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PROGRAMA DE PÓS-GRADUAÇÃO EM GEOLOGIA E GEOQUÍMICA**

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**TESE DE DOUTORADO Nº 179**

**A CAPA CARBONÁTICA MARINOANA DO SUL DO  
CRÁTON AMAZÔNICO: *MULTIPROXY* APLICADOS NA  
RECONSTITUIÇÃO PALEOCEONOGRÁFRICA E  
GEOBIOLOGICA DO INÍCIO DO EDIACARANO**

**Tese apresentada por:**

**RENAN FERNANDES DOS SANTOS**

**Orientador: Prof. Dr. Afonso César Rodrigues Nogueira (UFPA)**

**Coorientador: Prof. Dr. Pierre Sansjofre (*Muséum National d'Histoire Naturelle*)**

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**TESE APRESENTADA POR:**

**RENAN FERNANDES DOS SANTOS**

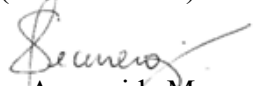
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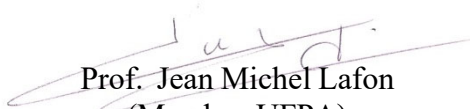
**Banca Examinadora:**

  
Prof. Afonso Cesar Rodrigues Nogueira  
(Orientador-UFPA)

  
Prof.ª Dr.ª Marly Babinski  
(Membro-USP)

  
Prof.ª Dr.ª Evelyn Aparecida Mecenero Sanchez  
(Membro-UFVJM)

  
Prof. Ricardo Trindade  
(Membro-USP)

  
Prof. Jean Michel Lafon  
(Membro-UFPA)

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*Eu sou o sonho dos meus pais  
Que eram sonhos dos avós  
Que eram sonhos dos meus ancestrais  
Emicida*

## RESUMO

A extensa deglaciação pós Marinoano (~650-635Ma), associada ao evento *Snowball Earth*, induziu alterações profundas na química dos oceanos, registradas em sucessões de capa carbonática distribuídas globalmente. Estes eventos desencadearam grandes alterações paleoceanográficas, principalmente pelos efeitos da eustasia glacial (nível do mar global), ajuste glacioisostático (GIA) e *ice gravity*, e expansão térmica dos oceanos em condições de efeito estufa, impactando o nível relativo do mar. A rápida deglaciação causou uma estratificação de densidade estável com condições geoquímicas complexas, composta por águas profundas hipersalinas e uma camada superficial de água de degelo. A escala de tempo para a desestratificação oceânica varia de dezenas de milhares a milhares de anos. A capa carbonática Puga (~635 Ma), relacionados ao contexto dos depósitos basais da bacia Araras-Alto Paraguai no sul do Cráton Amazônico, é revisitado nas seções clássicas de Tangará da Serra e Mirassol d'Oeste, no Estado de Mato Grosso. Esta sucessão exemplifica esse fenômeno paleoceanográficos pós-Marinoano, e é um dos melhores registros para avaliar os eventos de supersaturação sob condições de GIA e transgressão que controlaram o espaço de acomodação no sul do Cráton Amazônico. Dados sedimentológicos e estratigráficos foram integrados com novos dados paleoceanográficos e paleoredox, combinados com resultados diagenéticos, cristalográficos, geoquímicos (principalmente elementos terras raras e metais traços) e isotópicos ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\epsilon\text{Nd}(t)$ ,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , Sm/Nd) em rocha total são fornecidos para a sequência de capa carbonática Puga. A sucessão de capa carbonática Puga ocorre com aproximadamente 90 metros, sendo os 10 primeiros metros composto por depósitos glaciomarinho, diamictitos e dropstones, da Formação Puga, a capa dolomítica, Formação Mirassol d'Oeste, aproximadamente 40 metros, está em contato direto e apresenta evidências de deformações sinsedimentar na base, é compostos principalmente por: 1) Ds - doloboundstones estratiforme com pseudomorfo de gipso; 2) Dd - doloboundstones dômicos com estruturas tubulares, essa associação de fácies é interpretadas como uma plataforma rasa com intensa atividade microbiana. A porção superior da capa dolomítica é composta por 1) Dp - dolomudstone/dolopackstone peloidal com laminações paralelas ao plano, 2) Dq - dolograinstones/dolomudstone peloidal com laminações quasi-planar e truncamento de baixo ângulo, essa associação é interpretada como plataforma rasa influenciada por onda. A capa calcária (50 m de espessura da Formação Guia) recobre de forma concordante os depósitos de capa dolomítica, o contato é uma camada com espessuras descontínua de marga dolomítica e calcário com leques de cristais de calcita (pseudomorfo de aragonita) intercalados com calcário com

*megaripples*. A associação de fácies da capa calcária indica um ambiente moderadamente profundo dominado por ação de ondas e tempestades que passam para uma plataforma profunda supersaturada com  $\text{CaCO}_3$ . A mineralogia destes depósitos carbonáticos marinhos tem sido um fator crucial na restrição da composição dos oceanos durante a transgressão pós-Marinoana. Desta forma, as restrições diagenéticas, são uma etapa prévia crucial para demonstrar os impactos dos fluidos pós-deposicionais. Um estudo diagenético de alta resolução foi conduzido nestes depósitos, demonstrando maior influência dos processos sin/eodiagenéticos, indicados tanto nos padrões mineralógicos, quanto nos cristalográficos e texturais. O principal processo registrado é a dolomitização, que ocorre em pelo menos duas etapas principais, dolomitas si deposicionais e dolomitas de soterramento raso. Além disso, os testes geoquímicos e isotópicos aplicados neste estudo, corroboram a interpretação da preservação dos sinais sindeposicionais. Os padrões de elementos terras raras + ítrio no carbonato de capa de Puga oferecem *insights* sobre as condições marinhas pós-*Snowball Earth*. As baixas razões  $\text{Y}/\text{Ho} > 36$  na capa dolomitica sugerem mistura de água de degelo com água do mar, no entanto a base registra altos valores da razão  $\text{Y}/\text{Ho}$  de até 70, e anomalias de  $\text{Eu}/\text{Eu}^*$  até 3, indicam ressurgência de água do mar hipersalina com interação de fluido hidrotermal (*vents*), corroborando com a interpretação de que a capa dolomitica precipitou durante o processo de desestratificação dos oceanos. As composições isotópicas de Nd radiogênico, combinadas com outros proxies como  $\delta^{13}\text{C}$  e  $^{87}\text{Sr}/^{86}\text{Sr}$ , indicou a influência de contribuições continentais e marinhas durante a precipitação do carbonato de capa de Puga. O sistema isotópico de Nd, menos suscetível a trocas diagenéticas, revelou assinaturas distintas de massas de água e intenso intemperismo do Cráton Amazônico durante a deglaciação, conforme indicado pelas tendências geoquímicas, ex.  $\text{Y}/\text{Ho}$ , e valores de  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\epsilon\text{Nd}(t)$ ,  $\delta^{13}\text{C}$ . Os nossos dados de  $^{87}\text{Sr}/^{86}\text{Sr}$  na capa dolomitica variam de 0.7264 a 0.7084, e esses valores são mais altos do que os valores de  $^{87}\text{Sr}/^{86}\text{Sr}$  pré e pós-glaciais da água do mar. A associação de valores de  $^{87}\text{Sr}/^{86}\text{Sr}$  mais radiogênico com os valores de  $\epsilon\text{Nd}(t)$  menos radiogênico, similares aos encontrados nos diamictitos, reforça a conexão com a contribuição do intemperismo continental na água de degelo. Esta abordagem *multiproxies* reconcilia-se com o modelo anterior de precipitação rápida de carbonato de capeamento, seguindo a escala de tempo de curto prazo para a desestratificação do oceano. Os dados de metais traços redox-sensíveis, U, Mo, V, Ni, Cu, P e isótopos de  $\delta^{13}\text{C}$  indicaram condições paleoredox e paleoprodutividade durante a transgressão pós-glacial. A capa dolomitica precipitou em condições oxigenadas com extensa contribuição das comunidades microbianas, passando para condições predominantemente disóxicas com ação de ondas na última fase de deposição na plataforma dolomitica. O aprofundamento das regiões costeiras relacionado ao aumento abrupto do nível do

mar, que levou à modificação do ciclo biogeoquímico. Nossos dados demonstram uma relação direta da produção de oxigênio e a rápida colonização das comunidades microbianas. A rápida elevação do nível do mar interrompeu a precipitação disseminada de dolomita, à medida que íons de Mg se dispersaram, levando à substituição de plataformas dolomíticas por mares supersaturados em  $\text{CaCO}_3$ . Além disso, os dados geoquímicos demonstram um baixo conteúdo de siliciclástico na capa dolomitica, coerente com o modelo de fome de siliciclástico, e o aumento abrupto nestes depósitos, coincide com evolução das condições paleoceanográficas, declínio das comunidades microbianas, predomínio de condições disóxicas e mudança da fábrica carbonática. Durante a transição Criogeniano-Ediacarano processos sedimentares e geoquímicos anômalos geraram uma das mais complexas perturbações paleoambientais no ciclo biogeoquímico associadas a transição *Icehouse-Greenhouse*. A análise de cenários pré-cambrianos no Cráton Amazônico, desvendando os climas extremos, lança uma luz crítica sobre a proliferação de vida em condições extremas e tem fortes implicações para a compreensão de outras superfícies planetárias

**Palavras-chaves:** ediacarano; estratificação oceânica; produtividade primária; paleoredox; capa dolomitica

## ABSTRACT

The post-Marinoan glaciation (~650-635 Ma) was the most severe event from the late Cryogenian period of the planet. The snowball Earth conditions induced a climate anomaly, triggering major changes in the paleoenvironmental and ocean chemistry recorded in the carbonate cap sequences. The dramatic effects on the global sea level were caused by glacial-isostatic adjustment (GIA) and ice gravity on the coastal zones associated with the ocean thermal expansion under greenhouse conditions. The fast input of meltwaters contributed to a stable density ocean stratification formed by hypersaline deep waters and meltwater surface layers. The ocean desatratification occurred in a timescale ranging from tens of thousands to thousands of years. The Puga cap carbonate (~635 Ma), the basal deposits of the Araras-Alto Paraguai basin from the southern Amazon Craton, is revisited in the classical sections from the Tangará da Serra and Mirassol d'Oeste, Mato Grosso State. This succession is one of the best records for evaluating the supersaturation events under GIA and transgression conditions that controlled the accommodation space in the southern Amazon Craton. Sedimentological and stratigraphic data were integrated with new paleoceanographic, and paleo-redox data combined with diagenetic, crystallographic, geochemical (primarily rare earth elements and trace metals), and isotopic (whole rock  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\epsilon\text{Nd(t)}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , Sm/Nd) results providing further insights to understand the post-Marinoan conditions. The Puga cap carbonate sequence spans approximately 90 meters, with the first 10 meters composed of glaciomarine deposits, diamictites, and dropstones from the Puga Formation. The basal contact with diamictites is plastically deformed, indicating rapid carbonate precipitation. The cap dolostone consists of stratiform doloboundstones with gypsum pseudomorphs and domal doloboundstones with tubestone, which were deposited in a shallow platform with intense microbial activity. Peloidal dolomudstone/dolopackstone with laminations parallel to bedding planes and peloidal dolograinstones/dolomudstone with quasi-planar laminations and low-angle truncation were formed in a wave-influenced shallow platform. The cap limestone conformably overlies the cap dolostone deposits, marked by dolomitic marlstone with calcite crystal fans (aragonite pseudomorphs) interbedded with mega-rippled limestone. The facies association of the cap limestone indicates moderately deep-water conditions dominated by waves and storms transitioning to a deep platform supersaturated with  $\text{CaCO}_3$ . The main diagenetic process is dolomitization during syn-depositional and shallow burial stages. Rare earth element + yttrium patterns have been analyzed in these deposits. Low Y/Ho ratios (<36) in the cap dolostone suggest a mixture of meltwater and seawater, while the base records superchondritic Y/Ho values up to 70 and high Eu/Eu\* values up to 3, indicating upwelling of hypersaline seawater with hydrothermal fluid interaction, suggesting dolomite precipitation



during ocean destratification. The radiogenic isotopic compositions of Nd, combined with other proxies such as  $\delta^{13}\text{C}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ , indicate the influence of continental and marine contributions. The Nd isotopic system, less susceptible to diagenetic exchanges, revealed distinct signatures of water masses and enhanced weathering of the Amazon Craton during deglaciation. This process is indicated by geochemical trends (e.g., Y/Ho) and  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\epsilon\text{Nd(t)}$ ,  $\delta^{13}\text{C}$  values.  $^{87}\text{Sr}/^{86}\text{Sr}$  data in the cap dolostone range from 0.7264 to 0.7084, higher than pre- and post-glacial seawater values. More radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  values associated with less radiogenic  $\epsilon\text{Nd(t)}$  values, similar to those found in diamictites, reinforce coastal weathering contribution to meltwaters. This multiproxies approach is a reconciliation with the previous rapid cap carbonate precipitation model following the short-term timescale for ocean destratification. Redox-sensitive trace metal data, U, Mo, V, Ni, Cu, P, and  $\delta^{13}\text{C}$  isotopes, indicated paleo-redox states and paleoproductivity during the post-glacial transgression. The cap dolostone precipitated under oxygenated conditions with extensive microbial community contributions, transitioning to predominantly dysoxic conditions with wave action in the last deposition phase. The abrupt sea-level rise altered the biogeochemical cycle, indicating a direct relationship between oxygen production and rapid microbial community colonization. The rapid sea-level rise and continental weathering reduced seawater Mg/Ca ratios with substantial  $\text{Ca}^{2+}$  input, also demonstrated by  $\epsilon\text{Nd(t)}$  values, causing the change of dolomitic platform to  $\text{CaCO}_3$ -supersaturated seas in the Amazon Craton margin. Additionally, low siliciclastic content in the cap dolostone is consistent with the siliciclastic starvation model, and the abrupt increase caused the decline of microbial communities coincident with the predominance of dysoxic conditions and long-term transgression. During specific Cryogenian-Ediacaran deglaciation scenarios, anomalous sedimentary and geochemical processes generated one of the most complex paleoenvironmental disturbances in the biogeochemical cycle. They strongly influenced the rapid primary productivity, directly impacting microbial life. The analysis of Precambrian scenarios in the Amazon Craton unraveling the extreme climates sheds critical light on extremophile life proliferation and has strong implications for understanding other planetary surfaces.

**Keywords:** oceanic stratification; paleocoastal; primary productivity; paleoredox; cap dolostone

## LISTA DE ILUSTRAÇÕES

### CAPÍTULO 1 INTRODUÇÃO

Fig. 1.1- Paleogeografia do período Criogeniano e a Fragmentação de Rodínia. Reconstruções paleogeográficas globais na projeção de Mollweide para (A) o término da glaciação Marinoana (~635 Ma) e (B) o início Esturtiana (~ 717 Ma). Linhas vermelhas representam os sistemas de cristas e falhas transformantes oceânicas, e linhas azuis escuras com barbatanas indicam zonas de subducção inferidas. As estrelas são formações glacial-periglaciais, estrelas vermelhas são formações com formação de ferro sin-glacial, e estrelas verdes indicam ocorrências de barita autigênica e/ou no fundo do mar em dolomitos de capa pós-glacial Marinoanos. A glaciação Criogeniana foi contemporânea com a fragmentação do supercontinente Rodínia. O paleocontinente Laurência (Laur) está fixado em latitude e declinação a 720 Ma por dados paleomagnéticos do LIP de Franklin (linha tracejada roxa) no Árctico canadense. Os paleocontinentes são: Austrália do Sul (SA), China do Sul (SCh), Amazônia (Amaz), Avalônia (Av), Báltica (Balt), Cadômia (Ca), Congo, Dzabkhan (Dz) na Mongólia, Antártica Oriental (EAnt), Svalbard Oriental (ESv), Índia (Ind), Kalahari (Kal), Cazaquistão (Kaz), Austrália do Norte (NA), China do Norte (NCh), Omã (Om), Rio de la Plata (P), São Francisco (SF), Sibéria (Sib), Tarim (Tm) e Oeste da África (WAfr). Extraído de Hoffman *et al.* (2017).  
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# 1 CAPÍTULO 1 INTRODUÇÃO

## 1.1 ORGANIZAÇÃO DA TESE DE DOUTORADO

A tese está organizada em nove capítulos que incluem uma introdução (Capítulo 1) apresentação da temática, objetivos, área de estudo, no (Capítulo 2), materiais e métodos aplicados enquanto no (Capítulo 3) e apresentado os aspectos geológicos da área de estudo. Os resultados estão apresentados na forma de quatro artigos científicos e um manuscrito em desenvolvimento. O primeiro artigo (Capítulo 4), denominado “*DIAGENESIS OF THE MARINOAN CAP DOLOSTONE, SOUTHERN AMAZON CRATON: AN UNCONVENTIONAL PETROLEUM SYSTEM IN THE EVOLUTION OF THE ARARAS-ALTO PARAGUAI BASIN*” O artigo está publicado no periódico *Marine and Petroleum Geology* 158 (2023): 106496, apresenta resultados de análise de microfácies e um estudo diagenético, determinando as condições paleoambientais, bem como as principais fases diagenéticas e implicações para o sistema petrolífero não convencional do Grupo Araras. O segundo artigo (Capítulo 5), intitulado “*RARE EARTH ELEMENTS AS INDICATORS FOR THE PALEOCEANOGRAPHIC CHANGES OF THE POST-MARINOAN SNOWBALL EARTH FROM THE AMAZON CRATON*” aborda a dinâmica paleoceanográfica a partir da geoquímica de elementos maiores e menores, principalmente elementos terras raras, combinados com dados isotópicos de  $\delta^{13}\text{C}_{\text{carb}}$ , discutindo a influência dos principais eventos pós-Marinoano na precipitação da sequência de capa carbonática Puga. O terceiro artigo (Capítulo 7) intitulado “*UNRAVELING POST-MARINOAN SEAWATER EVOLUTION IN THE AMAZON CRATON*” apresenta restrições paleoceanográfica baseada nos dados isotópicos, de  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$ ,  $^{147}\text{Sm}/^{144}\text{Nd}$ ,  $\delta^{13}\text{C}$  e  $\delta^{18}\text{O}$ , demonstramos indicativos de proveniência para os depósitos glaciomarinho da Formação Puga e o impacto da água de degelo na precipitação de capa dolomítica, trazendo *insights* sobre a rápida precipitação, sob influência deglacial. O quarto artigo (Capítulo 6), com título “*POST-MARINOAN PALEOREDOX AND PALEOPRODUCTIVITY RECORD IN PUGA CAP CARBONATE: IMPLICATION FOR COASTAL LIFE COLONIZATION FROM THE AMAZON CRATON MARGIN*” apresenta resultados de metais traços que possibilitaram a discussão dos parâmetros redox e indicadores de paleoprodutividade durante a precipitação da capa dolomítica, e demonstramos como as comunidades microbianas contribuíram para a manutenção de ambientes oxigenados e como auxiliaram na recuperação dos ciclos biogeoquímicos na margem sul do cráton Amazônico pós-Snowball Earth. O Capítulo 8 intitulado “*HIGH-RESOLUTION MAPPING AND CRYSTAL ARCHITECTURE OF MARINOAN CAP DOLOSTONE (~635 MA): INSIGHTS INTO THE*

*DOLOMITE PROBLEM AND ITS POTENTIAL AS AN ASTROBIOLOGICAL ANALOG*” apresenta um manuscrito em desenvolvimento que abrange feições petrográficas, refinamento mineralógico por meio de catodoluminescência e MEV e mapeamento geoquímico *in situ* por microsonda e nano-fluorescência de raios-x (FRX) por luz síncrotron, além disso um estudo cristalográfico por meio de Difração de raios-X (DRX) em rocha total e *in situ* por microscopia Raman. Este manuscrito em desenvolvimento trará *insights* sobre o processo de dolomitização durante a precipitação de capa dolomítica e o seu potencial como análogo astrobiológicos. O último capítulo (Capítulo 9) refere-se às considerações finais e conclusões dos temas abordados nos artigos científicos.

Os materiais suplementares que compõem essa tese de doutorado são anexados nos seus respectivos manuscritos.

## 1.2 ENUNCIADO DO PROBLEMA

Rochas sedimentares pré-cambrianas ocorrem preservadas em várias áreas cratônica e registram importantes eventos paleoceanográficos, paleoclimáticos e bioevolutivos na transição Neoproterozoico-Paleozoico (Kaufman & Knoll 1995, Jacobsen & Kaufman 1999, Knoll 2000, Nogueira *et al.* 2007, 2019, Santos *et al.* 2017). Condições de temperaturas extremas caracterizam o fim do Neoproterozoico, registrando glaciações do tipo *Snowball Earth*, onde vastas extensões de terra foram cobertas por gelo, alcançando até mesmo as baixas paleolatitudes (Trindade *et al.* 2003, Hoffman *et al.* 2017). Este cenário glacial, condições *Icehouse*, foi abruptamente interrompido por um rápido aquecimento, impulsionado pelo efeito estufa, condições de *greenhouse* (Hoffman *et al.* 1998, 2017). De acordo com Fairchild & Kennedy (2007) o Criogeniano é um período chave para o entendimento dos eventos climáticos extremos, pois são amplamente registrados dois episódios de glaciação em escala global, sendo eles o evento Esturtiano (~717-660 Ma) e o Marinoano (~650 - 635 Ma), amplamente descritos em várias regiões ao redor do mundo (Fig. 1.1).

Durante o período glacial, a espessura das geleiras foi estimada em 0,7–1,4 km para as camadas de gelo continentais (Liu & Peltier, 2010, Benn *et al.* 2015), enquanto geleiras marinhas atingiram até ~1 km (Fig. 1.2 A) (Tziperman *et al.* 2012). Estes eventos glaciais desencadearam grandes alterações nos sistemas oceânicos, principalmente pelos efeitos do degelo, seguidos pela eustasia glacial (nível médio do mar global), ajuste isostático glacial (GIA), impactando o nível relativo do mar durante as fases pré, sin e pós-glaciais (Fig. 1.2 B-C) (Allen & Hoffman 2005, Benn *et al.* 2015, Creveling & Mitrovica 2014, Hoffman *et al.* 2017, 2021, Mitchell *et al.* 2021, Rame & Marotzke 2022). O volume de água de fusão dependia do estado da

água nas geleiras, os oceanos eram compostos parcialmente de gelo marinho (água do mar congelada) e gelo meteórico (neve compactada) (Li & Pierrehumbert 2011, Yang *et al.* 2017, Hoffman *et al.* 2017, Wu *et al.* 2021). O intenso sequestro de água durante a formação das capas de gelo, gerou uma salinidade até duas vezes maior do que a do oceano moderno (Fig. 1.2 A) (Yang *et al.* 2017). A deglaciação das camadas de gelo continentais foi provavelmente a principal fonte de água de degelo para o oceano (Liu & Peltier 2010, Tziperman *et al.* 2012, Benn *et al.* 2015, Wu *et al.* 2021). A ablação completa das espessas capas de gelo marinho é estimada em um máximo ~300 a 1500 anos (Zhao *et al.* 2022). A deglaciação rápida e o aquecimento causaram uma estratificação de densidade estável formada por águas profundas hipersalinas contrastando com uma camada superficial de água de degelo (Fig. 1.2 B) (Shields 2005, Gidding & Wallace 2009, Liu *et al.* 2014, 2018, Yang *et al.* 2017, Hoffman *et al.* 2017, 2021, Wei *et al.* 2019).

O Ajuste isostático glacial (GIA) gerou o soerguimento de áreas continentais e subsidência nas bacias, gerando uma excepcional criação gradual de espaço de acomodação pós-*Snowball Earth* (Creveling & Mitrovica 2014). Estes eventos associados a transgressão sin-deglacial são responsáveis pela súbita elevação do nível do mar durante a transição Criogeniano-Ediacarano (Creveling & Mitrovica 2014, Hoffman *et al.* 2017). No entanto, ao longo do período deglacial, uma queda local no nível do mar pode ter superado momentaneamente a taxa global (eustática) de aumento do nível do mar, relacionada a redução da carga de gelo e diminuição gravitacional (*ice-gravity*) (Creveling & Mitrovica 2014). Esse processo intensificou o soerguimento local das áreas continentais, mantendo algumas plataformas rasas e isoladas durante a transgressão sin-deglacial. A contribuição eustática do derretimento de camadas de gelo distantes foi mais significativa do que a queda local do nível do mar impulsionada por efeitos ação da gravidade (Creveling & Mitrovica 2014), seguindo um padrão deposicional de migração significativa da linha costeira durante a transgressão de longa duração (Hoffman *et al.* 2017). As mudanças ambientais associadas a esses eventos incluem a transformação de um oceano globalmente congelado (*Icehouse*) para um oceano livre de gelo (*greenhouse*) (Hoffman *et al.* 2017, 2021). A escala de tempo para a desestratificação oceânica varia de dezenas de milhares (Yang *et al.* 2017) a milhares de anos (Rame & Marotzke 2022). Eventos de ressurgência, combinado com o GIA, causou uma mistura gradual e alteração na estratificação oceânica (Hoffman *et al.* 2017, Ramme & Marotzke 2022). Além disso, segundo Hoffman *et al.* (2017), a capa dolomítica precipitou diacronicamente aos processos de mistura de água, e a mistura



completa dos oceanos coincide com o avanço da transgressão de longa duração e a expansão térmica dos oceanos (Fig. 1.2 B).

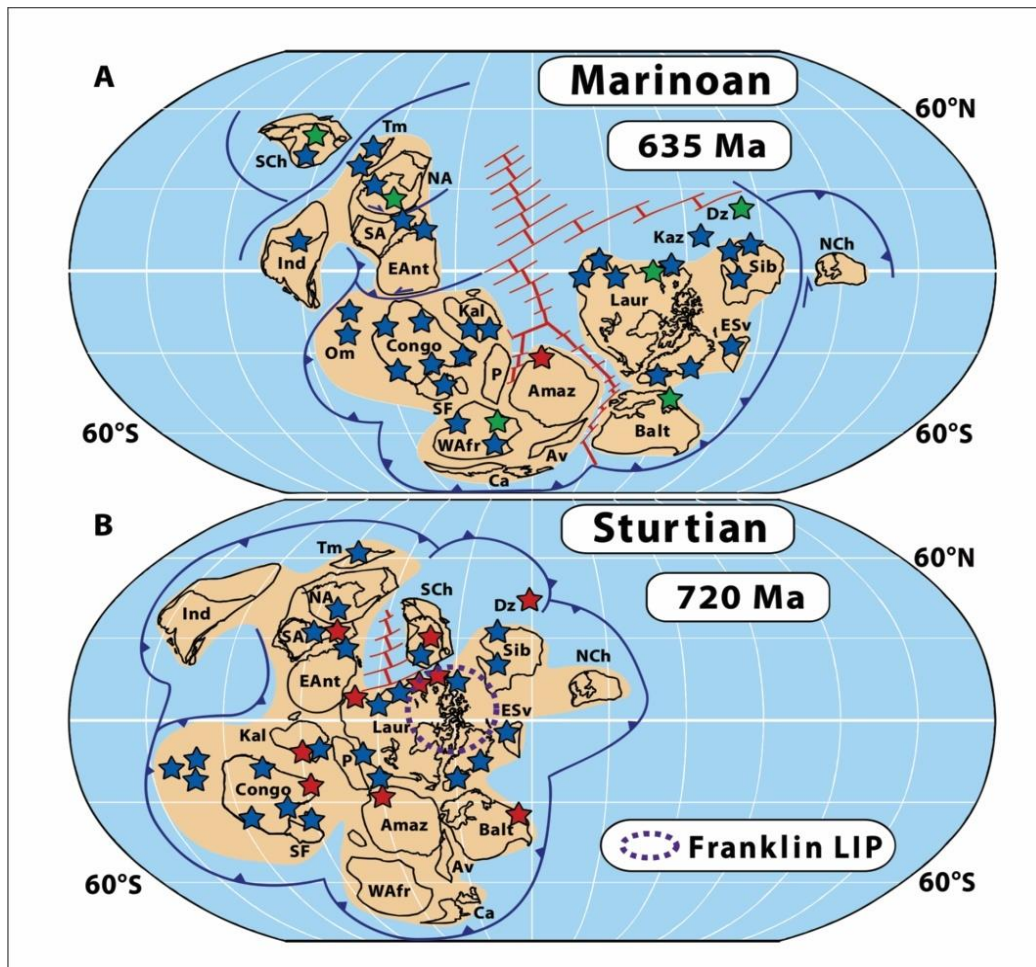


Fig. 1.1- Paleogeografia do período Criogeniano e a Fragmentação de Rodínia. Reconstruções paleogeográficas globais na projeção de Mollweide para (A) o término Marinoano a 635 Ma e (B) o início Sturtiano a 720 Ma. Linhas vermelhas representam os sistemas de cristas e falhas transformantes oceânicas, e linhas azuis escuras com barbatanas indicam zonas de subducção inferidas. As estrelas são formações glacial-periglaciais, estrelas vermelhas são formações com formação de ferro sin-glacial, e estrelas verdes indicam ocorrências de barita autigênica e/ou no fundo do mar em dolomitos de capa pós-glacial Marinoano. A glaciação Criogeniana foi contemporânea com a fragmentação do supercontinente Rodínia. O paleocontinente Laurência (Laur) está fixado em latitude e declinação a 720 Ma por dados paleomagnéticos do LIP de Franklin (linha tracejada roxa) no Ártico canadense. Os paleocontinentes Austrália do Sul (SA) e China do Sul (SCH). Outros paleocontinentes são: Amazônia (Amaz), Avalônia (Av), Báltica (Balt), Cadômia (Ca), Congo, Dzabkhan (Dz) na Mongólia, Antártica Oriental (EAnt), Svalbard Oriental (ESv), Índia (Ind), Kalahari (Kal), Cazaquistão (Kaz), Austrália do Norte (NA), China do Norte (NCh), Omã (Om), Rio dela Prata (P), São Francisco (SF), Sibéria (Sib), Tarim (Tm) e Oeste da África (WAfr). Extraído de Hoffman *et al.* 2017

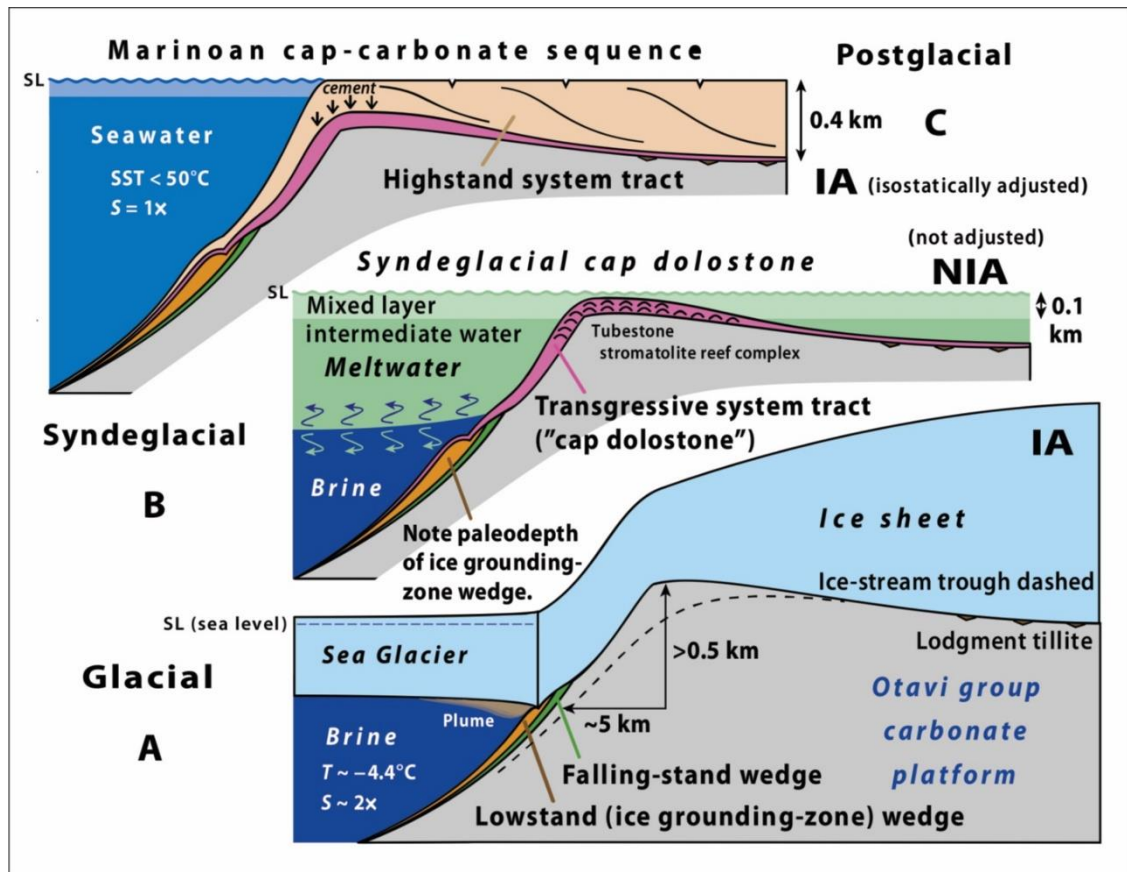


Fig. 1.2- Modelo Paleoceanográfico de Três Estágios para Sequências de Cap-Carbonato Marinoano A) Durante o evento *Snowball Earth*, a queda líquida do nível de base (eustasia glacial > isostasia glacial + gravidade do gelo). A salinidade da água do mar pode dobrar como resultado do sequestro de água doce nas camadas de gelo e no glacial marinho. (B) Durante a deglaciação, a produção de água de degelo e o aquecimento da superfície criam uma estratificação estável de densidade. A camada de água de degelo com espessura de quilômetros, inclui uma camada mista oxigenada e uma água intermediária que é pelo menos regionalmente anóxica, presumivelmente devido à respiração da produção orgânica exportada da superfície. A escala de tempo para a subida do nível de base pode exceder a escala de tempo de derretimento da camada de gelo por causa do aquecimento do oceano inteiro e da expansão térmica à medida que a desestratificação na escala de tempo do ajuste isostático (IA). (C) Após o derretimento das camadas de gelo, a camada de água de degelo se mistura com a salmoura evoluída do Snowball, que finalmente aquece. A HST das sequências de cap-carbonato preenche as áreas onde a acomodação líquida permanece após os ajustes isostáticos glacio e hidro isostáticos. A progradação para o interior é inferida a partir das

As sequências de capas carbonáticas são os principais registros da transição das condições *icehouse- greenhouse*, registradas em várias regiões cratônica ao redor do mundo (Fig. 1.1) (Hoffman *et al.* 2017, Yu *et al.* 2020). São caracterizadas por apresentarem camadas contínuas com espessuras métricas, compostas principalmente de dolomitos e calcários, em contato abrupto com diamictitos glaciais, sem evidências de retrabalhamento ou hiatos deposicionais (Hoffman *et al.* 1998) (Fig. 1.3). A capa carbonática Esturtiana ( $\sim 717$  Ma) é caracterizada por depósitos ricos em matéria orgânica, finamente laminados, com laminações rítmicas, estruturas *roll-up* e valores negativos de  $\delta^{13}\text{C}$  na base, que aumentam rapidamente para valores positivos em alguns metros da sequência (Hoffman *et al.* 2011, 2017). A capa carbonática Marinoana

(~635 Ma), (foco deste estudo), por sua vez, é comumente caracterizada por dolomitos e calcários finos, apresentando estruturas anômalas, como estruturas tubulares (*tubestone*) associadas a estromatólitos, *megaripples*, macropeloides, leques de cristais (pseudomorfo de aragonita ou barita), além dos valores negativos de  $\delta^{13}\text{C}$  (Hoffman & Scharg 2002, Hoffman *et al.* 1998, 2017, Allen & Hoffman 2005).

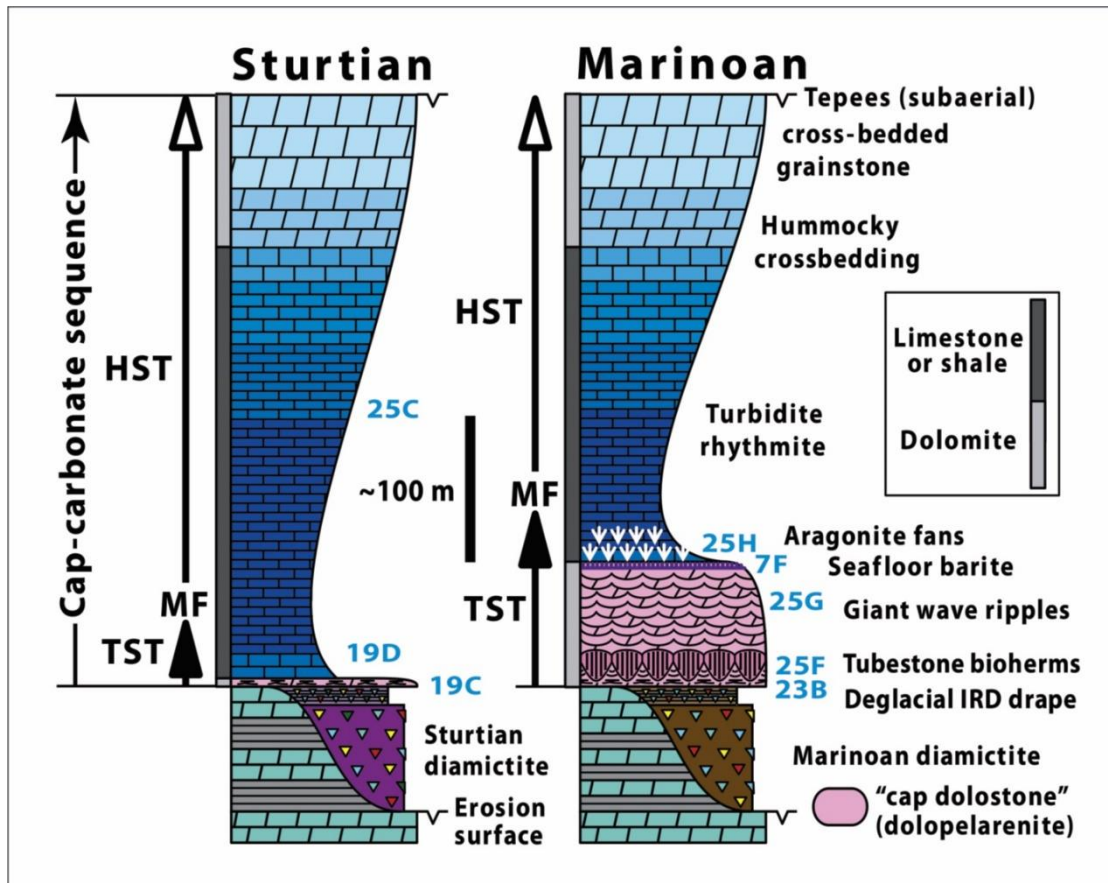


Figure 1.3- Comparação litoestratigráfica de seqüências de capa carbonática idealizadas relacionadas ao evento Esturtiano (710Ma) e Marinoano (635Ma) TST=Trato de Sistema transgressivo, HST=Trato de Sistema de Mar Alto e MF=Superfície de Inundação Máxima. Extraído de Hoffman *et al.* (2017).

A mineralogia destes depósitos carbonáticos marinhos tem sido um fator crucial na restrição paleoceanográfica da transgressão pós-glacial durante o final do Neoproterozoica. A relação mineralógica destes depósitos sugere condições marinhas supersaturadas (Fabre *et al.* 2013, Nogueira *et al.* 2019). A abordagem *multiproxies* tem sido essencial em estudos voltados para reconstruções paleoambientais, mudanças climáticas registrados em rochas sedimentares (Hohl *et al.* 2015, Caxito *et al.* 2018, Wang *et al.* 2023). Esta abordagem abrangente envolve a análise de diversos proxies, como fácies, estratigrafia, geoquímica, isótopos instáveis e estáveis, conteúdo fossilífero e restrições geocronológicas. A busca por interpretações amplas e precisas tem

incentivado uma abordagem multidisciplinar. Recentemente, muitos estudos têm adotado essa perspectiva, visando mitigar as tendências de interpretações baseadas em evidências isoladas. Para compreender os registros de carbonatos Ediacaranos, em particular, tem-se observado um avanço substancial impulsionado por múltiplas abordagens. Estudos que incorporam análises como: elementos maiores e menores *in situ* e em rocha total, isótopos instáveis e estáveis, por exemplo,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$ , e  $\delta^{13}\text{C}$ , em rocha total, além das restrições geocronológicas com datações Pb/Pb e U-Pb *in situ*. Essa abordagem integrada oferece uma visão mais completa e detalhada, contribuindo significativamente para o entendimento das condições paleoambientais pós-*Snowball Earth*.

Na literatura são encontrados diversos modelos para tentar explicar a formação de carbonato de capa marinoana, principalmente, os fatores controladores da alcalinização, que ainda são alvo de discussões, principalmente relacionados à origem do carbonato micritico, comumente associados a intensas atividades microbianas ou, excepcionalmente, precipitados inorgânicos (Nogueira *et al.* 2003; 2019, Nédélec *et al.* 2006, Font *et al.* 2010, Fabre *et al.* 2013). Um dos modelos sugere que o aumento da alcalinidade da água do mar desempenhou um papel crucial na precipitação e dolomitização generalizada observada durante a deposição do dolomito de capa. Esses fatores incluem a ressurgência das águas oceânicas profundas e anóxicas (Hoffman *et al.* 1998, James *et al.* 2001), intenso intemperismo químico pós-glacial (Hoffman *et al.* 1998, Higgins & Scharg 2003, Fabre *et al.* 2013), modelo de alcalinidade hidrotermal: aumentos de alcalinidade ligados a atividade hidrotermal extensiva ao longo de falhas delimitadoras de bacias (Gernon *et al.* 2016), desestabilização e liberação maciça de metano (Jiang *et al.* 2003, Jiang *et al.* 2006, Kennedy *et al.* 2008, Wang *et al.* 2008), aumentos de alcalinidade associados à atividade microbiana (por exemplo, redução de sulfato) (Nogueira *et al.* 2003, 2007, 2022, Font *et al.* 2006) e plumas de água derretida, densidade estável (Shields 2005, Yang *et al.* 2017, Liu *et al.* 2014, Santos *et al.* 2021, 2023). No entanto, a relação da cinética de precipitação, possíveis mecanismos que condicionaram a modificação da fábrica carbonática ou mesmo da dolomitização sindeposicional ainda é constantemente debatida (Hoffman *et al.* 2017, Ahm *et al.* 2018, Santos *et al.* 2023). A seguir uma tabela resumindo modelos e as principais referências, bem como um esquema evolutivo dos modelos retirados do trabalho de revisão de Yu *et al.* (2020).

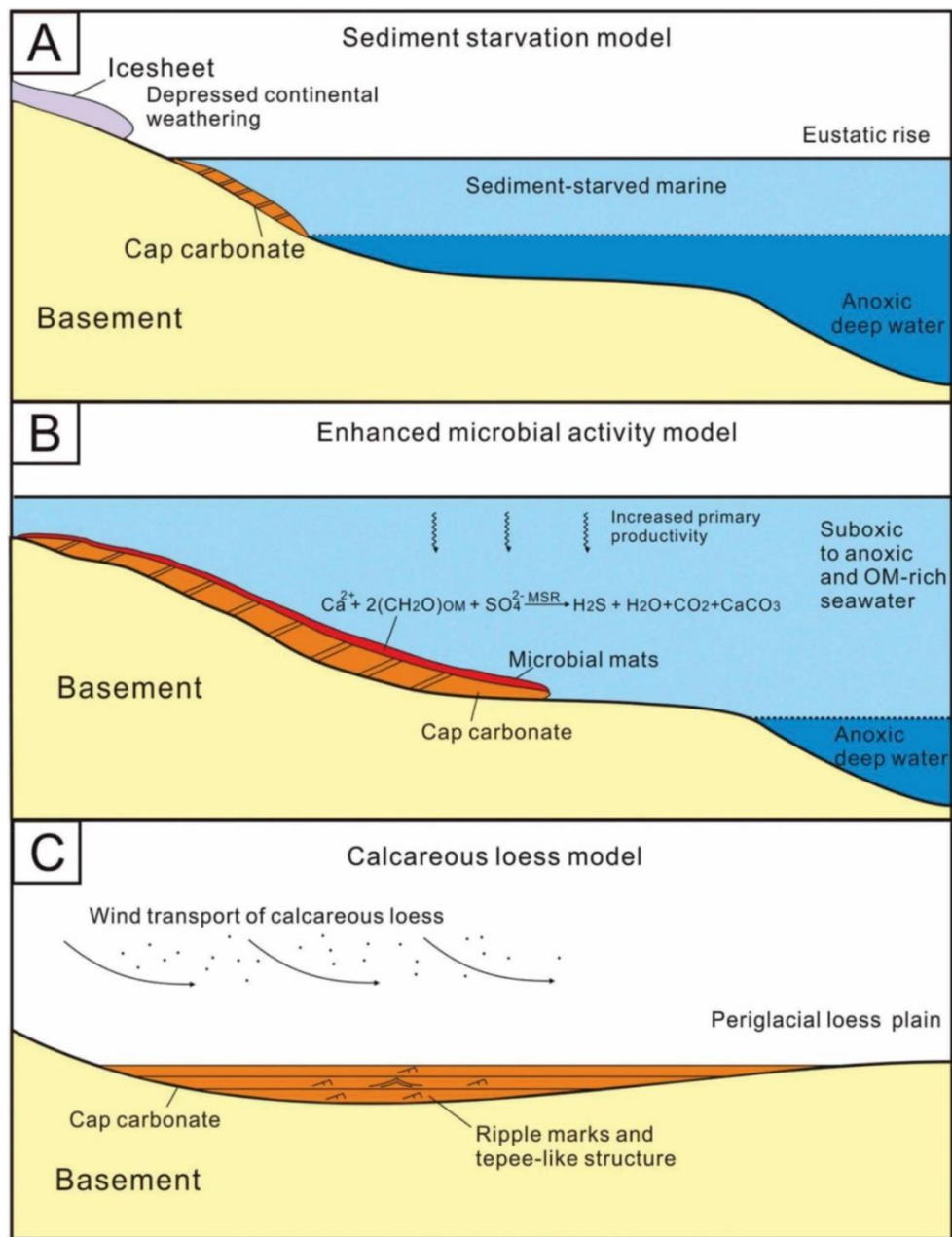


Figure 1.4- Esquemas dos modelos de precipitação da capa carbonática relacionadas a processo de formação lenta dos depósitos. (A) Modelo de fome de sedimentos. (B) Modelo de atividade microbiana aprimorada. OM = matéria orgânica. (C) Modelo de Loess calcário. Veja o resumo dos modelos, bem com as principais referências na tabela 1.1. Extraído de Yu *et al.* 2020.



Tabela 1.1- Resumo dos modelos de precipitação da capa carbonática.

| Nome do Modelo                           | Ponto Principal                                                                                                                                                                                                                                                                                                                                                   | Fonte de Alcalinidade                                                                                                                                                       | Tempo de deposição                                                                                                    | Oceano pós-glacial                                                                                    | Principal Referência                                |
|------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|-----------------------------------------------------|
| <i>Oceanic overturn</i>                  | A transgressão pós-glacial e a ressurgência fornecem água profunda rica em alcalinidade para as prateleiras continentais e bacias interiores, resultando em precipitação de carbonato. (Fig. 1.5A)                                                                                                                                                                | (1) HCO3- e CO32- gerados pela redução microbiana do sulfato (RMS) da matéria orgânica, (2) Oxidação da matéria orgânica                                                    | Deposição rápida (10 <sup>3</sup> - 10 <sup>4</sup> anos)                                                             | Oceano fortemente estratificado durante a glaciação e amplo afloramento durante a deglaciação         | Grotzinger & Knoll, 1995, Knoll <i>et al.</i> 1996  |
| <i>Continental weathering-alkalinity</i> | Alta pCO2 atmosférica levou a uma deglaciação catastrófica e rápida, intensificação do intemperismo de plataformas de carbonato expostas ao ar e loess causaram um tremendo influxo de detritos de carbonato finamente graduados para o oceano em expansão e aquecimento. A dissolução do detrito de carbonato resultou em precipitação de carbonato. (Fig. 1.5B) | Dissolução de detritos de carbonato finamente graduados terrígenos                                                                                                          | Deposição rápida (10 <sup>3</sup> - 10 <sup>4</sup> anos)                                                             | Oceano fortemente estratificado devido à camada de água doce derretida e "salmoura" subjacente        | Hoffman & Schrag, 2002, Hoffman <i>et al.</i> 2017  |
| <i>Gas hydrate destabilization</i>       | A deglaciação desencadeou a destabilização local do metano e liberou grande quantidade de metano de permafrost. A oxidação anaeróbica do metano pela MSR levou à precipitação de carbonato. (Fig. 1.5C)                                                                                                                                                           | Oxidação anaeróbica do metano                                                                                                                                               | Deposição rápida (10 <sup>3</sup> - 10 <sup>4</sup> anos) ou deposição lenta (10 <sup>4</sup> - 10 <sup>5</sup> anos) | Oceano fortemente estratificado em termos de redox, com camada oxa superior e camada anóxica inferior | Kennedy <i>et al.</i> 2001, 2008                    |
| <i>Plumeworld</i>                        | Capas carbonáticas formados rapidamente na camada de água doce derretida durante a deglaciação da Terra Bola de Neve. (Fig. 1.5D)                                                                                                                                                                                                                                 | Produtos de intemperismo químico, tempestades de poeira massiva, mistura de água do mar e água doce, e emissões submarinas de metano                                        | Deposição rápida (10 <sup>3</sup> - 10 <sup>4</sup> anos)                                                             | Oceano fortemente estratificado devido à camada de água doce derretida e "salmoura" subjacente        | Shields, 2005                                       |
| <i>Sediment starvation</i>               | No cenário prolongado e cíclico de deglaciação, o influxo supressor de detritos terrígenos levou à condição de fome marinha para o depósito contemporâneo de cap carbonato, assim os cap carbonatos formaram-se em uma taxa de acumulação muito baixa no substrato rochoso submarino. (Fig. 1.4 A)                                                                | Produtos de intemperismo químico, tempestades de poeira massiva, mistura de água do mar e água doce, e emissões submarinas de metano                                        | Deposição lenta (10 <sup>5</sup> - 10 <sup>6</sup> anos)                                                              | Um oceano mais homogêneo devido ao tempo de mistura suficiente para água doce e água do mar           | Spence <i>et al.</i> 2016                           |
| <i>Microbial activity</i>                | O crescimento microbiano durante a deglaciação levou à formação de estromatólitos e ao processo aprimorado de redução microbiana do sulfato (RMS). (Fig. 1.4 B)                                                                                                                                                                                                   | Matérias orgânicas foram degradadas pelas bactérias redutoras de sulfato                                                                                                    | Deposição lenta (10 <sup>5</sup> - 10 <sup>6</sup> anos)                                                              | Uma coluna de água estratificada, com uma camada superior oxa acima de uma camada euxínica            | Nédélec <i>et al.</i> 2007, Font <i>et al.</i> 2010 |
| <i>Calcareous loess</i>                  | As capas carbonáticas formaram-se por loess calcários que se acumularam na planície de deflação sob o clima sazonalmente congelado, frio a frígido e árido. (Fig. 1.4 C)                                                                                                                                                                                          | O modelo <i>Calcareous loess</i> invoca uma origem eólica terrestre. Deposição a partir de uma topografia preexistente relacionadas as morenas glaciais (loess periglacial) | Deposição lenta (10 <sup>5</sup> - 10 <sup>6</sup> anos)                                                              | Depósito siliciclástico                                                                               | Retallack, 2011                                     |

Extraído de Yu *et al.* (2020)

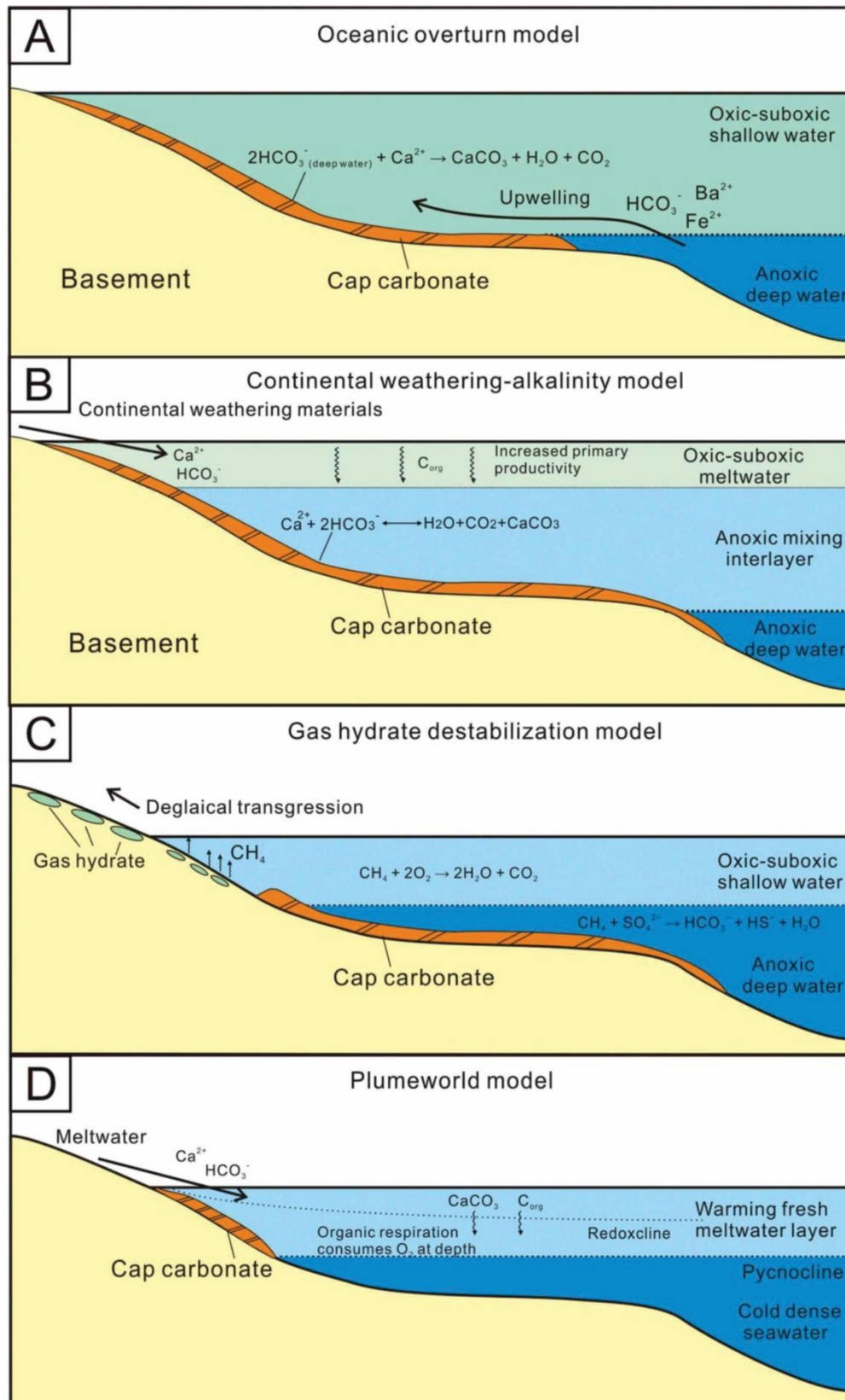


Figure 1.5- Esquemas dos modelos de precipitação da capa carbonática relacionadas a processo de formação lenta dos depósitos. (A) Modelo de ressurgência oceânica. (B) Modelo de intemperismo continental. (C) Desestabilização do hidrato de gás. (D) Modelo *Plumeworld*. Veja o resumo dos modelos, bem com as principais referências na tabela 1.1. Extraído de Yu *et al.* (2020).

O Sul do Cráton Amazônico (Fig. 1.6) registra uma sequência de capa carbonática relacionada, ao evento Marinoano (~ 650 - 635 Ma), comumente referida como sequência de capa carbonática Puga. A sucessão é composta por depósitos glaciomarinho, Criogeniano, da Formação Puga, e depósitos carbonáticos, Ediacarano, relacionados a base do Grupo Araras (Nogueira *et al.*2003, 2019, Font *et al.*2006, Sansjofre *et al.*2014, Soares *et al.*2020, Santos *et al.*2021). Esta sucessão marca o início da história deposicional da bacia intracratônica, Araras-Alto Paraguai, previamente incluída na evolução Criogeniana-Ediacarana da Faixa de dobramento Paraguai (Alvarenga & Trompette 1993, Nogueira *et al.*2007, McGee *et al.*2014, 2015). Estudos recentes incluem esses depósitos siliciclásticos-carbonáticos, na evolução da bacia intracratônica Araras-Alto Paraguai, deformados por tectônica transtensional, ligada à evolução dos mares epicontinentais primordiais do Gondwana Oeste (Nogueira *et al.*2019, Santos *et al.*2020). A tectônica de colisão está impressa apenas nas rochas metamórficas do Grupo Cuiabá que marcam a suturas dos crátons adjacente que representa a verdadeira Faixa Paraguai, ligada à Tectônica Pan-Africana-Brasileira (Alvarenga & Trompette 1993, McGee *et al.*2014, 2015; Nogueira *et al.*2019, Santos *et al.*2020). Sendo assim a porção norte da Faixa Paraguai previamente definida como “Faixa Paraguai Norte” foi redefinida por Nogueira *et al.*2019 como uma Bacia Intracratônica, denominada Araras-Alto Paraguai. As ocorrências de capa carbonática correspondem a parte inferior do Grupo Araras, nas regiões de Mirassol d'Oeste e Tangará da Serra, Estado do Mato Grosso, e em Espigão d'Oeste, Estado de Rondônia, margem Sul e Sudoeste do Cráton Amazônico respectivamente (Fig.1.6) (Nogueira *et al.*2003, 2019; Font *et al.*2006, Sansjofre *et al.*2011, 2014, Gaia *et al.*2017, Soares *et al.*2020, Santos *et al.*2021).



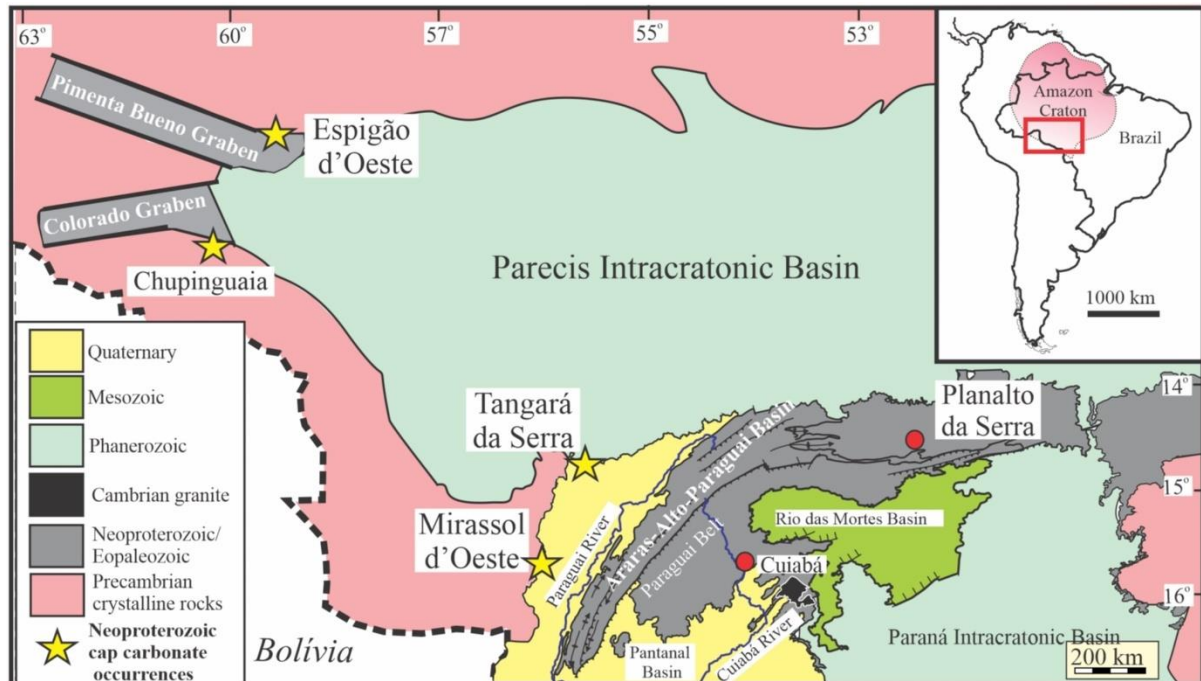


Figure 1.6- Mapa geológico simplificado do sudeste do Cráton Amazônico. Mostrando o contexto da bacia intracratônica, Araras Paraguai, a norte da faixa de dobramentos Paraguai e Sudeste do Cráton Amazônico. Destaque para a localização das ocorrências de capa carbonática Puga. Extraído de Nogueira *et al.* (2019).

Nas últimas duas décadas muitos estudos foram feitos principalmente na região de Mirassol d'Oeste (Fig.1.6), ocorrência clássica da capa carbonática, tais como: biomarcadores (Elie *et al.*2007, Sousa *et al.* 2016, van Maldegem *et al.*2018), isótopos de  $\delta^{13}\text{C}$  e  $\delta^{18}\text{O}$ , (Nogueira *et al.*2003,2007,2019, Alvarenga *et al.*2004,2008, Font *et al.*2006, Sansjofre *et al.*2011, Gaia *et al.*2017) Nd ( Dantas *et al.*2009, Souza *et al.*2024),  $^{87}\text{Sr}/^{86}\text{Sr}$  (Nogueira *et al.*2007, Alvarenga *et al.*2004,2008, Romero *et al.*2013, Souza *et al.*2024) Paleomagnetismo (Trindade *et al.*2006, Font *et al.*2010), Microfáceis e estratigrafia ( Nogueira *et al.*2003, 2019, Sansjofre *et al.*2014, Gaia *et al.*2017, Soares *et al.*2020, Romero *et al.*2020, Santo *et al.*2021) estudos diagenéticos ( Soares *et al.*2020, Santos *et al.*2023). Apesar de todas as ocorrências de capas carbonáticas no Cráton Amazônico (Fig.1.6), serem bem estudadas do ponto de vista estratigráfico e sedimentológico ainda são incipientes o entendimento paleoceanográfico integrados destes depósitos. A maioria das interpretações paleoambientais das unidades do Grupo Araras, basearam-se em dados obtidos nas porções sudoeste e central da Bacia Araras-Alto Paraguai (Nogueira *et al.*2003, 2007,2019). A integração destes dados nesta pesquisa de doutorado permitirá o estabelecimento de um arcabouço quimioestratigráficos, viabilizando um modelo paleoceanográfico inédito para a porção sul do Cráton Amazônico.

O entendimento do papel das comunidades microbianas nas mudanças biogeoquímicas (ex. paleoredox e paleoprodutividade) dos mares ediacaranos encontra-se na fronteira científica

de entendimento da expansão da vida no planeta. A presença de biostramas gigantes associados a capa dolomítica, na porção SE do Cráton Amazônico, sugere um aumento nas atividades metabólicas, que provavelmente alteraram as condições físico-químicas marinhas (Santos *et al.* 2021). Os microbialitos são constantemente mencionados nos depósitos de capa carbonática Puga (Nogueira *et al.* 2003, 2007, 2019, Font *et al.* 2006, Romero *et al.* 2020, Santos *et al.* 2021). No entanto, o mecanismo de precipitação do dolomicrito ainda é intrigante, se são relacionados a uma dolomitização precoce ou são realmente de origem primária ligada ao metabolismo de bactérias redutoras de sulfato. O papel da vida microbiana na recuperação dos ciclos biogeoquímicos, bem como sua participação na precipitação de dolomita ainda é pouco compreendida (Font *et al.* 2010, Sansjofre *et al.* 2014). A textura grumosa peloidal destes estromatólitos foram interpretadas como forma micritizadas de cianobactérias fotossintetizantes (Romero *et al.* 2020, Santos *et al.* 2021). Esta inferência, é condizente com a presença de biomarcadores de cianobactérias fotossintetizantes descritos por Elie *et al.* 2007, Souza *et al.* 2016, e van Maldegem *et al.* 2018). Sabe-se que as comunidades microbianas são compostas por diferentes microrganismos bem exemplificados pelos estromatólitos recentes de Shark Bay na Austrália e aqueles observados nas porções mais rasas da Lagoa Salgada no Rio de Janeiro- Brasil (Vasconcelos & Baniuk 2015). Os processos de organomineralização gerados pela comunidade microbiana foram fundamentais para superar as barreiras cinéticas na precipitação e nucleação de dolomita, mesmo em baixas temperaturas (Vasconcelos *et al.* 1995, Roberts *et al.* 2004, Sánchez-Román *et al.* 2008, McKenzie & Vasconcelos 2009, Dupraz *et al.* 2009, Deng *et al.* 2010, Kenward *et al.* 2013, Bontognali *et al.* 2014, Petrash *et al.* 2017, Liu *et al.* 2019, 2020, Han *et al.* 2022, 2024). Esta inovação biológica foi um dos gatilhos para o desenvolvimento das plataformas rasas dolomíticas que caracterizam o Ediacarano e ainda são pouco entendidas.

Uma das maiores dificuldades no estudo dos microbialitos ediacaranos é demonstrar diferentes microorganismos nestas comunidades, devido ao baixo potencial de preservação destes organismos. Desta forma, é necessário explorar ao máximo a mineralogia e os aspectos texturais dos microbialitos, e matéria orgânica, quando preservada para obter inferências biológicas. Outra prioridade é decifrar as zonas geoquímicas (Paleoredox e produtividade), visto que os processos diagenéticos, podem sobrepor e mascarar os sinais primários. Foi necessário um estudo diagenético de alta resolução combinado principalmente com a petrografia, catodolumiscência, microsonda e nano-Fluorescência de raios-X (luz sincrotron). Além disso um estudo cristalográfico foi conduzido utilizando difração de raios-X, microscopia Raman. Este compêndio de técnicas permitiu diferenciar as dolomitas formadas por organomineralização e

aquelas diageneticamente alteradas por dolomitização e/ou neomorfismo. Esta abordagem *multiproxies* que inclui dados isotópicos de  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$ ,  $^{147}\text{Sm}/^{144}\text{Nd}$ , além de geoquímica de elementos maiores e menores (principalmente elementos terras raras + ítrio e metais traços) permitiu a reconstrução paleoceanográfica das ocorrências de capa carbonática permitiu a elaboração de um arcabouço sequencial e geoquímico-isotópico para a sucessão de capa carbonática, decifrando os principais eventos paleoambientais, paleoceanográficos e paleoredox ocorridos na transição Criogeniano-Ediacarano.

### 1.3 OBJETIVOS

Este trabalho visa traçar uma evolução paleoambiental, paleoceanográfica e paleoredox da plataforma carbonática instalada na margem do Cráton Amazônico durante a transição Criogeniano-Ediacarano.

Objetivos Específicos:

1. Compreender a distribuição e a quimioestratigrafia das sequências de capas carbonáticas no Cráton Amazônico.
2. Estabelecer um arcabouço quimioestratigráficos, integrando novos dados e compilados, e propor uma curva de referência para o início do Ediacarano no Cráton Amazônico.
3. Inferir as condições paleoceanográficas que favoreceram a precipitação da capa carbonática Puga durante a transgressão sin-deglacial e a de longo prazo
4. Determinar as condições paleoredox e de paleoprodutividade durante a precipitação dos carbonatos de capa, e a participação das comunidades microbianas na recuperação dos ciclos biogeoquímicos pós-*Snowball Earth*.
5. Demonstrar a influência da água de degelo como fonte do intemperismo continental na plataforma carbonática durante a precipitação dos depósitos de capa.
6. Identificar e individualizar a origem das fácies biogênicas formadas por processos de organomineralização, sejam eles bioinduzidos ou bioinfluenciados, relacionando-as à evolução paleoceanográfica.
7. Sequenciar e definir as relações diagenéticas precoces, determinando a influência das comunidades microbianas na dolomitização precoce ou na manutenção de uma plataforma dolomítica.
8. Fornecer embasamento para a astrogeologia e astrobiologia para o entendimento de outras superfícies planetárias.

#### 1.4 LOCALIZAÇÃO E ACESSO

A Sucessão de capa carbonática estudada abrange furos de sondagem e afloramentos distribuídos no sul do Cráton amazônico, abrangendo as regiões de Tangará da Serra e Mirassol d'Oeste no Estado de Mato Grosso, no entanto outras ocorrências são descritas no Estado de Rondônia (Fig. 1.6). No entanto, este trabalho se concentrou principalmente em testemunhos de sondagem perfurados pela mina Calcário Tangará LTDA, no município de Tangará da Serra-Mato Grosso ( $14^{\circ} 45' 26''$  S,  $57^{\circ} 50' 02''$  W), a cerca de 240 km da capital Cuiabá (Fig. 1.7). Além dos testemunhos, sessões de afloramentos foram descrita e compõem a sucessão estudada, o acesso para a mina Calcário Tangará é feito pela da rodovia MT-358, km 18, saindo-se de Tangará da Serra em direção à cidade de Campo Novo e em seguida por 15 km em estrada vicinal até a entrada da mina. Adicionalmente, a ocorrência da mina Terconi na região de Mirassol d'Oeste-MT ( $15^{\circ}40'42''$  S,  $58^{\circ}04'32''$  W), também foram estudadas nesta tese, a ocorrência de Mirassol d'Oeste está a 210 Km da ocorrência de Tangará e 300km da capital Cuiabá, tendo acesso principalmente pela BR-070 e BR-174 (Fig. 1.7).

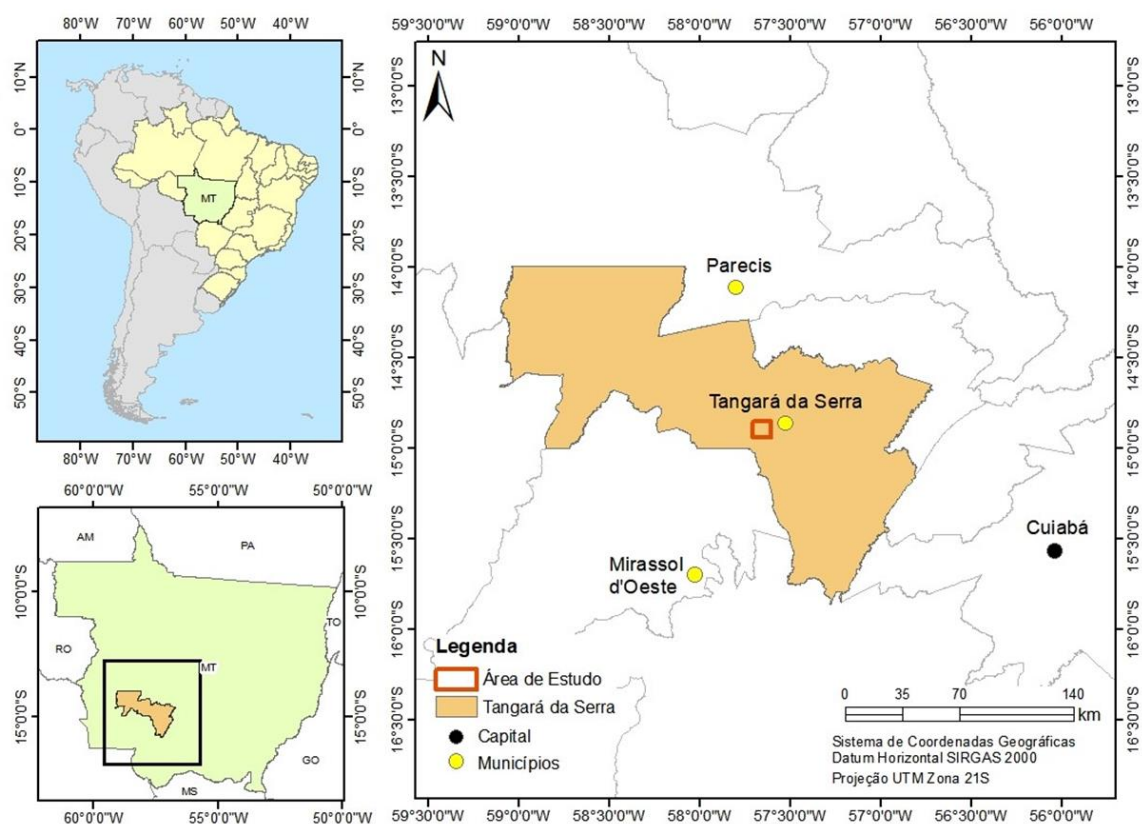


Figure 1.7- Mapa de localização e acesso a área de estudo no estado de Mato grosso, mina calcário Tangará, região de Tangará e mina Terconi na região de Mirassol d'Oeste. Principais vias BR – 363 e MT – 358

## 2 CAPÍTULO 2 MATERIAIS E MÉTODOS

### 2.1 LEVANTAMENTO BIBLIOGRÁFICO

Foi utilizado trabalhos relativos à geologia regional, geodinâmica e geoquímica da bacia Araras-Alto Paraguai, bem como de outras regiões do mundo com contexto do pós-*Snowball Earth*, principalmente glaciação Marinoana (~ 650 - 635 Ma). Além dos principais indicativos das feições texturais-mineralógicas e tratamento de dados geoquímicos e isotópicos em sequência de capas carbonáticas.

### 2.2 AMOSTRAGEM

As amostras de rocha deste estudo foram obtidas principalmente de dois testemunhos de sondagem, JOR (Fig. 2.1), referente à frente de lavra Ornamental e JBN (Fig. 2.2) referente à frente de lavra bananal, disponibilizadas pela mina Calcário Tangará Ltda, na região de Tangará da Serra, Mato Grosso (Fig.1.7). As amostras foram coletadas a cada 20cm, além das amostras de testemunhos outras amostras de afloramento das frentes de lavra, complementaram a amostragem dos perfis estudados.



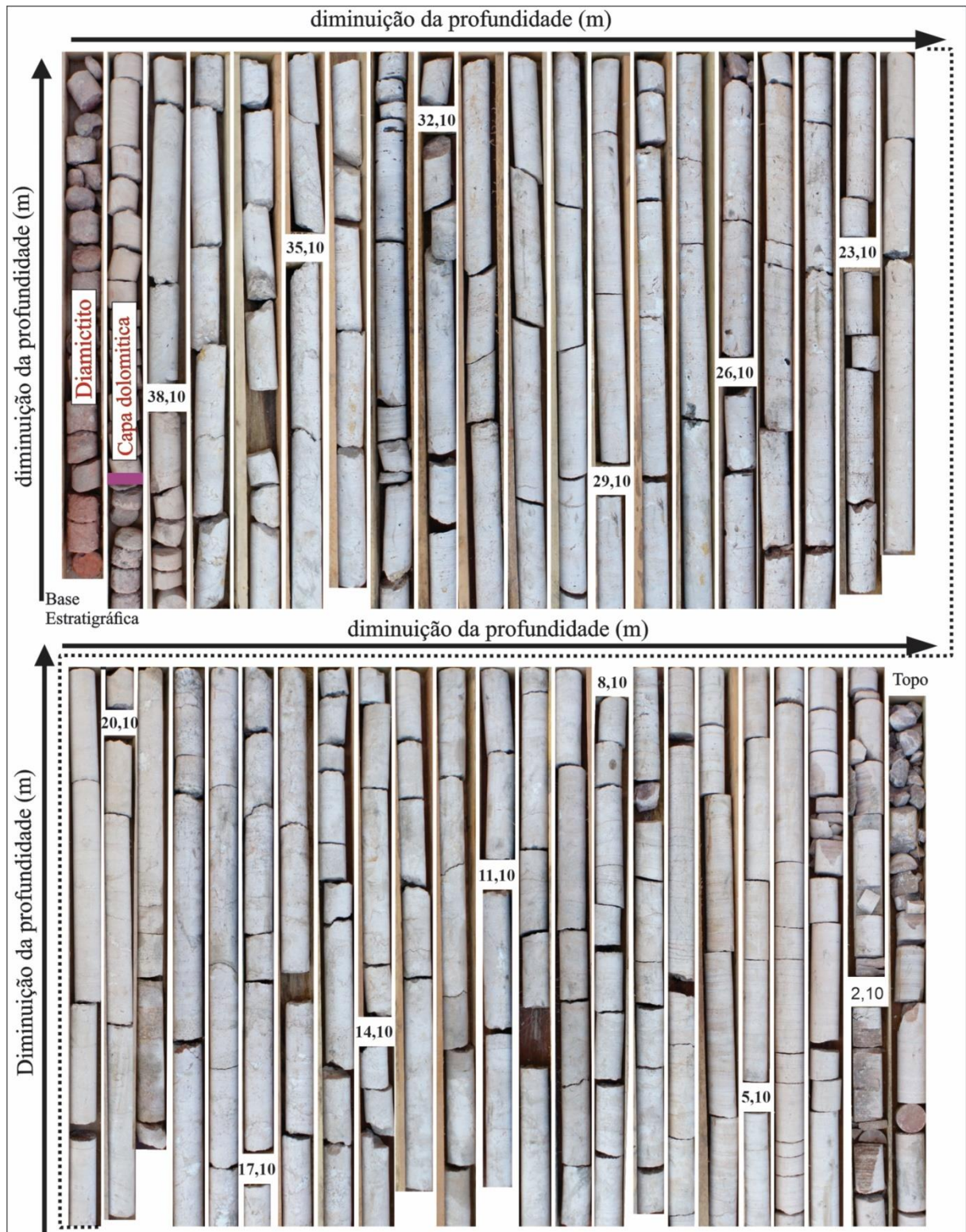


Figura 2.1- Fotografia do testemunho de sondagem JOR (frente de lavra Ornamental), mina Calcário Tangará, região de Tangará da Serra-Mato Grosso, ~40 metros de profundidade, mostrando o contato dos diamictitos glaciomarinho da Formação Puga com a capa dolomítica (Formação Mirassol d'Oeste).



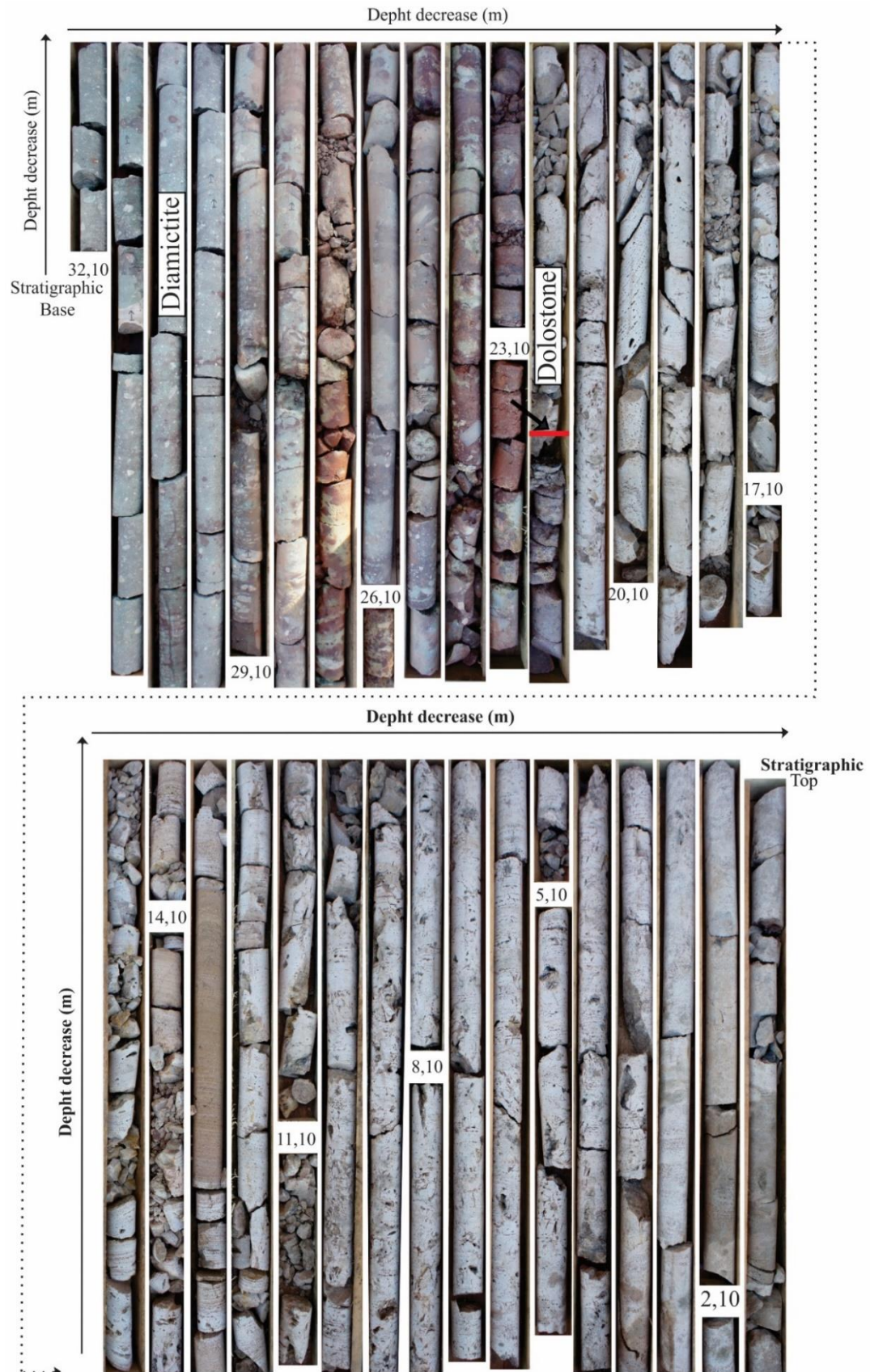


Figura 2.2- Fotografia do testemunho de sondagem JBN (frente de lavra Bananal) mina Calcário Tangará, região de Tangará da Serra-Mato Grosso, ~32 metros de profundidade, mostrando o contato dos diamictitos glaciomarinho da Formação Puga com a capa dolomítica (Formação Mirassol d'Oeste).

### 2.3 PETROGRAFIA

Foram descritas 93 seções polidas da capa dolomítica, da região de Tangará da Serra-Mato Grosso (MT), e cerca 50 seções polidas da sucessão de capa carbonática Puga foram revisadas das ocorrências da região de Mirassol d'Oeste-MT e Rondônia. A seleção de amostras para a confecção de lâminas delgadas ocorreu de acordo com as variações faciológicas observada e o respectivo nível estratigráfico. A definição de microfáceis carbonática e interpretação paleoambiental dos carbonatos, assim como dos principais processos diagenéticos a qual a rocha foi submetida, foram obtidas a partir da identificação das principais características como: texturas, componentes (cimento, grãos, poros) e feições diagenéticas. O termo microfáceis é aplicado a toda descrição e interpretação de dados sedimentológicos e paleontológicas obtidos através de seções delgadas de rochas sedimentares. A classificação de microfáceis seguiu a proposta modificada de Dunham (1962), com refinamentos baseados nos trabalhos de Wright (1992), Tucker (1992) e Flügel (2004). Além disso, os tipos de dolomita foram reconhecidos e classificados individualmente com base no tamanho dos cristais e na forma das bordas dos cristais, seguindo a proposta de Sibley & Gregg (1987) e Mazzulo (1992). enquanto a classificação da porosidade seguiu a proposta de Choquette & Pray (1970). Aproximadamente 300 pontos foram contados usando um contador de pontos para caracterizar as proporções dos constituintes, seguindo os métodos de Glagolev-Chayes (Galehouse 1971). Estas seções foram tingidas com alizarina vermelha S e ferrocianeto de potássio (0,2g/100 ml de 1,5% HCl) (Dickinson *et al.* 1966, Adams *et al.* 1984). Os litotipos foram descritos em microscópio petrográfico LEICA DM 2700 P do Laboratório de petrografia sedimentar do Grupo de Análise de Bacias Sedimentares da Amazônia (GSED) da Universidade Federal do Pará (UFPA). As novas lâminas representativas da região de Tangará da Serra-Mato Grosso, de microbialitos e estruturas associadas da capa dolomítica são listados a seguir na Tabela 2.1, e estão armazenadas na coleção didática de carbonatos do laboratório de Petrografia do GSED, do Instituto de Geociências da UFPA.



Tabela 2.1- Lista das seções polidas da capa dolomítica da região de Tangará da Serra-Mato Grosso, suas respectivas posições estratigráficas e classificação microfáciológica.

(continua)

| <b>Amos-<br/>tra</b> | <b>Profundi-<br/>dade</b> | <b>Amos-<br/>tras</b> | <b>Profundi-<br/>dade</b> | <b>Microfácies/Fácies</b>                            |
|----------------------|---------------------------|-----------------------|---------------------------|------------------------------------------------------|
| <b>JBN-1</b>         | 10,2                      | <b>JOR-2</b>          | 1,6                       | Estromatólitos estratiformes com gipso (DM2) e (R D) |
| <b>JBN-2</b>         | 10,4                      | <b>JOR-3</b>          | 1,8                       |                                                      |
| <b>JBN-4</b>         | 10,8                      | <b>JOR-4</b>          | 2,0                       |                                                      |
| <b>JBN-5</b>         | 11,0                      | <b>JOR-6</b>          | 2,4                       |                                                      |
| <b>JBN 6</b>         | 11,2                      |                       |                           |                                                      |
| <b>JBN 7</b>         | 11,4                      |                       |                           |                                                      |
| <b>JBN-8</b>         | 11,6                      | <b>JOR-7</b>          | 2,6                       |                                                      |
| <b>JBN-9</b>         | 11,8                      | <b>JOR-14</b>         | 4,0                       |                                                      |
| <b>JBN-10</b>        | 12,0                      | <b>JOR-24</b>         | 6,0                       |                                                      |
| <b>JBN 12</b>        | 12,4                      |                       |                           |                                                      |
| <b>JBN 14</b>        | 12,8                      |                       |                           |                                                      |
| <b>JBN-15</b>        | 13,0                      | <b>JOR-26</b>         | 6,40                      |                                                      |
| <b>JBN- 18</b>       | 13,6                      |                       |                           |                                                      |
| <b>JBN-21</b>        | 14,2                      | <b>JOR-33</b>         | 7,80                      |                                                      |
| <b>JBN 23</b>        | 14,6                      | <b>JOR 36</b>         | 8,40                      |                                                      |
| <b>JBN-28</b>        | 15,1                      |                       |                           |                                                      |
| <b>JBN-29</b>        | 15,3                      |                       |                           |                                                      |
| <b>JBN-33</b>        | 16,6                      | <b>JOR-41</b>         | 9,40                      |                                                      |
| <b>JBN 36</b>        | 17,2                      |                       |                           |                                                      |
| <b>JBN-38</b>        | 17,6                      | <b>JOR-50</b>         | 11,2                      |                                                      |
| <b>JBN-39</b>        | 17,8                      | <b>JOR-54</b>         | 12,0                      |                                                      |

(continuação)

| <b>Amos-<br/>tra</b> | <b>Profundi-<br/>dade</b> | <b>Amos-<br/>tras</b> | <b>Profundi-<br/>dade</b> | <b>Microfácies/Fácies</b>                       |
|----------------------|---------------------------|-----------------------|---------------------------|-------------------------------------------------|
| <b>JBN-43</b>        | 18,6                      | <b>JOR-58</b>         | 12,8                      |                                                 |
| <b>JBN-45</b>        | 19,0                      |                       |                           |                                                 |
| <b>JBN- 47</b>       | 19,4                      |                       |                           |                                                 |
| <b>JBN-49</b>        | 19,8                      | <b>JOR-66</b>         | 14,4                      |                                                 |
| <b>JBN -52</b>       | 20,4                      |                       |                           |                                                 |
| <b>JBN-57</b>        | 21,4                      | <b>JOR-67</b>         | 14,6                      |                                                 |
| <b>JBN-60</b>        | 22,0                      | <b>JOR-72</b>         | 15,6                      |                                                 |
| <b>JBN- 62</b>       | 22,4                      |                       |                           |                                                 |
| <b>JBN-68</b>        | 23,6                      | <b>JOR-76</b>         | 16,4                      |                                                 |
| <b>JBN-69</b>        | 23,8                      | <b>JOR-79</b>         | 17,0                      |                                                 |
| <b>JBN-71</b>        | 24,2                      | <b>JOR-93</b>         | 19,8                      |                                                 |
| <b>JBN-72</b>        | 24,4                      | <b>JOR-94</b>         | 20,0                      | Estromatólitos dômicos com estruturas tubulares |
|                      |                           | <b>JOR 98</b>         | 20,8                      |                                                 |
| <b>JBN-78</b>        | 25,6                      | <b>JOR-110</b>        | 23,2                      |                                                 |
| <b>JBN-80</b>        | 26,0                      | <b>JOR-121</b>        | 25,4                      |                                                 |
| <b>JBN-83</b>        | 26,6                      | <b>JOR-133</b>        | 27,8                      |                                                 |
| <b>JBN-88</b>        | 27,6                      | <b>JOR-146</b>        | 30,4                      |                                                 |
|                      |                           | <b>JOR 153</b>        | 31,8                      |                                                 |
| <b>JBN-91</b>        | 28,2                      | <b>JOR-160</b>        | 33,2                      |                                                 |
|                      |                           | <b>JOR 161</b>        | 33,4                      |                                                 |
| <b>JBN-93</b>        | 28,6                      | <b>JOR-171</b>        | 35,4                      |                                                 |
| <b>JBN-94</b>        | 28,8                      | <b>JOR-183</b>        | 37,8                      |                                                 |

(conclusão)

| <b>Amos-<br/>tra</b> | <b>Profundi-<br/>dade</b> | <b>Amos-<br/>tras</b> | <b>Profundi-<br/>dade</b> | <b>Microfácies/Fácies</b>                       |
|----------------------|---------------------------|-----------------------|---------------------------|-------------------------------------------------|
| <b>JBN-95</b>        | 29,0                      |                       |                           | Dolograinstone/Dolomudstone Peloidal            |
| <b>JBN-96</b>        | 29,2                      | <b>JOR-188</b>        | 38,8                      |                                                 |
| <b>JBN-97</b>        | 29,4                      | <b>JOR-191</b>        | 39,4                      |                                                 |
|                      |                           | <b>JOR-192</b>        | 39,6                      |                                                 |
| <b>G-1</b>           | Subsuperfície             |                       |                           | Estromatólitos dômicos com estruturas tubulares |
| <b>G1-B</b>          |                           |                       |                           |                                                 |
| <b>G1-C</b>          |                           |                       |                           |                                                 |
| <b>G-2</b>           | Subsuperfície             |                       |                           | Dolograinstone/Dolomudstone Peloidal            |
| <b>G-4</b>           |                           |                       |                           |                                                 |
| <b>G-5</b>           |                           |                       |                           |                                                 |
| <b>G5-B</b>          |                           |                       |                           |                                                 |

## 2.4 CATODOLUMINESCÊNCIA

Este estudo também contou com o auxílio da microscopia acoplada ao aparelho de catodoluminescência, que estimula a luminescência em seções polidas por meio do bombeamento de elétrons. A luminescência é influenciada pelas características composicionais (Hemmig *et al.* 1989). As imagens fornecem a distribuição espacial dos elementos traços, principalmente  $\text{Fe}^{2+}$  e  $\text{Mn}^{2+}$  em calcita e dolomita, contribuindo para detalhes sobre a composição e disposição dos tipos de cimento carbonático. Isso demonstra as diferenças nas fases de cimentação, permitindo o ordenamento de eventos diagenéticos e auxiliando na identificação de conteúdo siliciclástico quando presente, disperso na matriz das rochas estudadas. As imagens de catodoluminescência foram obtidas utilizando um microscópio óptico Leica, modelo DM 4500 PLED,

acoplado ao aparelho de catodoluminescência Optical CL 8200 mk5-2 do Laboratório de Catodoluminescência do Instituto de Geociências (LabCatodo-UFPA). As condições de análise foram as seguintes: corrente elétrica variando de 14,9 a 15,1 kV, voltagem de aceleração variando de 296 a 442 A, e tempo de exposição de 10,8 segundos. A interpretação dos dados de catodoluminescência, como zonação, crescimento anômalo, variação composicional das fases minerais e a gênese dos fluidos precipitados, será baseada em trabalhos anteriores de Machel (1985), Haberman *et al.* (1994), Pagel (2000), Budd *et al.* (2000), Richter (2003), Götze (2012) e Shuster *et al.* (2018).

## 2.5 MICROSCOPIA ELETRÔNICA DE VARREDURA (MEV)

A análise utilizando microscopia eletrônica de varredura (MEV) e imagens de elétrons retroespalhado (BSE), apoiada pela espectroscopia por dispersão de energia (EDS), foi realizada no Laboratório de Microanálise da Universidade Federal do Pará em seções delgadas previamente revestidas com ouro para caracterizar as fases minerais em termos texturais e químicos. As condições operacionais para as imagens de elétrons secundários e retroespalhado foram as seguintes: corrente do feixe de elétrons = 80  $\mu$ A, voltagem de aceleração constante = 20 kV, distância de trabalho = 8,5 mm. A análise EDS foi realizada utilizando o microscópio eletrônico de varredura Zeiss SIGMA-VP com o sistema EDS IXRF Sedona-SD acoplado. As condições operacionais para a análise EDS foram uma corrente do feixe de elétrons de 80  $\mu$ A, uma voltagem de aceleração constante de 20 kV, uma distância de trabalho de 10,1 mm e um tempo de contagem de análise de elementos de 30 segundos.

## 2.6 MICROSSONDA

As análises utilizando Micro-analizador de Sonda Eletrônica (EPMA) foram realizadas utilizando um JEOL 8230 com cinco espectrômetros de dispersão de energia (WDS) no Departamento de Geologia da Universidade Estadual Paulista (UNESP), Brasil. Foram utilizados blocos polidos. As condições para as análises pontuais quantitativas estão resumidas na Tabela Suplementar 8.2. Para as análises de mapeamento, a voltagem de aceleração foi ajustada para 15 kV e a corrente da sonda para 15 nA. Mg, Ca, Sr e Mn foram adquiridos no modo WDS, enquanto Al, Si, P e Fe foram adquiridos simultaneamente no modo EDS. Imagens de catodoluminescência, elétrons secundários e elétrons retroespalhado também foram adquiridas. O tamanho do passo e o tempo de permanência variaram dependendo do tamanho da área de mapeamento. O limite de detecção da análise por microsonda foi de aproximadamente 280 ppm para cada elemento.

## 2.7 ESPECTROSCOPIA MICRO-RAMAN

Os espectros Raman foram realizados no Laboratório de Astrobiologia-AstroLab do Instituto de Química da Universidade de São Paulo-USP, utilizando o Renishaw inVia Reflex acoplado a um microscópio Leica DM2500 M, contendo lasers com excitação a 632,8 nm (He-Ne, Renishaw) - 50 mW -, 785 nm (diodo laser, Renishaw) - 500 mW - e 532 nm (diodo laser, Renishaw) - 500 mW -. O equipamento também possui duas grades de difração, uma com 1200 linhas (usada com os lasers de 632,8 ou 785 nm) e outra com 2400 linhas (usada com o laser de 532 nm), e um detector CCD termoelétrico resfriado (1040 x 256 pixels). Para as análises foram utilizados a objetiva de 50x, um tempo de exposição de 2 segundos e 30 acumulações. Os dados coletados foram analisados no software SpectrGryph 1.2.

## 2.8 DIFRAÇÃO DE RAIOS-X

As análises de difração de raios-X foram realizadas no Laboratório de caracterização Mineral (LCM) no Instituto de Geociências da Universidade Federal do Pará. A difração de raios X em pó foi utilizada para caracterizar as fases presentes e determinar a composição e o grau de ordem dos cátions para as fases dolomita. Trinta amostras foram utilizadas para o método de pó total, com ~ 1g de cada amostra. Uma micro-broca foi utilizada para individualizar a matriz de cimento e as fases analisadas. Análises de difração de raios X (DRX) foram realizadas utilizando o Difractômetro de Raios X modelo Empyrean da PANalytical, com tubos de raios X cerâmicos, anodo de cobalto ( $K\alpha_1 = 1.789010 \text{ \AA}$ ), foco fino longo, filtro de Fe K $\beta$ , detector PIXCEL3D-Medpix3 1x1, em modo de varredura, com voltagem de 40 kV, corrente de 35 mA. O intervalo de varredura foi de 2° a 80° 2 $\theta$ , tamanho do passo de 0.026° em 2 $\theta$ , e um tempo/passagem de 31 s. Fenda divergente: 1/4° e fenda anti-dispersão: 1/2°, máscara: 10 mm. A aquisição de dados foi realizada utilizando o software X'Pert Data Collector, versão 5.1, e o processamento de dados com o software X'Pert HighScore Plus, versão 5.0, também da PANalytical. A identificação mineral foi realizada comparando o difratograma obtido com padrões (cartões) dos bancos de dados ICDD-PDF (International Center for Diffraction Data - Powder Diffraction File) e COD (Crystallography Open Database). O grau de ordem dos cátions é relatado como a razão dos picos de reflexão da superrede d015:d110 seguindo os métodos de Goldsmith & Graf (1958).

## 2.9 NANO FLUORESCÊNCIA DE RAIOS-X (LUZ SINCROTON)

As análises de nano-FRX foram realizadas no Laboratório Nacional de Luz Síncrotron, Sirius, na estação terminal Tarumã da linha de luz Carnaúba. O mapeamento por Fluorescência de Raios X em Nanoescala ( $\mu$ -XRF) com radiação síncrotron foi conduzido em 14 lâminas polidas, empregando modo de microfeixe, com excitação policromática filtrada por folhas de Ca e Fe. As dimensões do feixe ( $12 \times 25 \mu\text{m}$ ) foram alcançadas utilizando um sistema de focalização KB na linha Carnauba feixe XRF do Laboratório Nacional de Luz Síncrotron (LNLS), Brasil. O mapeamento foi realizado com passos de  $20 \mu\text{m}$  e tempo de acumulação de 0,2 s/ponto. As medições foram realizadas utilizando um feixe monocromático com energia de 9 keV e 12 keV, com aquisição realizada em modo de varredura contínua. Os dados foram processados utilizando o software PyMca 4.6.0 (desenvolvido pelo *European Synchrotron Radiation Facility* ESRF, Solé *et al.* 2007) para gerar concentrações elementares em mapas semiquantitativos.

## 2.10 GEOQUÍMICA

No total, 97 amostras foram analisadas da capa dolomítica (Formação Mirassol d'Oeste) e capa calcária (Formação Guia) do carbonato de capa de Puga, no sul do Cráton Amazônico (Figura 2.1). Dessas 97 amostras, 37 foram coletadas em afloramentos da mina Terconi na região de Mirassol d'Oeste e 60 foram coletadas na mina Calcário Tangará, na região de Tangará da Serra com 42 amostras sendo retiradas de testemunhos de sondagem (JOR) e 19 amostras de afloramentos. As amostras seguiram a estratigrafia proposta e o critério de fácies/microfácies apresentado por Nogueira *et al.* (2003), Sansjofre *et al.* (2014), Santos *et al.* (2023).

### 2.10.1 Geoquímica de elementos maiores e menores

#### 2.10.1.1 Geoquímica - Dissolução Parcial

No total, 42 amostras do testemunho de sondagem JOR (Fig. 2.3), da capa dolomítica da seção de Tangará da Serra, foram preparadas para concentrações principais e menores para evitar contribuições de REE de componentes não carbonáticos (por exemplo, argilas e óxidos), seguindo o protocolo de digestão de Rongemaille *et al.* (2011). Aproximadamente 20 mg de pó da amostra foram pesados em tubos de micro-centrífuga de 2,5 mL limpos com ácido, e 0,5 mL de ácido acético de grau traço a uma concentração de 0,85 N (ou seja, 5%) foi adicionado e deixado para dissolver as amostras durante a noite à temperatura ambiente. As amostras foram centrifugadas, e alíquotas de 0,25 mL do sobrenadante foram diluídas em 4,75 mL de ácido

nítrico destilado em PFA preparado para uma concentração de 0,45 N HNO<sub>3</sub> (ou seja, 2%) com 10 ppb de índio como padrão interno para controlar o desvio instrumental. As análises foram conduzidas em um espectrômetro de massa de plasma acoplado indutivamente de alta resolução Thermo Scientific ELEMENT XR (HR ICP-MS) do Pôle Spectrométrie Océan (PSO) no Institut *Universitaire Européen de la Mer, Université de Bretagne Occidentale*, França. O uso de modos de baixa, média e alta resolução permitiu a medição de concentrações principais/menores/traços/REE + Y em um fator de diluição constante durante uma única sessão analítica. Análises repetidas do material de referência padrão CAL-S (N = 15) mostraram uma precisão de 1σ de 7-9%, com resultados dentro de 10% dos valores publicados. As concentrações foram determinadas por calibração externa com uma solução de calibração sintética compatível com a matriz.

#### 2.10.1.2 Geoquímica – Rocha total

Foram analisadas 56 amostras de afloramento, sendo 37 da seção Terconi e 19 da seção Tangará, utilizando dissolução total. Fragmentos de rocha livres de fraturas aparentes ou recristalização foram cuidadosamente selecionados e triturados em um almofariz de ágata. A análise química foi realizada por ICP-AES (elementos principais e menores) e ICP-MS (elementos traços) no laboratório espectroquímico (SARM) do Centre de Recherches en Pétrographie et Géochimie em Vandœuvre-les-Nancy. As amostras foram preparadas por fusão com LiBO<sub>2</sub> (980 °C durante 60 min), seguida de dissolução em uma mistura de HNO<sub>3</sub> (1 mol L<sup>-1</sup>) - H<sub>2</sub>O<sub>2</sub> (~0.5% v/v) - glicerol (~10% v/v) para obter uma solução diluída (Carignan *et al.* 2001). A precisão e a exatidão foram melhores que 1% do valor medido (média de 0,5%) para elementos principais e menores e 8% para metais traços, conforme verificado por padrões internacionais e análise de amostras replicadas (Carignan *et al.* 2001).

### 2.11 ISÓTOPOS DE CARBONO E OXIGÊNIO

#### 2.11.1 δ<sup>13</sup>C e δ<sup>18</sup>O - testemunho JOR

No total, 44 amostras do testemunho de perfuração JOR (Fig. 2.1), da capa dolomítica da seção Tangará, foram preparadas para análises de isótopos estáveis e realizadas no Museu Nacional de História Natural em Paris, na plataforma SSMIM. As amostras foram primeiramente moídas em pó em um almofariz de ágata. O CO<sub>2</sub> foi extraído por dissolução com H<sub>3</sub>PO<sub>4</sub> a 100% a 70 °C sob vácuo primário. As composições isotópicas estáveis de carbono e oxigênio do CO<sub>2</sub> produzido foram medidas usando um dispositivo Kiel IV Carbonate. Os padrões NBS-

19 (internacional), MarbreLM (interno ao SSMIM) e CAMIL-21 foram utilizados para corrigir a linearidade dos espectrômetros de massa e calibrar os dados. Utilizando os padrões, uma curva de referência foi projetada para determinar a porcentagem de carbonatos na amostra. Por fim, os resultados são expressos em ‰ na escala V-PDB. Os resultados são apresentados em notação  $\delta$  em relação aos Padrões Internacionais V-PDB para  $\delta^{13}\text{C}$  e  $\delta^{18}\text{O}$ . A reprodutibilidade externa para medições de  $\delta^{13}\text{C}$  e  $\delta^{18}\text{O}$  é de 0,1‰ e 0,15‰, respectivamente ( $1\sigma$ ).

### 2.11.2 $\delta^{13}\text{C}$ e $\delta^{18}\text{O}$ - testemunho JBN

Cinquenta amostras foram coletadas de um testemunho JBN-10 (Fig. 2.2), correspondendo à capa dolomítica, porção basal da Formação Mirassol d'Oeste na seção de Tangará da Serra-MT. Um almofariz e pistilo de ágata foram utilizados para pulverizar aproximadamente 3 g de cada uma das seis porções mais homogêneas de cada amostra. Para obter uma maior precisão foi utilizado uma broca de diamante com diâmetro aproximado de 1 mm, para evitar porções recristalizadas ou aquelas afetadas por fluidos diagenéticos. As amostras foram analisadas no Laboratório de Químioestratigrafia e Geoquímica Orgânica (LGQM) da Universidade Estadual do Rio de Janeiro (UERJ) usando um Dispositivo de Carbonato Kiel IV e um analisador de Espectrômetro de Massa de Razão de Isótopos Delta V Plus (Thermo Scientific). Foram seguidos os procedimentos recomendados por Craig (1957). Inicialmente, as amostras foram colocadas em recipientes plásticos, previamente lavados com água destilada e álcool, e deixadas secar ao ar. Posteriormente, foram reagidas com ácido ortofosfórico a 100% a 25°C por 12 horas. Os resultados são apresentados em notação  $\delta$  (‰) calibrada para V-PDB (*Vienna Pee Dee Belemnite*).

## 2.12 ISÓTOPOS ESTRÔNCIO-NEODÍMIO

As análises de isótopos de rocha total foram realizadas no Laboratório de Geologia Isotópica (LGI) do Centro de Estudos em Petrologia e Geoquímica (CPGq), Universidade Federal do Rio Grande do Sul (UFRGS) e no Laboratório de Geocronologia do Instituto de Geociências, Universidade de Brasília (UNB), sendo 18 amostras na UFRGS, 10 em diamictitos e 8 em carbonatos, enquanto 6 amostras de carbonatos foram analisadas na UNB.

Aproximadamente 10-20 ml da solução estoque de lixiviação com ácido acético foram utilizados para medidas da composição isotópica de Sr e Nd em rochas carbonáticas. As alíquotas foram secas, tratadas três vezes com 1 ml de  $\text{HNO}_3$  concentrado a 110°C, e equilibradas em HCl 2,5 M. Para amostras de diamictitos, alíquotas contendo aproximadamente 100 mg de amostra foram pesadas em uma balança de alta precisão e dissolvidas em etapas, incluindo o



uso de uma mistura ácida concentrada de HNO<sub>3</sub> e HF em frascos de PFA Savillex® e uma placa quente, seguida por tratamento com HCl concentrado. Para as análises de Sm/Nd dos diamictitos, aproximadamente 100 µg de pó da amostra foi misturado com uma solução de spike de <sup>149</sup>Sm/<sup>150</sup>Nd em frascos Savillex. Quaisquer resíduos foram dissolvidos com água régia até que a solução ficasse clara. Após secagem, o material foi diluído em HCl 2,5 M para gerar uma solução estoque. Os reagentes foram pré-diluídos, e as diluições foram feitas com água Milli-Q ultrapura. A extração de Sr e REE foi realizada utilizando lavagens ácidas em colunas de Teflon com resina de troca catiônica Biorad AG® 50W-X8. A partir da fração de REE concentrada, o Nd foi separado usando colunas de quartzo e resina Eichron Ln Spec. Os concentrados de Sr e Nd foram coletados em frascos Savillex® e secos em uma placa quente para análise subsequente por espectrometria de massa.

### 2.12.1 Procedimentos Analíticos

Para análise, os sais de Sr e Nd foram dissolvidos em 2 µL de ácido fosfórico (H<sub>3</sub>PO<sub>4</sub>, 0,25 M) e 2 µL de ácido nítrico (HNO<sub>3</sub>, 0,25 M), respectivamente. Filamentos duplos de rênio pré-desgaseificados foram utilizados. As análises foram realizadas utilizando o espectrômetro de massa de ionização térmica multicoletor Thermo Scientific™ TRITON (TIMS) na UFRGS. Simultaneamente, ICP-MS (Espectrômetro de Massa de Plasma Induzido por Alta Resolução da Série Neptune) equipado com 9 detectores de copo Faraday, um multiplicador de elétrons central e 5 contadores de íons do tipo MIC (multi-ion channel) foi utilizado na UNB. Para Sr, foram obtidas razões isotópicas de 150 para cada amostra, integradas e normalizadas para  $^{86}\text{Sr}/^{88}\text{Sr} = 0,1194$ . Para Nd, foram obtidas razões isotópicas de 210 para cada amostra sempre que possível, com base em análises repetidas do padrão internacional JNdi. A razão  $^{146}\text{Nd}/^{144}\text{Nd}$  foi normalizada para a razão  $^{146}\text{Nd}/^{144}\text{Nd}$  de 0,7219. A análise dos materiais de referência NBS-987 (Sr) e JNdi (Nd) para monitoramento de variação instrumental forneceu resultados dentro da faixa histórica do laboratório, consistentes com relatórios da literatura. Não foi necessária correção para desvio analítico instrumental. Análises de branco e material de referência (BHVO-2 e BCR-2) são rotineiramente realizadas para monitoramento de controle de qualidade. Após a redução, os valores de TDM são calculados usando o modelo de De Paolo (1981).

### 3 CAPÍTULO 3 CONTEXTO GEOLÓGICO

#### 3.1 BACIA ARARAS ALTO PARAGUAI

As sucessões carbonáticas e siliciclasticas do sul do Cráton Amazônico foram consideradas exclusivamente de idade Ediacarana e incluídas em uma única bacia do tipo *foreland* com áreas offshore profundas em direção ao sudeste (Almeida 1964). Esses depósitos foram inicialmente inseridos no contexto da Faixa de dobramento Paraguai, associado ao Evento Brasileiro / Pan-Africano, que envolveu os blocos continentais Amazônia, São-Francisco-Congo e Paraná (Almeida 1964, Trompette *et al.*1998, Trindade *et al.*2003, Alvarenga *et al.*2007, Nogueira *et al.*2007, Tohver *et al.*2010, Bandeira *et al.*2012, McGee *et al.*2015). No entanto, estudos recentes demonstraram que as sucessões siliciclasticas-carbonáticas foram deformadas por tectônica transtensional (Nogueira *et al.*2019, Santos *et al.*2020). A tectônica colisional foi observada apenas nas rochas metamórficas do Grupo Cuiabá (Faixa Paraguai) que marcam a suturas dos crátons adjacente (Nogueira *et al.*2019, Santos *et al.*2020). Sendo assim a porção norte da Faixa Paraguai previamente definida como “Faixa Paraguai Norte” foi redefinida por Nogueira *et al.* (2019) como uma Bacia Intracratônica, denominada Araras-Alto Paraguai (Fig. 3.1).

A Bacia Araras-Alto Paraguai foi instalada durante o Criogeniano-Ordoviciano no Sudeste do Cráton Amazônico, influenciada por um regime de subsidência termal extensional (Cordani *et al.*2013, Nogueira *et al.*2019, Santos *et al.*2020). Essa bacia sobrepõe rochas do embasamento cristalinas e metamórficas do Grupo Cuiabá que caracterizam a Faixa de dobramentos Paraguai. O preenchimento basal desta bacia é composto por rochas do Criogeniano da Formação Puga (pelitos, arenitos e diamictitos glaciais) sobreposta por rochas carbonáticas do Ediacarano do Grupo Araras que consiste em quatro formações (Fig. 3.4): 1) Formação Mirasol d'Oeste, composta por capas dolomíticas interpretado como ambiente de plataforma rasa, 2) Formação Guia composta por carbonatos e folhelhos, interpretados como plataforma moderadamente profunda, 3) Formação Serra do Quilombo, composta por plataformas dolomíticas rasa a moderadamente profunda, e 4) Formação Nobres que consiste em dolomitos relacionado a ambiente de maré (Nogueira & Riccomini 2006, Nogueira *et al.*2007, Rudnitzki *et al.*2016, Nogueira *et al.*2019).

O soerguimento progressivo culminou com a erosão da sucessão sedimentar superior do Grupo Araras, Formação Nobres, com idade máxima estimada em 614 Ma (Nogueira *et al.*2022, Romero *et al.*2022). Esta erosão ficou registrada em uma discordância no Grupo

Araras Superior, sobreposta por depósitos siliciclásticos do Grupo Alto-Paraguai do Cambriano-Ordoviciano (Nogueira *et al.* 2019, 2022, Santos *et al.* 2017, Romero *et al.* 2022). O Grupo Alto Paraguai foi previamente interpretado como de idade Ediacarana (Bandeira *et al.* 2012), no entanto uma idade Cambriana foi inferida para a Formação Raizama, base dos depósitos, com base na presença de traços fósseis da icnofácies *Skolithos* (Santos *et al.* 2017). Estes novos indícios, colocam uma complexidade na história de sedimentação da bacia, uma discordância de aproximadamente 80 milhões de anos na bacia intracratônica Araras-Alto Paraguai (Santos *et al.* 2017, Nogueira *et al.* 2019, 2022).

As rochas siliciclasticas, Cambriano-Ordoviciano, do Grupo Alto Paraguai, encerra o registro de sedimentação da bacia Araras-Alto Paraguai (Bandeira *et al.* 2012, Santos *et al.* 2017, Nogueira *et al.* 2022). A sucessão siliciclástica do Grupo Alto Paraguai foi depositada em discordância sobre o Grupo Araras, interpretada como depósitos fluvio-costeiro e de plataforma rasa, relacionados as formações Raizama e Sepotuba, e depósitos lacustres-deltaicos da Formação Diamantino (Bandeira *et al.* 2012, Santos 2018). A descoberta da idade Cambriano-Ordoviciano (?) para o Grupo Alto Paraguai também abre perspectiva de se entender a implantação da Bacia no contexto do Gondwana Oeste, formado após a quebra do Rodinia no final do Neoproterozoico (Hoffman, 1999, Li *et al.* 2008, Cordani *et al.* 2013, Santos *et al.* 2014, Shields-Zhou *et al.* 2016 Spence *et al.* 2016, Santos *et al.* 2017, Santos *et al.* 2020).

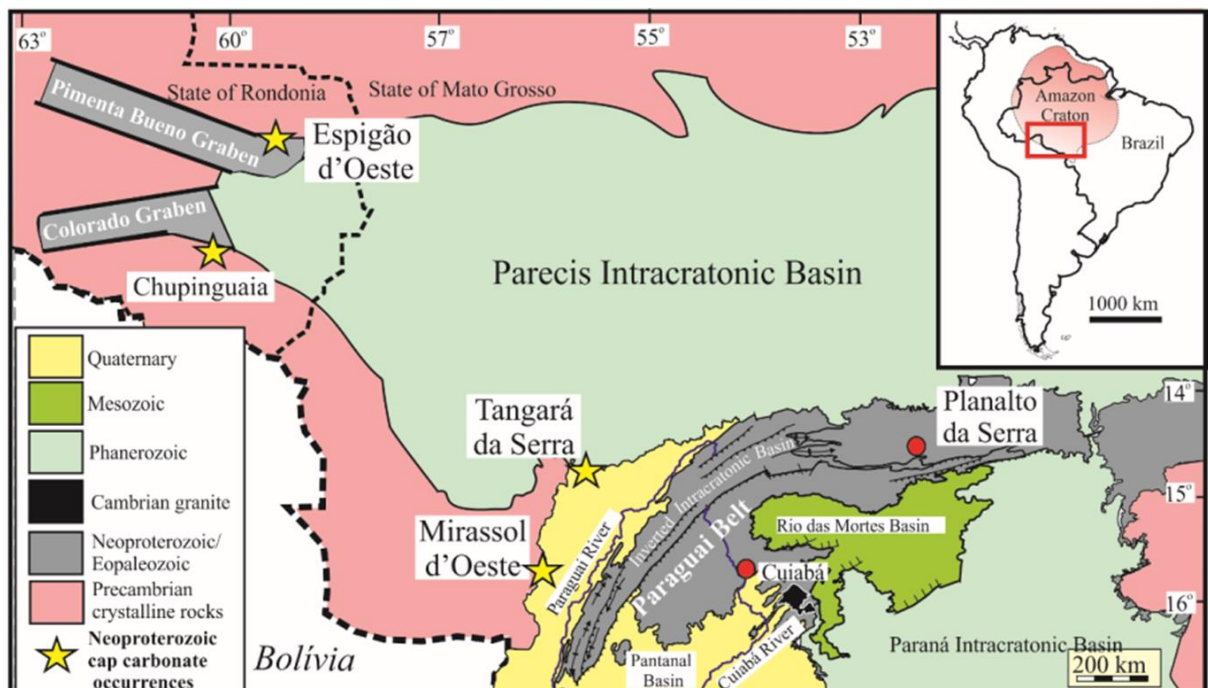


Figura 3.1- Mapa geológico simplificado do sudeste do Cráton Amazônico. Mostrando o contexto da bacia intracratônica, Araras Paraguai, a norte da faixa de dobramentos Paraguai e Sudeste do Cráton Amazônico. Destaque para a localização das ocorrências de capa carbonática Puga. Extraído de Nogueira *et al.* (2019).

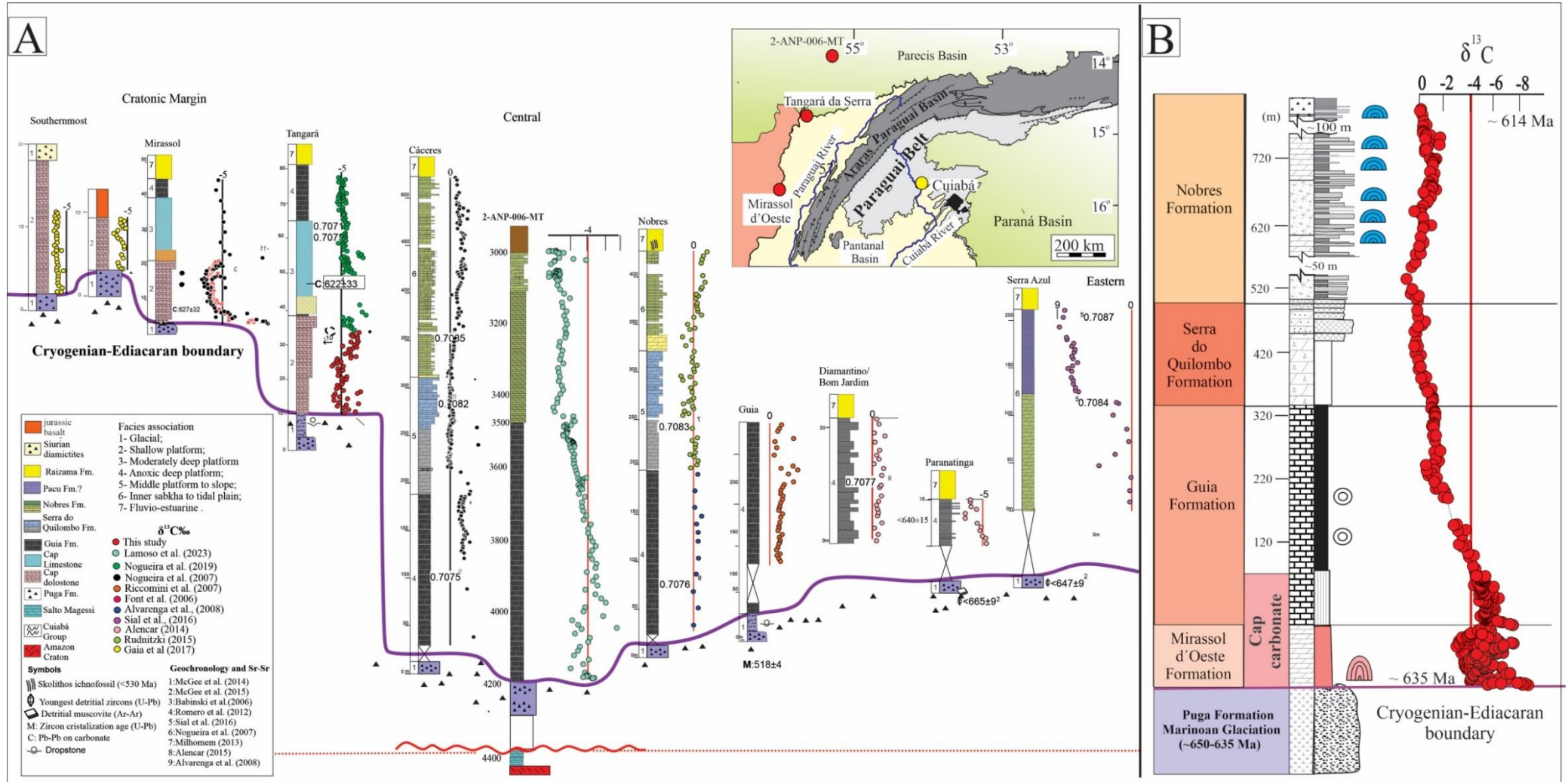


Figura 3.2- A) Correlação estratigráfica de sequência carbonática e quimioestratigrafia do Grupo Araras, na bacia Araras-Alto Paraguai, com proposta de uma curva de referência de  $\delta^{13}C$  para o Cráton Amazônico para o intervalo ~ 635–614 Ma em B). Grupo Araras seguindo a estratigrafia proposta por Nogueira & Riccomini, 2006. Correlação lito-, quimio- e estratigráfica da sucessão de capa carbonática Puga (área cratônica) Nogueira *et al.* 2003, 2019, Font *et al.* 2006, Gaia *et al.* 2017, Soares *et al.* 2020, Santos *et al.* 2021. Correlação litoestratigráfica, quimioestratigráfica e estratigráfica de sequência do Grupo Araras no domínio norte do Cinturão Paraguai (Nogueira *et al.* 2007, Rudninski, 2015, Alvarenga *et al.* 2004, 2008, Brelaz 2012, Alencar 2017, Souza 2015). Grupo Araras na bacia Parecis (Lamoso *et al.* 2023). Idade Pb/Pb capa dolomítica 10) (Babinski 2011), 11) por Babinski *et al.* (2006): e idade Pb/Pb da capa calcária por 12) Romero *et al.* (2013), 13) Souza *et al.* (2024), e U/Pb *in situ* em leques cristalinos por 14) Carvalho *et al.* (2023).

### 3.2 CAPA CARBONÁTICA PUGA, SUL DO CRÁTON AMAZÔNICO.

A sucessão de capa carbonática Marinoana (~635 Ma) ocorre em ao menos quatro localidades no Cráton amazônico, na região de Mirassol d'Oeste, Tangará da Serra em Mato Grosso, Espigão d'Oeste e Chupinguaia em Rondônia. As fácies são similares e correlacionáveis lateralmente por centenas de km (Nogueira *et al.* 2003, 2019, Gaia *et al.* 2017, Soares *et al.* 2020). As unidades basais da Bacia Araras-Alto Paraguai constituem a sucessão de capa carbonática Puga, iniciada por depósitos glaciomarinho da Formação Puga, sobrepostos a estes ocorrem depósitos carbonáticos com estruturas anômalas relacionado as capas carbonáticas, a capa dolomita é associada a Formação Mirassol d'Oeste enquanto a capa calcária a base da Formação Guia. (Nogueira *et al.* 2003, 2007, 2019, Soares *et al.* 2013, 2020, Romero *et al.* 2020, Santos *et al.* 2021). A base da capa dolomítica é predominantemente composta por estromatólitos estratiformes com pseudomorfo de gipso, estromatólitos dômicos gigantes com estruturas tubulares associadas, *Dolomudstone* peloidal com laminação paralela, *Dolograinstone* peloidal com laminação quasi-planar e *Dolopackstone* peloidal com *megaripples*. A capa calcária é composta principalmente por calcários com *megaripples*, laminações onduladas, quasi-planar e leques de cristais de calcita (pseudomorfo de aragonita), e pelitos laminados subordinados (Nogueira *et al.* 2003, 2019, Soares *et al.* 2020, Romero *et al.* 2020, Santos *et al.* 2021)

Estes depósitos carbonáticos depositados sobre diamictitos indicam as mudanças das condições climáticas pós-Marinoana, *Icehouse* para *Greenhouse*, no sudeste do Cráton Amazônico (Hoffman & Scharg 2002, Nogueira *et al.* 2003, 2007, 2019). As idades obtidas para a capa carbonática Puga foi através de datação Pb-Pb, e obteve idades de  $627 \pm 32$  Ma e  $622 \pm 33$  Ma para capa dolomita e capa calcária, respectivamente, indicando uma idade Ediacarana inferior (Babinski *et al.* 2006, Romero *et al.* 2013). Estas idades foram corroboradas por valores isotópicos de  $\delta^{13}\text{C}$  de -5 ‰ na capa dolomítica a -2 ‰ na capa calcária, além dos valores de  $^{87}\text{Sr}/^{86}\text{Sr}$  entre 0,7074 e 0,7089 comparáveis com curvas globais (ex. Grupo Otavi, Namíbia) (Nogueira *et al.* 2019).



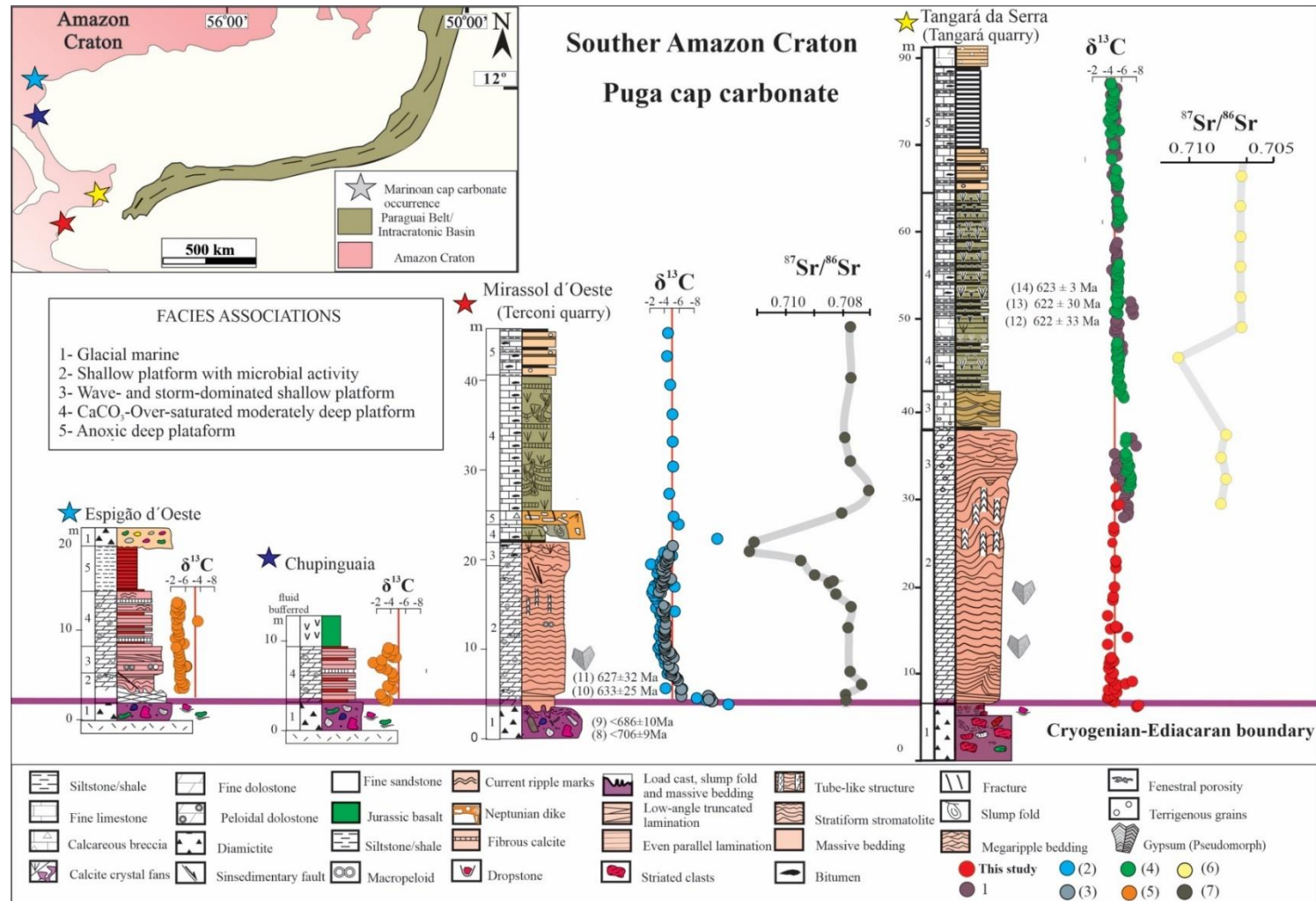


Figura 3.3- Seções estratigráficas da sucessão de capa carbonática Puga, Marinoana ~635 Ma, Sul do Cráton Amazônico. pedreira RMC, região de Espigão d'Oeste, Estado de Rondônia, afloramento na região de Chupinguaia, Estado de Rondônia, pedreira Terconi, região de Mirassol d'Oeste, Estado de Mato Grosso, e pedreira Calcário Tangará, região de Tangará da Serra, Estado de Mato Grosso. As curvas de  $\delta^{13}\text{C}$  e  $^{87}\text{Sr}/^{86}\text{Sr}$  da capa carbonática no Cráton Amazônico, com valores em ‰, foram obtidas por 1) Nogueira *et al.* (2019), 2) Nogueira *et al.* (2019), 3) Font *et al.* (2006), 4) Sansjofre *et al.* (2011), 5) Gaia *et al.* (2017), 6) Romero *et al.* (2013), 7) Nogueira *et al.* (2007). Interpretação paleoambiental (associação de fácies) da capa carbonática Puga (Nogueira *et al.* 2003, 2007, 2019, Sansjofre *et al.* 2014, Gaia *et al.* 2017, Soares *et al.* 2020, Santos *et al.* 2021, 2023). Idades máximas de deposição de zircão detriticos para os diamictito da Formação Puga são reportadas como <706 ± 9 Ma por 8) Babinski *et al.* (2013) e <686 ± 10 Ma por 9) McGee *et al.* (2018) e idade Pb/Pb da capa dolomítica por 10) Babinski, 2011, 11) por Babinski *et al.* (2006): e idade Pb/Pb capa calcária por 12) Romero *et al.* (2013), 13) Souza *et al.* (2024), e U/Pb *in situ* em leques de cristais de pseudomorfos de aragonita por 14) Carvalho *et al.* (2023).

### 3.3 FORMAÇÃO PUGA

A Formação Puga, base da sucessão, compreende uma associação de fácies relacionadas a um ambiente glaciomarinho, diamictitos maciços e estratificado, polimítico e *dropstones*, a unidade faz contato erosivo aos depósitos metamórficos do Grupo Cuiabá (Faixa de dobramentos Paraguai) com uma discordância erosiva e angular (Nogueira *et al.* 2003, 2019, Alvarenga *et al.* 2011). Os clastos estão dispersos em uma matriz siliciclástica fina de cor cinza-esverdeada a cinza-avermelhada, com diâmetros variando de alguns centímetros a 1 metro. Os clastos consistem principalmente de rochas do embasamento (por exemplo, granito, gnaiss, quartzito, quartzos, xistos), alguns desviando laminações subjacentes, facetados e estriados, e abundante mica detrítica. O diamictito maciço exibe variações nas proporções da matriz (areia lamacenta) e clastos (Alvarenga & Trompette, 1992, Nogueira *et al.* 2003, Dantas *et al.* 2009, Alvarenga *et al.* 2011, Santos *et al.* 2023). O diamictito estratificado inclui camadas de alguns centímetros de espessura de diamictito maciço associado a pelitos exibindo estratificação graduada e clastos desviando laminações subjacentes (Nogueira *et al.* 2003, Alvarenga *et al.* 2011). A matriz de siltito/areia ocorre com *dropstones* de milímetros a centímetros de tamanho e varia em composição (por exemplo, arenito, gnaiss, granito, vulcânica) (Alvarenga & Trompette, 1992, Nogueira *et al.* 2003, Santos *et al.* 2023). A Formação Puga é interpretada como depósitos glaciomarinho associados aos eventos glaciais Marinoano (~650 - 635 Ma) no Cráton Amazônico (Nogueira *et al.* 2003, Alvarenga *et al.* 2011, Santos *et al.* 2021, 2023) e o estabelecimento da Bacia intracratônica Araras Alto-Paraguai (Nogueira *et al.* 2019, 2022, Santos *et al.* 2020). Idades máximas de deposição de zircão detríticos de  $706 \pm 9$  Ma foram relatadas por Babinski *et al.* (2013), enquanto McGee *et al.* (2018) obtiveram idades de  $< 686 \pm 10$  Ma para a mesma unidade. Além disso, Dantas *et al.* (2009), empregando Sm/Nd, demonstraram que as idades-modelo das diamictites são compatíveis com fontes predominantemente do Cráton Amazônico. Os diamictitos e *dropstones* caracterizam a Formação Puga, e são sobrepostos pelos depósitos de capa carbonática (Alvarenga *et al.* 2004, 2011, Nogueira *et al.* 2007, 2022). Os carbonatos da bacia Araras-Alto Paraguai são associados ao contexto do Grupo Araras (Nogueira & Riccomini 2006).

### 3.4 GRUPO ARARAS

O Grupo Araras é dividido em quatro formações de acordo com a proposta de Nogueira & Riccomini, 2006, da base para o topo: Formação Mirassol d'Oeste: Formação Guia, Formação Serra do Quilombo e Formação Nobres. A seguir, as principais características sedimentológicas e estratigráficas de cada unidade:

### 3.4.1 Formação Mirassol d'Oeste (Capa dolomítica)

A Formação Mirassol d'Oeste, capa dolomítica, exibe espessura de até 40 m, sendo constituída por *dolomudstone* rosado finamente laminado, disposto em camadas lateralmente contínuas por centenas de metros. Esta unidade está em contato com os diamictitos glaciais da Formação Puga, marcando a transição Criogeniano-Ediacarano, apresentam deformações sin-sedimentares no contato. Predominam neste litotipo estromatólitos planares fenestrais, dômicos com estruturas tubulares (Nogueira *et al.* 2003, Font *et al.* 2006, 2010, Soares *et al.* 2020, Romero *et al.* 2020, Santos *et al.* 2021, 2023). São reconhecidas duas associações de fácies para esta unidade, sugerindo deposição em um ambiente de plataforma rasa com atividade microbiana, que transita para uma plataforma rasa a moderadamente profunda, influenciada por ondas. As microfácies dentro da associação de plataforma rasa com atividade microbiana incluem: 1) Ds - doloboundstones estratiforme com pseudomorfo de gipso; 2) Dd - doloboundstones dômicos com tubestone. As microfáceis dentro da associação de plataforma rasa influenciada por ondas incluem: 1) Dp - dolomudstone/dolopackstone peloidal com laminações plano paralelas, 2) Dq - dolograstone/peloidal dolomudstone com laminações quasi-planar com truncamento de baixo ângulo. Restrições diagenéticas tem demonstrado a excelente preservação dos aspectos mineralógicos e texturais, os processos diagenéticos registrados nesta unidade estariam majoritariamente relacionados aos eventos Sin-Eodiagenéticos (Soares *et al.* 2020, Santos *et al.* 2021, 2023).

### 3.4.2 Formação Guia (Capa Calcária)

A capa calcária é associada a base da Formação Guia, apresenta uma espessura de ~40m, apresenta duas principais microfáceis, *Cements* e *Mudstone*, que formam camadas distintas e estão, portanto, intimamente associados. Subordinadamente, ocorrem marga dolomíticas, folhelhos betuminosos e brechas associadas a sucessão basal da Formação Guia. O folhelho é predominantemente calcítico (calcita microcristalina) com fissilidade bem desenvolvida, por isso é considerado pertencente à fácies argilito calcário. A marga dolomítica marca o contato entre as formações Mirassol d'Oeste (capa dolomítica) e Guia (capa calcária). A microfáceis *Mudstone* é caracterizada pela presença de calcita microcristalina e localmente intercalados com grãos terrígenos. A microfáceis *cementstone* é caracterizada exclusivamente pela ocorrência de cristais arborescentes de calcita nucleados na base de uma camada de finas crostas de cimento em escala milimétrica, formando leques com irradiação ascendente. Os leques de cristais de calcita ocorrem em arranjos isolados e em escala decimétrica, sendo considerados



pseudomorfos de aragonita. A associação de fácies da capa calcária indica plataformas rasas dominadas por ondas e ondas tempestades que transitam para uma plataforma profunda supersaturada em  $\text{CaCO}_3$  (Nogueira *et al.* 2003, 2007, 2019, Sansjofre *et al.* 2014, Soares *et al.* 2020, Carvalho *et al.* 2023). Os processos diagenéticos da capa calcária incluem: precipitação de pirita, cimentação de calcita, micrito e leques de cristais neomorfizados, dissolução parcial dos leques de cristais, dolomitização local, compactação química, fraturamento, precipitação de dolomita ferrosa e calcita (Soares *et al.* 2020, Carvalho *et al.* 2023).

### 3.4.3 Formação Guia

A Formação Guia é constituída por camadas tabulares, lateralmente contínuas por dezenas de quilômetros, representadas principalmente por calcários finos e folhelhos betuminoso de coloração cinza e, subordinadamente, brechas sinsedimentares., com mais de 400 m de espessura em afloramento. A Formação Guia nos domínios da faixa Paraguai Norte, os calcários ocorrem em contato com diamictitos glaciais da Formação Puga. Os calcários são principalmente *mudstones* calcíferos finamente laminados e calcários cristalinos subordinados (Nogueira & Riccomini 2006). O abundante desenvolvimento de planos de estilólitos paralelo ao acamamento muitas vezes forma uma fábrica fitada (*fitted fabric*) com concentrações de grãos terrígenos, oxic-hidróxido de ferro e matéria orgânica associados aos eventos de mesodiagenese (Soares *et al.* 2020). Estilólitos são comuns nas unidades basais do Grupo Araras. Na Formação Guia, fraturas são preenchidas com cimento de calcita e delimitadas por estilólitos paralelos ao estrato. Estas relações indicam precipitação prévia de calcita antes do sepultamento profundo desta unidade (Soares *et al.* 2020). Estudos recentes descrevem estilólitos tectônicos (subverticais) na Formação Guia, associados a um evento transtensional relacionado à geração de falhas sinistrais nos depósitos calcários da região de Paranatinga-MT (Seoane & Domingos 2021). Esta região foi afetada por eventos extensionais na Bacia Araras-Alto Paraguai (Santos *et al.* 2020). Por outro lado, os depósitos de capa carbonática não apresentam estilólitos tectônicos (subverticais), provavelmente devido à sua restrição geográfica à margem sul do Cráton Amazônico, região menos afetada por eventos extensionais (Nogueira *et al.* 2019, Santos *et al.* 2020, Santos *et al.* 2023).

Camadas de folhelhos betuminosos de até 1 m de espessura ocorrem intercalados aos calcários, muitas vezes formando ritimitos. A cor escura dos *mudstones* calcíferos e a presença de folhelhos betuminosos revelam a predominância de condições redutoras (anóxicas) e estagnantes, que proporcionaram o acúmulo e preservação da matéria orgânica, associada a cristais autigenicos de pirita (Nogueira & Riccomini 2006, Nogueira *et al.* 2007, Brelaz 2012, Soares *et*

*al.*2020, Sansjofre *et al.*2014, Soares *et al.*2020).

A Formação Guia seria composta por uma plataforma *offshore* anóxica e supersaturada em  $\text{CaCO}_3$ , representando o depocentro da Bacia Guia (Nogueira & Riccomini 2006, Nogueira *et al.*2007, Brelaz, 2012, Sansjofre *et al.*2014, Soares *et al.*2020). Em direção a esta porção observa-se o desenvolvimento de depósitos (Nogueira *et al.*2007). A plataforma profunda grada para fácies de plataforma rasa, configurando o Mar Guia (Alencar 2017). Lamoso *et al.*2023, descreveram a ocorrência de um testemunho 2ANP 0006 MT na bacia do Parecis, estes autores relacionam a porção basal, constituídas por depósitos calcários com porções dolomitizada como Formação Mirassol d'Oeste, no entanto como descrito anteriormente a Formação Mirassol d'Oeste é constituídas por dolomicrito primários (Nogueira *et al.*2003, Santos *et al.*2023). Desta forma, estes depósitos basais do testemunho 2ANP 0006 MT estão mais bem relacionados à Formação Guia, estendendo lateralmente a ocorrência da Bacia Araras-Alto Paraguai.

As principais feições diagenéticas encontradas na Formação Guia são: *Aggrading neomorphism* do micrito, maturação da matéria orgânica, dissolução e geração de porosidade, compactação física, dolomitização, cimentação de calcita, compactação química, dolomita-sela e migração de hidrocarbonetos. Estas feições estão relacionadas principalmente à Eo-Mesodiagênese (Alencar 2017, Soares *et al.*2020, Santos 2022).

#### 3.4.4 Formação Serra do Quilombo

A Formação Serra do quilombo é constituída predominantemente por dolomitas está em contato com a Formação Guia, a unidade tem espessura ~70 m e tem suas melhores exposições ocorrem na região de Cáceres-MT. A zona de contato entre as formações Guia e Serra do Quilombo é marcada por intenso fraturamento nos dolomititos e calcários finos associados com brechas cimentadas por dolomita. As brechas formam acumulações descontínuas, com espessuras de 2 até mais de 30 m de espessura, se intercalam com dolomito fino laminado ou apresentam contato lateral brusco com este, provavelmente por falhas sinsedimentares. Muitas vezes, as brechas exibem clastos com perfeito ajuste (*fitting*), sendo possível reconstituir a camada fraturada. A parte superior da Formação Serra do Quilombo apresenta camadas com espessuras centimétricas a métricas de dolomito grosso (dolomito cristalino). A estratificação plano-paralela associa-se com a estratificação cruzada *hummocky*, de até 3 m de comprimento e amplitude de 0,5 m, formando bancos amalgamados em sucessões de até 5 m de espessura. As marcas onduladas são simétricas e assimétricas e a laminação cruzada. Serra do Quilombo Formation, é interpretada como a sucessão dolomítica de plataforma rasa a moderadamente profunda (Nogueira & Riccomini 2006, Nogueira *et al.*2007, Milhomen *et al.*2013). Os principais processos

diagenéticos registrados é a dolomitização, silicificação e hidotermalismo (Milhomen *et al.* 2013, Sepeda 2024), no entanto trabalhos em andamento com o mesmo detalhe das unidades basais poderão restringir melhor o impacto dos fluidos pós deposicionais na unidade.

### 3.4.5 Formação Nobres

A Formação Nobres, unidade de topo do Grupo Araras, é dominada por camadas de dolomitas e sílica expostas principalmente na região de Cáceres-Mato Grosso. A parte inferior da Formação Nobres é caracterizada pela predominância de ciclos formados por: 1) dolomito fino (*dolomudstone*) e 2) dolomito arenoso e brecha dolomítica intraclástica (*dolorudstone* intraclástico). O dolomito fino forma camadas maciças e/ou laminadas de até 5 m de espessura, cuja base desenvolve um contato brusco com o ciclo subjacente, enquanto a passagem superior para os dolomititos arenosos com camadas enterolíticas é geralmente transicional. As camadas enterolíticas são complexas, geralmente associadas a moldes de evaporitos e estrutura *chicken-wire* e nodular, algumas vezes rompidas e dobradas por estruturas de injeção. Dolomititos arenosos com acamamento heterolítico, formado por laminações onduladas e deformadas, formam pacotes de até 4 m de espessura (Nogueira & Riccomini 2006, Nogueira *et al.* 2007, 2019, Rudninski *et al.* 2016). Os estromatólitos são formados por lâminas de 1-2 mm de espessura, quando substituídas por sílex, essas lâminas são ressaltadas em alto relevo. Três morfologias de estromatólitos foram observadas: 1) dômica a estratiforme, 2) estratiforme, e 3) rugosa (cerebroide) (Nogueira & Riccomini 2006, Rudninski *et al.* 2016, Romero *et al.* 2022). Os ciclos métricos da porção superior da Formação Nobres são formados por dolomito fino (*dolomudstone*) e, subordinadamente, dolomito oolítico (*dolopackstone/dolograinstones* oolítico) na base, e dolomito fino com estromatólitos (*doloboundstones*), dolomito arenoso e brecha com intraclastos (*dolopackstone* e *rudstone* intraclástico) na parte superior (Nogueira & Riccomini 2006, Rudninski *et al.* 2016).

A Formação Nobres apresenta uma série de evidências de processos diagenéticos capazes de obliterar por completo o sinal primário de carbono como dolomitização, recristalização, dissolução de componentes carbonáticos e siliciclásticos, e diferentes fases de cimentação de dolomita, calcita e sílica. Os processos mais significativos são a substituição dos depósitos calcários, que iniciou a dolomitização na fase Eodiagenética e se estendeu a fases de diagênese de soterramento, evidenciados por de cristais de dolomita com hábitos e relações paragenéticas diferenciadas. Além dos eventos de silicificação, silicificação com níveis maciços e nódulos de *chert*. O processo de silicificação é mais expressivo representado por quartzo microcristalino e cimento de quartzo fibrous-radial, esta fase mais pervasiva são associadas aos eventos

hidrotermais tardios (Rudnitzki 2015, Nogueira *et al.* 2022).

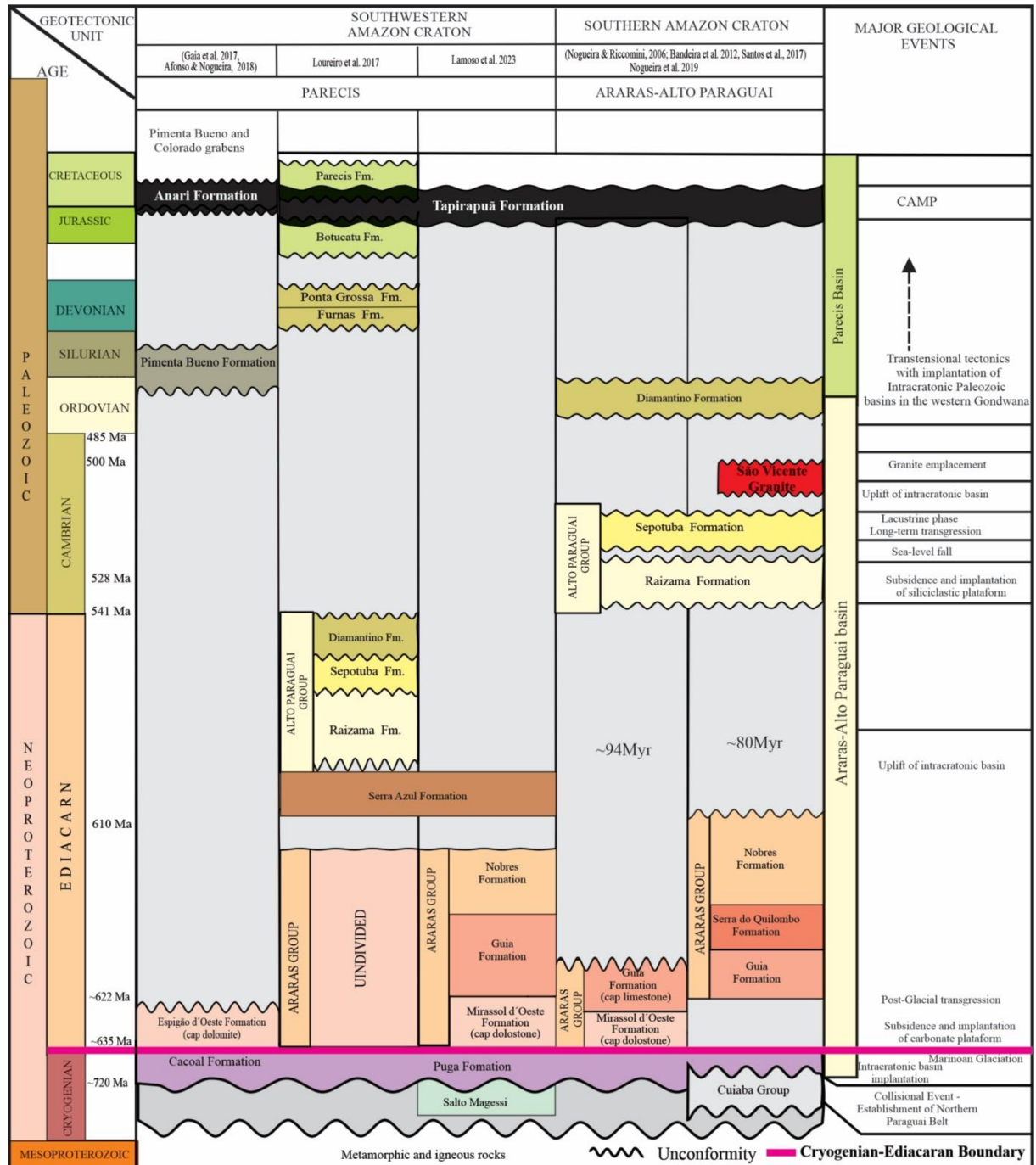


Figura 3.4- Litoestratigráfica da margem sul do Cráton Amazônico e Faixa Paraguai, em destaque o limite Crio-geniano/Ediacarano da Bacia Araras-Alto Paraguai. Modificado de Nogueira *et al.* (2019).

### 3.5 INDICAÇÕES PALEOREDOX DA PLATAFORMA ARARAS

O modelo da Terra de Bola de Neve postula glaciações extremas com um oceano anóxico, seguido por uma deglaciação abrupta sob condições climáticas quentes (Hoffman *et al.* 2017). Nesse contexto, há uma antecipação de precipitação generalizada, maciça e rápida de capa carbonática durante a deglaciação, juntamente com a estabilização da anoxia pré-existente nas águas mais profundas (Hoffman & Scharg 2002, Nogueira *et al.* 2003, Font *et al.* 2006, Hoffman *et al.* 2017, 2021). A capa carbonática Puga depositados no Sul do cráton amazônico estão associados a microbialitos, sugerindo a importância das comunidades microbianas em ambientes rasos (Nogueira *et al.* 2003, 2007, 2019, 2022, Font *et al.* 2006, Sansjofre *et al.* 2014, Romero *et al.* 2020, Santos *et al.* 2021, 2023, 2024).

Após a glaciação Marinoana, a coluna d'água na plataforma de Araras provavelmente passou a condições predominantemente oxigenadas, com anoxia restrita à água dos poros do sedimento e à interface água-sedimento nas regiões mais profundas da plataforma, com base em metais traços (Sansjofre *et al.* 2014). Ao usar a especiação de ferro Sansjofre (2011) encontrou o ferro principalmente em um estado altamente reativo, com razões  $\text{Fe}_{\text{Hr}}/\text{Fe}_{\text{T}}$  com média de 0,82 para a capa dolomítica e 0,74 para a capa calcária. Esse ferro reativo é abundante em formas oxidadas e carbonatadas ( $\text{Fe}_{\text{ox}}$ ) ( $\text{Fe}_{\text{carb}}$ ). Na base dos capa calcária, o ferro está predominantemente na forma de pirita ( $\text{Fe}_{\text{pyr}}$ ), resultando em uma mistura das três fases,  $\text{FeOx}$ ,  $\text{Fe}_{\text{carb}}$  e  $\text{Fe}_{\text{pyr}}$ , na porção superior, com concentrações de 0,35%, 0,55% e 0,10%, respectivamente (Sansjofre 2011). Ader *et al.* (2014) ilustraram que o Grupo Araras exibe valores de  $\delta^{15}\text{N}$  variando entre +2,2 e +10,5%, e que o  $\delta^{15}\text{N}$  mostra uma boa correlação entre COT e N, atribuindo uma contribuição significativa da matéria orgânica para o *pool* de nitrogênio. Os valores variam entre 2,4 e 9,9‰. A parte basal da capa dolomítica mostra inicialmente uma diminuição de 4,2 para 2,4‰ e na parte superior dos microbialitos com tubestone, os valores passam abruptamente para 9,9‰. A parte superior capa dolomítica e capa calcária mostram um valor  $\delta^{15}\text{N}$  constante em torno de 5‰, exceto o último valor de 2,5‰. A hipótese mais plausível sugere um ciclo de nitrogênio semelhante ao oceano contemporâneo, onde o nitrato permanece estável ao longo do mar, exceto em Zonas Mínimas de Oxigênio anóxicas e bacias anóxicas localmente confinadas. Esta inferência implica a presença de oxigênio dissolvido suficiente para estabilizar o nitrato na maioria dos oceanos do Neoproterozoico tardio. Consistente com as interpretações de Sansjofre *et al.* (2014), essas condições implicam diretamente na preservação matéria orgânica na capa dolomítica, como demonstrado anteriormente por Elie *et al.* (2008), Souza *et al.* (2016) e van Maldegem *et al.* (2019). No entanto, as condições anóxicas ao menos na interface água-

sedimento estão registrados na porção superior, transição capa dolomitica-calcária, no entanto, tais condições são mais bem desenvolvidos nos depósitos de capa calcária, aumentando o potencial de preservação da MO (Sansjofre *et al.*2014).

Estudos de fósseis orgânicos na capa carbonática Puga retrataram a transição de comunidades bentônicas para planctônicas coincidindo coma mudança de fábrica carbonática (dolomitica-aragonitico) (Elie *et al.*2007, Sousa *et al.*2016, van Maldegem *et al.*2019). A queda na abundância de BNG no contato dolomito-calcário sugere uma ligação potencial entre a atividade biológica do ecossistema pós-glacial inicial e a mineralogia dos carbonatos depositados (van Maldegem *et al.*2018). A capa calcária marca o início de alta produção e preservação de organismos fototróficos e um aumento preservação de organismos eucarióticos sobre comunidades bacterianas, como evidenciado pela relação molecular colestanos ( $\Sigma dia + reg$ )/hopanos ( $\Sigma Ts + Tm + BNH$ ). O sinal forte de esteranos C27 e níveis indetectáveis de C28 e C29, combinados com níveis traços de hopanos e terpenos tricíclicos (TTs) de C19 a C39, indicam a prevalência de algas vermelhas como a matéria orgânica primária. A presença de isoprenoides C13-C26 2,3,6-trimetil aril isoprenoides, juntamente com uma baixa razão Pr/Ph, sugere bactérias fotossintéticas de enxofre verde (Summons & Powell 1987, Brocks *et al.*2005) em um ambiente marinho rico em sulfato. Uma característica particular do calcário cap na região sudeste do cráton amazônico é sua composição molecular, muito diferente da região sul. Apenas nesta região está registrada a presença de gammacerano (36,73-47,74), que, combinada com baixas razões Pr/Ph (0,56 e 0,61), indica que as condições provavelmente eram muito mais anóxicas e hipersalinas. A diferença mais significativa ocorre na série de terpanos. Na região de Mirassol d'Oeste, os terpanos tricíclicos estão quase exclusivamente presentes, com ausência de hopanos. Em contraste, na região de Tangará da Serra, a série de terpanos é mais completa, indicando biodegradação ou (mais provavelmente) a prevalência de tapetes microbianos, enquanto florescimentos de algas vermelhas ocorriam na região de Mirassol d'Oeste. Isoprenoides I21 a I25, escaleno I30, gammacerano e norcolestanos C-21 a C-27 sugerem oscilações em condições hipersalinas (Souza *et al.*2017, van Maldegem *et al.*2018).

### 3.6 GEOQUÍMICA ISOTÓPICA E REGISTRO PALEONTOLOGICOS DO GRUPO

#### ARARAS: RELACIONADOS AS MUDANÇAS DO NÍVEL DO MAR DURANTE O INÍCIO DO EDIACARANO.

A bacia Araras-Alto Paraguai (Fig. 3.1) tem sido extensivamente estudado através de estudos sedimentológicos, paleontológicos e de litoestratigrafia de alta resolução, além de quimioestratigráficos (Nogueira *et al.*2007, 2019, 2022). Particularmente, uma atenção especial

foi dada às microbialitos e fósseis orgânicos que representam os principais registros de vida no Grupo Araras, Ediacarano Inferior (Fig. 3.6 E) (Nogueira *et al.* 2003, 2022, Font *et al.* 2006, Elie *et al.* 2007, Sousa *et al.* 2016, van Maldegem *et al.* 2018, Romero *et al.* 2020, 2022, Santos *et al.* 2021). Até o momento, um grupo raro e mal preservado de acritarcas foi descoberto na seção dolomítica superior capa carbonática Puga (Formação Mirassol d'Oeste) e nos estratos calcários da Formação Guia (Hidalgo 2007, Brelaz 2012). No entanto, devido à sua má preservação e aos desafios em sua classificação, esses acritarcas fornecem uma resolução bioestratigráfica limitada e uma interpretação paleoambiental não diagnóstica. As ocorrências fósseis com valor bioestratigráfico são escassas na Formação Guia. As espécies primárias identificadas dentro do gênero *Leiosphaeridia* são *L. crassa* e *L. minutissima*, enquanto as espécies de acritarcas esféricos permanecem indeterminadas (Hidalgo 2007, Brelaz 2012, Nogueira *et al.* 2019). Este conjunto foi correlacionado com a Biozona Palinoflora do Ediacarano (ELP) proposta por Grey (2005) para o período Ediacarano Inferior.

As associações de microfósseis na Formação Nobres, depósitos superiores do Grupo Araras, revelam uma complexidade maior do que aquelas encontradas na base dos depósitos carbonáticos. A unidade ocorre com uma presença abundante de matéria orgânica e microfósseis degradados. Entre os táxons de acritarcas identificados, destacam-se *Cavaspina acuminata* (Kolosova 1991), *Chlorogloeopsis sp.*, *Obruchevella sp.*, *Ericiasphaera sp.*, *Appendisphaera barbata* (Grey 2005), *Tanarium irregulare*, *Tanarium conoideum* e *Micrhystridium pisinnum*. O tamanho significativo desses acritarcas os classifica como acantomorfos, e uma forte correlação foi estabelecida com os microfósseis da Biozona ECAP, conforme descrito por Grey (2005) na Austrália, provavelmente associada à Zona de Associação *Tanarium irregulare-Ceratospaeridium glaberosum-Multifronsphaeridium pelorium*. Esta associação também pode estar relacionada à associação Volhyn/Redkino (Amadeusiana) proposta por Vidal & Moczydlowska (1997). Os acantomorfos da biozona ECAP emergiram pelo menos 20 milhões de anos após o fim da glaciação Marinoano (Rudniski *et al.* 2017), consistente com a proposta de idade de Nogueira *et al.* (2019, 2022) para esta unidade de 614 Ma inferida através de correlações quimioestratigráficas com a Formação Nama (Nogueira *et al.* 2019).

Os avanços na geocronologia em carbonatos trouxeram uma melhor calibração com idades radiométricas que trouxeram melhores restrições para os eventos ediacaranos das unidades do Grupo Araras. Idades Pb/Pb obtidas para capa dolomítica, de  $633 \pm 30$  Ma (Babinski 2011) e  $627 \pm 32$  Ma (Babinski *et al.* 2006), enquanto para capa calcária,  $622 \pm 33$  Ma (Romero *et al.* 2013) e  $622 \pm 30$  (Souza *et al.* 2024), indicando uma idade Ediacarana Inferior (Babinski *et al.* 2006, Romero *et al.* 2013). Recentemente, uma idade U-Pb *in situ* de  $622 \pm 3$  Ma foi obtida

para os leques de cristais pseudomorfo de aragonita, da capa calcária (Carvalho *et al.*2023). Esta idade foi interpretada como uma restrição à transição da diagênese de soterramento raso dos depósitos de capa carbonática Puga. Além disso, os valores de  $^{87}\text{Sr}/^{86}\text{Sr}$  variam de 0,7074 a 0,7089 (Nogueira *et al.*2007, Alvarenga *et al.*2008, Alencar, 2017, Lamoso *et al.*2023) com valores mais baixos de 0,7070–0,7077, relatados por Romero *et al.* (2013) e Souza *et al.* (2024), que foram interpretados como indicativos da composição isotópica primária, típica do Ediacarano (Fig. 3.4 C). Eles sugeriram que os valores mais altos observados em estudos anteriores podem ser atribuídos à incorporação de estrôncio a partir de componentes siliciclásticos nas rochas carbonáticas. Essas assinaturas isotópicas de  $^{87}\text{Sr}/^{86}\text{Sr}$  são compatíveis com os valores mais baixos registrados em outros lugares para carbonatos pós-Marinoano, que geralmente estão entre 0,7072–0,7087 (Kaufman *et al.*1995, Jacobsen & Kaufman 1999, Halverson *et al.*2007, 2010).

Nesse sentido, o Grupo Araras surge como o principal candidato para a construção de uma curva de referência  $\delta^{13}\text{C}$  do Ediacarano Inferior (~635-614 Ma) (Estágios 1 e 2) para o Cráton Amazônico. Essa significância é particularmente evidente no Grupo Araras inferior (Mirassol d'Oeste e base da Guia), compreendendo a sequência carbonática de tampa de Puga. Apesar das incertezas quanto à origem dos sinais de  $\delta^{13}\text{C}$  ou seu uso na correlação quimioestratigráficas globais, dados da capa carbonática Puga e de todo o Grupo Araras exibem sinais bem preservados, exibindo tendências distintas para cada unidade. Carbonatos ediacaranos comumente exibem excursões isotópicas de carbono ( $\delta^{13}\text{C}$ ) caracterizadas por desvios negativos e positivos distintos, em acordo com as tendências estratigráficas e as mudanças do nível do mar. A curva  $\delta^{13}\text{C}$  da sucessão carbonática de Araras é interpretada como representativa da química original da água do oceano, exibindo uma tendência com valores de  $\delta^{13}\text{C}$  fortemente esgotados na base e composições enriquecidas na parte superior. A tendência de enriquecimento observada nos carbonatos de Araras é indicativa de um retorno às composições sindeposicional, provavelmente associado ao restabelecimento da atividade biológica. Durante a elevação do nível do mar, a superfície da plataforma se expandiu rapidamente, promovendo uma produtividade orgânica abundante e aumentando a retenção de  $\delta^{12}\text{C}$  pelos organismos (Mitchell *et al.*1996, Nédélec *et al.*2007).

Nos depósitos de capa dolomítica, Formação Mirassol d'Oeste, os valores de  $\delta^{13}\text{C}$  são mais negativos, variando de aproximadamente -8 a -5 ‰ (média =  $-4.46 \pm 1.25$  ‰,  $n = 307$ , com baixa correlação entre  $\delta^{13}\text{C}$  e o  $\delta^{18}\text{O}$   $R^2 = 0.23$ ) (Nogueira *et al.*2003, 2007, 2019, Alvarenga *et al.*2004, 2008, Font *et al.*2006, Sansjofre *et al.*2011). Esses valores isotópicos de  $\delta^{13}\text{C}$  confirmaram a interpretação anterior do paleoambiente marinho raso pós-glacial com condições



favoráveis para a colonização microbiana comumente encontrada nas camadas do Ediacarano Inferior. À medida que a transgressão continuou, formando uma plataforma moderadamente supersaturada em  $\text{CaCO}_3$ , ocorreu precipitação de micrito registrada nos depósitos de capa calcária (Formação Guia), que mostram valores de  $\delta^{13}\text{C}$  um pouco menores, de aproximadamente -6 a -2‰ (média =  $-5.4 \pm 0.65$  ‰,  $n=168$ ), com baixa correlação entre  $\delta^{13}\text{C}$  e o  $\delta^{18}\text{O}$  ( $R^2 = 0.05$ ) (Nogueira *et al.* 2003, 2007, 2019, Alvarenga *et al.* 2004, 2008, Sansjofre *et al.* 2011, Soares *et al.* 2020, Carvalho *et al.* 2023). Os depósitos de capa calcária são restritos na região cratônica. No entanto, a porção superior da Formação Guia é interpretada como um calcário de plataforma profunda anóxica ocorrem por toda bacia, esta unidade registra um aumento gradual nos valores de  $\delta^{13}\text{C}$  de -2,5 a -1‰ até o topo da sucessão (valores médios =  $-2.6 \pm 1.49$  ‰,  $n=200$ ) com baixa correlação entre  $\delta^{13}\text{C}$  e o  $\delta^{18}\text{O}$  ( $R^2 = 0.3$ ) (Nogueira *et al.* 2007, Alencar, 2017, Lamoso *et al.* 2023). Além disso, os robustos dados de Lamoso *et al.* (2023) foram predominantemente reinterpretados aqui como sendo da Formação Guia, considerando que a unidade de Mirassol d'Oeste é tipicamente descrita como dolomítica, desta forma os calcários com porções dolomitizada é mais bem interpretado como Formação Guia. Esses calcários e folhelhos betuminosos registram o desenvolvimento de uma plataforma *offshore* representando o depocentro da Bacia Araras Alto Paraguai. Adicionalmente, os dados reinterpretados por Lamoso *et al.* (2023) estende a ocorrência da Plataforma carbonática Araras no cráton amazônico).

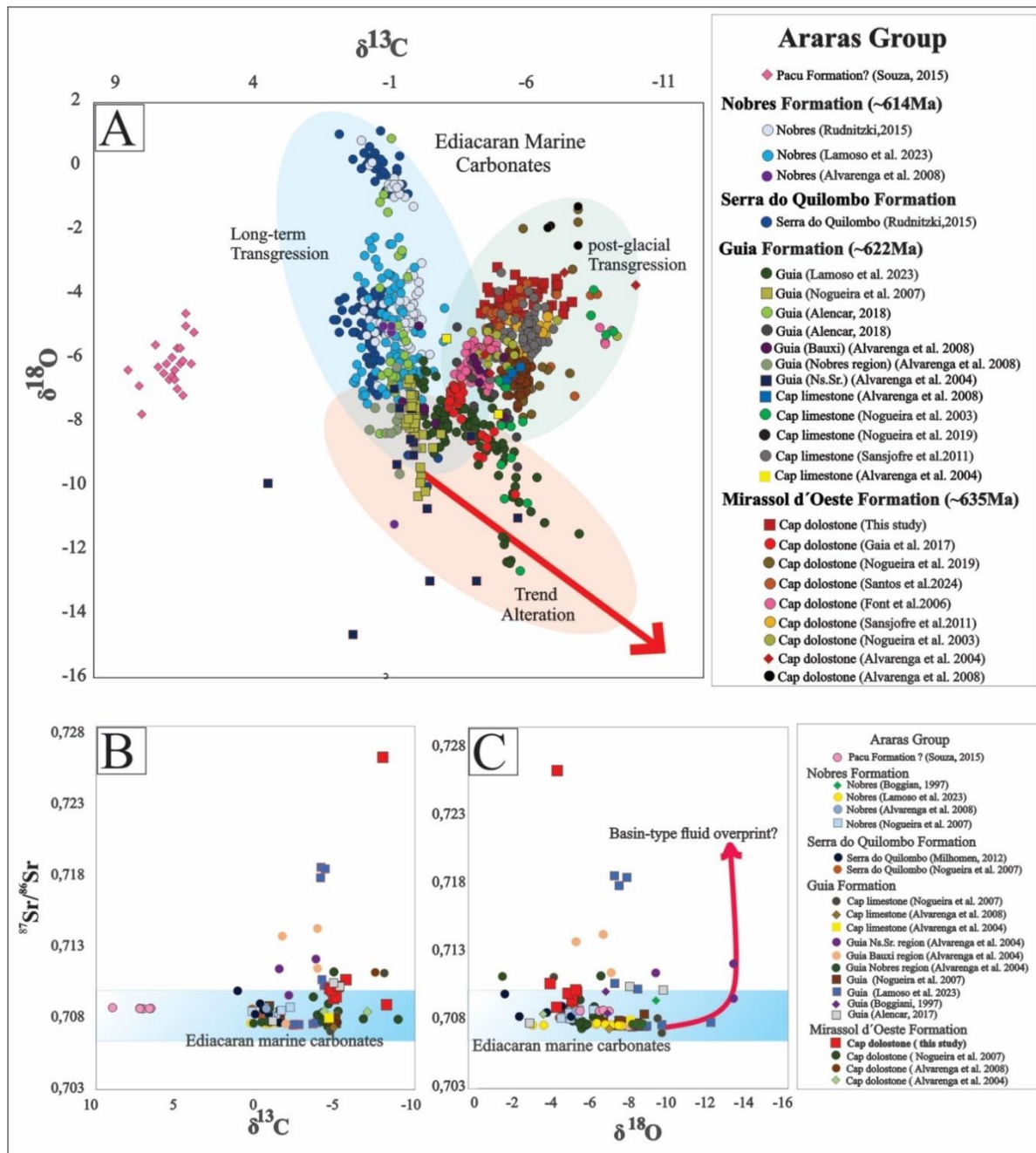


Figura 3.5- A) Gráfico cruzados das composições isotópicas estáveis de  $\delta^{13}\text{C}$  e  $\delta^{18}\text{O}$  dos carbonatos do Grupo Araras. Note as tendências dos valores de  $\delta^{13}\text{C}$  para os depósitos de capa carbonática, relacionados a transgressão pós-glacial e as tendências dos carbonatos relacionados a transgressão a longo prazo, e a excelente preservação dos sinais indicada pela baixa correlação com  $\delta^{18}\text{O}$ . B) Diagramas de dispersão das composições isotópicas estáveis de  $^{87}\text{Sr}/^{86}\text{Sr}$  e  $\delta^{13}\text{C}$  dos carbonatos do Grupo Araras. C) Diagramas de dispersão das composições isotópicas estáveis de  $^{87}\text{Sr}/^{86}\text{Sr}$  e  $\delta^{18}\text{O}$  da fração carbonática do Grupo Araras. Os valores estão próximos aos esperados para o Ediacarano inicial, com baixa correlação com o  $\delta^{18}\text{O}$ , demonstrando um baixo impacto de fluidos pós-deposicionais (diagenéticos) nos valores de  $^{87}\text{Sr}/^{86}\text{Sr}$ .

A subsequente diminuição do nível do mar desencadeou a progradação de ambientes costeiros, ocorrendo simultaneamente com condições extremas de estufa com precipitação de evaporitos (Nogueira *et al.*2022). Esse evento causou exposição parcial e o desenvolvimento de *flatstidais* e ambientes de Sabkha com a proliferação de montículos microbianos em pequena escala, marcando o limite entre as zonas intertidal e subtidal (Nogueira *et al.*2007, 2022, Romero *et al.*2022). A sucessão de plataforma dolomítica sobrejacente (Formação Serra do Quilombo inferior) apresenta valores de  $\delta^{13}\text{C}$  em torno de 0‰ (valores médios =  $0 \pm 0.5$  ‰, n= 117) com baixa correlação entre  $\delta^{13}\text{C}$  e o  $\delta^{18}\text{O}$  ( $R^2 = 0.04$ ) (Nogueira *et al.*2007, Milhomen, 2012). Os valores são ligeiramente positivos nos depósitos de plataforma rasa (parte mais alta da Formação Serra do Quilombo) com uma correlação pobre entre  $\delta^{13}\text{C}$  e  $\delta^{18}\text{O}$  (Nogueira *et al.*2007). Os valores de  $\delta^{13}\text{C}$  levemente negativos nas fácies peritidais (Formação Nobres) com uma correlação pobre entre  $\delta^{13}\text{C}$  e  $\delta^{18}\text{O}$  (valores médios =  $-0.75 \pm 0.76$  ‰, n= 224) com baixa correlação entre  $\delta^{13}\text{C}$  e o  $\delta^{18}\text{O}$  ( $R^2 = 0.04$ ) (Nogueira *et al.*2007, Rudninski 2014, Lamoso *et al.*2023). Além disso, valores positivos de  $\delta^{13}\text{C}$  são encontrados para os depósitos descritos como Formação Pacu, 6,5 a 8.91‰ (valores médios =  $7.2 \pm 0.6$  ‰, n= 22) com baixa correlação entre  $\delta^{13}\text{C}$  e o  $\delta^{18}\text{O}$  ( $R^2 = 0.2$ ) (Souza 2015, Sial *et al.*2016), estes valores são distintos daqueles encontrados para o Grupo Araras, sendo considerados uma unidade a parte. No entanto, os valores de  $^{87}\text{Sr}/^{86}\text{Sr}$  são consistentes com o esperado para o período Ediacarano. Nogueira *et al.* (2022) indicaram que essa unidade poderia fazer parte da evolução do Grupo Araras, correlacionada com os ambientes rasos da Formação Nobres. No entanto, a definição lateral e o contato da unidade, bem como as restrições geocronológicas, precisam ser melhor definidos para encaixá-la na evolução da bacia Araras-Alto Paraguai. Um progressivo soerguimento causou uma inversão na bacia que culminou com a erosão da sucessão sedimentar com idade máxima estimada em 614 Ma (Nogueira *et al.*2019). Esta ascensão e erosão geraram uma discordância no Grupo Araras Superior, sobreposta por depósitos siliciclásticos do Cambriano-Ordoviciano do Grupo Alto-Paraguai (Nogueira *et al.*2019, 2022). A idade Cambriano foi proposta para a base do Grupo Alto Paraguai, Formação Raizama, com base na ocorrência de fósseis de traços *Skolithos* (Santos *et al.*2017). Esta discordância representa um intervalo de aproximadamente 80 milhões de anos na bacia Araras-Alto Paraguai (Nogueira *et al.*2019).

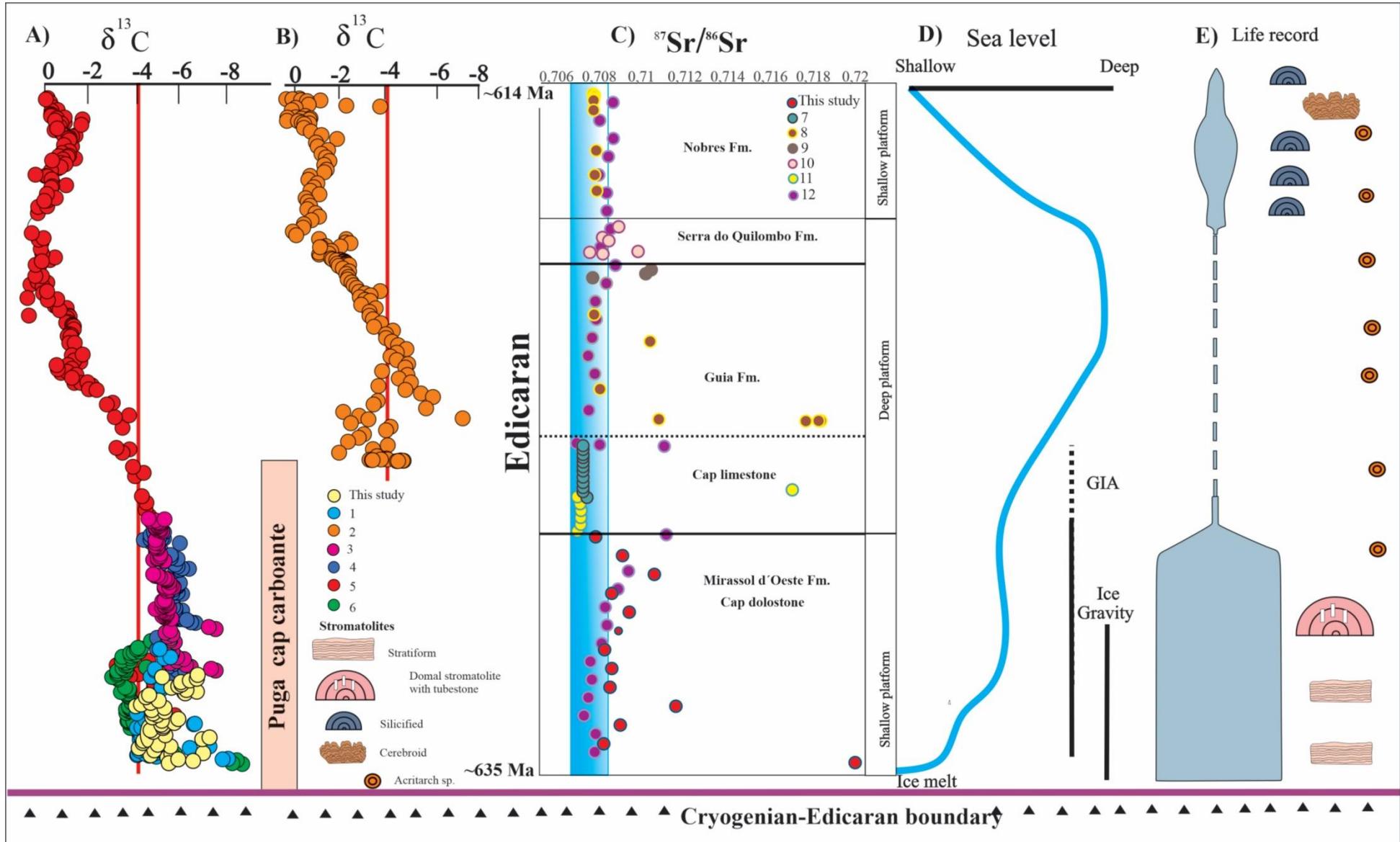


Figura 3.6- A) Curva de referência de  $\delta^{13}\text{C}$  para o cráton amazônico para o início do Ediacarano ~ 635–614 Ma. B) comparação com os valores  $\delta^{13}\text{C}$  do Grupo Araras no testemunho 2ANP00006MT, na Bacia Parecis (Lamoso *et al.* 2023). C) Razões  $^{87}\text{Sr}/^{86}\text{Sr}$  de cada unidade dentro do Grupo Araras. D) Variação do nível do mar na plataforma Araras no contexto da evolução inicial do Ediacarano. E) Registro fóssil do Grupo Araras, incluindo acritarcas e microbialitos, destacando a relação entre microbialitos e variação do nível do mar. 1) Font *et al.* 2004, 2) Lamoso *et al.* 2023, 3) Sansjofre *et al.* 2011, 4) Nogueira *et al.* 2019, 5) Nogueira *et al.* 2007, 6) Este estudo. 7) Souza *et al.* 2024, 8) Lamoso *et al.* 2023, 9) Alencar 2017, 10) Nogueira *et al.* 2007, 11) Romero *et al.* 2013, Nogueira *et al.* 2007.

# DIAGENESIS OF THE MARINOAN CAP DOLOSTONE, SOUTHERN AMAZON CRATON: AN UNCONVENTIONAL PETROLEUM SYSTEM IN THE EVOLUTION OF THE ARARAS-ALTO PARAGUAI BASIN

Renan F. dos Santos<sup>1</sup>, Afonso C. R. Nogueira<sup>1,4</sup>, Juliane B. da Costa<sup>1</sup>, Leandro F. Sepeda<sup>1</sup>, Juliana Okubo<sup>2</sup>, Isabele S. Barros<sup>1</sup>, Argel A. N. Sodré<sup>1</sup>, Pedro G. A. Oliveira<sup>1</sup>, Ivan A. R. Barrera<sup>1</sup>, Pierre Sansjofre<sup>3</sup>

<sup>1</sup>*Programa de Pós-Graduação em Geologia e Geoquímica, Faculdade de Geologia, Instituto de Geociências, Universidade Federal do Pará, Rua Augusto Corrêa s/n, CEP 66075-110, Belém-PA, Brasil*

<sup>2</sup>*Departamento de Geologia, Universidade Estadual Paulista – UNESP, Rio Claro, SP 13506-900, Brasil*

<sup>3</sup>*Muséum National d'Histoire Naturelle, 41 rue Buffon 75005, Paris, France*

<sup>4</sup>*Research Productivity of CNPq*

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## Highlights

1. Ediacaran unconventional petroleum system formed during the assembly of Gondwana.
2. Post-Marinoan transgression allowed the hydrocarbon accumulation in the Amazon Craton
3. Destructive diagenetic are typical features in the microbial dolostone reservoir.
4. Ediacaran petroleum plays can be a secondary hydrocarbon source for the Phanerozoic System.

#### 4 DIAGENESIS OF THE MARINOAN CAP DOLOSTONE, SOUTHERN AMAZON CRATON: AN UNCONVENTIONAL PETROLEUM SYSTEM IN THE EVOLUTION OF THE ARARAS-ALTO PARAGUAI BASIN

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<sup>1</sup>*Programa de Pós-Graduação em Geologia e Geoquímica, Faculdade de Geologia, Instituto de Geociências, Universidade Federal do Pará, Rua Augusto Corrêa s/n, CEP 66075-110, Belém-PA, Brasil*

<sup>2</sup>*Departamento de Geologia, Universidade Estadual Paulista – UNESP, Rio Claro, SP 13506-900, Brasil*

<sup>3</sup>*Muséum National d'Histoire Naturelle, 41 rue Buffon 75005, Paris, France*

<sup>4</sup>*Research Productivity of CNPq*

#### ABSTRACT

The post-snowball Earth world favors the development of hydrocarbon source rock intimately linked to periods of post-glacial marine transgression generating important potential petroleum plays. In the Southern Amazon Craton, hydrocarbons occur in one of the most spectacular examples of post-Marinoan cap carbonate, related to the mid-Ediacaran to Early Cambrian (c. post 635 Ma) interval associated with the early stabilization of the Gondwana Supercontinent. The Puga cap carbonate consists of the basal portion of the Araras Group exposed in the Araras Alto-Paraguai Basin inserted as a reservoir in an unconventional petroleum system. The cap dolostone overlies diamictites and is overlaid by bituminous limestone and shales (source-rock), and dolostone in the top of a 700m-thick depositional sequence. The cap dolostone has a diachronic relation with the limestone beds typifying as a secondary reservoir characterized by bitumen-filled fenestral and interpeloidal porosity. The upper dolostone has a closed framework and acts as sealing rocks. This study aims to establish paragenesis sequence and decipher its control on the quality of the cap dolostone as a microbialites-dominated reservoir. Drill core and outcrop samples were analyzed using microfacies, scanning electron microscopy, and cathodoluminescence to unravel the diagenetic history. Aftermath, the Marinoan events favored dolomuds precipitation in the shallow platforms, preserving primary porosity and permeability reduced by early gypsum cementation during oversaturation events. Other destructive processes, such as mechanical and chemical compaction (e.g., stylolites) and

authigenesis of pyrite and low-Mg ferroan calcite cementation, occurred during burial and mesodiagenesis. The low permeability restricts hydrocarbon migration concentrated in the upper cap dolostone, and the early cementation increases the potential for preserving these carbonate deposits. Hydrocarbon maturation was triggered during the burial and uplift of the Araras-Alto Paraguai basin. The cementation phases described here enhance our understanding of the mechanisms behind syndepositional diagenesis in microbially-induced reservoirs. This study uses proxies associated with diagenetic studies to quantify the quality of microbially induced dolostone reservoir linked to the evolution of the Neoproterozoic unconventional petroleum system. In addition, this conception will promote a guide for future exploration and understanding of petroleum plays and suggests a possible Precambrian source rocks component of traditional Phanerozoic Petroleum systems in the central part of Brazil.

**Keywords:** cap carbonate; fibrous dolomite; early cementation; dolomitization syndepositional; reservoir; migrabitumen

#### 4.1 INTRODUCTION

Carbonate reservoirs are important in the oil and gas industry, accounting for 50% of exploited plays (Lucia 2003, Mazzullo 2004, Ehrenberg *et al.*2005, 2009, Burchette 2012, Sagbana *et al.*2022). Microbialite carbonates have attracted significant interest due to their immense potential in hydrocarbon reservoirs (Mancini *et al.*2013, Lipinsk *et al.*2013, Słowakiewicz *et al.*2013, Grotzinger and Al-Rawahi 2014, Bosence *et al.*2015, Zhu *et al.*2020, Tang *et al.*2022, Xu *et al.*2022). These carbonate strata exhibit significant reservoir potential, with pore spaces resulting from constructive diagenetic processes (Kerans 1988, Sun 1995, Ehrenberg *et al.*2006, Ronchi *et al.*2012, Hu *et al.*2020, Wang *et al.*2022). However, these reservoirs are primarily influenced by sedimentation, diagenesis, and tectonic processes, contributing to their inherent complexity. This complexity is characterized by reservoir heterogeneity, the evolution of pore systems, multiple stages of tectonic movements, and hydrocarbon generation (Tang *et al.*2019, Yang *et al.*2020, Hu *et al.*2020). Therefore, understanding the evolution of pore structures requires the reconstruction of fluid circulation events and the diagenetic history of reservoirs. In recent decades, the potential exploration of Precambrian reservoirs has gained attention. Their geological complexity in the reservoirs can be recorded in prolonged thermal degradation, diagenesis, and phase overlap periods, occurring in tectonic contexts distinct from Phanerozoic reservoirs (Fowler and Douglas 1987).

Numerous oil and gas reservoirs have been identified in Meso-Neoproterozoic rocks,

especially in China, Siberia, India, Oman, and Australia (Murray *et al.*1980, Hao and Feng 1982, Grantham *et al.*1988, 1990, Wang and Simoneit 1995, Terken and Frewin 2000, Volk *et al.*2005, Dutta *et al.*2013, Jiang *et al.*2020, Wang *et al.*2020b, Xiao *et al.*2022). One of these Precambrian reservoirs is the Araras petroleum system (APS), an unconventional petroleum system formed in the Araras-Alto Paraguai basin, southern Amazon craton (Fig. 4.1A) (Nogueira *et al.*2001, Elie *et al.*2007, Souza Jr. *et al.*2017, Bezerra Jr. 2018, Santos *et al.*2018, van Maldegem *et al.*2019, Santos 2022). In this system, the Guia Formation (Fig. 4.1B) has been interpreted to be the source rock, primarily due to the presence of bitumen along its carbonate succession (Nogueira *et al.*2001). Hydrocarbons are limited to a small percentage of pores (~2%) and rarely occur in fractures in the Guia Formation. At the same time, the Mirassol d'Oeste Formation is limited to the top of the unit (Fig. 4.1C) (Soares *et al.*2020). Although this hydrocarbon accumulation is not economically viable, it represents an unconventional petroleum system (Nogueira *et al.*2001, Soares *et al.*2020). Unconventional petroleum systems have gained significant attention due to their potential as alternative energy resources (Law and Curtis, 2002, Ji *et al.*2016, Zhou *et al.*2017). These systems involve complex geological processes, including the formation and diagenesis of reservoir rocks and the distribution of cementation phases within them.

The paragenetic restriction in reservoirs plays a crucial role in unraveling the complexities of unconventional petroleum systems, even in cases where there may be limited economic potential. Early cementation can profoundly impact reservoir quality, porosity, and permeability, including the precipitation and compaction of cementation phases such as calcite, dolomite, and silica. Understanding the spatial distribution of the diagenetic products is essential to determine the factors controlling the reservoir properties and to be predictive (Morad *et al.*2012, 2018, Whitaker and Frazer 2018). Recently, Soares *et al.* (2020) proposed a diagenetic event sequence for the carbonate succession of Puga, highlighting its potential as an unconventional petroleum system. However, the study primarily focused on the cap limestone, which serves as the source rock and main reservoir, and the upper part of the cap dolostone, which acts as a secondary reservoir. Due to the restricted exposition of the unit in the region, the exposure studied by the authors only partially revealed the unit, including the depositional history and diagenesis of the contact with the diamictite and the relationship between the cap dolostone and the Araras petroleum system. In this study, we aim to provide a detailed analysis of the cap dolostone (Mirassol d'Oeste Formation) by examining samples from two drill cores and outcrops within the Puga cap carbonate occurrence in the southeast region of the Amazon craton (Fig. 4.2). We integrate sedimentological and petrographic features within the geological



evolution and chemostratigraphy context to establish a stratigraphy of events, investigate the impact of constructive and destructive processes, and gain insights into how these factors influenced the unconventional petroleum system associated with the Araras-Alto Paraguai Basin on the Southern Amazon Craton.

## 4.2 GEOLOGIC SETTING

The carbonate-siliciclastic deposits of the Araras Alto-Paraguai Basin occur on the southern edge of the Amazon Craton and form a discontinuous outcrop area in the Paraguai belt (Fig. 4.1A) (Nogueira and Riccomini 2006, Nogueira *et al.* 2019, Santos *et al.* 2020). The Araras Group was deposited after the Puga glacial event (Cryogenian) within the context of low-latitude glaciations according to the snowball Earth hypothesis (Nogueira *et al.* 2003, Allen and Hoffman 2005, Hoffman *et al.* 1998, 2011), and unconformably overlain (~80 Myr) by the siliciclastic rocks (Cambrian-Ordovician) of the Alto-Paraguai Group (Nogueira and Riccomini 2006, Soares *et al.* 2020, Santos *et al.* 2017, Nogueira *et al.* 2019, 2022). The Araras Group, which is 700 m thick, consists of dolomites and limestones from four formations: Mirassol d'Oeste, Guia, Serra do Quilombo, and Nobres (Fig. 4.1B) (Nogueira *et al.* 2003, 2019, 2022, Nogueira and Riccomini, 2006, Soares and Nogueira 2008, Rudnitzki *et al.* 2017, Soares *et al.* 2013, 2020, Romero *et al.* 2020, 2022, Santos *et al.* 2021). The Puga cap carbonate, represented by the Mirassol d'Oeste Formation and the base of the Guia Formation (Fig. 4.1B), was deposited after the Puga glacial event (Cryogenian), correlated with the Marinoan glaciation (~650-635 Ma) (Nogueira *et al.* 2003, Allen and Hoffman 2005, Hoffman *et al.* 1998, 2011). The post-glacial transgression was characterized by microbial colonization in shallow platforms, as evidenced by cap dolostone in the Mirassol d'Oeste Formation (Fig. 4.1B). The ongoing transgression and glacioisostatic adjustments led to moderately deep environments associated with the Guia and lower Serra do Quilombo formations. Subsequently, a gradual decrease in sea level led to the establishment of coastal environments within greenhouse conditions, featuring tidal flats and sabkha settings in the Nobres Formation (Rudnitzki *et al.* 2017, Soares *et al.* 2013, 2020, Romero *et al.* 2020, 2022, Santos *et al.* 2021, Nogueira *et al.* 2022).

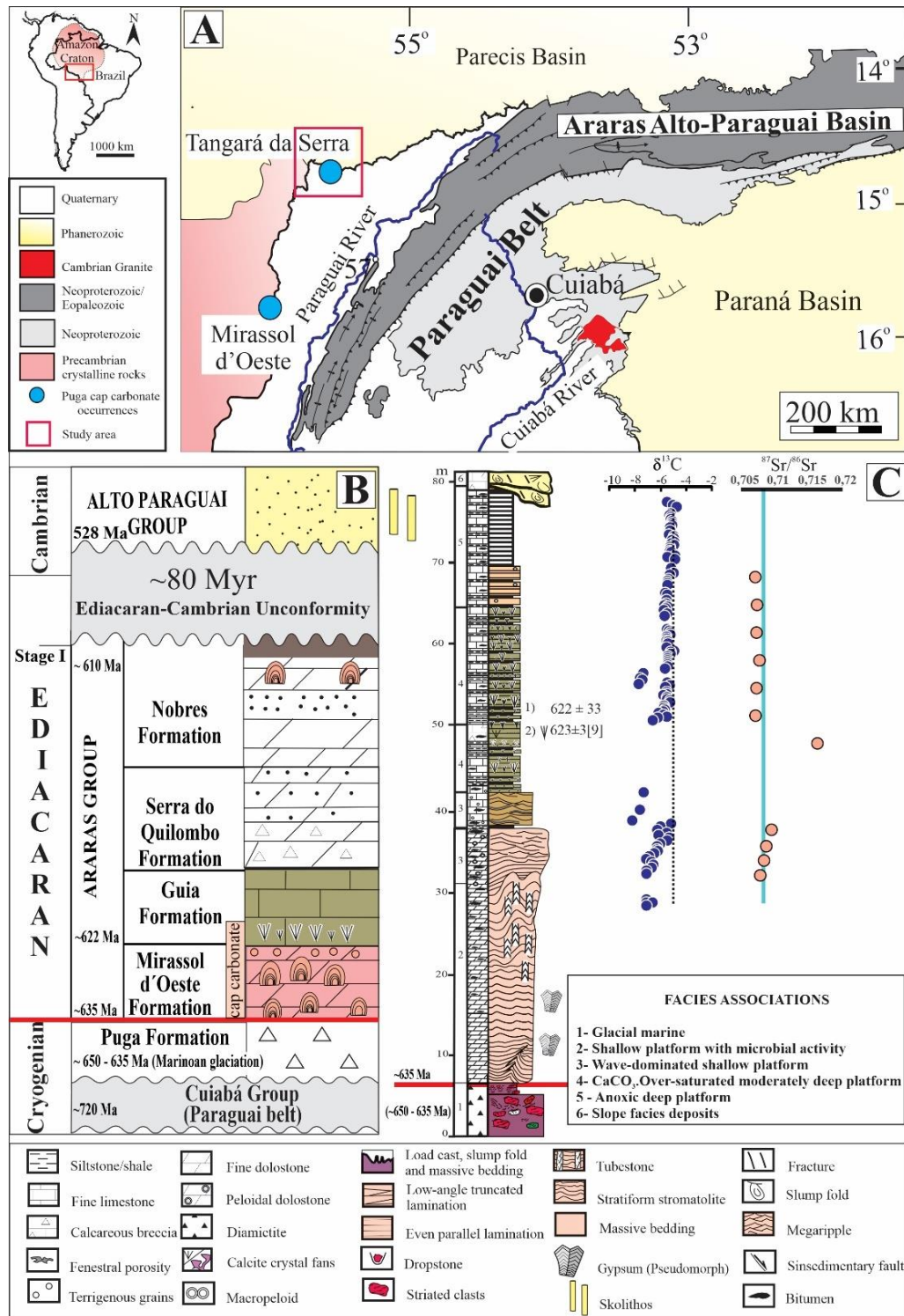


Figure 4.1- Geological map of the southwestern Amazon Craton, indicating the Araras-Alto Paraguai Basin, Paraguai Belt, and the occurrences of Puga cap carbonate (PCC) with the study area (Calcário Tangará quarry) highlighted by stars in the Tangará da Serra-Mato Grosso, Central-Western Brazil. B) Lithostratigraphy of the Neoproterozoic-Cambrian deposits of the Araras-Alto Paraguai basin (adapted from Nogueira and Riccomini, 2006 and Nogueira *et al.*, 2019). C) Marinoan cap carbonate sections (Tangará region).  $\delta^{13}\text{C}$  curves and paleoenvironmental interpretation (Facies association) of the Puga cap carbonate (adapted from Nogueira *et al.* 2019, Soares *et al.* 2020, Santos *et al.* 2021). Age of Guia Formation (Cap limestone): 1) Pb/Pb and  $^{87}\text{Sr}/^{86}\text{Sr}$  by Romero *et al.* 2013 and age 2) U/Pb in situ crystal fans by Carvalho *et al.* 2023.

#### 4.2.1 Mirassol d'Oeste Formation (Cap dolostone)

The Mirassol d'Oeste Formation is the basal unit of the Araras Group. It corresponds to a dolomitic interval known as cap dolostone (Fig. 4.1C), restricted to the southern edge of the Amazon Craton (Fig. 4.1 A), without extending into the Paraguai Belt (Nogueira and Riccomini 2006). In contrast, the basal portion of the Guia Formation corresponds to the cap limestone (Fig. 4.1C) of the Puga cap carbonate sequence (Nogueira *et al.* 2003, 2019, Soares *et al.* 2020, Santos *et al.* 2021). The Mirassol d'Oeste Formation overlies the Puga Formation (Fig. 4.1C and Fig. 4.2), marking the transition from glacial (icehouse) to greenhouse conditions, as proposed by the Snowball Earth hypothesis during the Cryogenian-Ediacaran transition (Nogueira *et al.* 2003, Hoffman *et al.* 2017). The upper contact with the Guia Formation is interpreted as a maximum flooding surface (Nogueira *et al.* 2003, 2019, Santos *et al.* 2021) and represents a thermal expansion of the oceans after the Marinoan event (Hoffman and Schrag 2002, Hoffman *et al.* 2017). The Puga cap carbonate sequence represents an important stratigraphic milestone, recording the beginning of the Ediacaran Period (Nogueira *et al.* 2003, 2019, 2022, Soares *et al.* 2020, Santos *et al.* 2021).

This unit is best exposed in the Terconi Quarry Mirassol d'Oeste-MT region, where its parastratotype is located, and in the Calcário Tangará Quarry, Tangará da Serra-MT, where the hypostratotype is found (Fig. 4.1A) (Nogueira and Riccomini 2006, Nogueira *et al.* 2019, Soares *et al.* 2020). However, cap dolostone is reported in the Chupinguaia and Espigão d'Oeste regions, Rondônia state, associated with the Espigão d'Oeste Formation (Gaia *et al.* 2017). These pink dolomites occur with the same contact relationships and are considered correlates of the Mirassol d'Oeste Formation (Gaia *et al.* 2017, Nogueira *et al.* 2019).

The Mirassol d'Oeste Formation represents a cap dolostone, approximately 40 meters thick (Fig. 4.1C and Fig. 4.2), consisting of pink microcrystalline peloidal dolomudstone, displaying low-angle planar lamination and tubestones (tube-like structures). It also contains dolopackstone with megaripples bedding (Fig. 4.3 A-D). This cap dolostone is succeeded in the upper section by the cap limestone layer (base of the Guia Formation) (Fig. 4.2 and Fig. 4.3 C-D), comprising laminated mudstone rich in silt-sized terrigenous grains (quartz) and subordinate bituminous shale, dolomitic marlstone, intraformational breccias, and large calcite crystal fans (aragonite pseudomorphs) (Nogueira *et al.* 2019, Soares *et al.* 2020, Santos *et al.* 2021, Carvalho *et al.* 2023). Recently, Santos *et al.* (2021) described the occurrence of stratiform stromatolites with gypsum pseudomorphs and giant stromatolites with tubestone (Fig. 4.3 A-B) in the Tangará da Serra region (Fig. 4.1 A). The cap dolostone (Mirassol d'Oeste Formation) is interpreted as a shallow to moderately deep platform environment influenced by biological activity,

grading into a moderately deep platform with local wave influence (Nogueira *et al.* 2003, 2019, Romero *et al.* 2020, Santos *et al.* 2021). The cap dolostone records the sin-deglacial transgression event in contracts, and the cap limestone transitions to long-term transgression, indicating the establishment of a supersaturated environment in  $\text{CaCO}_3$  (Nogueira *et al.* 2019).  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio values ranging from 0.7074 to 0.7085 for the Mirassol d'Oeste Formation (Fig. 4.1 C) are similar to the other Marinoan cap carbonate (Nogueira *et al.* 2007, Romero *et al.* 2013), while Pb/Pb dates of  $627 (\pm 32)$  Ma (Babinski *et al.* 2006), and  $622 (\pm 33)$  Ma obtained on samples from the lowest Guia Formation (Romero *et al.* 2013). Recently an age of  $622 \pm 3$  Ma U–Pb *in situ* in seafloor crystal fans from the Guia Formation was obtained by Carvalho *et al.* (2023). This age was interpreted as a refined constraint on the transition from shallow to intermediate burial diagenesis of the Puga cap carbonate (Fig. 4.1).

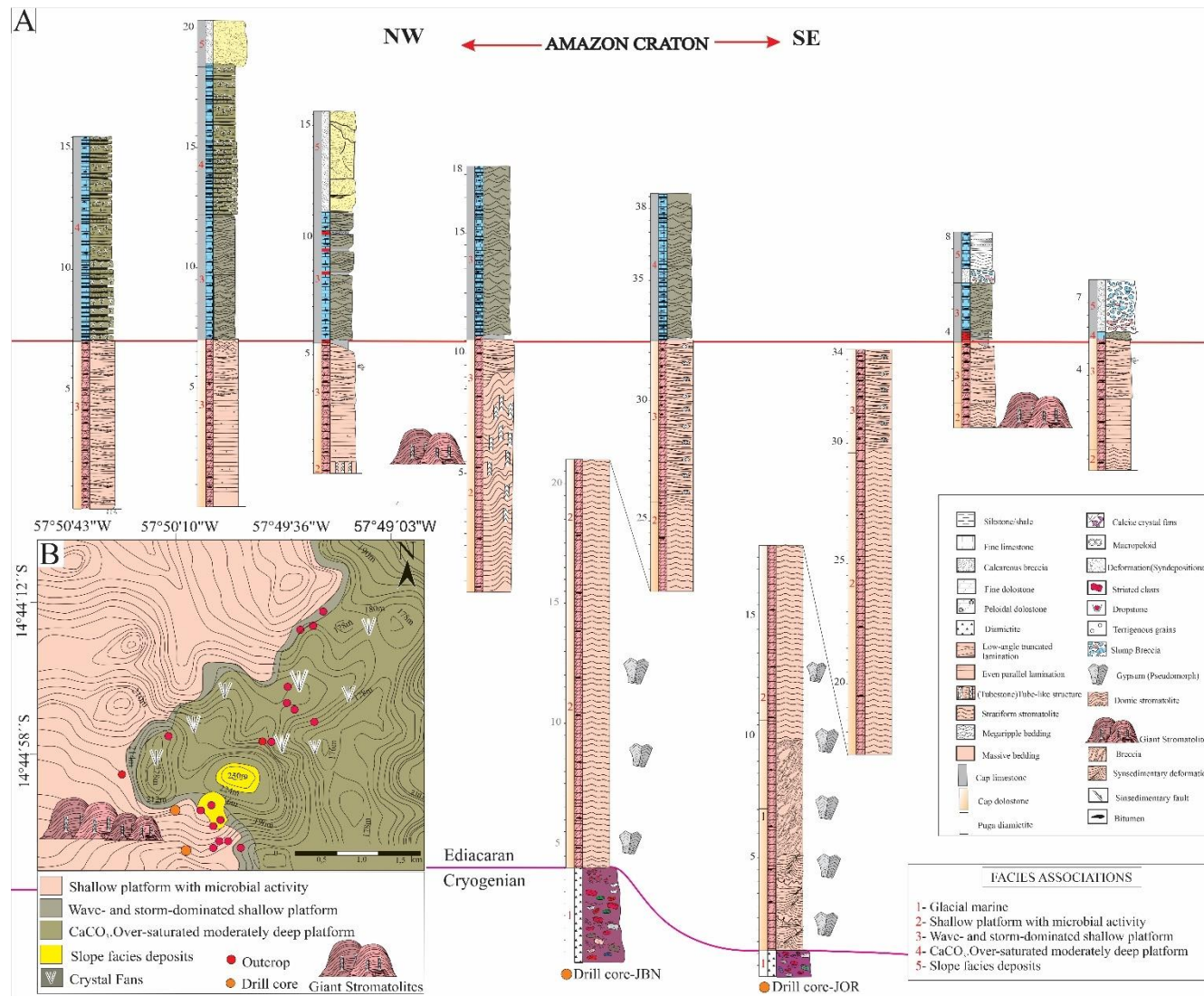


Figure 4. 2- Complete set of outcrops and drill cores (core-JBN and core-JOR) based sedimentary logs of the Puga Cap Carbonate Sequence in the Calcário Tangará quarry, in Tangará da Serra region-Mato Grosso, Central-Western Brazil, showing the interpreted lateral relationship and distribution of the facies associations with giant stromatolite with tubestone (domic doloboundstones with tubestone). The positions of the recorded sections are shown in the facies map on the left.

### 4.3 MATERIALS AND METHODS

We analyzed eighty-three (83) polished thin sections of the cap dolostone (Mirassol d'Oeste Formation). The samples were obtained from two drill cores and an outcrop (Fig. 4.2) from Calcário Tangará Quarry in the Tangará da Serra region of Mato Grosso, Central-Western Brazil (Fig. 4.1A). The modified classification by Dunham (1962) was used for microfacies classification, with refinements based on the works of Wright (1992), Tucker (1992), and Flügel (2004). Dolomite types were recognized and classified individually based on crystal size and shape of crystal boundaries, following the proposal by Sibley and Gregg (1987) and Mazzulo (1992), while the classification of porosity followed the proposal of Choquette and Pray (1970). Approximately 300 points were counted using a point counter to characterize the proportions of constituents following the Glagolev-Chayes methods (Galehouse 1971)

Mineralogical refinement is performed through scanning electron microscopical energy dispersive spectros (SEM/EDS) and cathodoluminescence (CL). CL was utilized to investigate diagenetic features further. CL analysis was performed using the LEICA DM 4500 P LED optical microscope coupled to the Optical cathodoluminescence CL 8200 MK5-2. s at the Cathodoluminescence Laboratory of the Federal University of Pará. The analysis conditions were as follows: electric current ranging from 14.9 to 15.1 kV, acceleration voltage ranging from 296 to 442 A, and exposure time of 10.8 seconds. In carbonate rocks, cathodoluminescence provides a basis for understanding the fundamental diagenetic relationships between grains, matrix, types of cement, porosity evolution, and common substitution reactions occurring in these rocks. CL also provided data on the spatial distribution of  $\text{Fe}^{+2}$  and  $\text{Mn}^{+2}$  in calcite, dolomite, and cement (Hiatt and Pufahl, 2014).

Additionally, analysis using scanning electron microscopical (SEM) and backscattered electron imaging (BSE), supported by energy-dispersive spectros (EDS), was carried out at the Microanalysis Laboratory of the Federal University of Pará on thin sections previously coated with gold to characterize the mineral phases texturally and chemically. The operating conditions for the secondary electrons and backscattered electrons imaging were as follows: electron beam current = 80  $\mu\text{A}$ , constant acceleration voltage = 20 kV, working distance = 8.5 mm. EDS analysis was performed using the Zeiss SIGMA-VP scanning electron microscope with the IXRF Sedona-SD EDS system attached. The operating conditions for EDS analysis were an electron beam current of 80  $\mu\text{A}$ , a constant acceleration voltage of 20 kV, a working distance of 10.1 mm, and an element analysis

counting time of 30 seconds.

## 4.4 RESULTS

### 4.4.1 Stratigraphy and Sedimentology

The first 10 m of the studied cores comprise diamictite and dropstone beds of the Puga Formation. Dolomites of the Mirassol d'Oeste Formation directly cover these deposits (Fig. 4.2), which form ~40m thick the cap dolostone layer. The cap dolostone is in sharp contact with glacial diamictite and exhibits synsedimentary deformation (deformed laminations, micro-faults, and incipient breccias (Fig. 4.3A-B). The cap dolostone presents stratiform stromatolites in the basal portion, transitioning to giant domed stromatolites associated with tubestone (Fig. 4.3A-E). These deposits are superimposed by onlap geometry deposits with wave-dominated dolostone facies (Fig. 4.3G, Fig. 4.4F-G) and horizontal stylolite's (Fig. 4.4H), which mark the last five meters of the unit (Fig. 4.2). Spathic calcite cement fills dissolution features throughout the cap dolostone succession. However, at the top, it is much more pronounced (Fig. 4.4C and 4.4D). The cap limestone (50 m thick of Guia Formation, Fig. 4.1C and Fig. 4.2) is the top of the succession composed of discontinuous layers of dolomitic marlstone that are concordantly superimposed on the cap dolostone (Fig. 4.3 E) and multi-interbedded limestone with fans of calcite crystals (for more details see Soares *et al.*2020 and Santos *et al.*2021). Facies analysis, description, and interpretation of processes are presented in Table 4.1, which summarizes the main facies of the Puga cap carbonate.



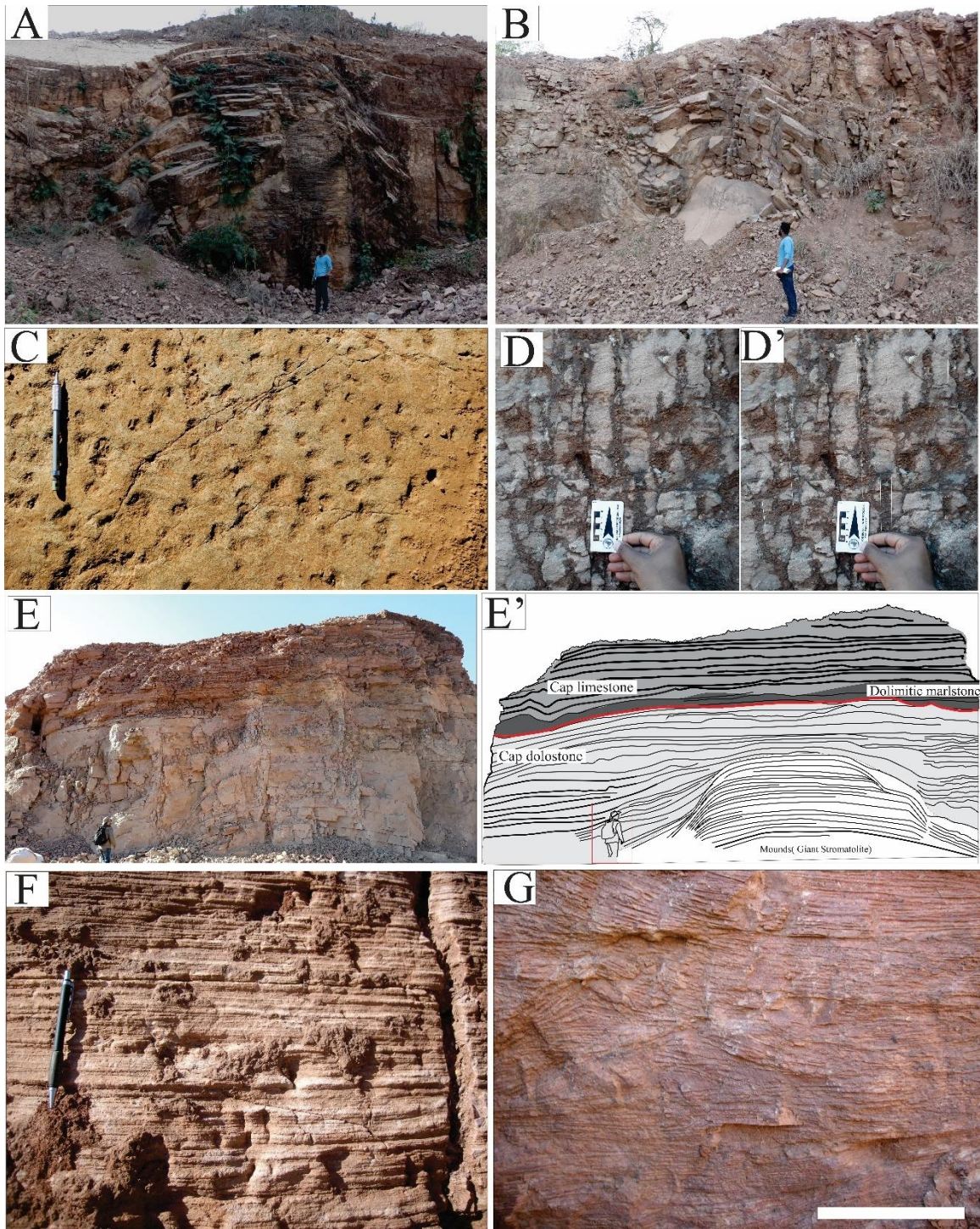


Figure 4.3- The giant biostrome with tubestone of the cap dolostone (Domic doloboustone with tubestone (Dd). A) and B) Large-scale domical mound, scale = 1.88 m. C) and D) Tubestone associated with the giant stromatolite is vertically oriented in the axial zone of the domes. C) Plain view of tubestone as circular structures 2 cm in diameter. D) Detail of tubestone and D') Arrows indicating tubestone. E and F) Wave dominate facies dolostone. E) Quasi-planar laminations F) Symmetrical wave lamination truncated by quasi-planar lamination (scale = 18cm).



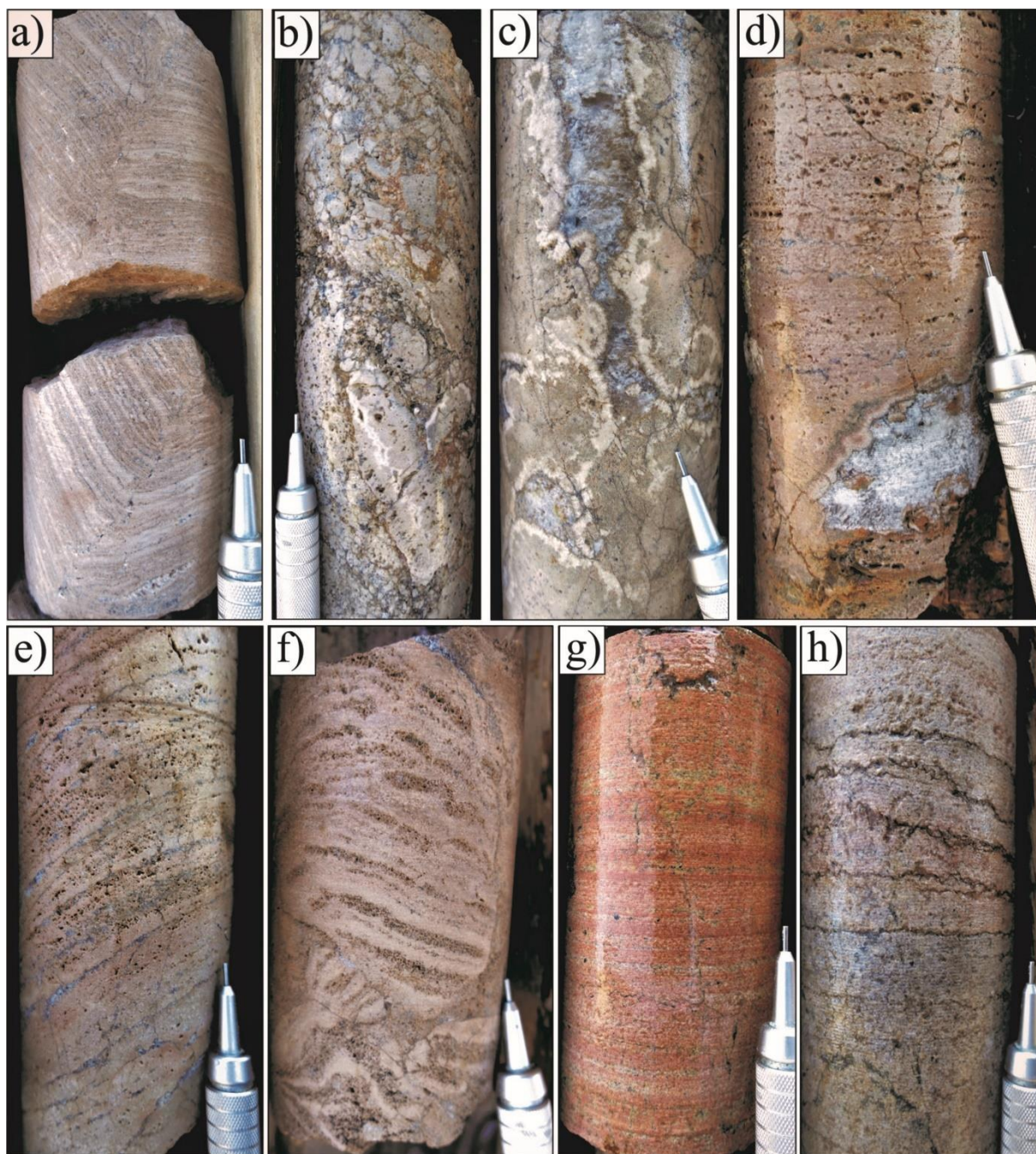


Figure 4.4- Details of the drill core showing the main features of the cap dolostone (Mirassol d'Oeste Formation): A) Deformed synsedimentary contact (Deformed bedding and microfaults). B) Incipient breccias. C) and D) Dissolution features filled with sparry calcite cement..D), E), and F) Laminoid fenestral porosities. G) Pink dolomite has a predominance of macropeloids. H) Chemical compaction features (stylolites).

Table 4.1- Summary of depositional facies and microfacies, structures, and processes recorded by the Puga cap carbonate sequence.

(continue)

| Facies/micro-facies                                                                     | Description                                                                                                                                                                                                                   | Process                                                                                                                                                                      |
|-----------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b><u>Df-Foliated Diamictite</u></b>                                                    | <u>Polymictic matrix-supported conglomerate (sandstone, gneiss, granite and volcanic clasts) poorly sorted, with faceted and striated coarse sand to pebble-grained clasts and clay-rich matrix with incipient foliation.</u> | <u>Abrasion over basement and sedimentary rocks, subsequent deposition from ablation and deformation produced by glaciogenic.</u>                                            |
| <b><u>Drm-Massive dropstone</u></b>                                                     | <u>Siltite / sandy matrix, with millimeter to centimeter size dropstone, of varying composition (sandstone, gneiss, granite and volcanic, and etc.).</u>                                                                      | Subaqueous origin for suspension processes, flow or rain traction debris and resedimentation.                                                                                |
| <b><u>Ds-Stratiform doloboundstone with gypsum pseudomorph</u></b>                      | <u>Stratiform organosedimentary structures with syndepositional cement filled laminate fenesters with gypsum.</u>                                                                                                             | <u>Dolomite precipitation through microbial communities, without hydrodynamics influence.</u>                                                                                |
| <b><u>Dd-Domic doloboundstone with tubestones</u></b>                                   | <u>Domical organosedimentary biostroma. The fenestral are predominantly irregular, filled with spathic calcite cement. Tubestone structures are common in the upper portions of the domes.</u>                                | <u>Precipitation of dolomite by microbial community, with strong hydrodynamics influence. Incipient trapping and bidding processes at the top of the giant stromatolite.</u> |
| <b><u>Dp – Peloidal dolomudstone/ dolopackstone with plane-parallel laminations</u></b> | <u>Parallel laminations, low-angle laminations, stylolites, micro- and macro-peloids.</u>                                                                                                                                     | Predominance of suspended material with sporadic oscillatory flows. Nucleation of carbonates and rapid cementation.                                                          |

(continuation)

| Facies/micro-facies                                                                                             | Description                                                                                  | Process                                                                                                            |
|-----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|
| <b><u>Dq</u></b> – Dolograinstone/ peloidal dolomudstone with quasi-planar laminations and low-angle truncation | <u>Quasi-planar lamination with low angle truncation, micro-ripples, micro-macropeloids.</u> | High-velocity oscillatory flow. Nucleation of carbonates and rapid cementation.                                    |
| <b><u>Pm</u></b> -Peloidal dolograine with megaripple bedding                                                   | <u>Symmetrical and asymmetrical megaripple. Micro and macro-peloids.</u>                     | Carbonate nucleation and rapid cementation during bedform migration by oscillatory flow.                           |
| <b><u>Lw</u></b> – Limestone with wavy bedding laminations.                                                     | <u>Asymmetric wavy mega-ripple marks, convolute laminations and mud drapes.</u>              | <u>Migration of bed shapes generated by currents and waves. Periodic continental influx of terrigenous grains.</u> |
| <b><u>Lq</u></b> – Limestone with quasi-planar laminations and bituminous marl                                  | <u>Quasi-planar laminations and bituminous marl layers.</u>                                  | <u>Calcite precipitation with sporadic high-speed unidirectional flows and impregnation by hydrocarbons.</u>       |
| <b><u>Li</u></b> – Limestone with irregular laminations                                                         | <u>Irregular laminations, rare and sparse crystals fans and pockets of bitumen.</u>          | <u>Calcite precipitation in deep, relatively calm and anoxic waters. Impregnation by hydrocarbons.</u>             |

| (conclusion)                                                                   |                                                                                                       |                                                                                                                    |
|--------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|
| Facies/micro-facies                                                            | Description                                                                                           | Process                                                                                                            |
| <u><b>Ls</b> – Limestone with slump structures</u>                             | <u>Slip structures, fractures, metric blocks, syn-sedimentary faults, and convoluted laminations.</u> | <u>Gravitational movement of masses. Fracturing and slip caused by earthquakes.</u>                                |
| <u><b>MI</b> – Dolomitic marlstone with laminations</u>                        | <u>Flat laminations, fissility, overload structures and dissolution seams.</u>                        | <u>Deposition from suspension.</u>                                                                                 |
| <u><b>SI</b> – Shale with laminations</u>                                      | <u>Parallel laminations, fissility and water leak structures.</u>                                     | <u>Deposition from suspension.</u>                                                                                 |
| <u><b>Lw</b> – Limestone with wavy bedding laminations.</u>                    | <u>Asymmetric wavy mega-ripple marks, convolute laminations and mud drapes.</u>                       | <u>Migration of bed shapes generated by currents and waves. Periodic continental influx of terrigenous grains.</u> |
| <u><b>Lq</b> – Limestone with quasi-planar laminations and bituminous marl</u> | <u>Quasi-planar laminations and bituminous marl layers.</u>                                           | <u>Calcite precipitation with sporadic high-speed unidirectional flows and impregnation by hydrocarbons.</u>       |
| <u><b>Li</b> – Limestone with irregular laminations</u>                        | <u>Irregular laminations, rare and sparse crystal fans, and pockets of bitumen.</u>                   | <u>Calcite precipitation in deep, relatively calm, and anoxic waters. Impregnation by hydrocarbons.</u>            |

#### 4.4.2 MICROFACIES OF CAP DOLOSTONE

The cap dolostone was subdivided from base to top into four microfacies: Microbialites: 1) stratiform doloboundstone with gypsum pseudomorph, 2) domical doloboundstone with tubestone), and wave-dominated dolostone facies, 3) peloidal dolograins/dolomudstone with quasi-planar laminations and low-angle truncations, and 4) peloidal dolograins with megaripples (Table 4.1).

##### 4.4.2.1 Stratiform doloboundstones with gypsum pseudomorph (Ds)

This microfacies is mainly dolomite, with a dolomicritic/microspathic matrix supporting the framework (Fig. 4.5A-D) with well-preserved lamination, mainly composed by dolomicrite peloids clustered in coalesced microclots (grumose texture). Alternatively, resembling a shrub pattern (Fig. 4.5A) like those described by Frasier and Corsetti (2003), these textures are eventually obliterated by neomorphism processes, forming the hipidiotopic texture (Fig. 4.5E and 4.5F).

##### 4.4.2.1.1 Porosity (Ds)

Four types of pores are present in these microfacies, which differ in morphology, distribution, and size: 1) fenestral, 2) interpeloidal, 3) vuggy, and 4) intracrystalline. Fenestral pores are predominant and characterized by laminar (Fig. 4.6 A-D) and discontinuous irregular shapes (Fig. 4.5B), varying sizes between 0.2 and 0.4 mm. These pores are filled with pseudomorph gypsum cement (Fig. 4.6 E-H), calcite cement (Fig. 4.6B and 4.9), and Fe/Mn oxy-hydroxides. Interpeloidal pores associated with shrub textures are more distributed, characterized by irregular shapes frequently filled with pseudomorph gypsum cement (Fig. 4.5 C). Vuggy pores are well distributed in these microfacies. They have irregular shapes and vary between 0.2 – 0.6 mm in width and 0.4 – 0.8 mm in length and are filled with Fe/Mn oxy-hydroxides (Fig. 4.11 C) and organic matter (Fig. 4.12 D). The intracrystalline pores observed within calcite cement (Fig. 4.11 A) and gypsum pseudomorphs (Fig. 4.6 G) present irregular shapes with a moderate distribution, usually ranging between 0.1 – 0.3 mm in width and 0.2 – 0.4 mm in diameter filled by hydrocarbon or Mn-Fe/oxy-hydroxide (Fig. 4.12 E-F).

#### 4.4.2.2 Domic doloboundstone with tubestone (Dd)

This microfacies is characterized by an open framework supported by a dolomicritic matrix associated with tubular structures (Fig. 4.5 H). The lumpy texture predominates in these microfacies, observed in the form of coalesced lumps (Fig. 4.5 G-H), being occasionally modified by neomorphic processes, which form the hypidiotopic texture. In the upper portion of this microfacies, a change in textural organization was observed, marked by rhythmic laminae, alternating between submillimetric, thinner, darker layers and lighter-colored, thicker layer, with irregular fenestrae filled with calcite (Fig. 4.5 G). These rhythmic laminae are always associated with fine terrigenous grains.

##### 4.4.2.2.1 Porosity (Dd)

Four types of pores were identified: 1) fenestral, 2) vuggy, 3) intracrystalline, and 4) tubestone. The fenestral pores, which are laminar and discontinuous with sizes ranging from 0.2 - 0.4 mm in width and 0.2 - 1 mm in length, are filled with spathic calcite cement (Fig. 4.5 G) and subordinately filled with Fe/Mn oxy-hydroxides. The tubestone infilling consists of massive dolomicrite (Fig. 4.7 C) compositionally like the dolomicrite matrix (host rock, Fig. 4.5 H and Fig. 4.7 A-B) and secondary spastic calcite cement (Fig. 4.7 D-H), where one can observe dissolution features (Fig. 4.7 G-H) and the incorporation of the host rock into the cement resulting in a dirty appearance near the walls of the tubestone (Fig. 4.7 E-H). The intracrystalline pores, with irregular shapes and restricted distribution, are observed unfilled inside calcite crystals, varying sizes between 0.1 – 0.2 mm in width and 0.1 – 0.4 mm in length. (Fig. 4.11 A).



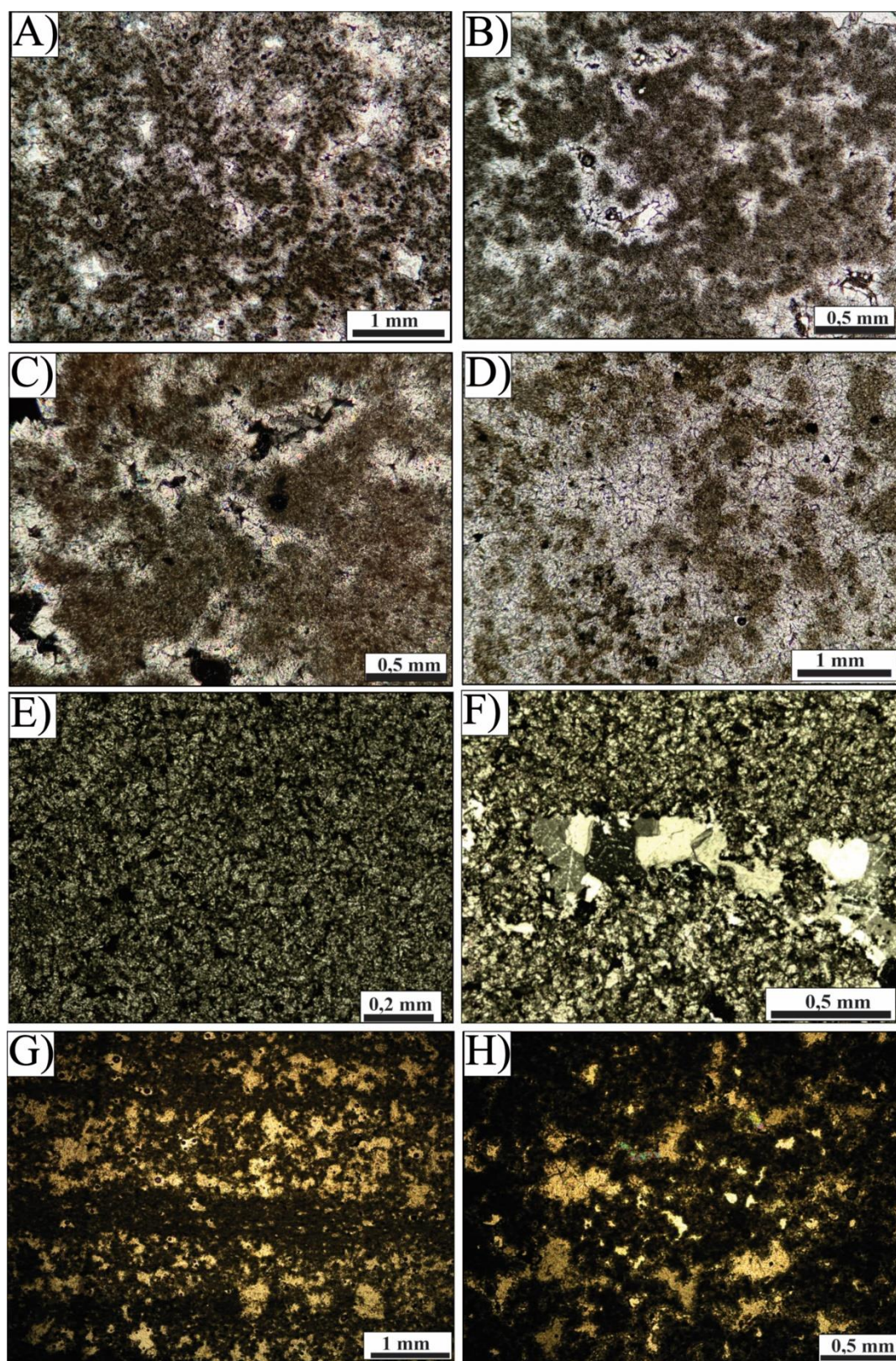


Figure 4.5- A) – F) Photomicrographs of the stratiform *doloboundstone* with *gypsum pseudomorph* (Ds). A) Coalescent grumose peloids with dendritic to dense patterns, similar to shrub facies. B) and C) Dolomicritic peloids clustered in micro-clots (grumose texture). D) Coalesced grumose with advanced neomorphism. E) and F) Dolomicrisparite (Replacive dolomite (RD)) forming a fine to medium planar-e to planar-s crystal mosaic. F) Dolomicrisparite with dissolution filling by calcite. G) and H) Domic doloboundstone with tubestones Dd. G) Dense dark laminae (opaque) alternating with irregular fenestral porosities filled with calcite. H) Dolomicritic peloids clustered in micro-clots (grumose texture). H) host rock is tubestone.



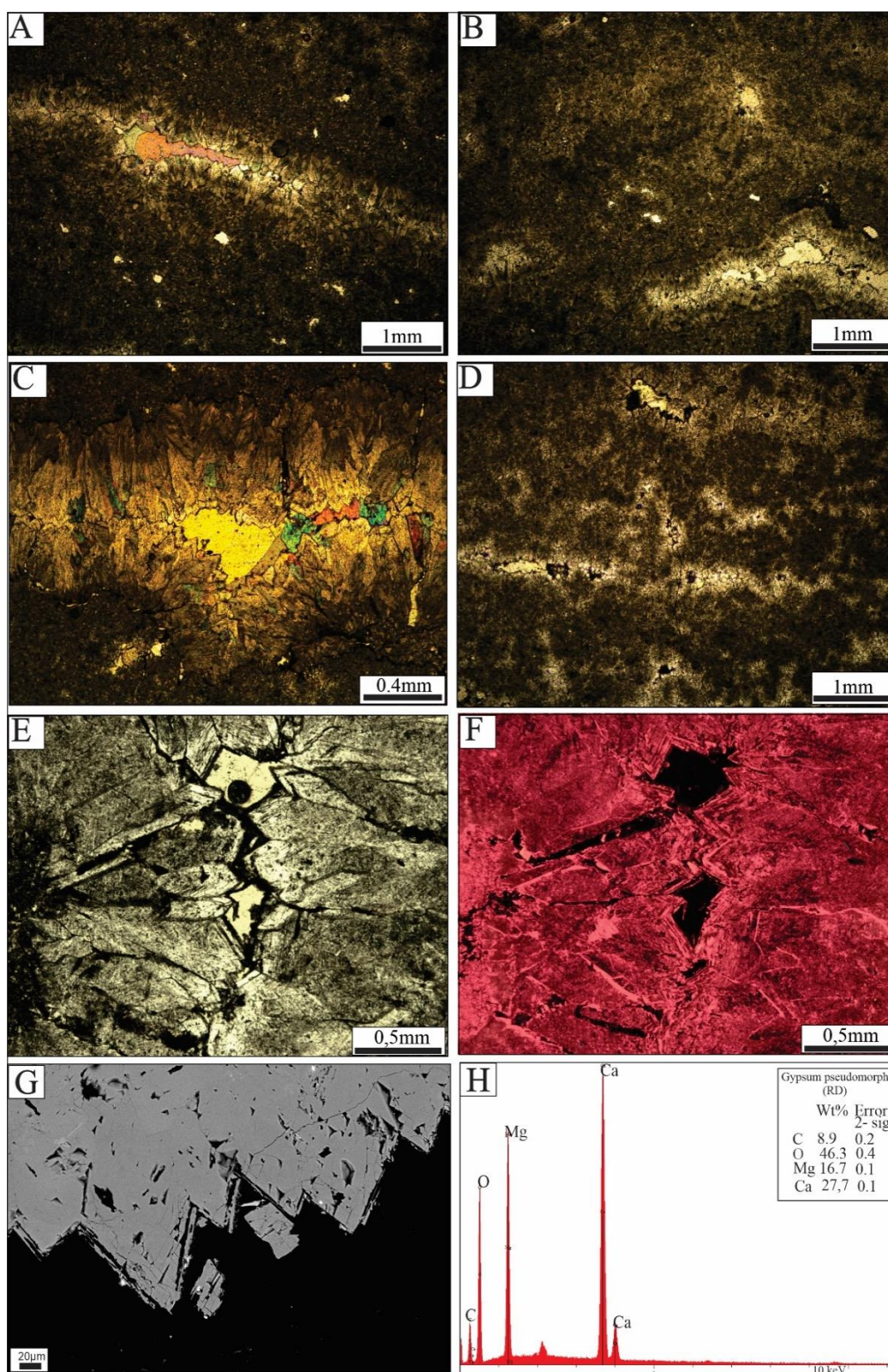


Figure 4.6- Photomicrographs of the textures of the dolomitized gypsum pseudomorph-bearing stratiform doloboundstones with gypsum pseudomorph (Ds). A) PL image of a mosaic of bladed crystals displaying swallowtail twinned gypsum pseudomorph filling fenestral porosity. B) Bladed crystals growing perpendicular to the peloids, forming a compromise contact and calcite among the swallowtail twinned crystal fan. C) Gypsum pseudomorph filling interpeloidal and fenestral porosity. D) Photomicrograph depicting peloidal (stratiform doloboundstones) characterized by micritic microclots exhibiting a grumous texture and fenestral porosity filled with gypsum pseudomorphs. E) Photomicrographs showing swallowtail twinned crystal fan. F) CL image of (E) illustrating details of the swallowtail twinned crystal fan. In CL the crystals showing a high iron content (dark color) and different stages of diagenetic growth. G) A backscattered electron (BSE) image showing details of swallowtail twin dolomitized gypsum. H) EDX spectra for the fribrous dolomite (gypsum pseudomorph)



#### 4.4.2.3 Peloidal dolomudstone/ dolopackstone with plane-parallel laminations (Dp)

These microfacies are characterized by presenting a dolomicritic matrix with a framework supported by peloidal grains, exhibiting millimeter quasi-planar laminations, sometimes low angle truncated (Fig. 4.8B). The laminations' thickness varies according to the size and quantity of the macropeloids (Fig. 4.8B and Fig. 4.8D). These microfacies mark the increase in siliciclastic grains in the cap dolostone rock matrix. Macropeloids have spherical to elliptical geometry, reaching up to 2.4 mm in diameter, with pores of up to 0.8 mm. The texture is predominantly lumpy and rarely hypidotopic. These microfacies exhibit diffuse grumous (Fig. 4.8) dense and dark lumpy texture, and well-defined macropeloids form thick laminations ranging from 1 to 4 mm. A frequent alternation between blades resembling fenestrae similar to microfacies (Ds and Dd) and macropeloid blades was observed (Figs. 4.8D).

##### 4.4.2.3.1 Porosity (Dp)

Three types of pores were identified: 1) interpeloidal, 2) vuggy, and 3) intracrystalline. The interpeloidal pores are filled with spastic calcite cement, hydrocarbon, and dolomite (Fig. 4.8B and Fig. 4.8 D). Their shape and size vary according to the geometry of the peloids/macropeloids and the thickness of the laminations. The vuggy pores occur dispersed along the matrix and within peloidal grains and present irregular shapes, variable sizes from 0.4 to 0.8 mm in diameter. They are sometimes filled with Fe oxyhydroxides and hydrocarbon (Fig. 4.8B). Intracrystalline pores occur exclusively within calcite crystals, have irregular shapes, occur with up to 0.2 mm, and are observed unfilled.

#### 4.4.2.4 Dolograinstone peloidal/ dolomudstone with quasi-planar laminations and low-angle truncation (Dq)

This microfacies is marked by a dolomicritic matrix with a framework supported by peloid grains and fine siliciclastic grains disseminated (Fig. 4.8 A). Exhibits wavy millimeter laminations that vary according to the size and quantity of macropeloids. Macropeloids are the most common throughout all microfacies. They usually have diffuse grain margins, thus preventing their characterization and forming the lumpy texture that

predominates in these microfacies. The macropeloids reach up to 2.4 mm in diameter, form up to 0.8 mm pores, have spherical to elliptical geometry, are moderately ordered, and have well-defined grain margins (Fig. 4.8 E-F). These thick laminations range from 1 – 4 mm. There is a frequent alternation between stromatolitic laminations, which resemble fenestrae (Fig. 4.8C), and wavy laminations marked by macropeloids (Fig. 4.8 A), suggesting wave excavations similar to Dp facies.

#### 4.4.2.4.1 Porosity (Dq)

Four types of pores were identified: 1) interpeloidal, 2) vuggy, 3) intracrystalline, and 4) fenestral. The interpeloidal pores (Fig. 4.8D) are predominantly filled with spathic calcite cement (Fig. 4.8 F), organic matter, and dolomite. Their shape and size vary according to the geometry of the micro/macropeloids and the thickness of the laminations. Within peloidal grains, the thickness varies from 0.4 - 0.8 mm, and they are filled with Fe oxy-hydroxide and hydrocarbon (Fig. 4.8 E). Intracrystalline pores occur exclusively within calcite crystals, have irregular shapes and poor distribution, and are usually up to 0.2 mm (Fig. 4.8 A). Finally, fenestral pores are irregular shapes, ranging from 0.1 - 0.3 mm in width and 0.2 - 1 mm in diameter (Fig. 4.8 C).

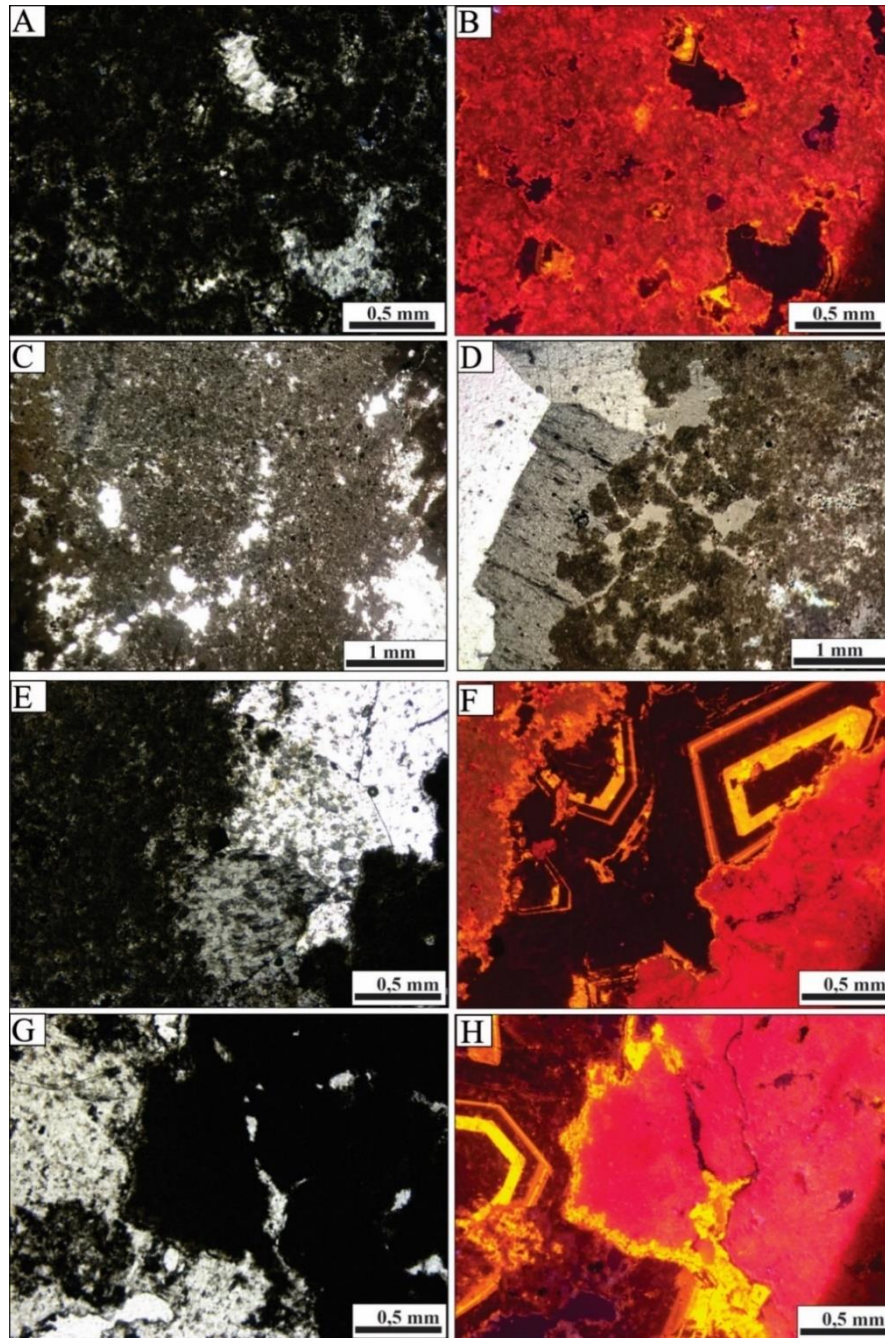


Figure 4.7- Photomicrographs of the petrographic characteristics of the tubestone structure. A) Photomicrograph depicting peloidal host rock (domic doloboustone) characterized by micritic microclots exhibiting a grumous texture with coalesced patterns and fenestral porosity filled with calcite cement. The replacive micritic pervasive dolomite exhibit irregular intercrystalline boundaries (non-planar) B) CL image of (A) illustrating the heterogeneous luminescence of dolomicrite. It exhibits a predominant red to orange luminescence, with the brightest luminescence occurring in the most replacive portions and dull luminescence in the most micritic portions. Note that calcite cement is mainly non-luminescent, although there are zones with concentric zoning of bright orange luminescence. (C) Fillings of the tube with dolomicrite (the same material as the host rock). (D) The cement of calcite fills the tubestone. Note that it engulfs and partially dissolves the tube wall. (E) Disrupted contact between the dolomicrite and the cement. (F) CL image of calcite cement showing concentric zoning with non-luminescent and bright yellow bands and dolomicrite exhibiting dull red to orange luminescence. (G) and (H) Paired PL and CL photomicrographs of rupture of the tube wall. Note that the bright yellow luminescence of the dolomicrite fragment edge shows a calcitization.



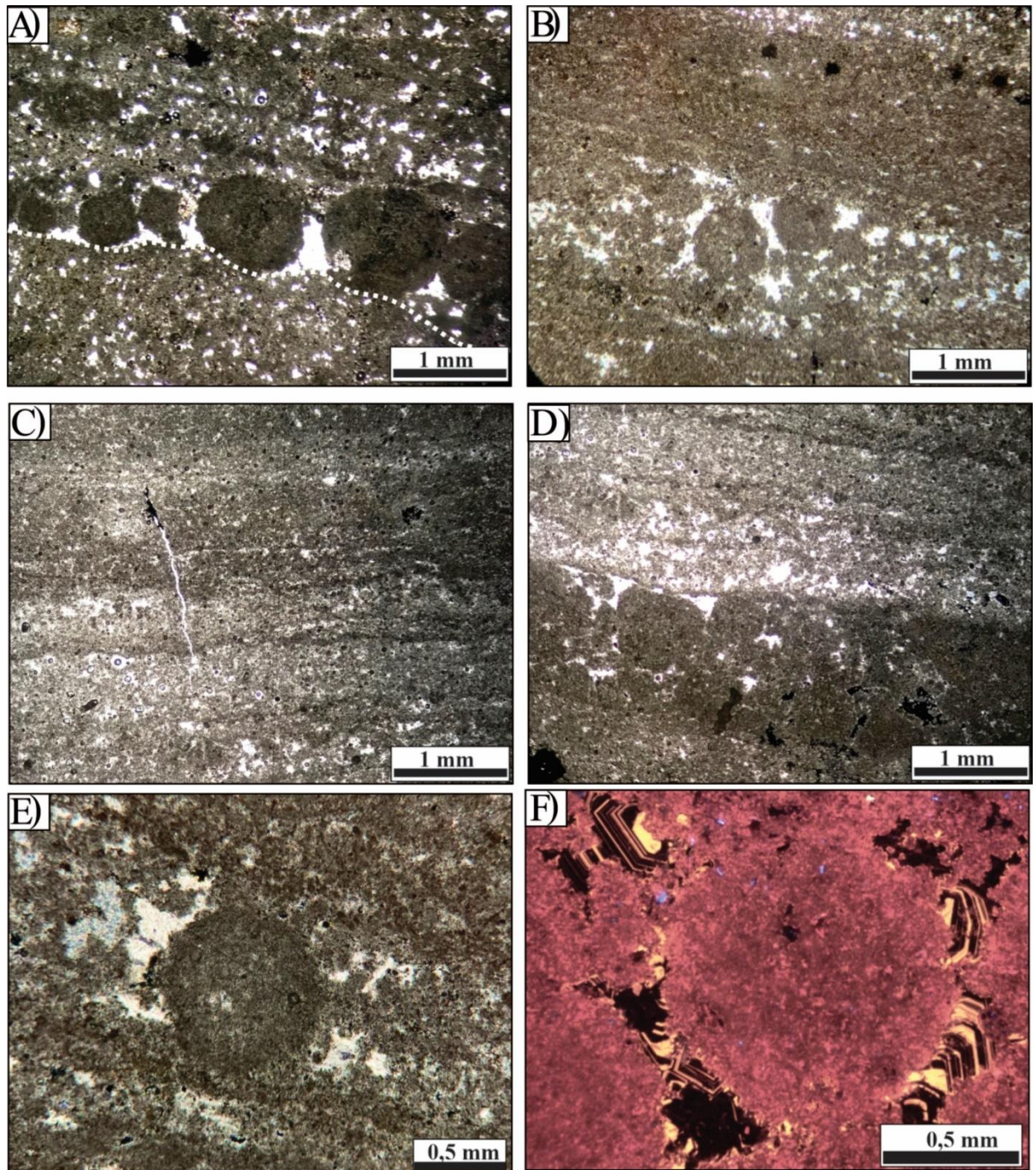


Figure 4.8- Photomicrograph of wave-dominated dolostone facies (macropeloids) from cap dolostone. A) and B) well-individualized macropeloids, filling in excavations (laminae base). C) detail of stromatolitic laminae. B and D) macropeloids intercalation with stromatolitic laminations. E) detail of the macropeloids, highlighting the calcitic cement. F) cementation phases in cathodoluminescence, dolomicrite in red and the ferrous calcitic cement in black

#### 4.4.3 Facies association

The microfacies have been classified into an association (Table 4. 2), suggesting deposition in an initially shallow platform environment with microbial activity, which later transitions to a shallow to moderately deep wave-influenced platform. The microfacies within the shallow platform environment with microbial activity association include the following. Ds – stratiform doloboundstones with gypsum pseudomorph 2. Dd – domical doloboundstones with tubestone. The microfacies within the shallow wave-influenced platform association include the following: 1) Dp–Peloidal dolomudstone/dolopackstone with plane-parallel laminations: 2) Dq–Dolograinstone/ peloidal dolomudstone with quasi-planar laminations and low-angle truncation. The facies association of the cap limestone (Table 4.2) indicates wave and storm-dominated shallow platforms transitioning into a CaCO<sub>3</sub>, over-saturated moderately deep platform (see Soares *et al.*2020 for more details).

Table 4. 2- Facies association and paleoenvironmental interpretation of the sequence of Puga Cap Carbonate

| <b><u>Formations</u></b>                 | <b><u>Facies Associations</u></b> | <b><u>Paleoenvironment</u></b>                                            |
|------------------------------------------|-----------------------------------|---------------------------------------------------------------------------|
| <b><u>Puga Formation</u></b>             | <b><u>Df and Drm-</u></b>         | <b><u>1-Glacial Marine</u></b>                                            |
| <b><u>Cap Dolostone</u></b>              | <b><u>Ds and Dd,</u></b>          | <b><u>2-Shallow Platform with microbial activity</u></b>                  |
| <b><u>Mirassol d'Oeste Formation</u></b> | <b><u>Dm, Dp and Dq</u></b>       | <b><u>3- Wave-influenced shallow platform</u></b>                         |
| <b><u>Cap Limestone</u></b>              | <b><u>Cm, CMq and MI</u></b>      | <b><u>3-Wave and storm-dominated shallow platform</u></b>                 |
| <b><u>Guia Formation</u></b>             | <b><u>Clc, Fl and Bd</u></b>      | <b><u>4-CaCO<sub>3</sub>, Over-saturated moderately deep platform</u></b> |
|                                          | <b><u>Bs, Cr and Cs</u></b>       | <b><u>5-Slop facies deposits</u></b>                                      |

#### 4.4.4 Petrography

##### 4.4.4.1 Dolomicrite (DM)

It consists of replacive micritic pervasive dolomite with irregular intercrystalline boundaries (non-planar) and exhibits bright red to orange luminescence (Fig. 4.7A-B). Texturally, a predominance of a grumose pattern is observed (Fig. 4.5), manifested in the form of diffuse peloids, clustered in no individualized micro aggregates or isolated

grumous (Fig. 4.5B and 4.5C), or rarely these peloids partly resemble shrubs (Fig. 4.5A).

#### 4.4.4.2 Gypsum pseudomorphs (Gy).

The fibrous dolomite cement is a gypsum pseudomorph (Gy) in a well-developed form (Fig. 4.6A-H and Fig. 4.9) with 0.5-0.8 mm in size, filling the majority of fenestral porosities within the rock (Fig. 4.6A-D and Fig. 4.9), with its occurrence limited to the base of the section (Fig. 4.2). The cement exhibits a fibrous habit, characterized by euhedral crystals that display two distinct growth forms: 1) fascicular (Fig. 4.6 C) and 2) radial/radiaxial, typical of swallowtail twinning (Fig. 4.6 E-G). This cement is replacive dolomite (D2). Under CL, the clear borders of the gypsum show dull red and bright orange luminescence rims with moderately corroded crystal borders (Fig. 4.6F and Fig. 4.9 C).

#### 4.4.4.3 Replacive dolomite (RD)

Replacive dolomite (RD) is present in all facies, forming a fine to medium planar- to planar-s crystal mosaic with 0.1-0.2 mm in size (Figs. 4.5E-F and 4.10A). RD represents a nonselective phase that retains tissue and often exhibits crystal formation characterized by a cloudy core (DM) and a clear outer part (Fig. 4.10A). This crystal structure displays CL zoning, with a non-luminescent core and a bright orange rim (Fig. 4.10 B). Primary DM crystal mosaics are commonly observed nested within mosaics of RD, indicating a textural transition between the two phases (Fig. 4.5 D). Moreover, RD directly influenced Gyp by modifying its composition while maintaining its original texture.

#### 4.4.4.4 Calcite Cement (CC)

The spathic cement CC consists of anhedral limpid crystals (Fig. 4.9) ranging from 0.4 to over 2 mm in size. It exhibits a concentric zonation in CL, alternating between non-luminescent and bright orange zones (Fig. 4.8F). Additionally, EDS data indicate a low magnesium ferrous calcite composition. Calcite cementation pervasively fills fenestral (Fig. 4.5G-H), tubestone (Fig.4.7D-H), interpeloidal (Fig. 4.8F) intercrystalline (Fig. 4.5 C), vuggy pores, dissolution seams (Fig. 4.5F and Fig. 4.10 E) and replacing dolomite rims (dedolomitization). CC engulfs and thus postdates all dolomite phases and pyrite crystals (Fig. 4.9).

#### 4.4.4.5 Other paragenetic phases

Non-carbonated cement, such as pyrite pseudomorphs (Fig. 4.9), Fe/Mn -oxy-hydroxides (Fig. 4.11 C-F), and fluorapatite (Fig. 4.11G-H), occur dispersed. Pyrite crystals are opaque minerals characterized by their typical cubic habit (Fig. 4.9) and represent the second cementation phase in the rock (Fig. 4.15 stage III), as indicated by well-formed crystal facies. In EDS, the pyrite crystal showed a predominance of oxygen and iron peaks (oxidation), with virtually no residual sulfide peaks (Fig. 4.9). Acicular or colloidal Fe/Mn oxy-hydroxides (todorokite pseudomorph) (Fig. 4.11 E-F) precipitate as a late-stage phase within vuggy and intracrystalline pores (Fig. 4.15 stage IV). In contrast, euhedral fluorapatite cement (Fig. 4.11G) typically occurs in vuggy pores.



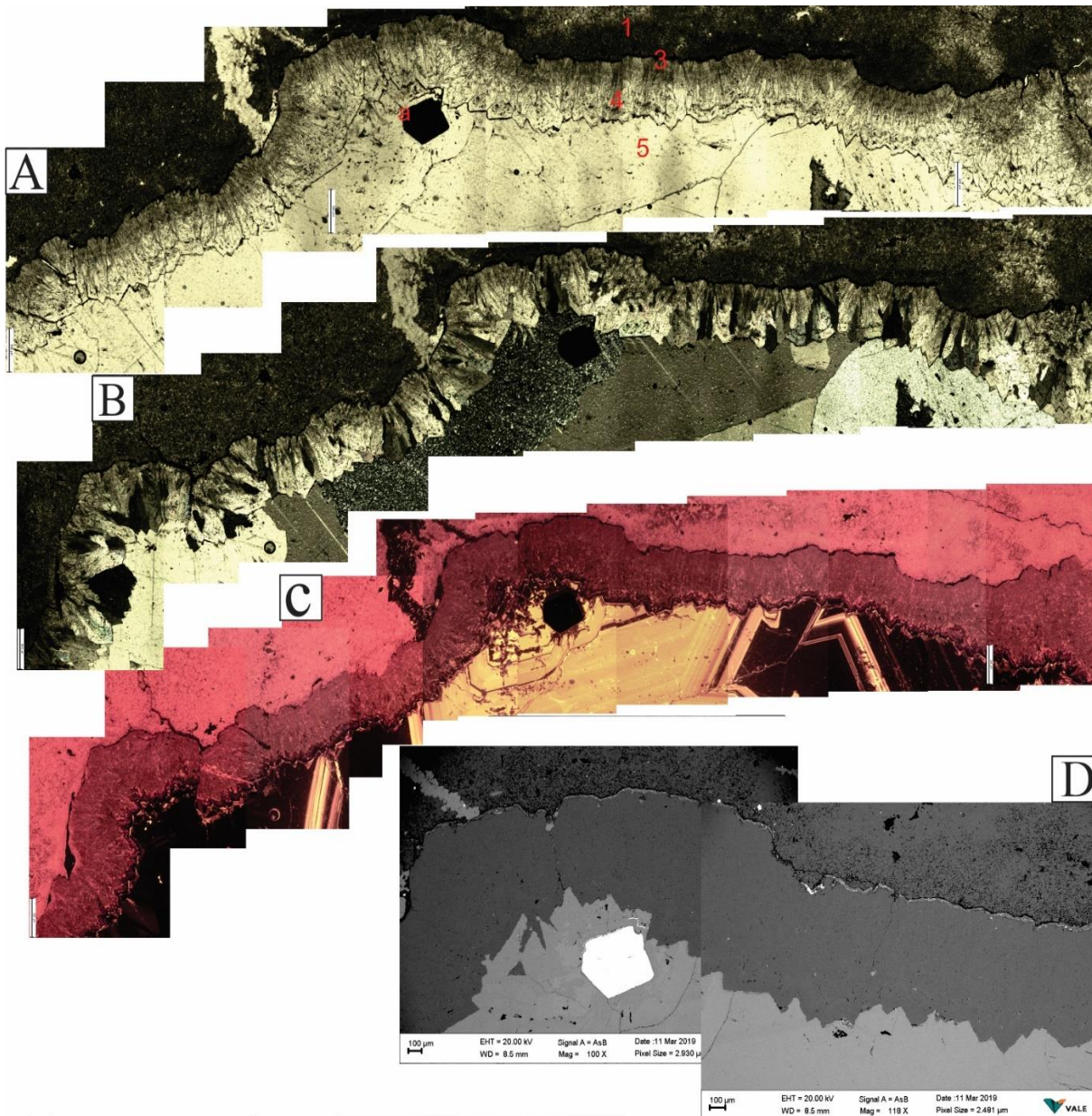


Figure 4.9- Photomicrographs of the gigantic fenestral pores filled with cement. (A-D) Image showing the precipitation order of the paragenetic phases, where the dolomicrite exhibits bright red-orange luminescence, while the gypsum pseudomorph and the most substituted part of the matrix display dull red luminescence. Note that the calcite cement engulfs the pyrite crystal and partially dissolves the pseudomorph faces. D) SEM images of the gigantic fenestral pores filled with cement.



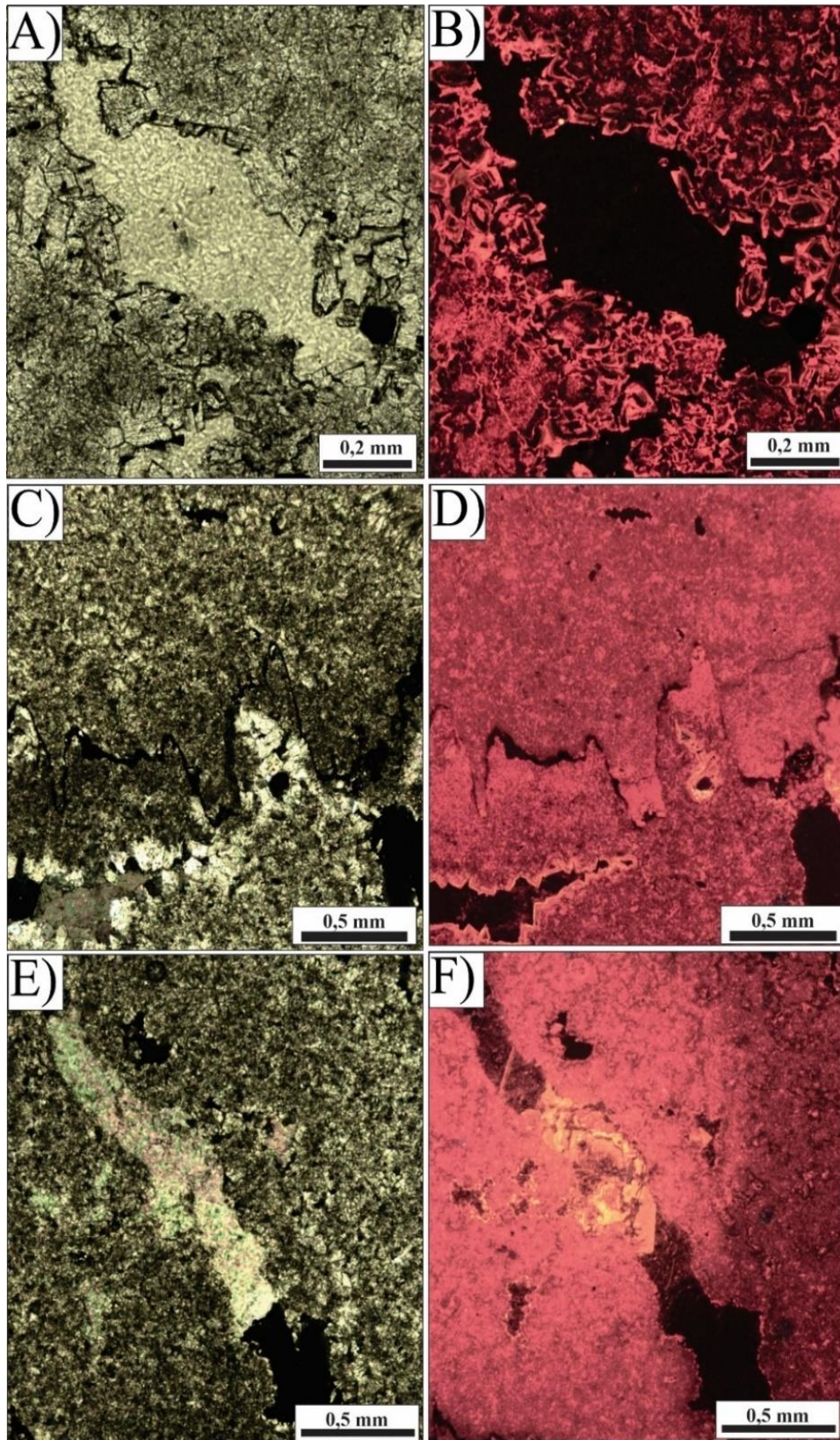


Figure 4.10- Petrographic and correspondent cathodoluminescence images of the main diagenetic features present in the Puga cap dolostone. (A, B) Neomorphism, (C, D) Stylolites, (E, F) Dissolution and calcite precipitation. The calcite filling the fracture shows a yellowish luminescence



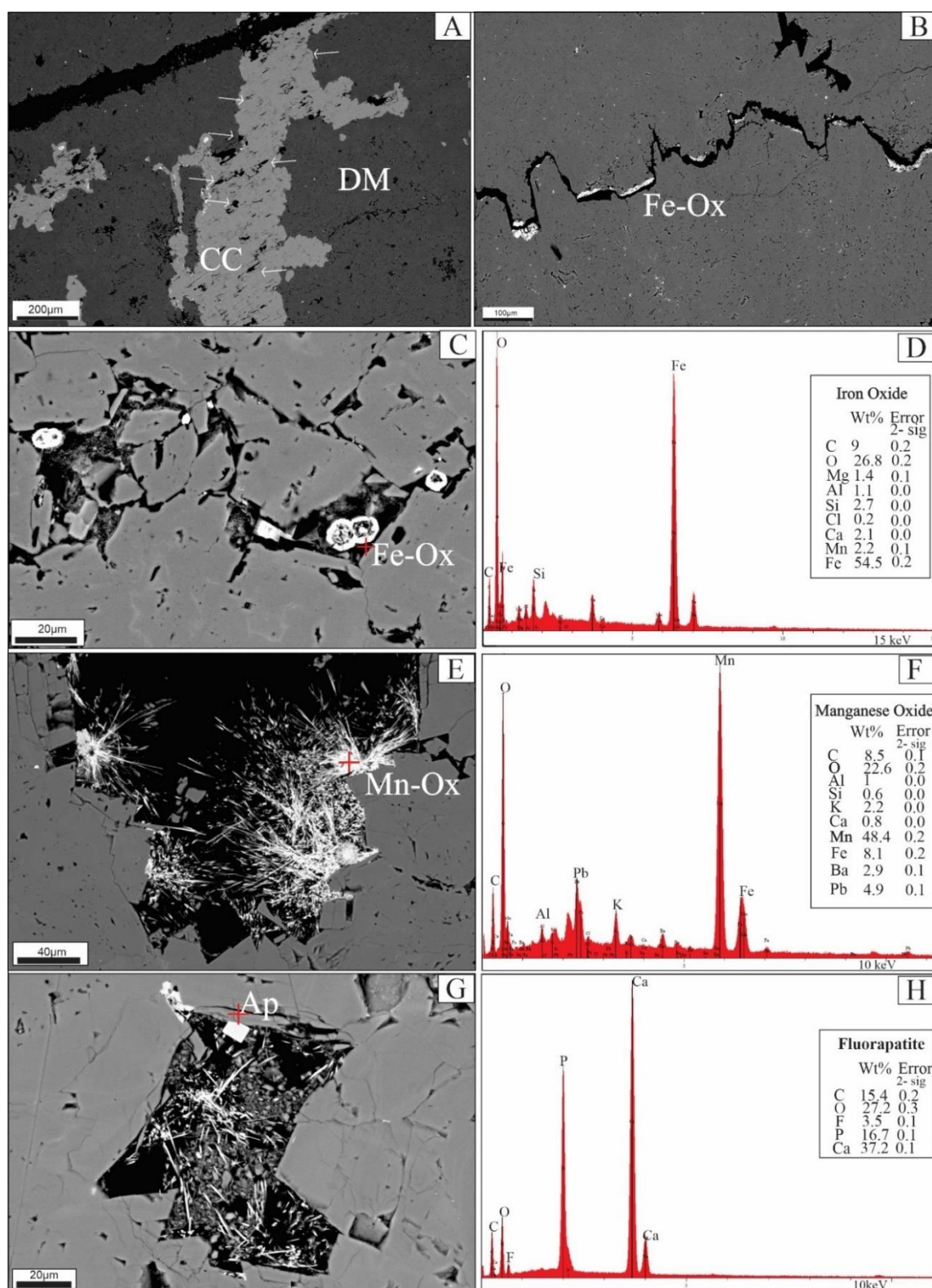


Figure 4.11- Petrographic features in SEM images. (A) Calcite cement filling dolomicrite dissolution seams and Arrows indicating calcite dissolution. (B) Horizontal stylolites in dolomicrite filled with iron oxide. (C) Intracrystalline pores of the dolomicrite filled by iron oxyhydroxide. (D) EDX spectra for the Fe oxyhydroxide. (E) Mn oxide with acicular habit growing towards the pore center without corroded border. (F) EDX spectra for the Mn oxyhydroxide. (G) Fluorapatite and Mn oxide in intercrystalline porosity. (H) EDX spectra for the Fluorapatite

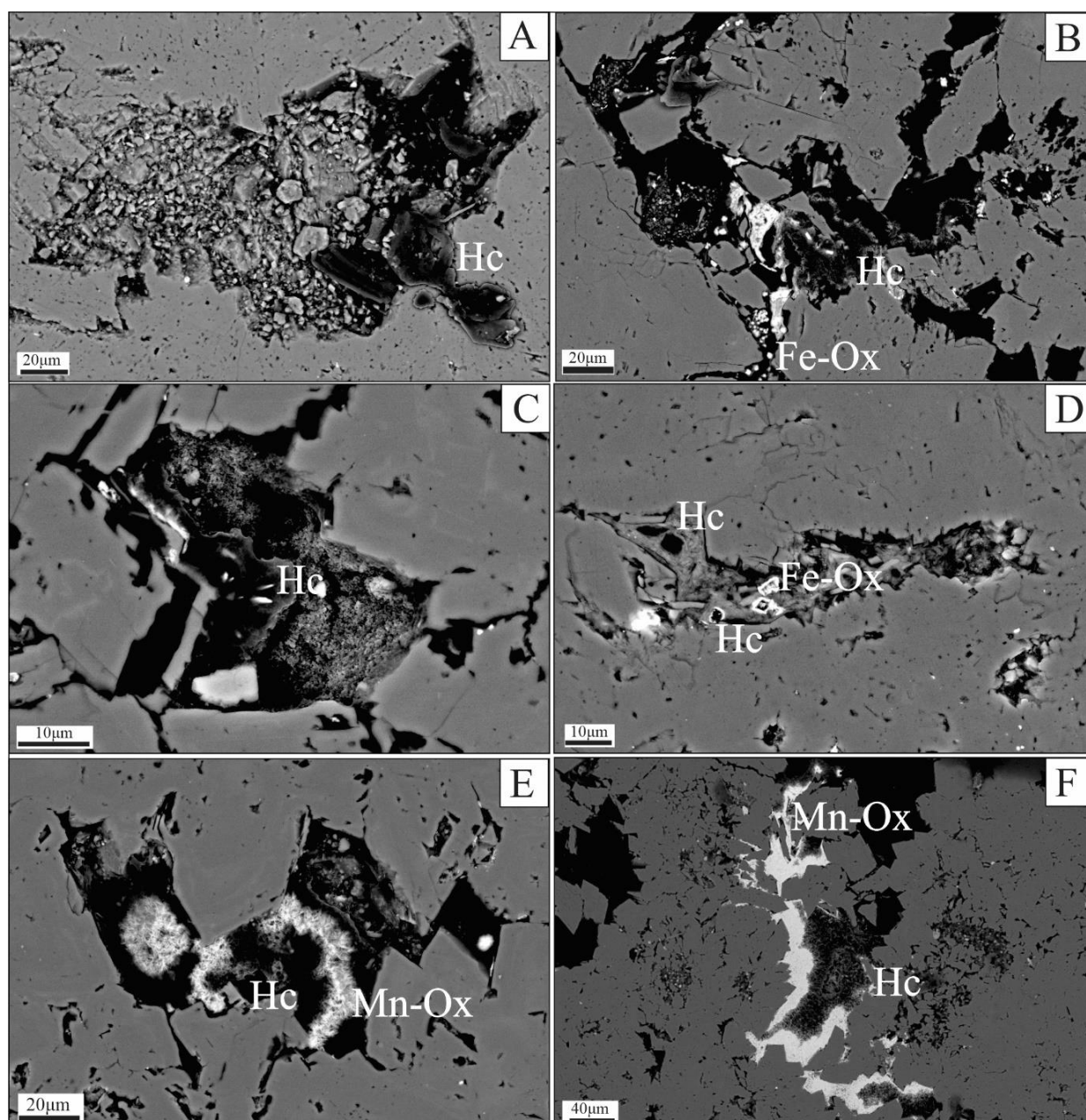


Figure 4.12- SEM and BES images showing bitumen (hydrocarbon) migration and sparry dolomite infilling in dolomite porosities. A) SEM image displaying hydrocarbon infilling of porosities in the dolomicrite. B) SEM image displaying hydrocarbon infilling of dolomite vuggy porosities, with a relationship to Fe oxyhydroxide. C) SEM image showing hydrocarbon infilling of dolomite intracrystalline porosities. D) Early bitumen oxidation processes (EDX analysis revealed that the lighter portions consist of iron oxides, while the darker portions exhibited characteristic peaks of organic matter (hydrocarbon)). E) and F) Hydrocarbon filling intracrystalline porosity in the Mn-oxide, note the dissolution features at the interface between hydrocarbon and Mn oxide.

## 4.5 DISCUSSION

### 4.5.1 Paleoenvironment

After the glacial cap retreat, a shallow carbonate platform established itself in the southern part of the Amazon craton a prelude of the assembly Gondwana (Nogueira *et al.* 2003, Sansjofre *et al.* 2014). The post-Snowball Earth environmental conditions were favorable for colonizing extensive microbial communities (Nogueira *et al.* 2003, 2022, Font *et al.* 2006, 2010, Romero *et al.* 2020, Santos *et al.* 2021). The contact between the stratiform doloboundstone with gypsum pseudomorph and the diamictites of the Puga Formation marks the Cryogenian-Ediacaran transition (Nogueira *et al.* 2003, 2019, Santos *et al.* 2021). The abundance of diffuse peloids forming a granular texture has been associated with intense microbial activity in the shallow platform (Nogueira *et al.* 2003, 2022, Font *et al.* 2006, 2010, Soares *et al.* 2020, Romero *et al.* 2020, Santos *et al.* 2021). The microbial communities colonize the substrate formed by diamicton, and the stratiform microbialites were developed under low hydrodynamic action (Santos *et al.* 2021). According to the model proposed by Yang *et al.* (2017), stable stratification formed after the deglaciation due to the density difference between the two distinct water layers: an upper layer of meltwater and a lower layer of intensely dense saline water. Furthermore, according to Hoffman *et al.* (2017), cap dolostone precipitates were diachronous with the water mixing processes caused by upwelling.

The upwelling combined with glacioisostatic adjustments caused gradual mixing and change of the ocean stratification (Hoffman *et al.* 2017, Ramme and Marotzke, 2022). Glacial Isostatic Adjustment (GIA) is generated by the uplift of continental areas and subsidence in basins, leading to the gradual creation of accommodation space associated with the GIA subsidizing sea-level rise caused by postglacial transgressions (Creveling and Mitrovica 2014, Hoffman *et al.* 2017). These phenomena mobilized deep hypersaline water toward the shallower upper portion of the platforms, which could have favored dolomicrite precipitation and gypsum cementation in fenestral porosities. The early cementation promoted rapid lithification and stabilization of the deposits. The brecciation and microfaulting observed in the basal portion of the drill core samples from the cap dolostone at the contact with the diamictites of the Puga Formation suggest synsedimentary deformation, similar to the deformed features described in the Mirassol d'Oeste region (Nogueira *et al.* 2003). The authors suggest that the deformation occurred while the

sediment was still unconsolidated as a response to the effects of glacial-isostatic adjustment. This evidence reinforces that the dolomite cap precipitated rapidly due to syn-deglacial transgression (Nogueira *et al.* 2003, 2019, 2022, Soares *et al.* 2013, Santos *et al.* 2021).

The hydrodynamic conditions increase, modifying the morphology and textural organization of microbialites (stratiform doloboundstones with gypsum pseudomorph). The chaotic growth of microbial texture at the base (e.g., shrubs and grumose in Ds, see Fig. 4.4 A-C) becomes more ordered toward the top of the domical doloboundstones with tubestone, alternating as dense, dark (mainly composed of peloids) and lighter laminae with irregular fenestral porosity (Fig. 4.4 G). Sporadic siliciclastic inputs created a well-marked lamination at the upper part of the large-scale biostrome (Fig. 4.3 B), evincing incipient trapping and binding with the accretion processes, including locally terrigenous grains within their microfabric (Suarez-Gonzalez *et al.* 2019, Santos *et al.* 2021, Vitek *et al.* 2022). The growth of giant stromatolites (along the coast of the Amazon Craton) after glaciation can be attributed to a combination of different factors, including shallow and clear coastal waters, high temperatures, increased carbonate production, and the continuous creation of accommodation space induced by GIA and postglacial transgression (Santos *et al.* 2021).

The progression of transgressive conditions and water mixing (seawater and melt-water) resulted in increased hydrodynamic effectiveness, with the environment becoming dominated by waves and currents, as reflected in the peloidal dolograins/dolomudstone microfacies with quasi-planar lamination and low-angle truncation, as well as the peloidal dolograins with megaripple beds. The occurrence of macropeloids is a product of the aggregation of micropeloids from the Dd microfacies during these erosive events, primarily influenced by waves. The macropeloids observed in the Dq and Dp microfacies are well preserved. However, finding well-preserved macropeloids is uncommon since they easily disaggregate after formation (Soares *et al.* 2020). Therefore, the presence of well-preserved macropeloids in the Dq and Dp microfacies indicates minimal or no transportation, and the deposition in situ was associated with rapid cementation increasing the potential of preservation (James *et al.* 2001, Halverson *et al.* 2004, Soares *et al.* 2020). The alternation of macropeloidal and microbialitic laminae suggests that during periods of lower energy, predominate microbial colonization on the substrate. In contrast, the high-energy conditions were recurrent reworking microbial communities (Santos *et al.* 2021, Suosaari *et al.* 2022).



Dolomitic marlstone observed in contact with the cap limestone indicates an increase in the influx of detrital components into the shallow platform, resulting in turbid waters that hinder light penetration. These new environmental conditions lead to the burial and decline of microbial communities and the consequent change in carbonate factories (Soares *et al.*2020, Romero *et al.*2020, Santos *et al.*2021, Nogueira *et al.*2022). The cap limestone predominantly comprises calcareous deposits with mega-ripple beds and aragonite crystal fans (see Soares *et al.*2020 for more details). This transition in carbonate fabric is interpreted as a record of  $\text{CaCO}_3$  supersaturation events, suggesting a more significant influence of inorganic precipitation (Nogueira *et al.*2003, 2022, Soares *et al.*2020). The upper contact of the cap dolostone with the cap limestone of the Guia Formation represents a maximum flooding surface recorded in all carbonate caps, indicating thermal expansion of the oceans and processes related to long-term transgression (Hoffman and Schrag, 2002, Yang *et al.*2017, Hoffman *et al.*2017, Soares *et al.*2020, Nogueira *et al.*2022).

#### 4.5.2 Diagenetic environment

Significant diagenetic features were observed in the cap dolostone within four diagenetic realms (Fig. 4.14). The sequence of each diagenetic phase can be inferred by paragenetic evidence. As the principal diagenetic process in the studied succession, dolomitization occurred during at least two main stages, from syndepositional to shallow burial settings. The major diagenetic realms are discussed below, emphasizing different types of dolomites and various dolomitization mechanisms/models. In conjunction with these syn-depositional and diagenetic stages, we propose a porosity evolution model for the cap dolostone, which involves multiple diagenetic processes (Fig. 4.15, stages I to IV). These processes can be further classified into constructive diagenesis, which involves pore formation and enlargement, and destructive diagenesis, associated with pore reduction.

##### 4.5.2.1 Syndepositional diagenetic realm

The processes preceding syndepositional diagenesis include synsedimentary dolomite precipitation, generation of primary porosities (fenestral, interpeloidal, intercrystalline, tubestone), gypsum cement precipitation, and collapse breccia formation (Fig. 4.15 stage I).

#### 4.5.2.2 Dolomite precipitation

Synsedimentary dolomite precipitation occurs in specific environments with relatively high temperatures, typically ranging from 35 to 40°C, high evaporation rates, and a high Mg/Ca ratio promoted by the precipitation of sulfates (Sibley and Gregg, 1987 and Warren, 2000). Dolomite can also result from early diagenetic alteration of Mg-rich limestone (Tucker 1983, Font *et al.* 2006). Thus, three genetic classifications are proposed, including primary precipitation mediated by 1) microbial communities through organomineralization processes (Dupraz *et al.* 2009), 2) early diagenetic dolomitization (replacement after deposition but before consolidation, predominantly controlled by fluids generated at the surface), and 3) late diagenetic dolomitization (replacement after consolidation or burial through the reaction of diagenetic fluids, such as hydrothermal influence) (Kaldi and Gidman 1982).

Despite the various proposed models, there has yet to be a consensus regarding the origin of the cap dolostone. Debate surrounds whether dolomite precipitated directly, preserving its primary characteristics and reflecting the chemistry of the water in which it formed (Kennedy 1996, Shields 2005, Nédélec *et al.* 2007, Font *et al.* 2006) or if it formed through secondary dolomitization, converting an aragonite or calcite precursor (Gammon *et al.* 2012, Gammon 2012, Fabre *et al.* 2013, Higgins *et al.* 2018, Ahm *et al.* 2018). It is worth noting that while carbonate caps undergo similar diagenetic processes globally, the creation of a global diagenetic model for carbonate caps is not possible due to the complete dependence of diagenetic processes, on the tectonic, thermal, and burial history of the sedimentary basin where the carbonate cap sequence was deposited (Soares *et al.* 2020). The recent study by Ahm *et al.* (2018) proposes a numerical diagenetic model that compiles new calcium and magnesium isotope measurements in marine cap carbonate successions (Canada, Arctic Alaska, Mongolia, and Bahamas). Based on these data, they argue that the cap dolostone was initially formed by inorganic aragonite precipitation, followed by early dolomitization of aragonite under a range of upwelling fluids during mixed water.



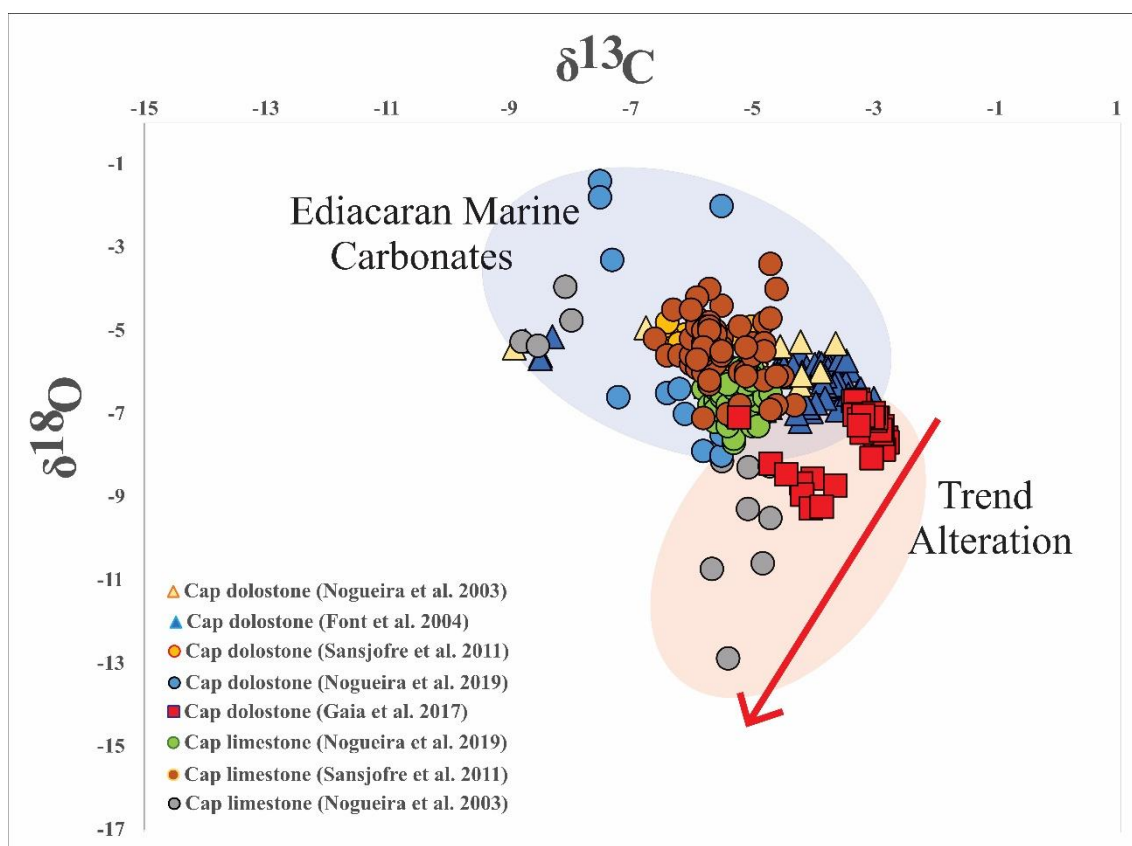


Figure 4.13- Cross plots of compiled  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for the cap dolostone and cap limestone from the Puga cap carbonate succession, southern Amazon Craton. The cap carbonate succession demonstrates preserved signatures of Ediacaran seawater. Data compiled from Tangará da Serra and Mirassol d'Oeste in Mato Grosso, and Chupinguaia and Espigão d'Oeste in Rondônia. Data compiled from Nogueira *et al.* 2003, 2019, Font *et al.* 2004, Sansjofre *et al.* 2011, Gaia *et al.* 2017.

However, the data presented here, along with previous works in the cap dolostone from the Amazon craton, suggest that the microcrystalline peloidal dolomite (dolomiticrite) is the result of organic dolomite precipitation (Nogueira *et al.* 2003, 2007, 2019, 2022, Font *et al.* 2006, Sansjofre *et al.* 2014, Soares *et al.* 2020, Romero *et al.* 2020, Santos *et al.* 2021). The abundance of peloids, the granular texture, and the presence of stromatolites in the geological record provide strong evidence for this organically derived precipitation, indicating that microbial community metabolism, particularly bacterial sulfate reduction, may be involved in the formation of this primary dolomite (Van Lith *et al.* 2003, Nogueira *et al.* 2003, Romero *et al.* 2020). Although syndepositional dolomite occurrences are rare in modern environments, numerous investigations under controlled conditions involve the removal of  $\text{SO}_4^{2-}$  through sulfate mineral precipitation (Baker and Kastner, 1981) or bacterial sulfate reduction (Van Lith *et al.* 2003). Sulfate ions are significant inhibitors of dolomite precipitation (Baker and Kastner 1981, Wright 1999, Warren 2000,

Van Lith *et al.* 2003, Vasconcelos *et al.* 2005, Mastandrea *et al.* 2006). In this regard, it is suggested that microbial activity acts to overcome the natural kinetic barrier to dolomite precipitation, creating a microenvironment with favorable conditions for the primary precipitation of this mineral.

Further evidence supporting the occurrence of primary synsedimentary precipitation is based on the size of dolomite crystals, as diagenetic dolomites formed later exhibit coarser grain sizes than depositional dolomites (Warren 2000). Additionally, the excellent preservation of depositional structures such as laminae, pores, and macro peloids indicates that the lithification of dolomicrite occurred rapidly, possibly within the precipitation environment. In later diagenesis, fluid percolation or mechanical compaction would partially or entirely obliterate these primary structures. Early dolomitization is consistent with the isotopic data from Puga cap carbonate (Fig. 4.13) presented by Nogueira *et al.* (2007, 2019), Font *et al.* (2006), Sansjofre *et al.* (2011), and Soares (2012), where most of the samples analyzed by these authors exhibit negative  $\delta^{18}\text{O}$  values (predominantly greater than -10‰), which do not systematically vary with the negative  $\delta^{13}\text{C}$  values (predominantly approximately -5‰), suggesting the preservation of the original isotopic composition of Neoproterozoic seawater. Furthermore, the lack of covariance between carbon and oxygen values suggests that subsequent alterations were minor (Kaufman and Knoll 1995). In contrast, the cap dolostone occurrence in the southwest region was more severely affected, as can be observed in both the textural aspects and the isotopic data of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  presented by Gaia *et al.* (2017). The covariance between the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  data confirms this greater heating,  $R^2 = 0.9$ , probably due to the interaction with the Jurassic diabase in this region (Gaia *et al.* 2017, Nogueira *et al.* 2019). We assume that dolomicrite is a syndepositional precipitate influenced by microbial communities along the southern margin of the Amazon craton during the syn-deglacial post-Marinoan transgression. This syndepositional stabilization favored the preservation of cap dolostone occurrences further south of the Amazon Craton.

#### 4.5.2.3 Origin of Primary Pore Systems (Fenestral, Intercrystalline, Interpeloidal, and Tubestone)

During carbonate precipitation, constructive diagenesis leads to the formation of primary pores, including fenestral, interpeloidal, intercrystalline, and tubestone pores. Fenestral pores can be interpreted as resulting from the growth of benthic microbial colonies on the diamictiton substrate, associated with forming oxygen gas pockets during the

photosynthesis of these communities or through the decomposition of organic matter (Grover and Read 1978, Mata *et al.*2012, Romero *et al.*2020). The preservation of these pores is possible due to early gypsum cementation and rapid lithification of dolomicrite in the depositional environment (Santos *et al.*2021).

The abundance of dense and uniform dolomicrite peloids reflects *in situ* carbonate nucleation driven by microbial activity (Flügel 2004, Font *et al.*2005, Nédélec *et al.*2007, Dupraz *et al.*2009, Soares *et al.*2020, Santos *et al.*2021, Vitek *et al.*2022). The alternating dark, dense micritic laminae, and irregular fenestral laminae (Fig. 4.4G), marked by siliciclastic grains on top of domical stromatolites, indicate initial trapping and binding processes resulting in laminated sediments (Santos *et al.*2021).

Vertical tubestones are commonly associated with giant stromatolites and are typically present in the flattest areas of the domes. This structural feature is also observed in the Terconi quarry, Mirassol d'Oeste region-MT, displaying similar relationships (Nogueira *et al.*2003, 2019, 2022, Romero *et al.*2020). The tubestone structures exhibit similar compositions for the filling (Fig. 4.7C) and the host rock (Fig. 4.7A). They display fracturing features consistent with the interpretation of layer rupture (Fig. 4.7G-H). In addition to micritic filling, the pores are filled with spathic calcite cement (Fig. 4.7A-H). The origin of tubestones is associated with gas escape, particularly methane, which can be attributed to the destabilization of methane hydrates or postglacial methane (Kennedy *et al.*2001). Contrasting with the previous explanation, Corsetti and Grotzinger (2005) proposed an alternative origin for tubular structures, suggesting a relationship between these structures and stromatolite growth. In the Puga cap carbonate, these structures have attributed gas escape (such as methane from the methanogenic zone of microbial communities) followed by subsequent filling with massive dolomicrite (Nogueira *et al.*2003, Font *et al.*2004, Romero *et al.*2016, Romero *et al.*2020). Here, we argue that tubular structures form through gas or fluid escape related to microbial mat activity, causing partial disruption of partially lithified sediments (Fig. 4.7G-H).

The well-preserved macropeloids laminae (Fig. 4.8) in the upper part of the carbonate succession is interpreted as a result of combined organic processes (microbial activity) and inorganic processes (hydrodynamic influence) (Santos *et al.*2021, Vitek *et al.*2022). The presence of excavated bases (Fig. 8A-B) suggests wave reworking and scouring at the base of these microbialites. The well-preserved macropeloids indicate that they formed *in situ* through the agglutination of micrite particles (Bosak *et al.*2013, Soares *et al.*2020, Santos *et al.*2021, Vitek *et al.*2022, Suosaari *et al.*2022). During periods

of lower energy, these macropeloids settle, generating interpeloidal porosities between the grains, which are filled with calcite cement (Fig. 4.15).

#### 4.5.2.4 Gypsum Precipitation – (Gy)

Cementation is one of the key factors contributing to pore destruction and reduction in reservoir rock porosity and is thus associated with destructive diagenesis processes (Figs. 4.13 and 4.14 A). Gypsum cement represents the initial cementation phase in the rock and can be inferred from observing crystal growth from the pore edges toward the center, exhibiting well-developed crystal facies with “swallowtail” terminations. This cement precipitates during the syndepositional stage within fenestral primary pores. During the gypsum precipitation, intercrystalline spaces are generated among the crystals, giving rise to intercrystalline porosity, which later undergoes dissolution, enhancing pore enlargement. Gypsum and its dehydrated form, anhydrite, are relatively common in the sedimentary geological record (Holland 1984, Bain 1990, Van Driessche *et al.* 2019). Typically, the formation of these gypsum crystals is attributed to evaporation processes occurring in hypersaline basins, sabkhas, and playas. However, an evaporative origin is unlikely for the gypsum crystals in the cap dolostone, as the overall trend of the succession is one of deepening, following the syn-deglacial transgression trends and continual accommodation space creation through glacioisostatic adjustment (GIA) (Nogueira *et al.* 2003, 2019, 2022, Soares *et al.* 2020, Santos *et al.* 2021). Gypsum cement has been used by Santos *et al.* (2021) as evidence of density stratification following the water plume model during deglaciation (Liu *et al.* 2014, Hoffman *et al.* 2017). However, the syndepositional coexistence of the dolomite and gypsum minerals needs to be better understood.

The precipitation of synsedimentary dolomite discussed earlier indicates an environment with low  $\text{SO}_4^{2-}$  content, whereas the gypsum filling the rock porosities suggests a more  $\text{SO}_4^{2-}$  enriched environment. According to Cui *et al.* (2022), early Precambrian seas were initially rich in Mg and poor in  $\text{SO}_4$ , which would favor widespread dolomite precipitation ( $\text{CaMg}(\text{CO}_3)_2$ ). However, it is common to find sulfate minerals associated with the cap dolostone context, such as barite ( $\text{BaSO}_4$ ) (Shields *et al.* 2007, Crockford *et al.* 2019, Okubo *et al.* 2018, 2020, Cai *et al.* 2023, Chen *et al.* 2023) and, in this study, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Therefore, the best explanation for the coexistence of these two minerals would be the addition of  $\text{SO}_4^{2-}$  from an external source. It is suggested that this possible source could be related to intense postglacial continental weathering, which mobilizes elements such as  $\text{SO}_4^{2-}$ , Sr, and rare earth elements (Cui *et al.* 2022, Cai *et al.* 2023),

or it could be related to upwelling hypersaline waters (Ramme and Marotzke, 2022) that could serve as sources of various ions and trace metals important for the recovery of coastal productivity after the Marinoan glaciation (Sansjofre *et al.* 2014).

Hypersaline waters are commonly found in deeper environments after the Marinoan glaciation (Liu *et al.* 2014, Hoffman *et al.* 2017, Yang *et al.* 2017). However, our facies analysis demonstrates precipitation in shallow marine settings. In this regard, the deeper hypersaline waters could be remobilized toward shallower coastal environments, leading to supersaturation of  $\text{SO}_4^{2-}$  and  $\text{Fe}^{2+}$  in fenestral pores. These elements deplete the water-sediment interface due to interactions with microbial community metabolism. The origin of gypsum is likely related to oceanic upwelling, which brings deep hypersaline waters to shallower portions of the marine platform (Yang *et al.* 2017, Ramme and Marotzke, 2022). The GIA event may have also contributed to the mobilization of these deep waters trapped within the fenestral pores of stratiform stromatolites (primary origin pores) and the pH difference between anoxic hypersaline waters and coastal water results in chemical changes in the fenestral porosity. The bottom water is hypersaline and has a different alkalinity than the water in which the dolomicrite precipitated. These relations could generate local dissolution processes, explaining enlarged fenestral pores with well-developed gypsum crystals. The supersaturation of sulfate ions derived from the hypersaline water leads to gypsum precipitation within the fenestral pores, driven by concentrations that exceed the solubility at the water-sediment interface. The alkaline nature reduces the solubility of sulfate ions, promoting gypsum precipitation by supersaturation in porewater.

### 4.5.3 Shallow burial diagenesis (Eodiagenesis)

#### 4.5.3.1 Early dolomitization

The fibrous dolomite cement (gypsum pseudomorph) fills the laminoid fenestrae of basal dolomitic deposits of the Puga cap carbonate succession (Fig. 4.15A, stage II). This cement, resembling typical evaporite mineral terminations known as “swallowtail” was called a “pseudomorph of gypsum”. The detailed mineralogical analysis confirmed the complete replacement of gypsum by dolomite, as evidenced by EDS analysis (dominance of Ca and Mg peaks) and cathodoluminescence examination (displaying the typical red luminescence of dolomite) (Fig. 4.9), establishing the paragenetic relationship

between these minerals. The close association between gypsum cement and dolomicrite and preservation of the original macrotextures indicates synsedimentary dolomitization of the cap dolostone (Zentmyer *et al.* 2011, Santos *et al.* 2021). This dolomitization event likely occurred shortly after gypsum cement precipitation, with minimal influence from deep burial processes. During gypsum cement precipitation, the reduction in  $\text{SO}_4^{2-}$  concentration and the increase in the Mg/Ca ratio of the interstitial water favored early dolomitization. These findings suggest a penecontemporaneous dolomitization process, possibly influenced by microbial communities and interaction with upwelling hypersaline fluids enriched in Mg during the mixed water aftermath of the Marinoan glaciation (Sanz-Montero 2006, Zentmyer *et al.* 2011, Bustillo *et al.* 2016, Hoffman *et al.* 2017, Ahm *et al.* 2018, Santos *et al.* 2021).

The penecontemporaneous nature of the fibrous dolomite cement described here aligns with the characteristics of synsedimentary dolomite marine cement, which is characterized by length-slow optical character and well-developed luminescence zoning, as observed in various Neoproterozoic successions (Tucker 1982, Hood *et al.* 2011, Hood and Wallace 2012, Wallace and Hood 2018, Shuster *et al.* 2018, Hu *et al.* 2020, 2022, 2023a, 2023b). The dolomitization of gypsum cement led to neomorphism of the host rock, resulting in the growth of dolomicrite crystals to dolomicrosparite size, discussed in detail in the next section.

#### 4.5.3.2 Neomorphism

Dolomicrosparite is commonly found in cap dolostone and is characterized by dense subhedral to amorphous crystals with planar boundaries (Fig. 4.10A). Many of these dolomites exhibit partially preserved grumose texture (Fig. 4.4D). This type of dolomite is equivalent to Mazzullo Planar-S (1992), hidiotopic (Gregg and Sibley 1984), and hipidiotopic (Friedman 1965). We interpreted this textural modification from dolomicrite to dolomicrosparite as a product of neomorphism. Neomorphic processes occur throughout the cap dolostone, but they have a limited impact and only partially obliterate the dolomicritic matrix through aggrading neomorphism. During this process, the microcrystalline peloidal dolomite crystals ( $< 4 \mu\text{m}$ ) enlarge, forming local microspar mosaics (5 to 10  $\mu\text{m}$  in size).

This evidence suggests that neomorphism results from shallow burial (Fig. 4.14) occurring during the syndepositional/eodiagenetic transition (Mazzullo 1992). The portions exhibiting more advanced neomorphism are the basal dolomicrites, which appear to

be a paragenetic association with gypsum pseudomorphs. This increased crystallinity characterized by planar boundaries could be related to slow crystal growth from its original state (grumose dolomicrite) due to the continuous diffusion of dolomitizing fluids at low temperatures (Sibley and Gregg 1987). In this sense, the transformation to dolomicrosparite could be primarily associated with the early dolomitization processes of gypsum cement. Mazzullo (1992) proposed various criteria to identify diagenetic dolomites as burial depth increases, including the transformation of initial dolomite with small crystals into (1) more stoichiometric and higher-order phases, (2) coarse crystalline mosaics, (3) depleted concentrations of  $^{18}\text{O}$ , Sr, and Na, and (4) homogenization under cathodoluminescence. However, the possibility of some contribution from early mesodiagenesis cannot be disregarded, given the migration of organic matter within the cap dolostone and shallow burial processes.

#### 4.5.4 Mesodiagenesis

The mesodiagenetic processes in the cap dolostone include chemical compaction, pyrite precipitation, sparry calcite precipitation, organic matter migration, and dedolomitization. Two common diagenetic subdivisions are utilized (Morad *et al.* 2000): shallow mesodiagenesis (depths of 2 to 3 km, temperatures of 70 to 100 °C) and deep mesodiagenesis (depths >3 km, temperatures >100 °C). Our findings, which are correlated with the depositional history of the Araras-Alto Paraguai basin, are more consistent with early mesodiagenesis.

##### 4.5.4.1 Chemical compaction

Stylolites are frequently observed (at macro/microscopic scales) along planes parallel to the sedimentary strata studied in the cap dolostone (Fig. 4.4H, Fig. 4.10C-D), indicating chemical compaction processes due to directed pressure from overlying sedimentary layers (Park and Schot 1968, Buxton and Sibley 1981, Railsback 1993, Koehn *et al.* 2016, Bah 2023). This pressure leads to continuous and irregular dissolution within the dolomite matrix, generating these diagenetic structures with a “sutured and serrate” morphology (Fig. 4.10 C). During the matrix dissolution process, insoluble mineral residues such as iron oxide and organic matter accumulate, highlighting the morphology of these structures and setting them apart from the surrounding matrix (Fig. 4.11 B).

The chemical compaction process begins in late eodiagenesis and extends into early mesodiagenesis (Fig. 4.14). The significant presence of these structures in the cap



dolostone implies a reduction in rock volume, as part of the original calcium carbonate was removed through dissolution (Soares *et al.*2020). On the other hand, they suggest a reduction in primary porosities formed during sediment deposition (syn-depositional) due to compaction in the rock during this diagenetic stage (Park and Schot 1968, Koehn *et al.*2016, Bah 2023). Stylolites are common in the basal units of the Araras Group. In the Guia Formation, fractures are filled with calcite cement and bounded by stylolites parallel to the bedding. These relations indicate prior calcite precipitation before the effective burial of this unit (Soares *et al.*2020). Recent studies describe tectonic stylolites (sub-vertical) in the same formation associated with a related transtensional event and generation of sinistral strike-slip faults in limestones in the Paranatinga-MT region (Seoane and Domingos, 2021). This region was affected by extensional events in the Araras-Alto Paraguai Basin (Santos *et al.*2020). On the other hand, the Mirassol d'Oeste Formation does not exhibit tectonic stylolites (sub-vertical), likely due to its geographic restriction on the southern margin of the Amazon craton, a region less affected by extensional events (Nogueira *et al.*2019, Santos *et al.*2020).

#### 4.5.4.2 Pyrite precipitation – Py

Cubic pyrite represents the second cementation phase in the rock (Fig. 4.15A, stage III) and occurs locally. Semiquantitative chemical analysis using EDS on the pyrite crystal showed a predominance of oxygen and iron peaks, with virtually no residual sulfide peaks, suggesting that the pyrite was oxidized during the percolation of meteoric fluids in the rock. Only the cubic habit of pyrite is preserved, classifying it as a pyrite pseudomorph (Fig. 4.9).

Euhedral pyrite crystals form extensively in marine settings, and the morphology is controlled by temperature, pH, and chemical composition of interstitial water. In marine hydrothermal systems, cubic and pyritohedron are the dominant forms of authigenic pyrite. The formation of pyrite occurs under suitable conditions, typically in reducing environments with an adequate supply of sulfur sources (Jørgensen *et al.*2004, Large *et al.*2007, Li *et al.*2011 Zhang *et al.*2016, Li *et al.*2014, Chang *et al.*2022). Disseminated pyrite pseudomorphs suggest the presence of dissolved sulfate in the water and the preservation of large amounts of organic matter in an anoxic environment. The precipitation of pyrite in marine environments is associated with the activity of sulfate-reducing bacteria (Berner 1984, Tucker 1991, Pruss *et al.*2008, Okubo *et al.*2018, Soares *et al.*2020). However, pyrite can precipitate in mesodiagenetic environments rich in organic matter and

sulfur (Dayal 2017).

During mesodiagenesis, the interaction between fluid and rock leads to combining iron and sulfur ions, forming pyrite. In our interpretation, pyrite in the cap dolostone is a product of the interaction between mesodiagenetic fluids and thermal events associated with the maturation of organic matter in limestone and shale (source-rock). These fluids flow into the intracrystalline porosity of the cap dolostone before calcite cementation, suggesting that this pyrite is closely linked to the maturation processes affecting the organic-rich layers. Pyrite intergrowth with calcite (Fig. 4.9) also indicates formation in mesodiagenetic environments on the cap dolostone results from complex interactions between organic matter, sulfur sources, maturation events and migration (Fig. 4.14).

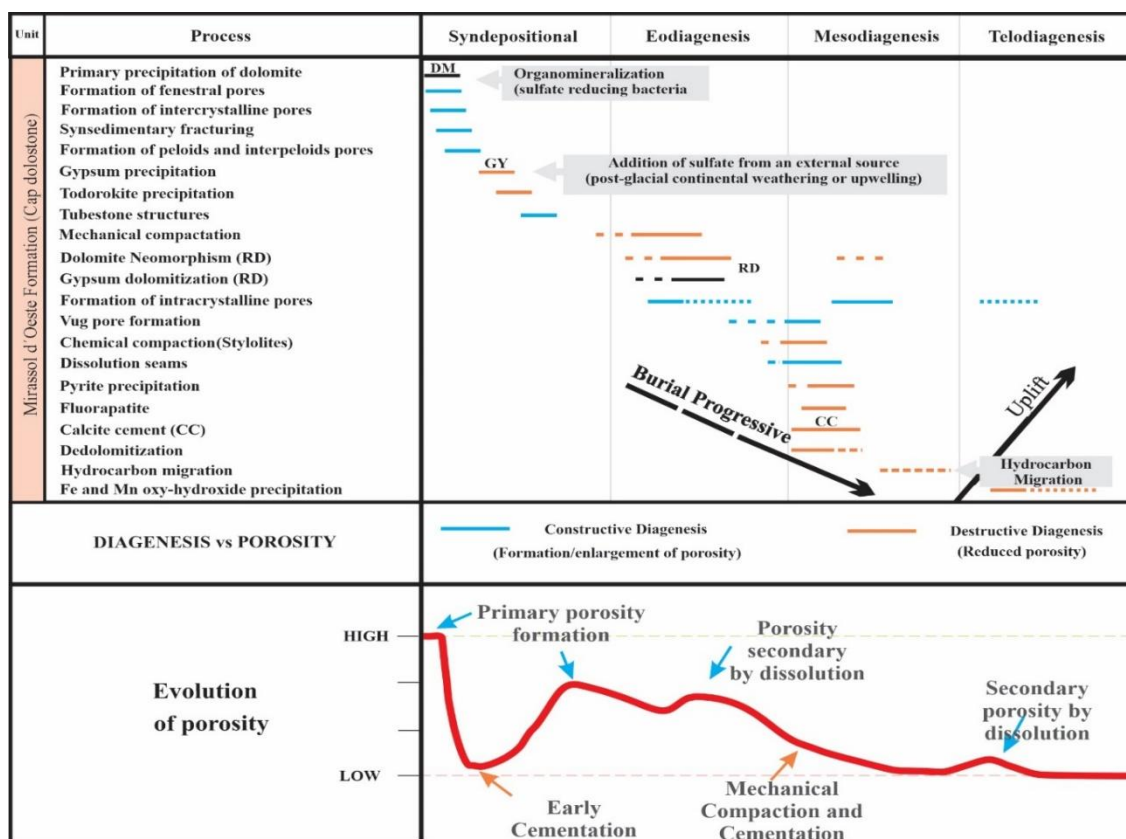


Figure 4.14- Main depositional and diagenetic processes occurred in cap dolostone of the Puga cap carbonatic, Tangará da Serra, following the division of syndepositional, eodiagenesis, mesodiagenesis, and telodiagenesis and the extent of these processes and their influence on the evolution of porosity in the secondary reservoir of the unconventional Araras system. Constructive and destructive diagenetic processes are represented by blue and orange lines, respectively.

#### 4.5.4.3 Burial Calcite Precipitation – CC

The spathic calcite cement (CC) is interpreted as the third phase of cementation in the rock (Figs. 4.14 and Fig. 4.15 A, stage III), commonly observed bordering Pyrite (Fig. 4.9). The precipitation of CC contributes to a significant reduction in both primary

and secondary porosities of the rock (Fig. 4.5F-G and Fig. 4.15, stage II). This calcite cement usually occurs in the center of the fenestrae (Fig. 4.5G and Fig. 4.6C), filling the enlarged pores previously formed by dissolution (Fig. 4.5F, Fig. 4.10 E-F, and Fig. 4.11A). Calcite cementation is most effective on top of the cap dolostone, where dissolution processes are more efficient, forming pockets (Fig. 4.4C-D and 4.10E). Additionally, calcite cement occurs filling the interpeloidal porosities (Fig. 4.8 E-F) and within the tube-like structures (Fig. 4.7), where one can observe dissolution features and the incorporation of the host rock into the cement resulting in a dirty appearance near the walls of the tubestone (Fig. 4.7G-H).

The spathic calcite cement exhibits well-developed crystalline aspects, typically appearing clear with indications of inclusions (Fig. 4.7D and Fig. 4.9). EDS analysis revealed a low Mg content in the calcite (Fig. 4.9 D), supporting a fluid origin distinct from the precipitating environment of the host dolomitic rock. Under CL, calcite has non-luminescent edges that transition to orange-to-yellow luminescence (Figs. 4.7E-H, 4.8F, and 4.9 C). These relationships commonly indicate a transition from an oxidizing environment, most likely shallow, where  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  remain in solution, to a predominantly reducing environment. The progressive burial of the host rock creates a favorable micro-environment for precipitation by incorporating  $\text{Mn}^{2+}$  into the calcitic cement (Hiatt and Pufahl 2014, Machel 1985, Tucker and Wright 1990).

Spathic cement frequently occurs throughout the Puga cap carbonate succession and is not restricted solely to cap dolostone. Soares *et al.* (2020) described the occurrence of spathic calcite in cap limestone deposits associated with mesodiagenetic events. Spathic cement is commonly associated with various stages in depositional and burial environments and is also commonly precipitated meteorically (Schole and Ulmer-Schole 2003). Other evidence supports the generation of cementation in burial environments, such as the previously described precipitation of diagenetic pyrite as a genetic phase preceding calcite. Furthermore, organic matter maturation and primary migration in the Araras Petroleum System are associated with mesodiagenetic events (Soares *et al.* 2020). In this regard, the fluid responsible for the dissolution and precipitation of calcite cement may have a direct relationship with the organic matter maturation events during the progressive burial of the Araras platform.

The paragenetic association of pyrite and spathic calcite cements may have a direct relationship with the thermal maturation of organic matter in the source rock during mesodiagenesis (Fig. 4.14). The co-migration of hydrothermal solutions and

hydrocarbons is common in the geological record (Guilhaumou *et al.* 2000, Lüders and Rickers 2004, Li *et al.* 2023) and has been experimentally simulated (Balitsky *et al.* 2007, Migdisov *et al.* 2017). Fluids associated with hydrocarbons can release fluids with hydrothermal characteristics and are considered independent mineralizing solutions during this process (Levresse *et al.* 2019). Fluids derived from shale that experience an increase in temperature can efficiently mobilize, accumulate, and transport dissolved silica, fluorine, and base metals through fluid-rock interactions. These fluids can precipitate minerals such as apatite and pyrite (Schneider *et al.* 2002, Fuchs *et al.* 2016, Bottoms *et al.* 2019, Li *et al.* 2023) within carbonate host rocks. Our cement stratigraphy above demonstrates the complex relationship between calcite cementation, hydrocarbon maturation, and migration (Figs. 4.13 and 4.14).

#### 4.5.4.4 Hydrocarbon migration – Hc

The upper cap dolostone exhibits accumulations of bitumen (Fig. 4.12), similar to occurrences described by previous studies (Elie *et al.* 2007, Souza Jr. *et al.* 2016, Soares *et al.* 2020). Hydrocarbon represents a fourth phase (Fig. 4.15), where the organic matter migrates through the host rock (reservoir) during early mesodiagenesis due to compaction processes (Figs. 4.14 and 4.15). It primarily accumulates within stylolites and dissolution seams and, to a lesser extent, in fenestral, interpeloidal, and vuggy pores, as the cementation of the rock hampers effective migration within the pores. Souza Jr. *et al.* (2016) and Soares *et al.* (2020) suggested that secondary migration may have occurred during late mesodiagenesis due to profound burial advancement. The cap dolostone is predominantly composed of microbialites, making it a potential candidate source rock and reservoir for the Araras petroleum system. However, only the top of the succession preserves organic matter, despite the initial constructive processes favoring the formation of primary porosity, especially fenestral pores (Figs. 4.14 and 4.15). The continuous cementation of gypsum significantly reduces primary fenestral porosity and interconnectivity between the pores (Fig. 4.15A). Shallow burial and early diagenetic stage evolution decrease rock permeability and consequently hinder the migration of organic matter at the base of the Araras Group (Figs. 4.14 and 4.15) (Bezerra Jr. 2018, Santos *et al.* 2018, Soares *et al.* 2020).

#### 4.5.5 Telodiagenesis

The fifth and final cementation phase involves the precipitation of oxides (Fig. 4.15). These oxides can be observed on all rock constituents in intracrystalline pores. They are found at the edges of certain porosities, exhibiting stylolite features (Fig. 4.10 C). The percolation of meteoric waters is believed to induce diagenetic alteration by oxidizing minerals such as pyrite pseudomorphs and Mn oxides such as todorokite pseudomorphs (Figs. 4.8 and 4.10H). Intracrystalline porosity is also associated with the percolation of meteoric fluids (Tucker and Wright, 1990). These fluids cause small dissolutions, mainly in calcite cement (Fig. 4.11A). Petrographic evidence, such as the dissolution of calcite cement and precipitation of Fe and Mn oxyhydroxide on this burial cement, indicates that telodiagenesis occurs after mesodiagenesis (Figs. 4.13 and 4.14).

##### 4.5.5.1 Telodiagenetic Events

The depositional history of the Araras-Alto Paraguai Basin demonstrates continuous carbonate precipitation on the Araras platform during the early stage of the Ediacaran period (Nogueira *et al.* 2007, 2022). The upper unit of the Araras Group, the Nobres Formation, can be correlated with an age of 610 Ma and shows unconformable contact with the siliciclastic units of the Alto Paraguai Group, with a time gap of at least 80 Myrs, based on the presence of *Skolithos* that provide a Cambrian age to this group (Santos *et al.* 2017, Nogueira *et al.* 2019, 2022, Romero *et al.* 2022). In this context, all the characteristics of the telodiagenetic stages described here may be related to major tectonic-stratigraphic events, such as inversion, uplift, and erosion of the intracratonic Araras-Alto Paraguai Basin (cf. Nogueira *et al.* 2019, 2022, Santos *et al.* 2020, Rezende *et al.* 2021). The uplift and exposure of Araras platform deposits caused the secondary migration of hydrocarbons in the intercrystalline pores can undergo degradation and release of metallic ions, including manganese ( $\text{Mn}^{2+}$ ) and iron (Fe). Two types of Mn-Oxide can be observed in secondary porosity precipitate before the hydrocarbon migration suggested by the hydrocarbon-mineral Mn oxy-hydroxides contact relationship (Fig. 4.12 E-F). This mineral was precipitated during the syngenetic–early diagenetic stages: 1) acicular crystals (Todorokite pseudomorph), growing towards the pore center without corroded border (Fig. 4.11 E), suggesting a low crystallinity and poor stability (Inversion todorokite into Mn-Oxide), 2) dense and smooth appearance crystal (Fig. 4.12 E), precipitated in the border pore with irregular contours, indicate low crystallinity and susceptibility to corrosion by hydrocarbon acid fluid. However, manganese oxide patterns known as "dendrites"

are observed throughout almost the entire exposure of the cap dolostone, and they are related to recent telodiagenetic processes.

These ions can interact with meteoric water that permeates the pores and channels of the rock framework. Manganese oxidation occurred under favorable geochemical conditions, such as appropriate pH, suitable concentrations of manganese ions, and oxidizing agents, among other factors. Manganese ( $\text{Mn}^{2+}$ ) was oxidized to its oxide form ( $\text{MnO}_2$ ), precipitating manganese oxide on pore walls and mineral surfaces.

During telodiagenetic events, hydrocarbon degradation increased due to the chemical weathering promoted by exposure to atmospheric conditions. In this regard, meteoric water can be an important agent in breaking the molecular bonds of hydrocarbons. In addition to water, interaction with acids in the atmosphere, such as carbon dioxide dissolved in rainwater, forming carbonic acid, can also occur. These acids can react with hydrocarbons, especially those more susceptible to oxidation, resulting in degradation and oxidation products. Meteoric water infiltrated the dolomite cap during prolonged telodiagenesis, creating slightly acidic oxygenated pore water, allowing for intense dissolution and oxidation of euhedral diagenetic pyrite present in the inter- and intracrystalline pores of the cap dolostone. Basin uplift, followed by erosion of the Araras Group, can lead to the infiltration of oxidizing surface waters into previously deeper sediments. These relationships are part of the history of most sedimentary basins worldwide. These phenomena are mainly well-developed at basin margins attributed to telodiagenesis (Worden and Burley 2003).

The occurrence of oxidized pyrite, and degraded organic matter associated with iron oxide, and manganese oxide confirms telodiagenesis in the cap dolostone, linked to the uplift and exposure events of the Araras Group during the Ediacaran-Cambrian transition, as proposed by Nogueira *et al.* (2018, 2022). We considered that only the events linked to the Upper Ediacaran uplift were registered if compared with the most significant uplift events associated with the Cretaceous tectonomagmatic event (200 Ma) and Cenozoic (c. 72-65 Ma) contractional pulse of the Peruvian orogeny that occurred since the late Campanian (Rezende *et al.* 2021).

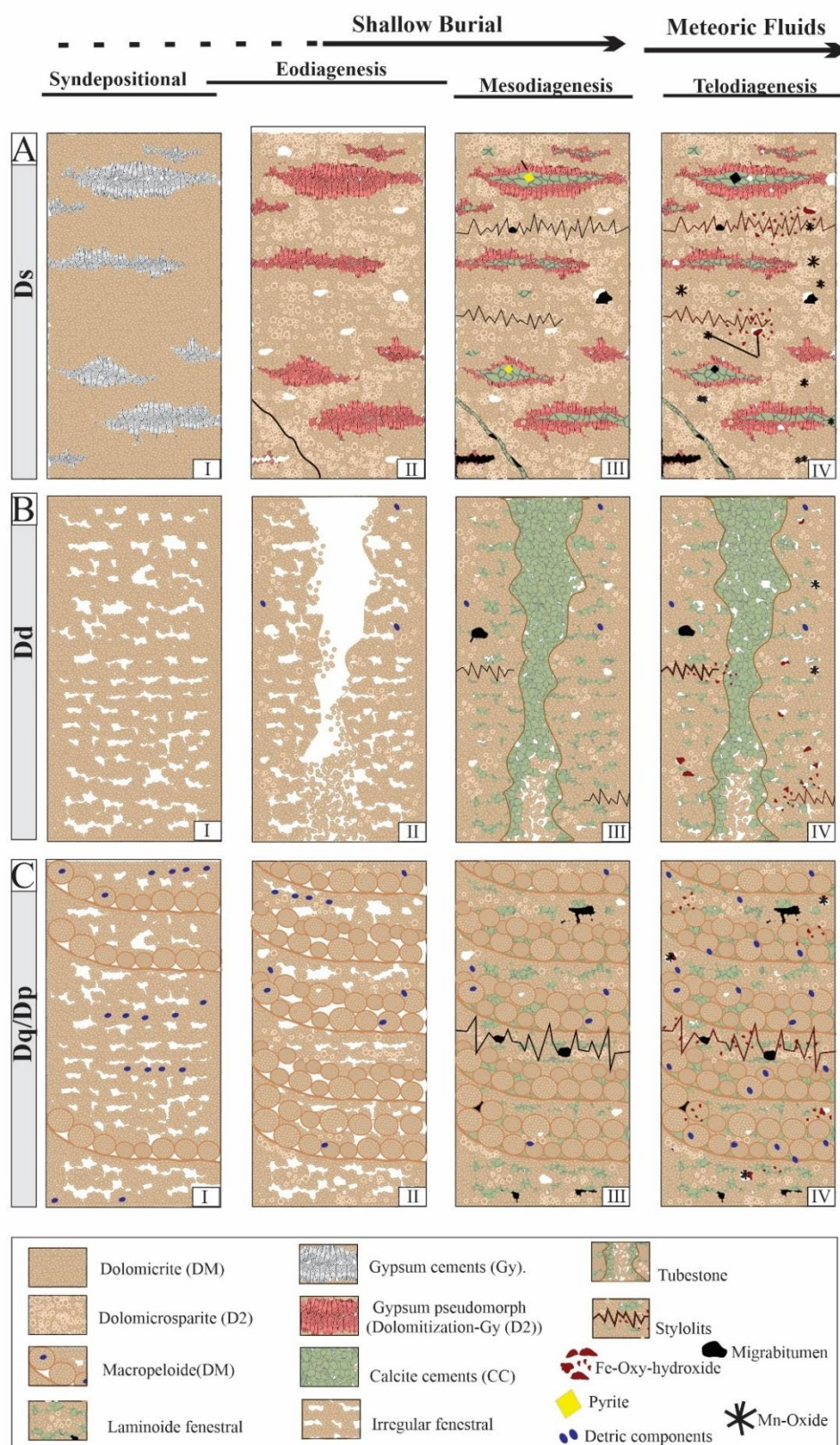


Figure 4.15- Model of porosity evolution for different facies of the Puga cap dolostone Diagenetic sequence and hydrocarbon migration in the cap dolostone (Mirassol d'Oeste Formation). I) Syndepositional II) Eodiagenesis. III) Mesodiagenesis IV) Telodiagenesis A) Ds- Stratiform doloboundstones with gypsum pseudomorph. B) Dd –Domic doloboundstone with tubestones. C) Wave-dominated dolostone facies (Dp)-Peloidal dolomudstone/ dolopackstone with plane-parallel laminations and (Dq) Dolograinsone/ peloidal dolomudstone with quasi-planar laminations and low-angle truncation).



#### 4.6 POROSITY AND PERMEABILITY

A reservoir rock contains empty spaces that determine its porosity, depending on factors such as shape, arrangement, grain size, and degree of cementation. Permeability, however, refers to the rock's capacity to transfer fluids and relies primarily on its pores' quantity, geometry, and interconnectedness (Lucia 2003, Ehrenberg and Walderhaug 2015, Al-Ramadan *et al.*2020, Abdullah *et al.*2022, Boutaleb *et al.*2022, Radwan *et al.*2022). Choquette and Pray (1970) classify rock porosity into two main groups: primary porosity, which forms during rock deposition, and secondary porosity, which develops after the rock's final deposition during diagenesis. Throughout and following rock formation, various factors can modify the size and interconnectedness of pore spaces.

The porosity of the cap dolostone was evaluated, and a qualitative visual analysis was conducted on the laminated dolomites comprising this unit (Table 4.3) by examining the morphology and interconnectedness of the pores, as well as the evidence of cementation found in each microfacies, along with an assessment of rock packing. Thus, despite carbonate deposits are generally considered excellent reservoir rocks, the evaluation of pore spaces in the laminated dolomites of the cap dolostone (Figs. 4.13 and 4.14) reveals that modifying factors, especially cementation (given the loose rock packing), have reduced the pore spaces and consequently affected their interconnectedness. As a result, the rock exhibits low porosity and permeability.

The precipitation of gypsum significantly reduces primary porosity, particularly fenestral porosity, and disrupts the interconnectedness of the pores. Consequently, as burial progresses and diagenetic stages evolve, the rock's permeability decreases, negatively impacting organic matter migration within the Araras Group. The presence of organic matter in the carbonate cap carries implications for petroleum geology. Based on petrographic analysis of morphology, pore interconnectedness, and evidence of cementation in the laminated dolomites, it is apparent that processes associated with constructive diagenesis primarily contribute to primary porosity, while secondary porosity plays a subordinate role. The secondary porosity (vuggy, microfracture dissolution seam, intracrystalline) is formed through the dissolution of dolomicrite and can also originate from the enhancement of pre-existing porosities. Its origin may be related to acidic fluids generated during the decarboxylation of organic matter, the released CO<sub>2</sub> combines with subsurface water to produce carbonic acid, and H<sub>2</sub>S produces sulfuric acid (Mazzullo and Harris 1992, Surdam *et al.*1984, Prochnow *et al.*2006), as evidenced by pyrite. These dissolution

processes initiate during early diagenetic stages and can extend into mesodiagenesis. Subsequently, there was telodiagenetic dissolution, which was less effective and generated by meteoric fluids. (Mazzullo 2004).

Destructive diagenesis processes obstruct these porosities, primarily influenced by gypsum cementation (Fig. 4.15A, Stage I) and secondarily by calcite cementation (Fig. 4.14 and Fig. 4.15 Stage III). Other agents such as Pyrite (Fig. 4.15A, Stage II) and compaction processes exert minimal influence on pore space reduction. Consequently, despite the presence of organic matter and carbonate deposits being generally regarded as excellent reservoir rocks, the evaluation of porosity in the laminated dolomites demonstrates that modifying factors, especially gypsum cementation, have reduced pore spaces and consequently affected their interconnectedness, resulting in a rock with low porosity and permeability.

Table 4. 3- Evaluation of porosity in the laminated dolomites of the cap dolostone (Mirassol d'Oeste Formation).

| <b><u>Porosity Type</u></b>      | <b><u>Porosity Formation</u></b> | <b><u>Microfacies</u></b> | <b><u>Cementation</u></b> | <b><u>Interconnectedness</u></b> |
|----------------------------------|----------------------------------|---------------------------|---------------------------|----------------------------------|
| <b><u>Primary Porosity</u></b>   | <u>Fenestral</u>                 | <u>Dd, Ds, Dq, and Dp</u> | <u>High</u>               | <u>Low</u>                       |
|                                  | <u>Intepeloidal</u>              | <u>Dp and Dq</u>          | <u>High</u>               | <u>Low</u>                       |
|                                  | <u>Intercrystalline</u>          | <u>Ds</u>                 | <u>Not observed</u>       | <u>Low</u>                       |
|                                  | <u>Tubestone</u>                 | <u>Dd</u>                 | <u>High</u>               | <u>Low</u>                       |
| <b><u>Secondary Porosity</u></b> | <u>Intracrystalline</u>          | <u>Dd, Ds, Dq, and Dp</u> | <u>Not observed</u>       | <u>Very low</u>                  |
|                                  | <u>Vuggy</u>                     | <u>Dd, Ds, Dq, and Dp</u> | <u>High</u>               | <u>Very low to low</u>           |
|                                  | <u>Dissolution Seams</u>         | <u>Dd, Ds, Dq, and Dp</u> | <u>High</u>               | <u>Low</u>                       |

#### 4.7 IMPLICATIONS OF THE UNCONVENTIONAL ARARAS PETROLEUM SYSTEM

The total organic carbon (TOC) content in the carbonate rocks of the Araras petroleum system (APS), southern Amazon craton is relatively low, ranging from 0.13% to 0.67% in the Tangará da Serra and Mirassol d'Oeste regions of Mato Grosso state (MT). In Cáceres (MT), TOC values range from 0.06% to 0.23%, while in Nobres, TOC values range between 0.05% and 0.27% (Nogueira *et al.*2001, Elie *et al.*2006, Sansjofre *et*

*al.*2011, Souza Jr. *et al.*2017, Bezerra Jr. 2018, van Maldegem *et al.*2019, Santos *et al.*2018, Soares *et al.*2020, Santos 2022). Although this hydrocarbon accumulation is not economically viable, it represents an unconventional petroleum system (Nogueira *et al.*2001, Soares *et al.*2020). These values are consistent with other Neoproterozoic reservoirs, which typically exhibit TOC values below 1% (Wang *et al.*2008, Ader *et al.*2009, Grosjean *et al.*2009, Hakhoo *et al.*2016, Soares *et al.*2020). The carbonates of the Araras Group are among the best thermally preserved deposits of the early Ediacaran periods, with Rock-Eval TMAX values below 440°C (average 417°C). These values indicate thermal immaturity from an oil window perspective, suggesting that these rocks should have retained indigenous polycyclic terpenoid biomarkers (Sansjofre *et al.*2014, Souza Jr. *et al.*2018, van Maldegem *et al.*2019).

In recent decades, the potential exploration of Precambrian reservoirs has gained attention. Their geological complexity in the reservoirs can be recorded in prolonged thermal degradation, diagenesis, and phase overlap periods, occurring in tectonic contexts distinct from Phanerozoic reservoirs (Fowler and Douglas, 1987). The Guia Formation has been associated with the Araras Petroleum System as the source rock, primarily due to the presence of bitumen along this carbonate succession (Nogueira *et al.*2001). Hydrocarbons are limited to a small percentage of pores (~2%) and rarely occur in fractures within the limestone and shale deposits. At the same time, the cap dolostone is nearly devoid of hydrocarbons (Soares *et al.*2020).

Aftermath of the Marinoan glaciation event (~635 Ma), intense continental weathering led to the input of nutrients into the shallow platform on the southern Amazon craton, promoting the proliferation of planktonic microorganisms and maintaining effective primary productivity (Elie *et al.*2007, Souza Jr. *et al.*2017, van Maldegem *et al.*2019). Organic matter was accumulated and preserved in the storm wave base moderately deep platform (Guia Formation), with anoxic conditions at the water-sediment interface (Sansjofre *et al.*2014). The organic matter content above 1% potential characterizes these deposits as source rock. The migration of hydrocarbons in these muddy rocks is low filling, mainly fractures, stylolites, and dissolution seams. Organic matter is degraded as migrabitumen (Souza Jr *et al.*2017). The cap dolostone overlies diamictites and is overlaid by bituminous limestone and shales (source-rock), and dolostone in the top of a 700m-thick depositional sequence. The cap dolostone has a diachronic relation with the limestone beds typifying as a secondary reservoir characterized by bitumen-filled fenestral and interpeloidal porosity. Although the contact relation between cap dolostone and

the source rock is incompatible with the couple source and reservoir rocks, we suggest a lateral relation between units, implying a lateral hydrocarbon migration. The contact between dolostone and limestone is a weak zone for percolating fluids that modify the closed packing of upper dolostone, allowing the accumulation of hydrocarbons. Furthermore, the dolomite-limestone contact zone provides a mechanical contrast conducive to developing small fracture corridors, serving as conduits for fluid flow (Mazzullo 2004, Koeshidayatullah 2022). The migration was facilitated by increased early cementation dissolution and the enlargement and connectivity of primary porosity. The upper cap dolostone occurs with calcitic cementation in the interpeloidal and fenestral pores, in contrast to the prevalent dolomitic cementation observed at its base. Calcite exhibits a higher propensity for dissolution than dolomite (Mazzullo 2004), elucidating the enhanced facilitation of secondary constructive diagenetic processes (Fig. 4.14) within the overlying Puga cap carbonate section (Fig. 4.1). In addition, anomalous isotopic values of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  (Fig. 4.13), which differ from  $\delta^{13}\text{C}$  trends usually found in the Araras succession, were recorded in this limit, confirming that it represents a corridor for diagenetic fluids before hydrocarbon migration (e.g., Nogueira *et al.* 2007). The migrabitumen concentration decreases downward, suggesting predominant dissolution close to the contact zone.

Permeability is a crucial rock property that directly affects the rate at which hydrocarbons can be recovered (Lucia 2003, Ehrenberg and Walderhaug 2015, Al-Ramadan *et al.* 2020, Abdullah *et al.* 2022, Boutaleb *et al.* 2022 ). The depositional and diagenetic processes control the petrographic characteristics of the cap dolostone, such as the distribution of dolomicrite and authigenic minerals, influencing reservoir homogeneity and heterogeneity. Diagenetic processes (Fig. 4.14 and Fig. 4.15) impact reservoir quality by controlling fluid storage and capacity (Taylor *et al.* 2010).

Several diagenetic events modified the primary porosity (Fig. 4.15), aligning with the findings presented by Soares *et al.* (2020), showcasing the major destructive and constructive processes that have influenced reservoir characteristics. Destructive diagenesis in a reservoir primarily involves compaction and cementation, which can modify the initial sedimentary framework and primary porosity. Despite the favorable precipitation conditions in the cap dolostone, the primary porosities and permeability were drastically obliterated by gypsum cementation (Gy), followed by calcite cementation (Fig. 4.14). Other destructive processes were mechanical and chemical compaction (e.g., stylolites) during mesodiagenesis. Pyrite and low-Mg ferroan calcite cementation occurred during this phase. The early stabilization of carbonate deposits at the base of the Araras Group,

as indicated by isotopic data (Fig. 4.13), favors their preservation and confirms the prevalence of destructive processes presented by Soares *et al.* (2020). The low permeability of the cap dolostone deposits restricts hydrocarbon migration, primarily conditioning accumulation in the source rock (shale and limestone) and the upper part of the cap dolostone (Santos *et al.* 2018, Soares *et al.* 2020, Bezerra *et al.* 2022, Santos 2022). Although the contact relation between cap dolostone and the cap limestone is incompatible with the couple source and reservoir rocks, we suggest more than a lateral relation between units, implying a lateral hydrocarbon migration.

Hydrocarbon maturation and migration in the Araras petroleum system result from the main events recorded in the Araras-Alto Paraguai basin, including burial and uplift (Fig. 4.14). These processes were directly linked to the geological evolution of the basin, leading to the formation and preservation of hydrocarbon reservoirs in the Araras petroleum system. According to Soares *et al.* (2020), hydrocarbon migration likely occurred in at least two distinct stages: 1) immediately after their formation, filling intercrystalline pores, and 2) after brittle deformation, when fractures became conduits for percolation. This relationship is exemplified more clearly in the limestone and shales (source rock), where hydrocarbons percolate through zones of low pressure represented by fractures and intercrystalline pores within fan-shaped crystal needles formed by dissolution. In the Mirassol Formation, this migration occurred after pyrite and spathic calcite precipitation. Our paragenetic relationships provided evidence of mesodiagenesis (Fig. 4.14). The fluids originating these types of cement may be directly related to the burial event that matured and initially generated the organic matter migration (Soares *et al.* 2020).

A second phase of migration may be related to the tectonic events of the southern margin of the Amazon Craton, associated with uplift events of the Araras Group, likely during the Ediacaran-Cambrian transition recorded in the 80 Myrs unconformity in the Araras-Alto Paraguai Basin (Santos *et al.* 2017, Nogueira *et al.* 2019, 2022). Another uplift event occurred during the Cretaceous-Cenozoic transition, associated with the emplacement of the CAMP magmatism during the opening of the Central Atlantic (Rezende *et al.* 2018, 2021), which may be related to the increased effectiveness of telodiagenetic events in the Puga carbonate cap. Although it caused more significant uplift in the southern region of the Amazon Craton, even though it has not been associated yet, the impact of this magmatic event on the maturation or degradation of organic matter in the Araras petroleum system appears to have been low, as confirmed by Rock-Eval T<sub>max</sub> values below 440°C (average of 417°C), indicating thermal immaturity from an oil window

perspective (Sansjofre *et al.* 2011, 2014, Souza Jr. *et al.* 2018, Van Maldegem *et al.* 2019). Furthermore, the textural evaluation presented here and by other authors (Nogueira *et al.* 2003, 2007, 2022, Soares *et al.* 2013, 2020, Santos *et al.* 2021) confirms that the rock framework of Araras deposits is completely lithified and not affected by phanerozoic diagenesis.

#### 4.8 CONCLUSIONS

The unconventional Araras petroleum system presents a complex history, primarily recorded in its multiple cementation relationships. The early stabilization of carbonate deposits at the base of the Araras Group has contributed to the potential preservation. In contrast, the early diagenetic processes caused the low permeability of cap dolostone despite the abundant primary porosity. This condition was modified during diagenesis, mainly in the contact zone between cap dolostone and cap limestone. The contact was a corridor for diagenetic fluids that altered the rock framework, causing dissolution and increased permeability. These conditions allowed the hydrocarbon migration from oil-rich limestone and shale deposits to the upper cap dolostone. Hydrocarbon maturation and migration in the Araras petroleum system result from significant events recorded in the Araras-Alto Paraguai basin, including burial and uplift. The understanding of the depositional and biological mechanisms of microbial communities represents a window of opportunity to evaluate the quality of dolomite reservoirs and the influence of early and mesodiagenetic processes in porosity and permeability. These data can guide future exploration of petroleum plays and integrate a more robust model of hydrocarbon migration in Neoproterozoic cap carbonate. Ongoing stratigraphic studies in the southern Amazon Craton to the same detail as those reported here for the Neoproterozoic Araras unconventional Petroleum system will hopefully give a more complete picture of the hydrocarbon migration events after the Snowball Earth conditions.

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CAPÍTULO 5: RARE EARTH ELEMENTS AS INDICATORS FOR THE PALEOCEANOGRAPHIC CHANGES OF THE POST-MARINOAN SNOW-BALL EARTH FROM THE AMAZON CRATON

Renan F. dos Santos<sup>1</sup>, Pierre Sansjofre<sup>2</sup>, Afonso C. R. Nogueira<sup>1,7</sup>, Peter W. Crockford<sup>3</sup>, Gabriel J. Uhlein<sup>4</sup>, Laurane Fogret<sup>2</sup>, Fábio S. Pereira<sup>1</sup>, Guilherme R. Romero<sup>5</sup>, Stefan V. Lalonde<sup>6</sup>

<sup>1</sup>*Programa de Pós-Graduação em Geologia e Geoquímica, Faculdade de Geologia, Instituto de Geociências, Universidade Federal do Pará, Rua Augusto Corrêa s/n, CEP 66075-110, Belém-PA, Brasil*

<sup>2</sup>*Muséum National d'Histoire Naturelle, Institut de Physique des Matériaux et de Cosmochimie, Sorbonne Université, Paris, France*

<sup>3</sup>*Department of Earth Sciences, Carleton University, Ottawa ON, Canada, K1S 5B6*

<sup>4</sup>*Universidade Federal de Minas Gerais, Programa de Pós-Graduação em Geologia, CPMTC-IGC, Campus Pampulha, Belo Horizonte, MG, Brazil*

<sup>5</sup>*Departamento de Geologia Sedimentar e Ambiental, Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil*

<sup>6</sup>*Institut Universitaire Européen de la Mer, Technopôle Brest-Iroise, France*

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HIGHLIGHTS

- 1 Early relative sea-level fall attributed to the loss of ice gravity.
- 2. Syndepositional dolomite is restricted to the post-Marinoan coastal environments.
- 3. Cap dolostone precipitates in mixed water influenced by hypersaline deep waters.
- 4. Factory changes are due to siliciclastic input variation and microbial proliferation.
- 5. Upwelling currents are the primary source of bioessential trace elements.

Precambrian Research

Renan Santos

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## 5 RARE EARTH ELEMENTS AS INDICATORS FOR THE PALEOCEANOGRAPHIC CHANGES OF THE POST-MARINOAN SNOWBALL EARTH FROM THE AMAZON CRATON

Renan F. dos Santos<sup>1</sup>, Pierre Sansjofre<sup>2</sup>, Afonso C. R. Nogueira<sup>1,7</sup>, Peter W. Crockford<sup>3</sup>, Gabriel J. Uhlein<sup>4</sup>, Laurane Fogret<sup>2</sup>, Fábio S. Pereira<sup>1</sup>, Guilherme R. Romero<sup>5</sup>, Stefan V. Lalonde<sup>6</sup>

<sup>1</sup>*Programa de Pós-Graduação em Geologia e Geoquímica, Faculdade de Geologia, Instituto de Geociências, Universidade Federal do Pará, Rua Augusto Corrêa s/n, CEP 66075-110, Belém-PA, Brasil*

<sup>2</sup>*Muséum National d'Histoire Naturelle, Institut de Physique des Matériaux et de Cosmochimie, Sorbonne Université, Paris, France*

<sup>3</sup>*Department of Earth Sciences, Carleton University, Ottawa ON, Canada, K1S 5B6*

<sup>4</sup>*Universidade Federal de Minas Gerais, Programa de Pós-Graduação em Geologia, CPMTIC-IGC, Campus Pampulha, Belo Horizonte, MG, Brazil*

<sup>5</sup>*Departamento de Geologia Sedimentar e Ambiental, Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil*

<sup>6</sup>*Institut Universitaire Européen de la Mer, Technopôle Brest-Iroise, France*

<sup>7</sup>*Research Productivity of CNPq*

### ABSTRACT

The extensive deglaciation linked to the snowball Earth climate that elapsed in the terminal Neoproterozoic caused dramatic changes in the ocean's chemistry, which are exceptionally recorded in globally distributed cap carbonate successions. One of the most spectacular examples is the Puga cap carbonate (~635 Ma), which was exposed in the Amazon Craton and associated with extensive sea level changes related to glacial-isostatic adjustment (GIA) and local ice gravity, resulting in continuous mixed waters. Coastal upwelling was succeeded by long-term transgression under a greenhouse climax. This study evaluates complex post-Marinoan dynamics using a comprehensive multiproxies approach. The rare earth element + yttrium patterns in the Puga cap carbonate reflect marine conditions in the aftermath of Snowball Earth. Specifically, the low Y/Ho ratios in the cap dolostone are consistent with seawater dilution due to meltwater influx. However, superchondritic Y/Ho ratios up to 70 and Eu/Eu\* values up to 3.6 suggest upwelling toward the coastal zone of hypersaline seawater with some hydrothermal fluids. These data indicate that ocean destratification is related to ocean circulation. The shallow-water recurrence influenced by ice gravity resulted in continuous coastal uplift, forming isolated shelves protected by ocean dynamics by undulating relief of substrate developed in diamicton morphologies. The recurrence of this post-glaciation scenario was succeeded by significant landward shoreline migration concomitant with rapid recovery of primary



productivity, with large microbial communities flourishing, inducing dolomite precipitation under restricted paleoenvironmental conditions on dolomitic platforms. The rapid rise in sea level led to the dispersion of Mg ions, leading to the definitive interruption of dolomicrite precipitation. Following the postglacial transgression, the stratified waters gradually became more mixed, resulting in the end of dolomitic platforms coinciding with the increase in detrital components, followed by abrupt replacement by oversaturated seas during extreme greenhouse conditions.

**Keywords:** cap dolostone; siliciclastic starvation; plumeworld; restriction; upwelling

## 5.1 INTRODUCTION

The extreme climatic transition between Snowball Earth episodes and their immediate post-glacial climate represents a pivotal interval of Earth geologic history. During the Cryogenian period, two global glaciations occurred, the Sturtian (~717–660 Ma) and Marinoan (~650–635 Ma) (Kirschvink 1992, Hoffman and Scharg 2002, Corsetti and Lorentz 2006, Fairchild and Kennedy 2007, Rooney *et al.* 2015, Hoffman *et al.* 2017, 2021). The environmental changes associated with these events include transforming from a globally frozen ocean to an ice-free (Hoffman *et al.* 2017, 2021). Such changes in ice cover would have manifested through long intervals of stable density stratification as well as large changes in sea level during the pre-, syn-, and postglacial stages, primarily driven by the effects of glacial eustasy (global mean sea level), ice gravity, glacial-isostatic adjustment (GIA), and the thermal expansion of the ocean (Allen and Hoffman 2005, Benn *et al.* 2015, Creveling and Mitrovica 2014, Hoffman *et al.* 2017, 2021, Yang *et al.* 2017, Mitchell *et al.* 2021, Rame and Marotzke 2022).

Globally deposited cap carbonate successions document a critical interval marking the terminal deglaciations of these ice ages, particularly the end of the Marinoan glaciation, which is recognized as the Cryogenian-Ediacaran boundary (Hoffman *et al.* 2017, 2021, Yu *et al.* 2020). Cap carbonates, which are found directly overlying Marinoan glacial diamictites, consist of either dolostone or limestone layers that are meter- to decameter-thick and laterally continuous and exhibit striking similarities across continents and have been globally correlated through geochronological and geochemical means (e.g., Nogueira *et al.* 2003, Halverson *et al.* 2005, Corsetti and Lorentz 2006, Rooney *et al.* 2015, Hoffman *et al.* 2017, 2021, Hohl *et al.* 2017, Crockford *et al.* 2018, Yu *et al.* 2020).

Despite the widespread distribution and intense study of these post-Marinoan successions and the various proposed models for cap carbonate formation, there has yet to

be a consensus regarding their origin. Current cap carbonate formation models have been proposed to explain the genesis of the Marinoan cap dolostones. According to one model, increased seawater alkalinity likely played a crucial role in the precipitation and widespread dolomitization observed during cap dolostone deposition (Higgins and Schrag 2003, Hoffman *et al.* 2011, 2017, Yu *et al.* 2020). This model is critical to forming a strongly stratified deglacial ocean where cap carbonate deposition occurs within the buoyant surface meltwater layer (Shields 2005, Liu *et al.* 2014, 2018, Yang *et al.* 2017, Hoffman *et al.* 2017). The continental weathering-alkalinity model generates alkalinity via intense chemical weathering of terrigenous materials during deglaciations (Hoffman *et al.* 2017). However, concerning the origin of the cap dolostones, it has been argued that continental weathering alone does not provide sufficient cations to account for the observed cap carbonate volume (Le Hir *et al.* 2009). Other triggers to consider include alkalinity increases associated with extensive hydrothermal activity along basin-bounding faults (Gernon *et al.* 2016), gas hydrate destabilization, and massive methane release (Jiang *et al.* 2003, Jiang *et al.* 2006, Kennedy *et al.* 2008, Wang *et al.* 2008). Alkalinity increases associated with microbial activity (e.g., sulfate reduction) (Nogueira *et al.* 2003, 2007, 2022, Font *et al.* 2006) and ocean warming have also been considered (Fabre *et al.* 2013).

Rare earth elements and yttrium (REE+Y) have been extensively utilized in paleoenvironmental and paleoceanographic studies to provide insights into the aftermath of Snowball Earth events (Font *et al.* 2006, Nédélec *et al.* 2007, Huang *et al.* 2009, Meyer *et al.* 2012, Wang *et al.* 2014, Viera *et al.* 2015, Hohl *et al.* 2015, 2017, Caxito *et al.* 2018, Verdel *et al.* 2018, Wu *et al.* 2019, Zhao *et al.* 2021, Cui *et al.* 2021, Ren and Li 2023). When analyzed in ancient nonskeletal carbonates such as microbialites, serve as proxies for reconstructing paleoenvironmental conditions and offer valuable information about past seawater conditions (Schere and Suits 1980, Shaw and Wasserburg 1985, Webb and Kamber 2000, Kamber and Webb 2001, Nothdurft *et al.* 2004, Huang *et al.* 2009, Ling *et al.* 2013, Hodgskiss *et al.* 2021). The incorporation of REEs+Y into carbonate minerals is controlled by various physicochemical processes, such as water chemistry, pH, and temperature (Wood 1990, Nozaki and Alibo 2003, Chen *et al.* 2015, Bolhar *et al.* 2015, Rahlf *et al.* 2021, Zhao *et al.* 2022). Consequently, the utility of marine carbonates as recorders of oceanographic conditions hinge upon their preservation quality, well-established diagenetic constraints, a comprehensive understanding of contamination by noncarbonate phases, and accurate placement in their depositional environment.

Abundant carbonate deposits with well-preserved primary textures occur in the southern Amazon Craton associated with the Marinoan Puga cap carbonate (Fig. 5.1). Previous studies have focused predominantly on microbial carbonate petrology, sedimentology, and isotopic characterization ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$ ) of these deposits (Fig. 5.2) (Nogueira *et al.* 2003, 2007, 2019, 2022, Font *et al.* 2006, 2010, Sansjofre *et al.* 2011, 2014, Romero *et al.* 2013, Gaia *et al.* 2017, Soares *et al.* 2020, Romero *et al.* 2020, Santos *et al.* 2021, 2023). However, despite well-established geological constraints, this succession lacks a comprehensive multiproxies study to constrain post-Marinoan conditions and test previous carbonate precipitation models, thereby refining our understanding of the factors driving changes in carbonate factories over this critical time interval. The evaluation of the Puga cap carbonate exposed in the southern part of the Amazon Craton represents an opportunity to achieve this end due to its exceptional preservation, largely unaffected by severe late-stage diagenetic modification (Sansjofre *et al.* 2014, Soares *et al.* 2020, Santos *et al.* 2021). Therefore, a comprehensive multiproxies study incorporating sedimentological observations (microfacies and facies) together with multiple geochemical proxies: rare earth elements (e.g., Y/Ho ratios and Eu/Eu\* and Ce/Ce\* anomalies),  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , may provide important insight into the post-Marinoan environment in this region.

## 5.2 GEOLOGICAL BACKGROUND

The focus of this study is the Puga cap carbonate, located in the southern Amazon Craton and associated with the basal deposits of the intracratonic Araras-Alto Paraguai Basin, installed during the late Cryogenian (Fig. 5.1 A and B) (Nogueira *et al.* 2003, 2019, Gaia *et al.* 2017, Santos *et al.* 2020, Soares *et al.* 2020, Romero *et al.* 2020, Santos *et al.* 2021, 2023). This basin overlies crystalline and metamorphic basement rocks of the Cuibá Group belonging to the Paraguai Belt (Nogueira *et al.* 2019, Santos *et al.* 2020). The basal fill of this basin is composed of Cryogenian rocks of the Puga Formation (pelites, sandstones, dropstones, and glacial diamictites) overlain by the earliest Ediacaran carbonate rocks of the Araras Group (Fig. 5.1C), which consists of four formations: 1) Mirassol d'Oeste (Cap dolostone), composed of dolomitic layers interpreted as a shallow platform environment, 2) Guia (Cap limestone), composed of carbonates and shales, interpreted as a moderately deep platform, 3) Serra do Quilombo, composed of shallow to moderately deep dolomitic platforms, and 4) Nobres, consisting of tidally influenced dolomites (Nogueira and Riccomini 2006, Nogueira *et al.* 2003, 2007, 2019, 2022, Rudnitzki

*et al.*2016, Romero *et al.*2020, 2022, Soares *et al.*2013, 2020, Santos *et al.*2021). The cap dolostone comprises stratiform stromatolites with gypsum pseudomorphs (Fig. 5.3), giant stromatolites with tubestone (Fig. 5.4 A-F), and wave-dominated dolostone facies (peloidal dolomudstone with parallel laminations, peloidal dolopackstone with quasi-planar laminations, and peloidal dolopackstone with megaripples beds) (Fig. 5.4G-I). The cap limestone is predominantly composed of limestones with megaripples, wavy laminations, calcite crystal fans (pseudomorphs after aragonite), and subordinate laminated shale (Fig. 5.5) (for more details, see Nogueira *et al.*2003, 2018, Sansjofre *et al.*2014, Soares *et al.*2020, Romero *et al.*2020, Santos *et al.*2021,2023). Post-Marinoan cap carbonate deposition in other localities around the world has previously been constrained through U–Pb zircon dating and, more recently, Re–Os dating, to between  $635.2 \pm 0.5$  Ma and  $632.3 \pm 5.9$  Ma, respectively (Condon *et al.*2005, Rooney *et al.*2015). (Condon *et al.*2005, Rooney *et al.*2015). Consistent with Pb/Pb ages obtained by Puga cap carbonate, for cap dolostone  $633 \pm 30$  Ma (Babinski, 2011) and  $627 \pm 32$  Ma (Babinski *et al.*2006), while for cap limestone  $622 \pm 33$  Ma (Romero *et al.*2013) and  $622 \pm 30$  (Souza *et al.*2024). An age of  $623 \pm 3$  Ma U–Pb in situ in seafloor crystal fans was obtained recently by Carvalho *et al.* (2023). This latter age is interpreted as a new constraint on the transition from shallow to intermediate burial diagenesis of the Puga cap carbonate (Fig. 5.1C). The isotopic values of  $\delta^{13}\text{C}$  range from -5‰ in the cap dolostone to -2‰ in the cap limestone and  $^{87}\text{Sr}/^{86}\text{Sr}$  between 0.7074 and 0.7089 (Fig. 5.1C) which are compatible with global curves (e.g., Otavi Group, Namibia) (Font *et al.*2006, Sansjofre *et al.*2011, Romero *et al.*2013, Nogueira *et al.*2019).

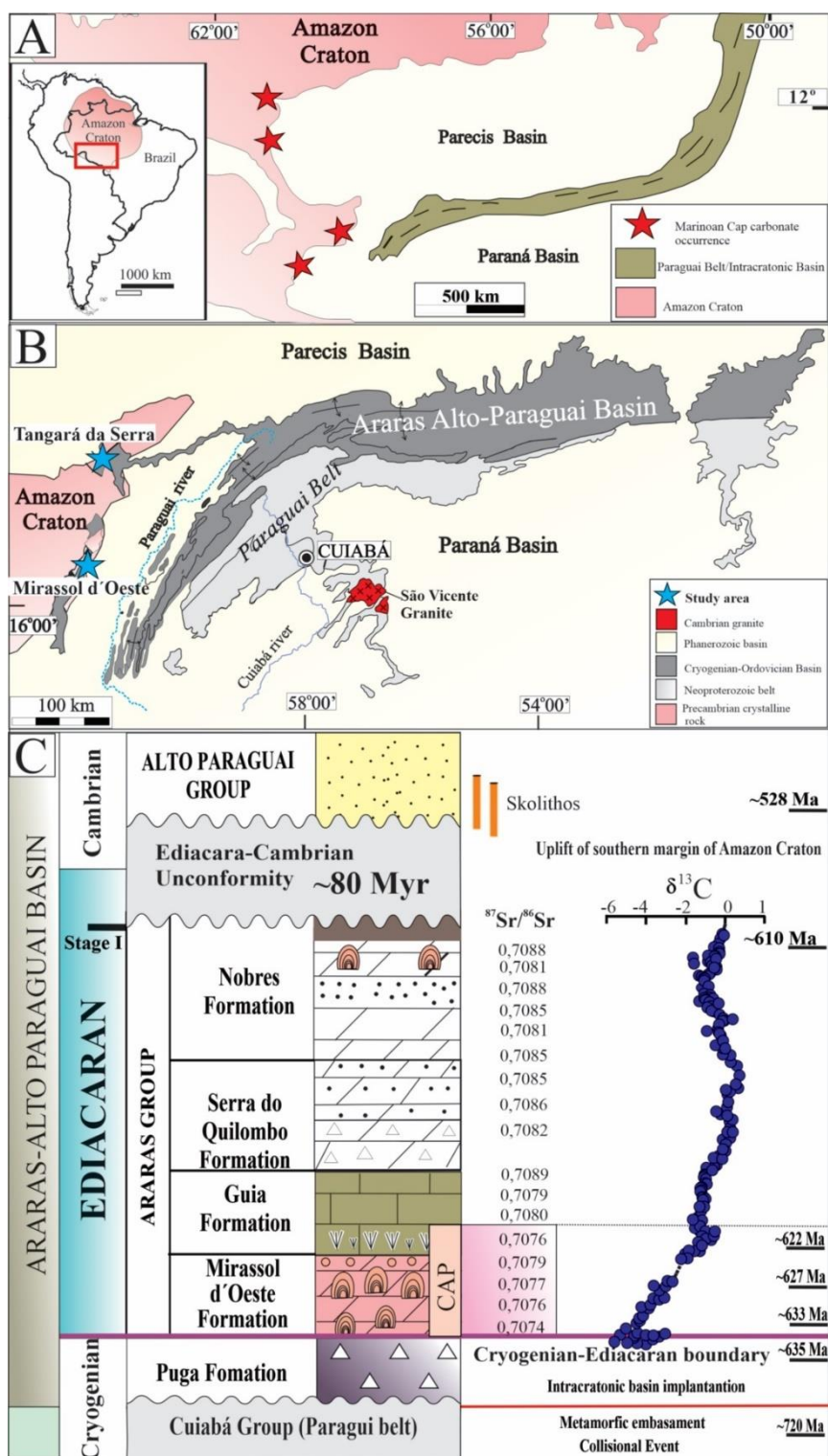


Figure 5.1- **A**) Location and simplified geologic map of the southwestern Amazon Craton with Neoproterozoic cap carbonate occurrences. The Cryogenian-Ediacaran boundary is exposed in the primary cap carbonate succession overlying crystalline and metasedimentary rocks of the Precambrian basement in the southwestern and southern portions of the Amazon Craton. **B**) Details of the geological context of the southern Amazon Craton, indicating the Araras-Alto Paraguai Basin, Paraguai Belt, and the occurrences of Puga cap carbonate (PCC) within the study area (the Calcário Tangará and Terconi quarries), highlighted by stars in the Tangará da Serra and Mirassol d'Oeste-Mato Grosso, Central-Western Brazil. **C**) Lithostratigraphy of the Neoproterozoic-Cambrian deposits of the Araras-Alto Paraguai basin (adapted from Nogueira and Riccomini, 2006 and Nogueira *et al.* 2019).  $\delta^{13}\text{C}$  curves and paleoenvironmental interpretation (facies association) of the Puga cap carbonate (adapted from Nogueira *et al.* 2019, Soares *et al.* 2020, Santos *et al.* 2021,2023). Age of the Guia Formation (Cap limestone): 1) Pb/Pb and  $^{87}\text{Sr}/^{86}\text{Sr}$  by Romero *et al.* (2013) and 2) U/Pb in situ crystal fans by Carvalho *et al.* (2023).

### 5.3 MATERIALS AND METHODS

In total, 97 samples were analyzed from the cap dolostone (Mirassol d'Oeste Formation) and cap limestone (Guia Formation) of the Puga cap carbonate in the southern Amazon Craton (Fig. 5.1). Of the 97 samples, 37 were collected from outcrops in the Terconi section at Terconi quarry in the Mirassol d'Oeste region, Mato Grosso state (15°40'42" S, 58°04'32" W). The remaining 60 samples were obtained from the Tangará Section at Calcário Tangará quarry in the Tangará da Serra region, Mato Grosso state (14° 45' 26" S, 57° 50' 02" W). In the Tangará Section, 42 samples were extracted from drill cores (JOR), while 19 samples were collected from outcrops. (Fig. 5.3 and Fig. 5.4). The stratigraphy of the samples was proposed, and the facies/microfacies criteria were previously presented by Nogueira *et al.* (2003, 2019), Sansjofre *et al.* (2014), and Santos *et al.* (2021,2023). Rock fragments free of apparent fractures or recrystallization were carefully selected. When greater precision was necessary to avoid recrystallized portions or those affected by diagenetic fluids, a diamond drill with a diameter of approximately 1 mm was used for micro-drilling, enhancing the accuracy of the selected areas for analysis.

#### 5.3.1 Trace elements

##### 5.3.1.1 REE geochemistry – Partial dissolution

In total, 42 drillcore JOR samples of cap dolostone from the Tangará section were measured for major and minor concentrations to avoid REE contributions from non-carbonatic components (e.g., clays and oxides) following the digestion protocol of Rongemaille *et al.* (2011). Approximately 20 mg of sample powder was weighed into acid-cleaned 2.5 mL microcentrifuge tubes, 0.5 mL of trace-metal grade acetic acid was then added at a concentration of 0.85 N (i.e., 5%), and the mixture was left to dissolve overnight at room temperature. The samples were centrifuged, and 0.25 mL aliquots of the supernatant were diluted in 4.75 mL of PFA-distilled nitric acid to a concentration of 0.45 N HNO<sub>3</sub> (i.e., 2%) with 10 ppb indium as an internal standard to control instrumental drift. Analyses were conducted on a Thermo Scientific ELEMENT XR high-resolution inductively coupled plasma mass spectrometer (HR ICP-MS) from the Pôle Spectrométrie Océan (PSO) at the Institut Universitaire Européen de la Mer, Université de

Bretagne Occidentale, France. Using low-, medium-, and high-resolution modes allowed for major, minor, trace and REE + Y element concentrations to be measured at a constant dilution factor during a single analytical session. Repeat analyses of the standard reference material CAL-S (N = 15) showed a 1 $\sigma$  precision of 7–9%, with results within 10% of published values. Concentrations were determined by external calibration with a synthetic, matrix-matched calibration solution.

#### 5.3.1.2 REE geochemistry – Bulk rock dissolution

In total, 56 outcrop samples were analyzed using total bulk dissolution, 37 from the Terconi section and 19 from the Tangará section. Rock fragments free of apparent fractures or recrystallization were carefully selected and crushed in an agate mortar. Chemical analysis was performed by ICP–AES (major and minor elements) and ICP–MS (trace elements) at the spectrochemical laboratory (SARM) of the Centre de Recherches en Pétrographie et Géochemie in Vandœuvre-les-Nancy. The samples were prepared by fusion with LiBO<sub>2</sub> (980 °C for 60 min), followed by dissolution in an HNO<sub>3</sub> (1 mol L<sup>-1</sup>)–H<sub>2</sub>O<sub>2</sub> (~0.5% v/v)–glycerol (~10% v/v) mixture to obtain a diluted solution (Carignan *et al.* 2001). The precision and accuracy were better than 1% of the measured values (mean 0.5%) for major and minor elements and 8% for trace metals, as determined by international standards and analysis of replicate samples (Carignan *et al.* 2001).

#### 5.4 STABLE ISOTOPES ( $\Delta$ 13C AND $\Delta$ 18O)

In total, 44 samples of drill core JOR, which captures cap dolostone from the Tangará section (Fig. 5.2), were prepared for stable isotope analyses performed at the National Museum of Natural Histories in Paris on the SSMIM platform. The samples were first ground to a powder in an agate mortar. CO<sub>2</sub> was extracted by dissolution with 100% H<sub>3</sub>PO<sub>4</sub> at 70 °C under a primary vacuum. Stable carbon and oxygen isotopic compositions of the product CO<sub>2</sub> were measured using a Kiel IV carbonate device. Standards of NBS-19 (international), MarbreLM (internal to SSMIM), and CAMIL-21 were used to correct the linearity of the mass spectrometer and calibrate the data. Using the standards, a reference curve was designed to determine the percentage of carbonates in the sample. Finally, the results are expressed in ‰ on the V-PDB scale. The results are presented in  $\delta$ -notation relative to the international Standard V-PDB for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . The external reproducibilities for the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements are 0.1‰ and 0.15‰, respectively (1 $\sigma$ ).



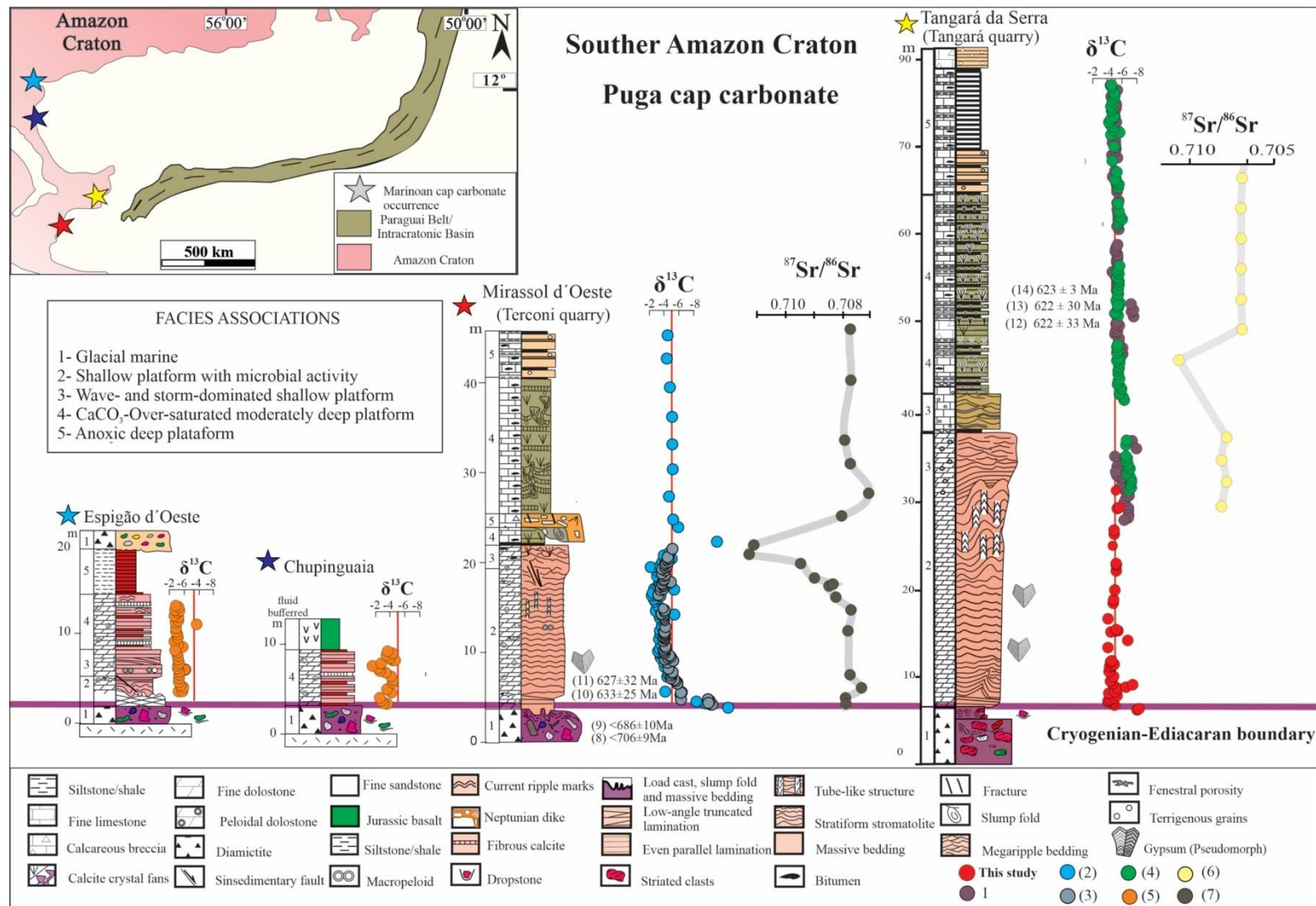


Figure 5. 2- Stratigraphic sections of the Marinoan Puga cap carbonate in the southern Amazon Craton. Open pit of the RMC quarry, Espigão d'Oeste region-Rondônia State, outcrop in the Chupinguaia region, Rondônia State, open pit in the Terconi quarry, Mirassol d'Oeste region, Mato Grosso state, and open pit in the Calcario Tangará quarry, Tangará da Serra region, Mato Grosso state. The  $\delta^{13}\text{C}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  curves of the carbonate platform deposits in the Amazon Craton with values in ‰ were obtained by 1) Nogueira *et al.* (2019), 2) Nogueira *et al.* (2019), 3) Font *et al.* (2006), 4) Sansjofre *et al.* (2011), 5) Gaia *et al.* (2017), 6) Romero *et al.* (2013), 7) Nogueira *et al.* 2007. Paleoenvironmental interpretation (facies association) of the Puga cap carbonate (Nogueira *et al.* 2003, 2007, 2019, Sansjofre *et al.* 2014, Gaia *et al.* 2017, Soares *et al.* 2020, Santos *et al.* 2021, 2023). Detrital zircon maximum depositional ages for the diamictite Puga Formation are reported as  $<706 \pm 9$  Ma by 8) Babinski *et al.* (2013) and  $<686 \pm 10$  Ma by 9) McGee *et al.* (2018) and Pb/Pb age of the cap dolostone 10) (Babinski 2011), 11) by Babinski *et al.* (2006): and Pb/Pb age of the cap limestone by 12) Romero *et al.* (2013), 13) Souza *et al.* (2024), and U/Pb in situ crystal fans by 14) Carvalho *et al.* (2023).



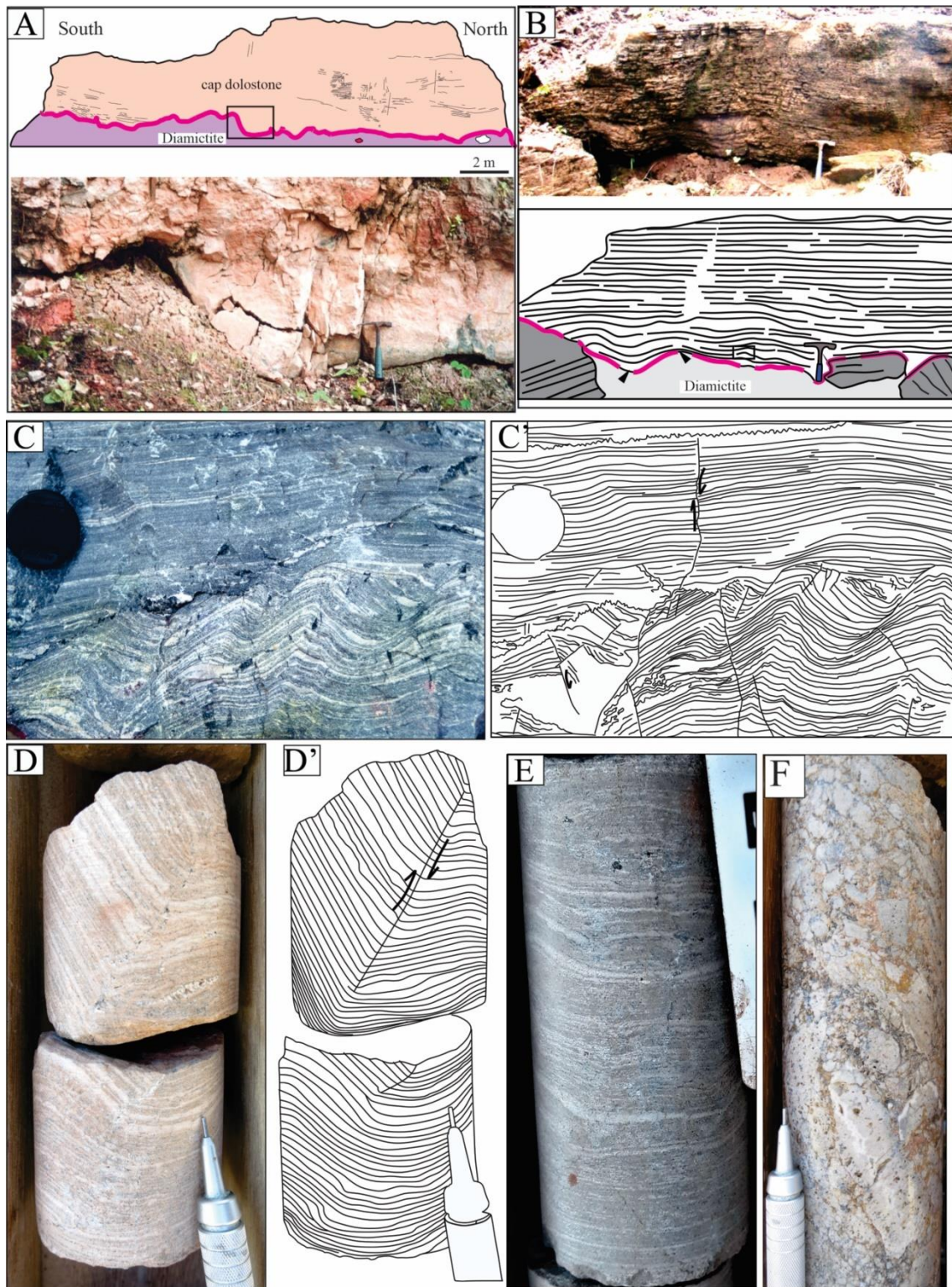


Figure 5. 3- The Cryogenian-Ediacaran boundary in South America. (A and B) Deformed contact between glaciogenic diamictites and cap dolostone in the Mirassol d'Oeste and Espigão d'Oeste regions, respectively. C) Domic and stratiform stromatolite in the Mirassol d'Oeste region (C) and interpretative diagram (C'). The striped appearance is caused by the intercalation of dolomitic laminae (light gray) with bituminous dolomitic laminae (dark gray). Deformed laminae occur between the domes associated with syndimentary faults. Note the abrupt transition from domal to planar stromatolites with the development of lateral stylolites at the contact. D) and E) Deformed synsedimentary contact (formed bedding and microfaults) in the drill core in the Tangará da Serra region. F) Incipient breccias.



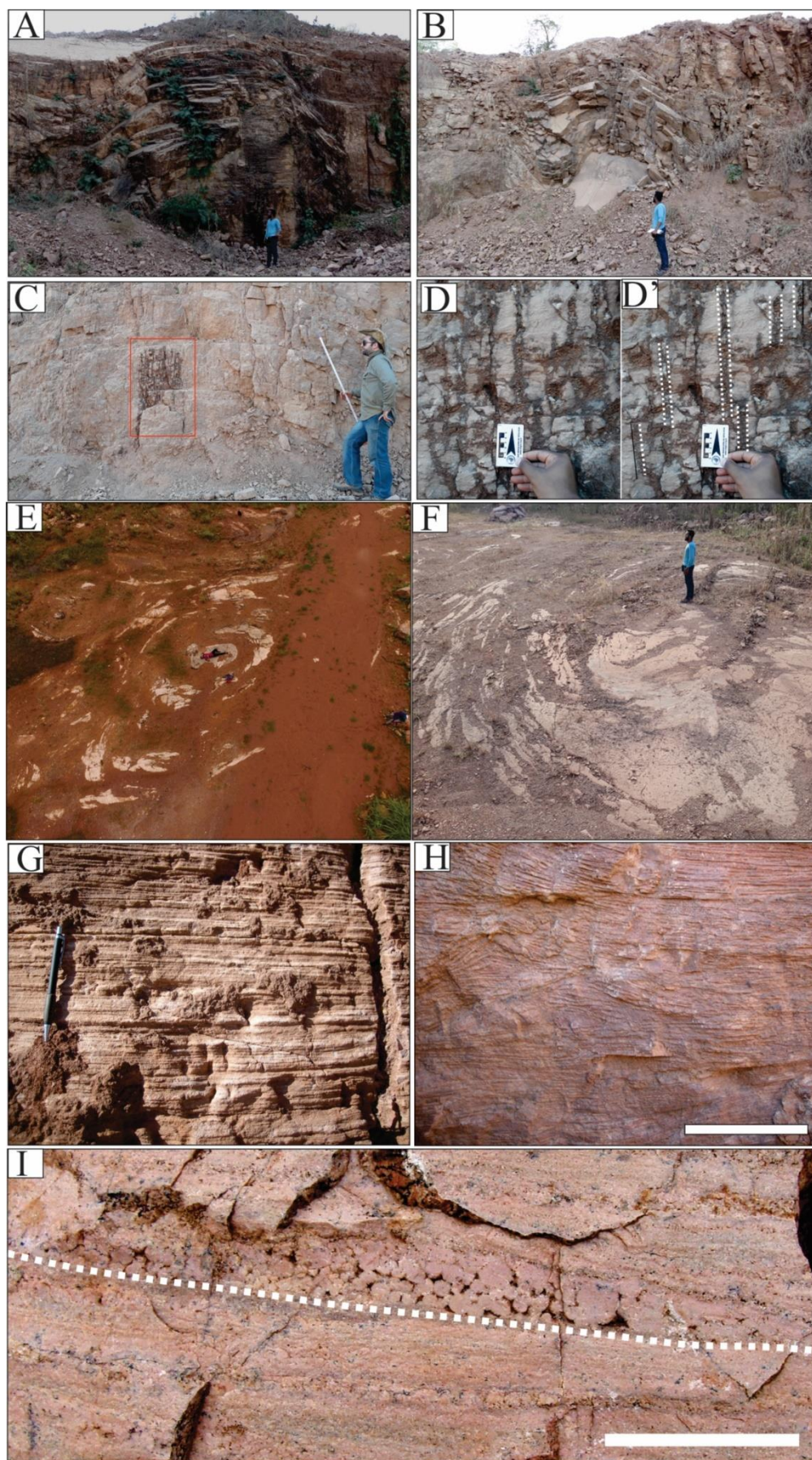


Figure 5. 4- The giant biostrome with tubestone of the cap dolostone (domic doloboustone with tubestone). A) and B) Large-scale domic mound, scale = 1.88 m. C) Tubestone associated with the giant stromatolite is vertically oriented in the axial zone of the domes. D) Detail of the C) Detail of the tubestone. D') Arrows indicating tubestones. E) and D) Drone flyover images outlining the elliptical pattern of the mounds (scale = 1.88 m).



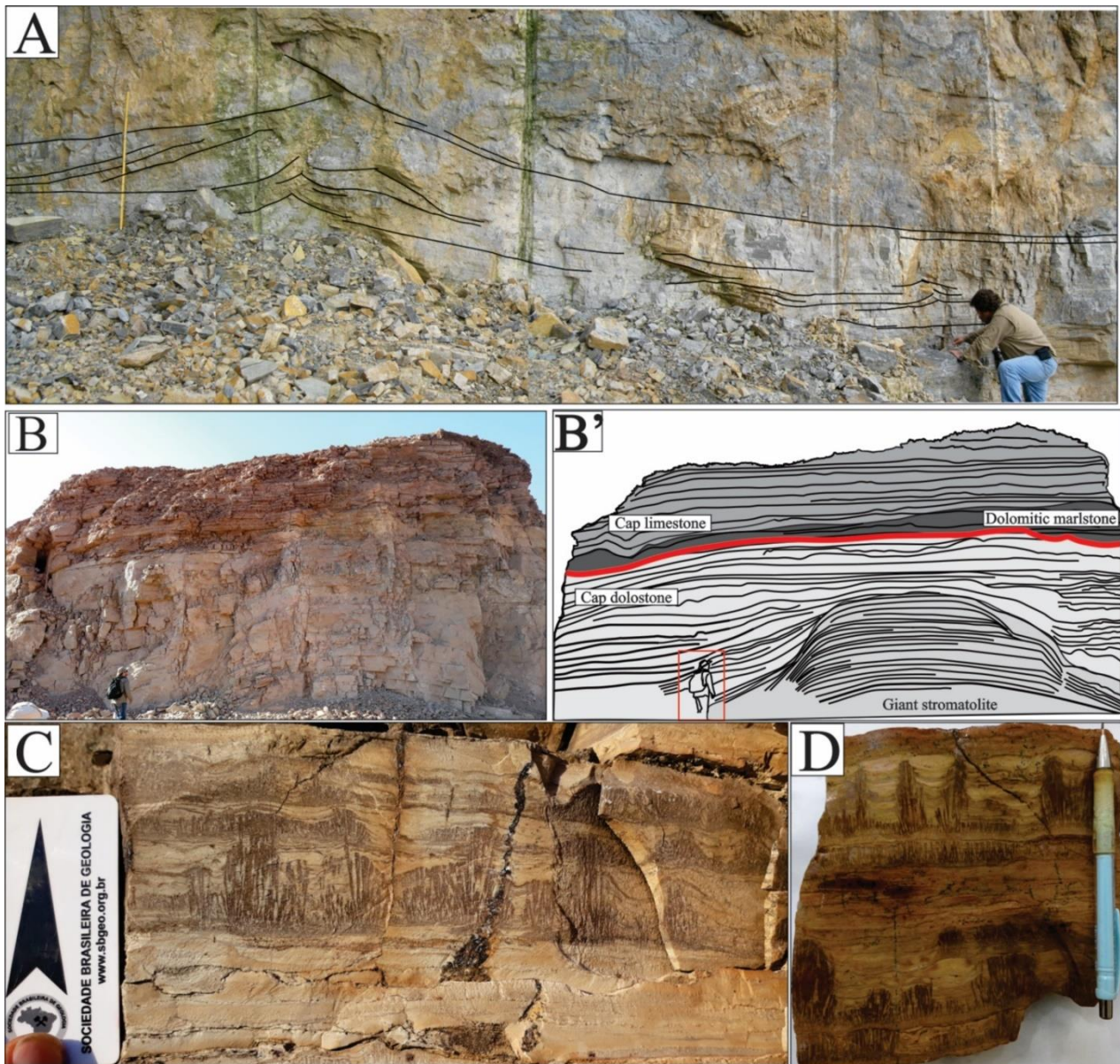


Figure 5.5- A) Giant-wave ripple. B) and B') Contact between cap dolostone and cap limestone. B) Upper part of the primary exposure of the giant stromatolite (domal doloboundstone with tubestone) transitioning into wave-dominated dolostone facies (peloidal dolomudstone/dolopackstone with plane-parallel laminations and Dolograinstone/peloidal dolomudstone with quasi-planar laminations and low-angle truncation) in contact with dolomitic marlstone and limestone beds (cap limestone). B') Interpret the facies boundaries of the Puga cap carbonate in B). C) and D) Calcite crystal fans (aragonite pseudomorphs).

## 5.5 RATIONALE FOR THE USE OF RARE EARTH ELEMENTS + YTTRIUM (REE+Y) AS PALEOCEANOGRAPHIC INDICATORS

Ancient nonskeletal carbonates, including microbialites, can record ambient seawater REE+Y concentrations, making them excellent potential archives for paleoenvironment proxies (Schere and Suits 1980, Shaw and Wasserburg 1985, Webb and Kamber 2000, Kamber and Webb 2001, Nothdurft *et al.* 2004, Huang *et al.* 2009, Ling *et al.* 2013, Hodgskiss *et al.* 2021). However, their ability to control for noncarbonate contamination and the impacts of diagenesis need to be evaluated (Bolhar and Van Kranendonk 2007, Rongemaille *et al.* 2011, Zhang *et al.* 2015, Van Kranendonk *et al.* 2003, Bolhar *et al.* 2004, 2015, Nothdurft *et al.* 2004, Olivier and Boyet, 2006). Additionally, evaluating the relative fractionation from different reservoirs and among individual REE+Y subgroups (enrichment of heavy REEs (HREE, from Ho to Lu) relative to light REEs (LREE, from La to Nd) is a significant tool that allows for a detailed tracing of biogeochemical processes and fluid chemistry constraints in both low- and high-temperature settings (Debruyne *et al.* 2016, Smrzka *et al.* 2019). These differences are among the primary causes of REE+Y concentration variations. Modern REE + Y compositions of oxic seawater are generally characterized by superchondritic ratios of Y/Ho and negative Ce and positive La anomalies (Nozaki, 2001). It is crucial to consider the subtle differences in the adsorption of LREE, MREE, HREE, and Ce onto organic particles, oxide phases, or mineral phases (German and Elderfield 1989, Sholkovitz *et al.* 1994, Alibo and Nozaki 1999), which can reveal oceanographic evolution. In this study, we primarily utilize Y/Ho ratios and Ce and Eu anomalies to explore the post-Marinoan record of the Amazon craton.

The Y/Ho ratio is a geochemical parameter that distinguishes between continental and marine influences on marine sediments (Bau *et al.* 1996, Nozaki *et al.* 1997, Wang *et al.* 2014). Freshwater samples typically reveal flat shale-normalized REE + Y patterns with weak Y anomalies with typical Y/Ho values of  $\approx 26$  (Taylor and McLennan, 1985, Kamber *et al.* 2005, Lawrence *et al.* 2006, Bolhar and Van Kranendonk 2007, Babechuk *et al.* 2014). In the estuarine context, the fractionation generates a significant positive La anomaly and a superchondritic Y/Ho ratio (Lawrence and Kamber, 2006). Seawater Y/Ho ratios  $< 36$  (Tostevin *et al.* 2016), and values between  $\approx 36$  and 26 typically relate to inland waters or mixed seawater-freshwater systems (Webb and Kamber, 2000, Van Kranendonk 2003, Bolhar *et al.* 2004, Shields and Webb 2004, Lawrence and Kamber 2006). Similarly, contamination by detrital components typically overestimates carbonate

concentrations of elements such as Al, Ti, Th, and Zr. It reduces Y/Ho ratios to  $\approx 27$ , which is similar to that of continental crust and much lower than the expected seawater Y/Ho (Webb and Kamber 2000, Nothdurft *et al.* 2004, Uhlein *et al.* 2021).

Cerium anomalies are valuable geochemical tools for assessing past redox conditions in sedimentary environments. Cerium exists in two oxidation states: Ce (III) and Ce (IV). Trivalent cerium is preferentially incorporated into sediments under reducing conditions, leading to a higher Ce anomaly and  $Ce/Ce^* > 1$ . Conversely, tetravalent cerium is more stable and retained in sediments under oxic conditions, resulting in a lower Ce anomaly and  $Ce/Ce^* < 1$ . Cerium anomalies in sedimentary records have been widely used to reconstruct marine redox conditions over time (Kamber and Webb, 2001, Bolhar *et al.* 2004, Bau and Alexander 2006, Bolhar and van Kranendonk 2007, Pourret *et al.* 2008, Planavsky *et al.* 2010, Ling *et al.* 2013, Hood and Wallace 2015, Rodler *et al.* 2016, Tostevin *et al.* 2016, Wallace *et al.* 2017, Zhang and Shields 2022).

The Eu anomaly is a valuable indicator for investigating changes in redox and hydrothermal-related parameters (Bau 1991, Klinkhammer *et al.* 1994a, Barrat *et al.* 2000, Lawrence *et al.* 2006, Alexander *et al.* 2008, Parsapoor *et al.* 2009). Under reducing conditions, such as hydrothermal systems influenced by high-temperature fluids associated with fumaroles, Eu (II) is preferentially incorporated into sediments, resulting in higher Eu/Eu\* anomalies. In contrast, Eu (III), under oxidizing conditions, leads to lower Eu/Eu\* anomalies. Positive Eu anomalies are typically absent from marine carbonates. Eu anomalies in sedimentary records allow one to infer past variations in hydrothermal activity or the presence of Eu in detrital sediments, especially within calcic plagioclase. This insight significantly enhances the understanding of its influence on sediment geochemistry and resulting shifts in redox conditions over time. (Michard 1986, Klinkhammer *et al.* 1994b, Bau and Dulski 1999, Barrat *et al.* 2000).

## 5.6 RESULTS

### 5.6.1 Stratigraphy and sedimentology

The first dozen meters of the studied cores comprise the Puga Formations glacio-genic diamictite and dropstone beds. Dolomites of the Mirassol d'Oeste Formation directly cover these deposits (Fig. 5. 3A-B), which form  $\sim 40$  m-thick cap dolostone layers (Fig. 5.2). The cap dolostone is in sharp contact with glacial diamictite and exhibits

syndimentary deformation (e.g., deformed laminations, microfaults, massive bedding, and incipient breccias, Fig. 5.3 A-E). The cap dolostone was subdivided from the base to top into four microfacies: 1) microbialites facies comprising of stratiform doloboundstones with gypsum pseudomorph (Fig. 5.3 C) and domical doloboundstones with tubestone (Fig. 5.4 A-F), 2) wave rippled dolostone consisting of two microfacies dolograinedstones/ peloidal dolomudstone with quasi-planar to low-angles lamination and peloidal dolomudstone/ dolopackstone with megaripple bedding (Fig. 5.4 G-H). The cap limestone (50 m- thick in the Guia Formation, Fig. 5.1C and Fig. 5.2) is the top of the succession and is composed of discontinuous layers of dolomitic marlstone that are concordantly superimposed on the cap dolostone (Fig. 5.5B) and limestone with calcite crystal fans (Fig. 5.5 C-F), interbedded with mega-rippled limestone (Fig. 5.5 A) (see Nogueira *et al.* 2003, 2019, Soares *et al.* 2020, and Santos *et al.* 2021, 2023 for more details).

## 5.6.2 MAJOR AND TRACE ELEMENTS

Trace element data from the Tangará and Terconi sections (Fig. 5.2 and Fig. 5.3) are listed in Supplementary Table 5.1, and they are described below, following the stratigraphy proposed by Nogueira *et al.* (2003) and Santos *et al.* (2021, 2023). The measured REE+Y data of all Puga cap carbonate samples were normalized to the values of the post-Archean Australian shale (PAAS) by McLennan (1989). La, Ce, and Eu anomalies were calculated following the equations by (1) Lawrence *et al.* (2006) and (2) Frimel 2009. Overall, the  $\Sigma$ REE+Y patterns from the Puga cap carbonate are similar in both sections (Fig. 5. 4 and Fig. 5. 5). The upper section of the Puga cap carbonate shows a progressive enrichment of REE+Y. In the Tangará Section,  $\Sigma$ REE+Y ranges from 1.58 to 60.4 ppm, with an average of 5.79 ppm (n = 61, Fig. 5.4). In the Terconi Section,  $\Sigma$ REE+Y ranges from 1.4 to 97.6 ppm, with an average of 11.4 ppm (n = 37, Fig. 5.5). However, these values are lower than those in the PAAS by at least two orders of magnitude.

### 5.6.2.1 Tangará section

#### 5.6.2.1.1 Cap dolostone- Tangará section

##### 5.6.2.1.1.1 Microbialites - Tangará section

In the Tangará section (Fig. 5.2 and Fig. 5.6), the microbialites (doloboundstones stratiform with gypsum pseudomorph cement and doloboundstones domical with tubestone (giant stromatolite)) of the cap dolostone have Mg/Ca ratios ranging from 0.6 to 1.0 (average =  $0.8 \pm 0.18$ ,  $n = 42$ ) and low Sr concentrations ranging from 22 to 87 ppm (average =  $50 \pm 13$  ppm) (Fig. 5.6). Stratiform doloboundstones with gypsum pseudomorph cement were found to have low  $\Sigma\text{REE} + \text{Y}$  concentrations ranging from 1.6 to 27 ppm (average =  $4 \pm 4.7$  ppm,  $n = 32$ ), show a flat  $(\text{REE} + \text{Y})_{\text{SN}}$  pattern with a depleted LREE pattern (average  $(\text{Pr}/\text{Yb})_{\text{SN}} = 1.0 \pm 0.3$ ,  $n = 33$ ) (Fig. 5.8A and Fig. 5.13) and negative La anomalies ( $\text{La}/\text{La}^* = 0.8$  to  $2.2$ , average =  $0.9 \pm 0.3$ ). Ce anomalies are mostly weakly negative, with  $\text{Ce}/\text{Ce}^* = 0.4$  to  $1.0$  (average =  $0.9 \pm 0.2$ ), and strongly positive Eu anomalies,  $\text{Eu}/\text{Eu}^* = 1.0$  to  $3.2$  (average =  $1.5 \pm 0.5$ ). These facies record slightly superchondritic Y/Ho ratios (average =  $32 \pm 10$ ,  $n = 32$ ), with some samples reaching Y/Ho values up to 70 (superchondritic) (Fig. 5.6 and Fig. 5.10). The Y/Ho ratios of these facies show an absence of correlation with Zr ( $R^2 = 0.023$ ), Th ( $R^2 = 0.0017$ ), Ni ( $R^2 = 0.0024$ ), and Pb ( $R^2 = 0.063$ ).

The domical doloboundstones with tubestones (giant stromatolites) exhibit  $\Sigma\text{REE} + \text{Y}$  concentrations between 3.0 and 34.8 ppm (average =  $3.7 \pm 0.97$ ,  $n = 10$ ) and have a flat  $(\text{REE} + \text{Y})_{\text{SN}}$  (Fig. 5.8 B) with a depleted LREE pattern (average  $(\text{Pr}/\text{Yb})_{\text{SN}} = 0.7 \pm 0.97$ ,  $n = 10$ ) (Fig. 5.13 B), occurring with 1) weakly negative Ce anomalies,  $\text{Ce}/\text{Ce}^* = 0.8$  to  $1.1$  (average =  $0.9 \pm 0.1$ ), 2) positive Eu anomalies,  $\text{Eu}/\text{Eu}^* = 1.0$  to  $1.9$  (average =  $1.3 \pm 0.3$ ), and 3) negative La anomalies,  $\text{La}/\text{La}^* = 0.8$  to  $1$  (average =  $0.9 \pm 0.1$ ) (Fig. 5.10). The Y/Ho ratios at this location range from 27 to 30 (average =  $29 \pm 1$ ) (Fig. 5.6 and Fig. 5.10) and show an absence of correlation with Zr ( $R^2 = 0.2$ ), Th ( $R^2 = 0.3$ ), Ni ( $R^2 = 0.24$ ), and Pb ( $R^2 = 0.30$ ).



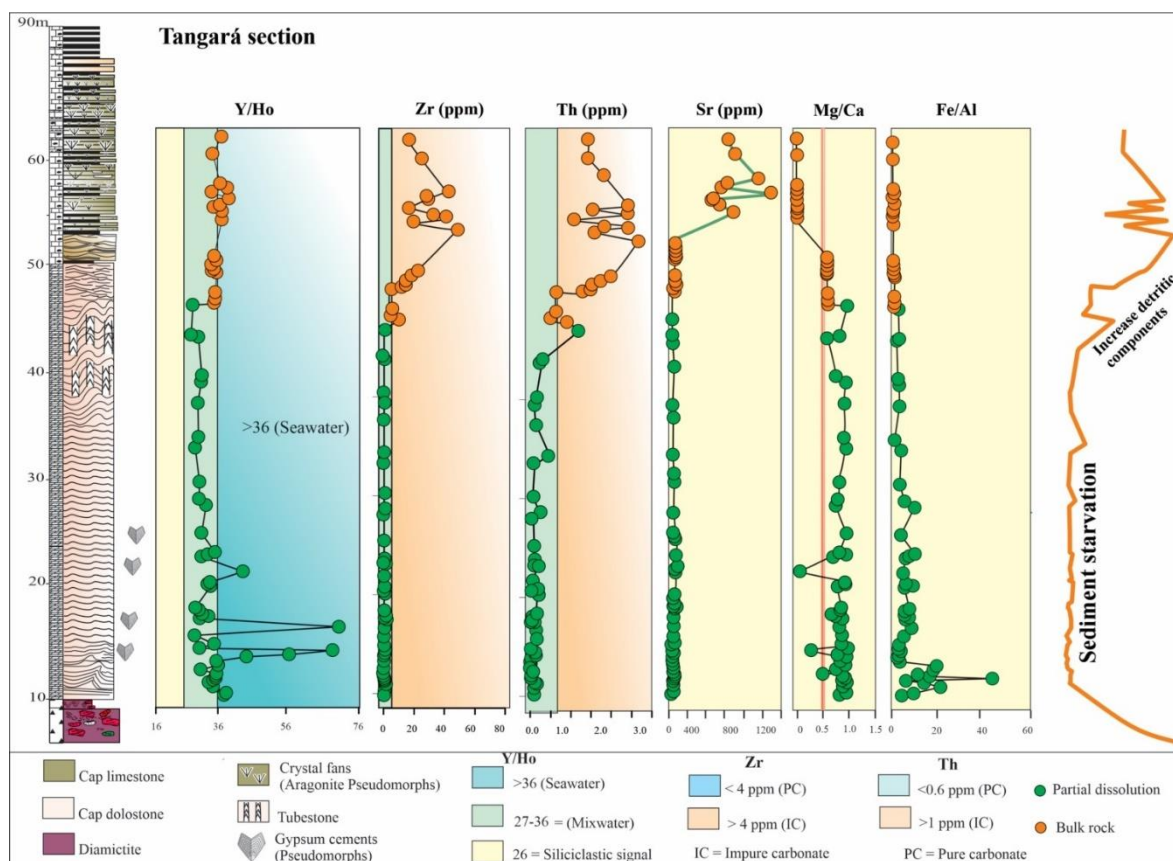


Figure 5.6- Stratigraphic and chemostratigraphic data of the Puga cap carbonate at the Tangará section. Y/Ho ratios, elemental contents of the zircon (Zr), thorium (Th), strontium (Sr), Mg/Ca, and Fe/Al ratios.

#### 5.6.2.1.1.2 Wave-rippled dolostone facies-Tangará section

The wave-rippled dolostone facies (microfacies dolograinstones/ peloidal dolomudstone with quasi-planar to low-angles lamination and peloidal dolomudstone/ dolopackstone with megaripple bedding) has Mg/Ca ratios ranging from 0.6 to 0.9 (average =  $0.6 \pm 0.11$ ,  $n = 9$ ) and low Sr concentrations ranging from 62.75 to 173 ppm (average =  $86.4 \pm 34$  ppm), which are similar to those of the basal section (Fig. 5.6). The upper part of the cap dolostone occurs with increased concentrations of the detrital component, with Al variations ranging from 12.34 to 37.88 ppm (average =  $25 \pm 9.7$ ), Zr from 7 to 20 ppm (average =  $13 \pm 5$  ppm) and Th from 0.59 to 1.77 (average =  $1.18 \pm 0.5$  ppm) (Fig. 5.6). The transition from the cap dolostone to the cap limestone records an increase in detrital content toward the top of the Puga cap carbonate. The wave-dominated dolostone facies exhibit  $\Sigma\text{REE} + \text{Y}$  concentrations between 12.3 and 39.02 ppm (average =  $26 \text{ ppm} \pm 8.3$ ,  $n = 10$ ) and have a flat (REE + Y) SN pattern (Fig. 5.8C) depleted in LREE (average (Pr/Yb) SN =  $1.0 \pm 0.1$ ) (Fig. 5.13 B). They show the following attributes: 1) absence of La anomalies  $\text{La}/\text{La}^* = 0.8$  to  $0.9$  (average =  $0.84 \pm 0.03$ ), 2) weakly negative Ce anomalies with  $\text{Ce}/\text{Ce}^* = 0.8$  (average =  $0.78 \pm 0.02$ ), 3) Eu anomalies are small to absent,



$\text{Eu}/\text{Eu}^* = 0.9$  to  $1.0$  (average =  $0.96 \pm 0.04$ ) (Fig. 5.10). 4)  $\text{Y}/\text{Ho}$  ratios vary from 32 to 34 (average =  $33.5 \pm 0.6$ ) (Fig. 5.6 and Fig. 5.10), and there is no correlation with  $\text{Zr}$  ( $R^2 = 0.085$ ),  $\text{Th}$  ( $R^2 = 0.16$ ),  $\text{Ni}$  ( $R^2 = 0.096$ ), and  $\text{Pb}$  ( $R^2 = 0.39$ ).

#### 5.6.2.1.2 *Cap limestone-Tangará section*

The cap limestone displayed higher  $\text{Sr}$  concentrations than cap dolostones with values between 549 and 1115 ppm (average =  $634 \pm 196$ ,  $n = 10$ ) (Fig. 5.6). The cap limestone is also associated with an increase in detrital components compared to the cap dolostone, evidenced by the contents of  $\text{Al}$ , which varies from 17.15 to 45.42 ppm (average =  $34.3 \pm 9.3$ ),  $\text{Zr}$ , from 18 to 48 ppm (average =  $28 \pm 10$ ), and  $\text{Th}$ , from 1.14 to 2.68 ppm (average =  $1.86 \pm 0.48$ ) (Fig. 5.6). The cap limestone has  $(\text{REE} + \text{Y})_{\text{SN}}$  patterns (Fig. 5.8 D) characterized by a high  $\Sigma\text{REE} + \text{Y}$  concentration, ranging from 34.9 to 60.4 ppm (average =  $47.2 \pm 8.1$ ,  $n = 10$ ), with depleted LREE patterns (average  $(\text{Pr}/\text{Yb})_{\text{SN}} = 0.87 \pm 0.07$ ) (Fig. 5.13B) and shows the following attributes: 1) negative  $\text{La}$  anomalies,  $\text{La}/\text{La}^* = 0.8$  to  $0.9$  (average =  $0.79 \pm 0.06$ ), 2) weakly negative  $\text{Ce}$  anomalies,  $\text{Ce}/\text{Ce}^* = 0.7$  to  $0.8$  (average =  $0.76 \pm 0.02$ ), and 3)  $\text{Eu}$  anomalies are minor to absent,  $\text{Eu}/\text{Eu}^* = 0.9$  to  $1.0$  (average =  $1.04 \pm 0.05$ ) (Fig. 5.10). 4)  $\text{Y}/\text{Ho}$  ratios show superchondritic values when contrasted with those of cap dolostone between 33 and 38 (average =  $35 \pm 1.6$ ) (Fig. 5.6 and Fig. 5.10) and occurs with an absence of correlation with  $\text{Zr}$  ( $R^2 = 0.069$ ),  $\text{Th}$  ( $R^2 = 0.35$ ),  $\text{Pb}$  ( $R^2 = 0.10$ ), and  $\text{Ni}$  ( $R^2 = 0.13$ ).

#### 5.6.2.2 Terconi Section

##### 5.6.2.2.1 *Cap dolostone- Terconi Section*

##### 5.6.2.2.1.1 **Microbialites-Terconi section**

The microbialites (stratiform doloboundstones with gypsum cement and domical doloboundstones with tubestone) of the cap dolostone in the Terconi section are similar to those of the Tangará Section, as follows: 1)  $\text{Mg}/\text{Ca}$  ratios ranging from 0.4 to 0.6 (average =  $0.6 \pm 0.05$ ,  $n = 18$ ), 2) low  $\text{Sr}$  concentrations between 40 and 60 ppm (average =  $49 \text{ ppm} \pm 6$ ,  $n = 17$ ), 3)  $\text{Zr}$  varying from 1.5 to 12.6 ppm (average =  $3.5 \pm 3.0$ ), 4)  $\text{Th}$  from 0.03 to 0.75 (average from  $0.19 \pm 0.17$ ), and 5)  $\text{Al}$  from 1.69 to 42.30 ppm (average =  $7.9 \pm 9.7$ ) (Fig. 5.7 and Fig. 5.10 B). The microbialites in the basal section exhibit low  $\Sigma\text{REE} + \text{Y}$  concentrations, ranging from 1.4 to 6.6 ppm (average =  $5.80 \text{ ppm} \pm 3.4$ ,  $n = 18$ ) and have flat  $(\text{REE} + \text{Y})_{\text{SN}}$  patterns (Fig. 5.9 A) with depleted LREE patterns (average  $(\text{Pr}/\text{Yb})_{\text{SN}}$

$\text{SN} = 0.82 \pm 0.15$ ,  $n=17$ ) (Fig. 5.13 B), and show the following attributes: 1) weakly negative Ce anomalies  $\text{Ce}/\text{Ce}^* = 0.7$  to  $1.1$  (average =  $0.93 \pm 10$ ), 2) Eu anomalies are small to absent  $\text{Eu}/\text{Eu}^* = 0.9$  to  $1.2$  (average =  $1.08 \pm 0.04$ ), and 3) weakly negative La anomalies,  $\text{La}/\text{La}^* = 0.7$  to  $1.0$  (average =  $0.94 \pm 0.09$ ) (Fig. 5.10). The Y/Ho ratio exhibited a superchondritic value when compared with the medium values of the microbialites from Tangará da Serra, ranging from 32 to 49 ppm (average =  $35.2 \pm 0.09$ ) (Fig. 5.3). These ratios show an absence of correlation with Zr ( $R^2 = 0.085$ ), Th ( $R^2 = 0.16$ ), Ni ( $R^2 = 0.096$ ), and Pb ( $R^2 = 0.39$ ).

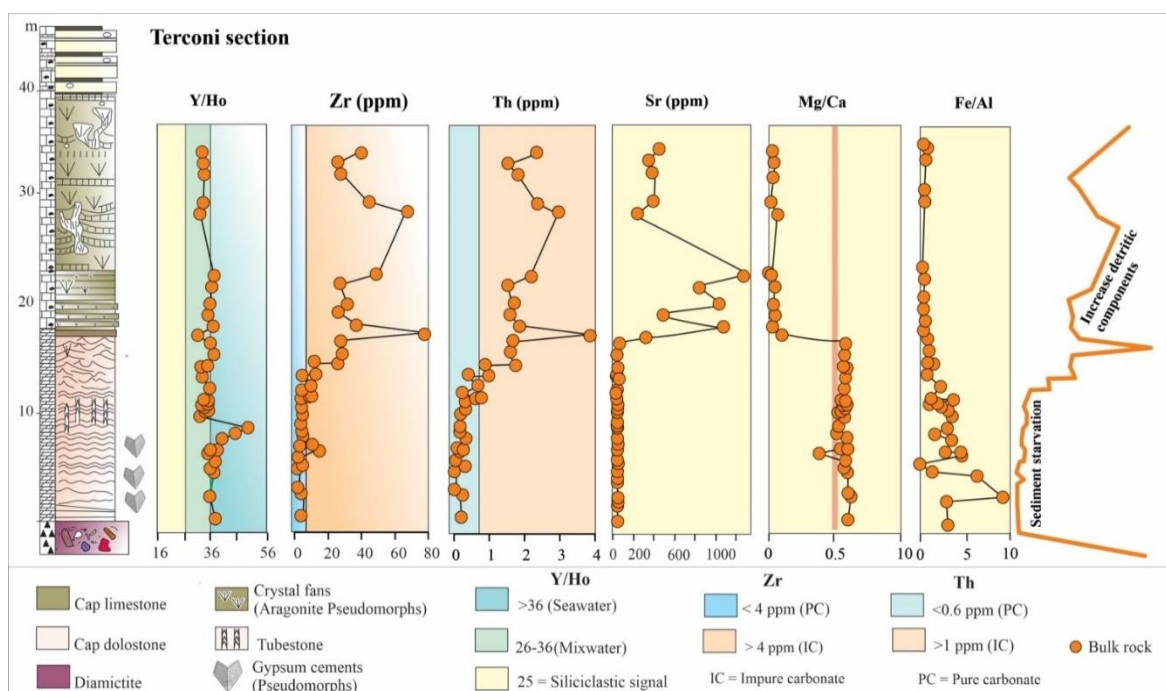


Figure 5.7- Stratigraphic and chemostratigraphic data of the Puga cap carbonate at the Tangará section. Y/Ho ratios, elemental contents of the zircon (Zr), thorium (Th), strontium (Sr), Mg/Ca, and Fe/Al ratios.

#### 5.6.2.2.1.2 Wave-rippled dolostone facies-Terconi section

The wave-rippled dolostone facies (e.g., peloidal dolopackstone with megaripple beds) have  $\text{Mg}/\text{Ca} = 0.5$  to  $0.6$  (average =  $0.6 \pm 0.01$ ,  $n = 8$ ) and low Sr concentrations similarly to the base of the section, between 63 and 87 ppm (average =  $59 \pm 8.4$  ppm). In these facies, there is an increase in detrital components compared to those of the basal microbialites, represented by values of  $\text{Al} = 10.59$  to  $83.65$  ppm (average =  $36.6 \pm 24.1$ ),  $\text{Zr} = 3.14$  to  $27.13$  ppm (average =  $12.6 \pm 9.25$ ), and  $\text{Th} = 0.24$  to  $1.54$  ppm (average =  $0.92 \pm 0.55$ ) (Fig. 5.7). These facies has higher  $\Sigma\text{REE}+\text{Y}$  concentrations than microbialites, ranging from 8.32 to 42.26 ppm (average =  $15.6$  ppm  $\pm 12.5$ ,  $n = 8$ ) and displays flat  $(\text{REE} + \text{Y})_{\text{SN}}$  patterns (Fig. 5.9 B) with a depleted LREE pattern (average  $(\text{Pr}/\text{Yb})_{\text{SN}}$

=  $0.9 \pm 0.1$ ,  $n = 8$ ) (Fig. 5.13 B). Additionally, they have the following attributes: 1) weakly negative Ce anomalies,  $Ce/Ce^* = 0.8$  to  $0.9$  (average =  $0.87 \pm 0.02$ ), 2) Eu anomalies minor to absent,  $Eu/Eu^* = 0.9$  to  $1.1$  (average =  $0.95 \pm 0.06$ ), 3) weakly negative La anomalies,  $La/La^* = 0.7$  to  $1.1$ , (average =  $0.96 \pm 0.05$ ) (Fig. 5.10 B), 4) slightly superchondritic Y/Ho ratios between 32 and 34 (average =  $34.2 \pm 1.6$ ) (Fig. 5.7 and Fig. 5.10 B) and there is a lack of correlation between Zr ( $R^2 = 0.14$ ), Th ( $R^2 = 0.03$ ), Ni ( $R^2 = 0.0002$ ) and Pb ( $R^2 = 0.074$ ).

#### 5.6.2.2.2 Cap limestone-Terconi section

The cap limestone has higher Sr concentrations between 315 and 1263 ppm (average =  $427 \pm 364$  ppm,  $n = 11$ ). The cap limestone is also associated with an elevated presence of detrital components compared to the cap dolostone, such as Al = 64 to 195 ppm (average =  $74 \pm 40$  ppm), Zr = 25 to 77 ppm (average =  $35 \pm 17$  ppm) and Th = 1.5 to 3.8 ppm (average =  $1.8 \pm 0.7$  ppm) (Fig. 5.7). The cap limestone has (REE + Y)<sub>SN</sub> patterns (Fig. 5.5C) characterized by a significantly greater concentration of  $\Sigma REE + Y$ , ranging from 36,4 to 97,6 ppm (average =  $46.3 \pm 17$  ppm,  $n = 12$ ), with a depleted LREE pattern (average (Pr/Yb)<sub>SN</sub> =  $0.9 \pm 0.05$ ,  $n = 12$ ) (Fig. 5.13 B), and shows the following attributes: 1) weakly negative Ce anomalies,  $Ce/Ce^* = 0.9$  (average =  $0.9 \pm 0.01$ ), 2) Eu anomalies are small to absent,  $Eu/Eu^* = 0.9$  to  $1.0$  (average =  $0.964 \pm 0.03$ ), and 3) weakly negative La anomalies,  $La/La^* = 0.8$  to  $1.1$  (average =  $0.86 \pm 0.07$ ) (Fig. 5.10 B). 4) Y/Ho ratios range from 31 to 37 (average =  $33 \pm 2$ ) (Fig. 5.7 and Fig. 5.10 B) and are weakly correlated with Zr ( $R^2 = 0.29$ ), Th ( $R^2 = 0.47$ ), Ni ( $R^2 = 0.34$ ) and Pb ( $R^2 = 8.10^{-6}$ ).

### 5.6.3 Carbon and oxygen isotope stratigraphy of the cap dolostone from the Tangará section

The  $\delta^{13}C$  and  $\delta^{18}O$  results for the Tangará section are presented in Fig. 5.2 and Fig. 5.10 and are listed in Supplementary Table 2. The isotopic composition is found to be relatively homogeneous. In the basal dolostone (stratiform doloboundstones with gypsum pseudomorphs), the  $\delta^{13}C$  values range from  $-4.1\text{‰}$  to  $-8.2\text{‰}$  (average =  $-4.8 \pm 1.1\text{‰}$ ,  $n = 33$ ), the  $\delta^{18}O$  values range from  $-4.1\text{‰}$  to  $-7.3\text{‰}$  (average =  $-5.1 \pm 0.7\text{‰}$ ,  $n = 33$ ), whereas in the domic doloboundstones with tubestones (giant stromatolite), the  $\delta^{13}C$  values range from  $-4.8\text{‰}$  to  $-5.7\text{‰}$  (average =  $-5.0 \pm 0.3\text{‰}$ ,  $n = 10$ ), while the  $\delta^{18}O$  values range from  $-3.7\text{‰}$  to  $-4.9\text{‰}$  (average =  $-4.7\text{‰} \pm 0.4$   $n = 10$ ). Our data complete the isotopic curve of the dolostone succession (Fig. 5.2) and reveal an absence of covariation between  $\delta^{13}C$  and  $\delta^{18}O$  ( $R^2 = 6 \times 10^{-5}$ ).

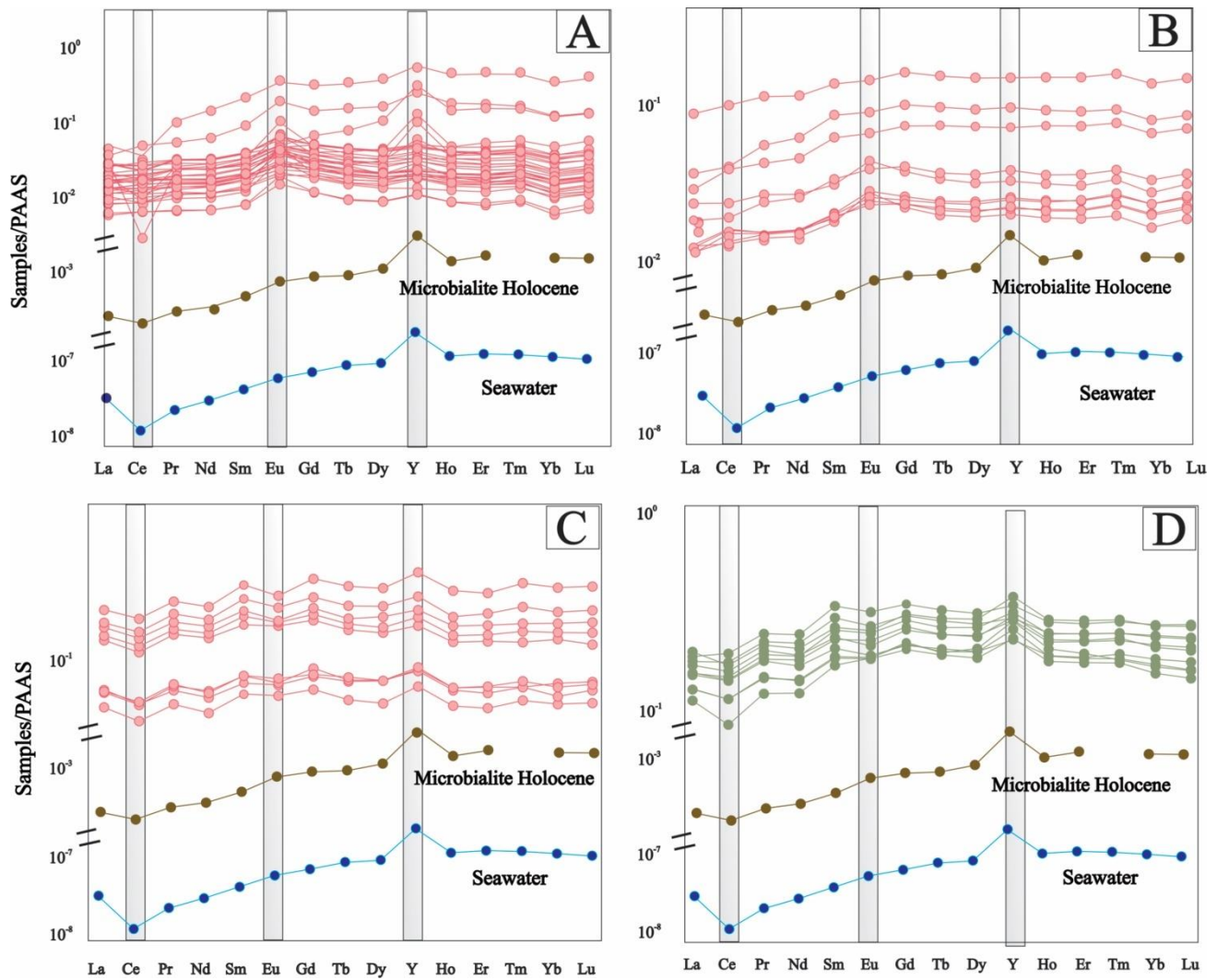


Figure 5.8- PAAS-normalized REE + Y diagram for the Puga cap carbonate in the Tangará section. The cap dolostone is shown as a pink line, and the green line represents the cap limestone. The blue dashed line shows modern seawater data from Alibo and Nozaki (1999), and the brown line indicates Holocene microbialite data from Webb and Kamber (2000). A) and B) Microbialite of the cap dolostone. A) Stratiform doloboundstones with gypsum pseudomorph cement. B) Domic doloboundstones with tubestone. C) Wave-rippled dolostone facies (peloidal dolograinstone/dolomudstone with quasiplanar to low-angle lamination and peloidal dolograinstone with megaripple bedding). D) Cap limestone (limestone with calcite crystal fans interbedded with mega-rippled limestone).

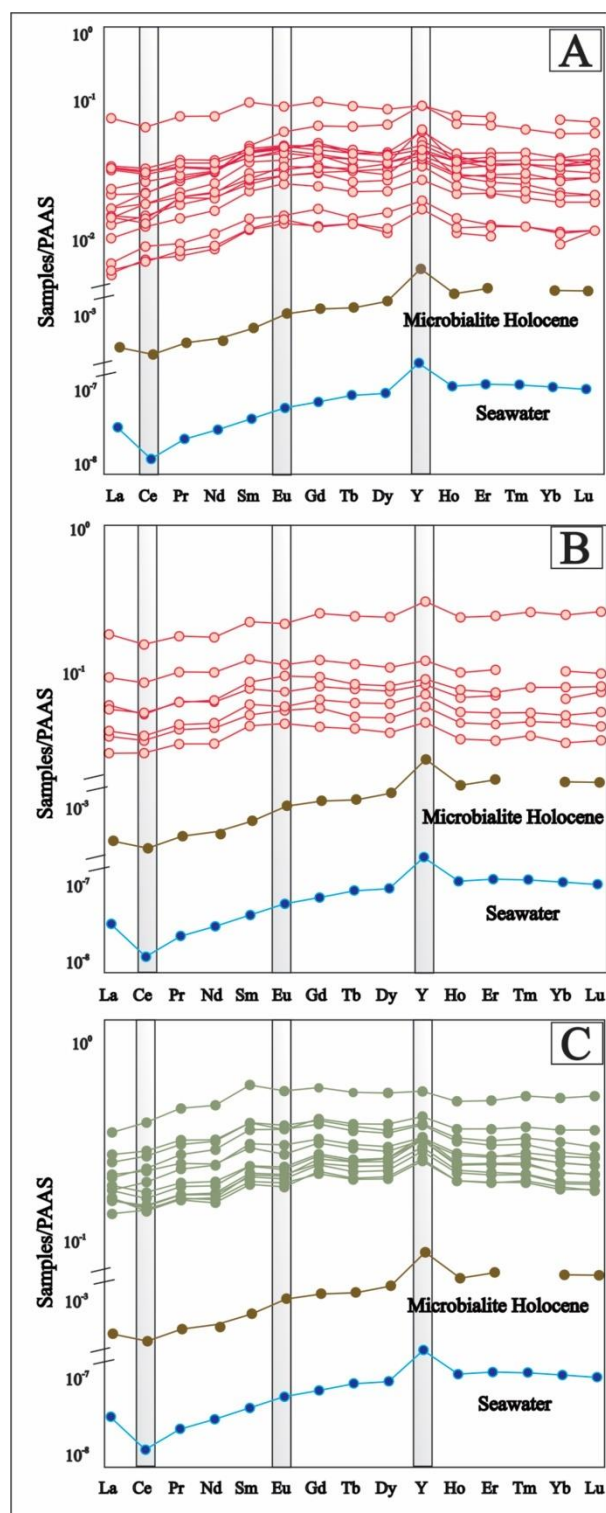


Figure 5.9- PAAS-normalized REE + Y diagram for the Puga cap carbonate in the Terconi section. The cap dolostone is shown as a pink line, and the green line represents the cap limestone. Modern seawater data from Alibo and Nozaki (1999) are shown as a blue dashed line, and the microbial Holocene data from Webb and Kamber (2000) are shown as a brown line. A) Microbialite of the cap dolostone (stratiform doloboundstones with gypsum pseudomorph cement and domical doloboundstones with tubestone). B) Wave-rippled dolostone facies (peloidal dolograinstones/dolomudstone with quasi-planar to low-angle lamination and peloidal dolograinstones with megaripple bedding. C) Cap limestone (limestone with calcite crystal fans interbedded with mega-rippled limestone).

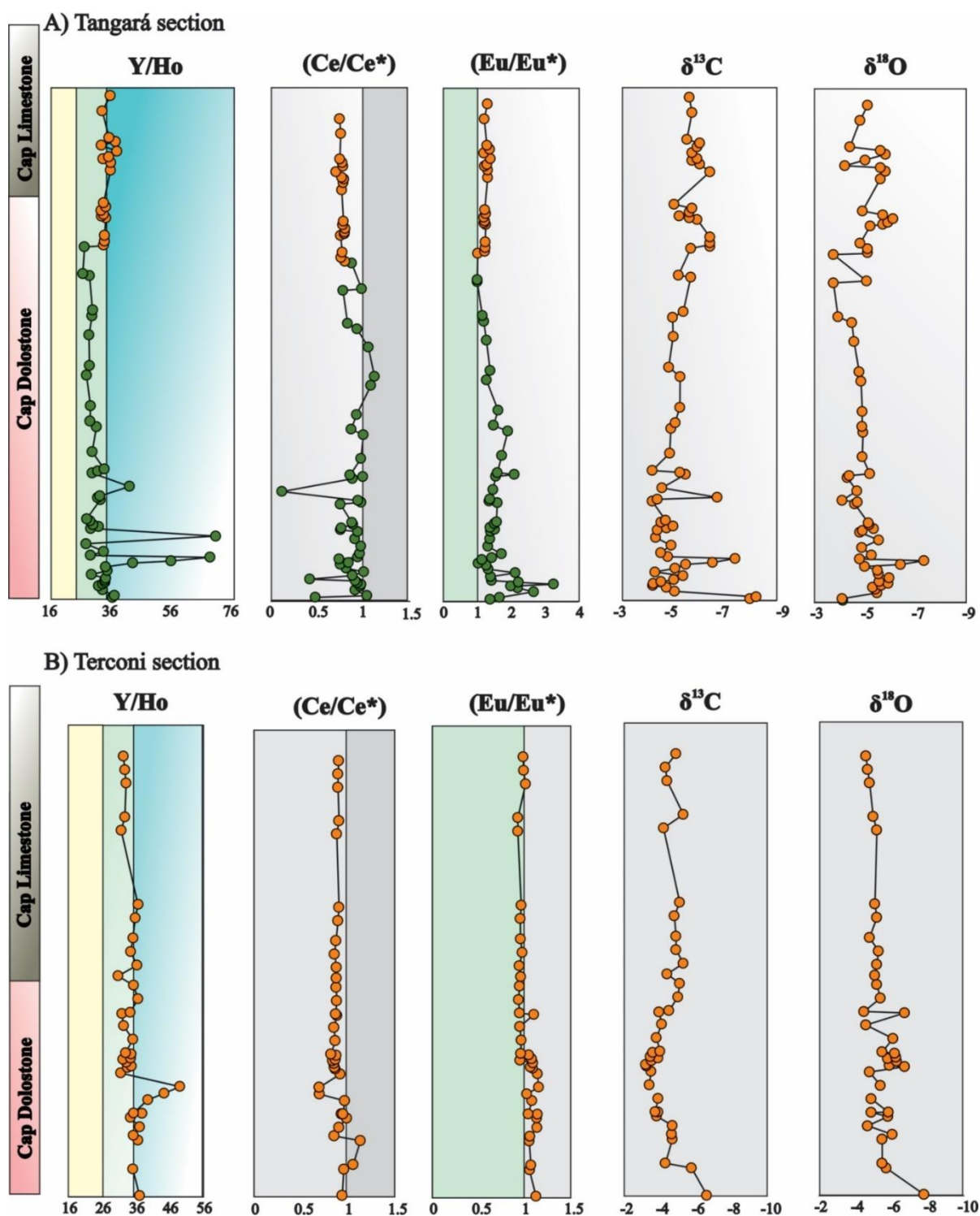


Figure 5.10- A) Chemostratigraphy of the Puga carbonate at the Tangará section. Y/Ho ratios, Ce/Ce\* and Eu/Eu\* anomalies, and  $\delta^{18}\text{O}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values normalized to VPDB. B) Chemostratigraphy of Puga carbonate at the Terconi section. Y/Ho ratios, Ce/Ce\* and Eu/Eu\* anomalies, and  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  normalized to VPDB.

## 5.7 DISCUSSION

### 5.7.1 Assessment of detrital input to Puga cap carbonate deposits

To assess the impact of detrital contributions on cap dolostone geochemistry (REE+Y anomalies), we evaluated the data using two dissolution techniques: total bulk rock dissolution and acetic acid leaching. The cap dolostone exhibited high purity in the Tangará section (Fig. 5.6) and Terconi section (Fig. 5.7). Previous microfacies studies have indicated that the Puga cap carbonate successions within the southern Amazon Craton occur with low detrital content in the matrix, especially in the cap dolostone (Nogueira *et al.* 2003, 2019, Font *et al.* 2004, Sansjofre *et al.* 2014, Soares *et al.* 2020, Santos *et al.* 2021, 2023). It is consistent with our geochemical data that indicated a clear covariance between the increase in insoluble particles (Zr, Al, and Th abundances) vs.  $\Sigma\text{REE+Y}$ . Zirconium concentrations are excellent markers of siliciclastic contamination. Once abundant in different detrital materials, contamination will drive carbonate [Zr] far above typical values of  $\sim 4$  ppm (Frimmel, 2009). Similarly,  $[\text{Th}] > 1$  ppm may indicate significant contributions from insoluble residues and thus are another marker of detrital contamination (Webb and Kamber 2000, Zhao and Zheng 2014, 2017).

In this study, binary diagrams were generated to determine the correlation between different element ratios and element concentrations to monitor the influence of diagenetic alteration and contamination by siliciclastic materials on  $\Sigma\text{REE+Y}$  distribution patterns (Kamber and Webb 2001, Nothdurft *et al.* 2004, Bolhar and Van Kranendonk 2007, Allwood *et al.* 2010, Wang *et al.* 2014, Zhao and Zheng, 2014, and Uhlein *et al.* 2021). Despite the clear influence on  $\Sigma\text{REE+Y}$ , there is no correlation, for example, between Y/Ho ratios, which would be the predicted behavior in carbonates significantly contaminated by terrigenous particles. An increase in the insoluble content of the cap dolostone was observed during the transition from microbialites facies to wave-dominated dolostone (Figs. 5.6 and 5.7). Conservative mixing lines between endmembers are based on Y/Ho vs. Zr, Th, Al, and  $\Sigma\text{REE} + \text{Y}$  (Fig. 5.11) data obtained using calcite cement from Nothdurft *et al.* (2004) and PAAS from Taylor and McLennan (1989). The calcite cement by Nothdurft *et al.* (2004) followed the criterion of purity and not its early diagenetic history.



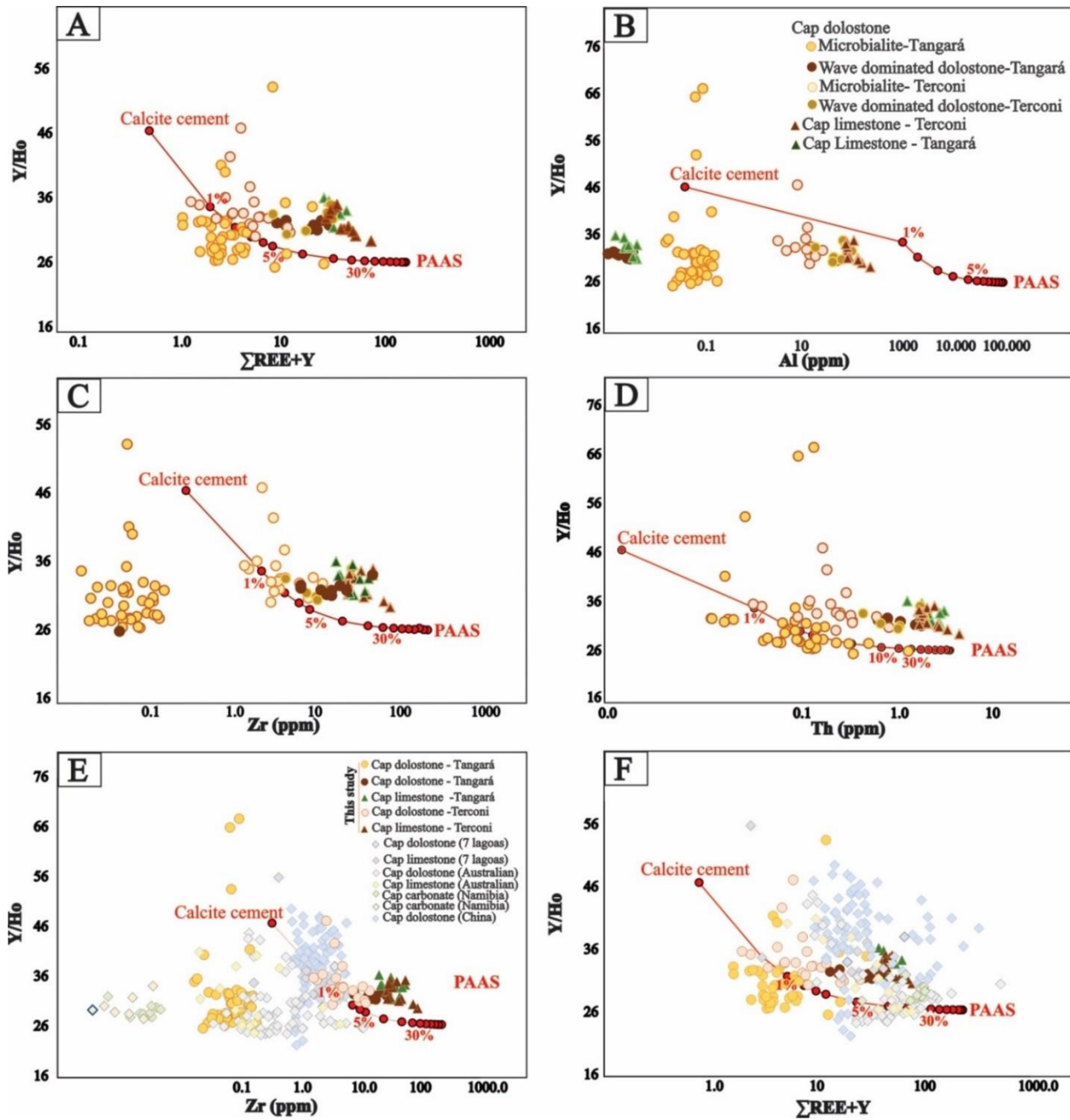


Figure 5. 11- Conservative mixing lines between endmembers based on Y/Ho versus A)  $\Sigma\text{REE} + \text{Y}$ , B) Al, C) Zr, D) Th, Fe, and Y data of the Puga cap carbonate (Terconi and Tangará quarries). The calcite cement from Nothdurft *et al.* (2004) and PAAS from Taylor and McLennan (1985) were used. Comparison of the purities of the Puga cap carbonate and other cap carbonates Sete Lagoas, Bambuí Group (Caxito *et al.* 2018), Central Australia (Verdel *et al.* 2018), Dou-shantuo cap carbonates in the Jiulongwan section in South China, Namibia, Otavi Group (Rodler *et al.* 2016).

When assessing the impact of detrital materials on total bulk rock dissolution analyses, we found that the cap dolostone was contaminated by 1–5% detrital particles (Fig.

5.11). However, Y/Ho vs. Al plot suggested less than 1% contamination (Fig. 5.11 B), whereas Y/Ho vs. Th indicates up to 10% contamination (Fig. 5.11 D). Our data reveal a minimal contribution of insoluble particles to the cap dolostone, especially within the microbialites intervals, and the limestone succession of the cap records the maximum detrital contribution. When analyzing the covariance of detrital components between Y/Ho and Zr and Th, for example, low correlation is demonstrated throughout the succession in total bulk rock dissolution (Fig. 5.11 A-D). Another critical factor is that the anomalies remain unaltered, as Y/Ho, Ce/Ce\*, and Eu/Eu\* show similarities throughout the entire succession. We further discuss these observations in detail below. However, when conservative mixing lines are applied between endmembers based on Y/Ho vs. Zr, Th, Al, and  $\Sigma\text{REE} + \text{Y}$  (Fig. 5.11), the cap limestone displays up to 30% contamination (Fig. 5.11 A-D). In comparison, Y/Ho vs. Al (Fig. 5.11 B) has a detrital contribution of up to 1%, and Y/Ho vs. Th indicates up to 30% contamination (Fig. 5.11 D).

### 5.7.2 Diagenetic influences on the Puga cap carbonate

Petrographic observations reveal that the matrix of the cap dolostone is predominantly composed of dolomicrite. It consists of replacive micritic pervasive dolomite with irregular intercrystalline boundaries (non-planar) and exhibits bright red to orange luminescence. Texturally, a predominance of the grumose pattern is observed, manifested in diffuse peloids clustered in individualized micro aggregates or isolated grumous. In rare instances, these peloids partly resemble shrubs, as Frasier and Corsetti (2003) described. Additionally, replacive dolomite is present in all facies, forming a fine- to medium- to planar-s-crystal mosaic with sizes ranging from 0.1 to 0.2 mm. The gypsum pseudomorph filling the fenestrae is well developed. Its size ranges from 0.5 to 0.8 mm, occupying the majority of fenestral porosities within the rock, with its occurrence limited to the base of the section. The cement exhibits a fibrous habit characterized by euhedral crystals that display two distinct growth forms: 1) fascicular and 2) radial/radiaxial, typical of swallowtail twinning. Subordinately, Fe-rich calcites occur mainly in fenestral, interpeloidal, and vug porosities. Furthermore, post-depositional alteration of the cap dolostone occurred primarily through processes such as dolomitization of gypsum, neomorphism of dolomicrite, development of vugs and intercrystalline porosity, euhedral dolomite precipitation, syndimentary fracturing, calcite and quartz precipitation, chemical compaction, Fe-Mn-oxide substitution, and precipitation (for more details, see Soares *et al.* 2020 and Santos *et al.* 2021, 2023). The diagenetic processes to which the cap limestone was

subjected are suggested to have occurred in the following sequence: pyrite precipitation, calcite cementation, neomorphism of micrite and crystal fan, partial crystal fan dissolution, dolomitization, chemical compaction, fracturing, ferrous dolomite and calcite precipitation, pyrite (pseudomorph) and micrite replacement with Fe oxide and replacement of rhombohedral dolomite by Mn oxides (Soares *et al.*2020, Santos *et al.*2023).

The paragenetic relationships of the Puga cap carbonate demonstrate consistent evidence of early diagenetic processes, with less influence on later mesodiagenetic events (Soares *et al.*2020, Santos *et al.*2023). The cap dolostone records a more significant impact of syndepositional cementation, which may have enhanced its preservation (Santos *et al.*2021., 2023). This exceptional preservation is observed in the well-preserved primary texture and interpreted primary  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  signals from new and previously published data (Nogueira *et al.*2003, 2019, Font *et al.*2006,2010, Sansjofre *et al.*2011, Soares *et al.*2020, Santos *et al.*2021,2023). We discuss the possible influences of late fluid-flow interactions in the Puga cap carbonate using mobile trace element,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  isotopic compositions to evaluate syn- or post-diagenetic fluid-rock interactions (Brand and Veizer 1981, Derry *et al.*1989, Banner and Hanson, 1990, Jacobsen and Kaufman 1999, McArthur 1994, Hohl *et al.*2015a,2015b). The overprinting of these fluids can mask the pristine geochemical compositions and thus must be thoroughly monitored (Hohl *et al.*2015, 2022). All the samples analyzed had negative  $\delta^{18}\text{O}$  values without systematic correlations with  $\delta^{13}\text{C}$  values, which indicates the preservation of primary signals (Fig. 5.11). The weak correlation ( $R^2 = 6 \times 10^{-5}$ ) between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  suggests that the carbon isotope system was not significantly disturbed (Folling and Frimmel, 2002). Post-depositional fluids can modify  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values (Jacobsen and Kaufman, 1999, Higgins *et al.*2018, Crockford *et al.*2021a). Many mechanisms have been proposed to explain this close covariance in altered  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, including early authigenesis in shallow marine sediments (Cui *et al.*2017) and post-depositional processes such as interactions with meteoric water and diagenetic fluids during burial diagenesis (Taylor 1977, Banner and Hanson 1999, Knuth *et al.*2017, Kennedy 2009, Zao *et al.*2020, Derry 2010).

Therefore, the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  signals of the cap carbonate occurrences in the southern region of the Amazon Craton do not present clear geochemical resetting, thus, we consider below a possible primary signal of these isotopic compositions. In most of the analyzed samples, the Mg/Ca ratios averaged  $0.8 \pm 0.18$ , indicating that dolomitization partially influenced the succession (Derry *et al.* 1994). However, the cross plot of  $\delta^{18}\text{O}$  vs. Mg/Ca shows a negligible correlation ( $R^2 = 0.0182$ ) (Fig. 5.12 B) and suggests that late dolomitization processes did not affect the  $\delta^{18}\text{O}$  values (Lu and Meyers, 1998). This weak correlation between Mg/Ca vs.  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  vs.  $\delta^{18}\text{O}$  suggested that the isotopes may have maintained pristine signals. Similarly, the weak correlation between the Mg/Ca ratio and the Mn/Sr and Fe ratios ( $R^2 = 0.015$ ) potentially indicates that the trace element concentrations did not change significantly during dolomitization (Chen *et al.* 2022).

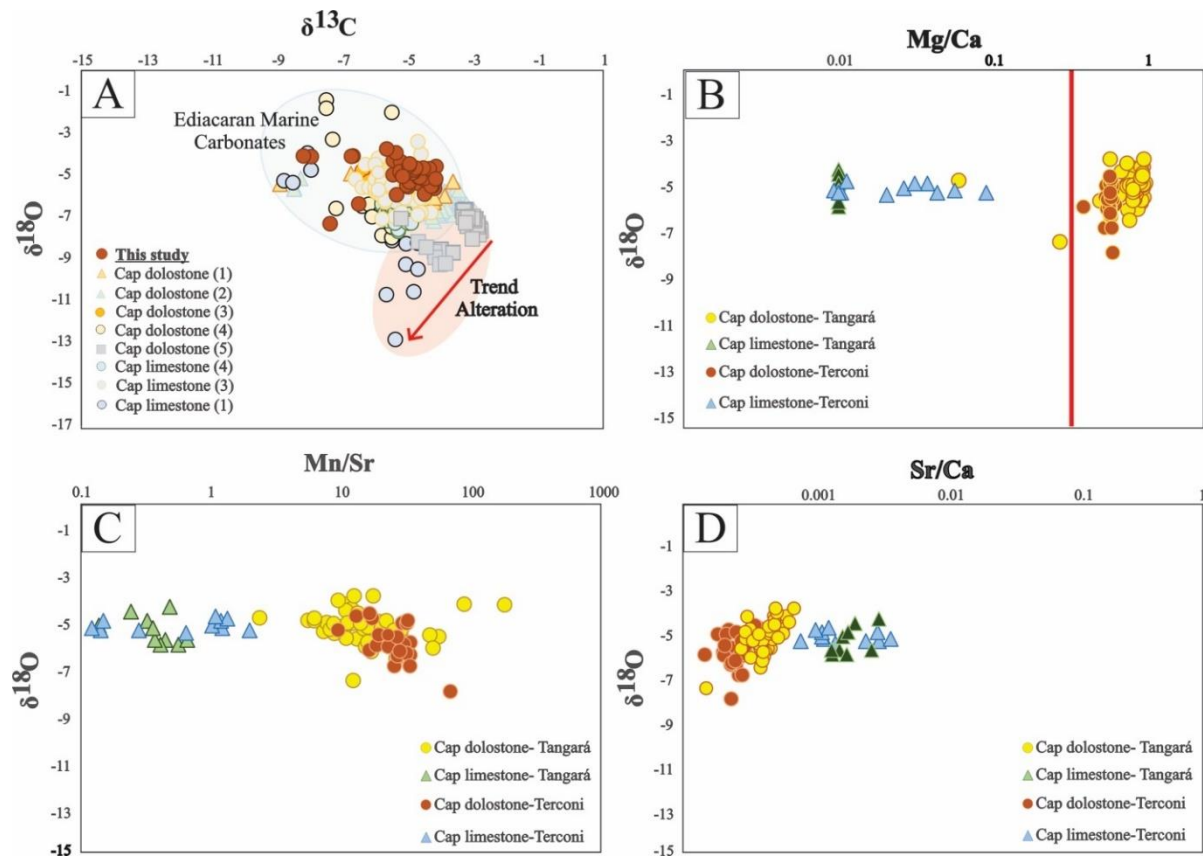


Figure 5.12- A) Cross plots of the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  stable isotopic compositions of the carbonate fraction in the Puga cap carbonate from the southern Amazon Craton. New data from this study and compiled data from 1) Nogueira *et al.* (2003), 2) Font *et al.* (2006), 3) Sansjofre *et al.* (2011), 4) Nogueira *et al.* (2019), 5) Gaia *et al.* (2017). B) Cross plots between  $\delta^{18}\text{O}$ . C) Mg/Ca, Cross plots between  $\delta^{18}\text{O}$  and Mn/Sr. D) Cross plots between  $\delta^{18}\text{O}$  and Sr/Ca ratios.

Mn/Sr and Sr/Ca variations can have two causes: post-depositional alteration or paleoenvironmental changes. The Mn/Sr ratio of the cap dolostone vs. the  $\delta^{18}\text{O}$  value (Fig. 5.12 C) showed no correlation ( $R^2 = 0.017$ ). On the other hand, a negligible correlation was observed for the Sr/Ca ratio when plotted against  $\delta^{18}\text{O}$  ( $R^2 = 0.43$ ) and the Mg/Ca ratio ( $R^2 = 0.40$ ). Despite these weak correlations, our data reveal a more significant relationship with syndepositional dolomitization (Sr/Ca and Mg/Ca) than post-stabilization changes in dolomite (late diagenesis). Therefore, Mn/Sr and Sr/Ca ratios may be explained by specific paleoceanographic conditions or the development of alteration processes by diagenetic fluids (Asmerom *et al.*1991, Derry *et al.*1992, Kaufman *et al.*1993, Kaufman and Knoll 1995, Melezhik *et al.*2001, Folling and Frimmel, 2002, Halverson *et al.*2007). Thus, the high Mn/Sr ratios obtained in many cap dolostones may be explained by increased Mn concentrations in bottom waters or anoxic porewaters (Hohl *et al.*2017, Chen *et al.*2022). Another possible explanation for the high Mn concentration in cap carbonates is that Mn-Fe-rich hydrothermal fluids were present in the coeval anoxic or suboxic deep ocean (Yoshioka *et al.*2003, Nédélec *et al.*2007, Shen *et al.*2005, Font *et al.*2006, Hurtgen *et al.*2006).

The relationship between our petrographic and isotopic data indicates that diagenetic processes may have occurred due to fluid (possibly seawater) interactions occurring during synsedimentary diagenesis or shallow burial (Nogueira *et al.*2003, Font *et al.*2004, Gilleaudeau *et al.*2018, Soares *et al.*2020, Santos *et al.*2021,2023). Evidence of early diagenesis demonstrated early stabilization of the Puga cap carbonate. This evidence is confirmed by dating aragonite crystal fans from the cap limestone, which provided a U–Pb age of  $623 \pm 3$  Ma (Carvalho *et al.*2023), indicating that post-depositional alteration occurred within the first  $\approx 10$  million years. In contrast, although cap carbonates have the same textural and compositional framework, the diagenetic history is regional and completely dependent on the tectonic, thermal, and burial history of the depositional basins where they were deposited (Ahm *et al.*2019, Soares *et al.*2020, Santos *et al.*2023). However, we suggest that the syndepositional signature of the cap carbonate succession is preserved. We showed that most post-depositional modifications occurred early, and there was no evidence of effective overprinting during succession. This exceptional preservation qualifies the Puga cap carbonate succession as an excellent candidate for tracing paleoceanographic dynamics after the Marinoan glaciation.

### 5.7.3 Diagenetic Overprint Interference in REE+Y Distributions

Previous diagenetic evaluations of the Puga cap carbonate demonstrated the predominance of early diagenesis (Soares *et al.* 2020, Santos *et al.* 2021). Diagenetic studies of REE+Y distributions in ancient carbonates suggest that  $\Sigma\text{REE+Y}$  patterns may be stable even during relatively intense diagenesis (Webb and Kamber, 2000, Liu *et al.* 2019) because  $\Sigma\text{REE+Y}$  concentrations are low in diagenetic fluids ( $10^{-6}$  to  $10^{-4}$  ppm) (Sholkovitz *et al.* 1989, Banner and Hanson 1990, McLennan *et al.* 2003), and the permeability and porosity of sedimentary carbonates are strongly reduced by calcite cement formation during early diagenesis (Tanaka and Kawabe 2006).

We analyzed Ce and Eu variations using binary diagrams (Fig. 5.14 A). Ce and Eu were chosen for investigation because of their high sensitivity to fluid mobilization processes.  $\text{Ce}^{3+}$  can oxidize to  $\text{Ce}^{4+}$ , while concurrently,  $\text{Eu}^{3+}$  can simultaneously undergo reduction to  $\text{Eu}^{2+}$  (Brookins 1989). Diagenetic overprinting of carbonate deposits leads to REE enrichment and a decrease in (Dy/Sm). These anomalies exhibit strong covariance between Ce anomalies and (Dy/Sm)<sub>SN</sub> (German and Elderfield 1990, Shields and Stille, 2001). These data could show a positive correlation between Eu/Eu\* anomalies and (Pr/Sm)<sub>SN</sub> (Bolhar and Van Kranendonk 2007). However, Ce/Ce\* anomalies do not covary with (Dy/Sm)<sub>SN</sub> (Fig. 5.14 C), and there is an anti-correlation between Eu/Eu\* anomalies and (Pr/Sm)<sub>SN</sub> (Fig. 5.13 A), suggesting low interference from post-depositional diagenetic fluids in the  $\Sigma\text{REE+Y}$  of the carbonates of the Puga cap carbonate.

The Puga cap carbonate successions show strong Eu/Eu\* anomalies reaching up to 3.2 (average =  $1.56 \pm 0.31$ ). Eu anomalies could be analytical artifacts due to interference from high Ba concentrations during ICP–MS measurements (Jiang *et al.* 2007). Our data show a low correlation with Ba ( $R^2 = 0.35$ ). Additionally, the Eu/Eu\* anomalies strongly correlate with Gd and Sm ( $R^2 = 0.9$ ), which is unrelated to isobaric interference with Ba. The positive Eu anomalies may occur because of plagioclase dissolution. Deng *et al.* (2017) and Langarica *et al.* (2020) discussed the influences of these variables on Eu anomalies and the flattening of REE+Y patterns. However, this is not the case in this study because we demonstrated the purity of cap dolostone in section 5.1. Our data show low covariance between Eu/Eu\* anomalies and Zr, Al, and Th. Another possible explanation for these anomalies could be syn- and post-depositional hydrothermal processes because hydrothermal fluids are potentially significant secondary flows of REEs+Y to the ocean and carry flat or heavy rare earth elements (HREEs) and excessive

concentrations of Eu (Bau and Dulski 1996, 1999, Douville *et al.* 1999, Douville *et al.* 1999, Barrat *et al.* 2000, Cui *et al.* 2019). Furthermore, the previous discussion demonstrated that the low covariance of  $\delta^{13}\text{C}$  vs.  $\delta^{18}\text{O}$  and the absence of a correlation between Mg/Ca and  $\delta^{18}\text{O}$  (Fig. 5.9) which suggests only minor modifications after dolomitization, which agrees with the diagenetic studies by Soares *et al.* (2020) and Santos *et al.* (2023). These observations indicate that the REE+Y patterns are most consistent with syn- or penecontemporaneous processes before cap dolostone stabilization.

#### 5.7.4 The Influence of Meltwater and Upwelling of Hydrothermal and Hypersaline Fluids.

The REE + Y patterns of the Puga cap carbonate (Fig. 5.8 and Fig. 5.9) have distinct PAAS-normalized patterns compared with those of modern marine environments, which are characterized by uniform LREE depletion and HREE enrichment, positive La anomalies, negative Ce anomalies, and high Y/Ho ratios (Bau and Dulski 1996, Webb and Kamber 2000, Kamber and Webb 2001, Van Kranendonk *et al.* 2003, Bolhar *et al.* 2004, Shields and Webb 2004, Zhang *et al.* 2016, Tepe and Bau 2016). As noted earlier, the Y/Ho ratio can distinguish between successions influenced by freshwater and those influenced by seawater (Bau *et al.* 1996, Nozaki *et al.* 1997, Wang *et al.* 2014, Hodgskiss *et al.* 2021). As a result, marine carbonates often exhibit elevated values, i.e., they are considered superchondritic (Bau *et al.* 1996, Zhang and Nozaki 1996, Nozaki *et al.* 1997). Conversely, REE + Y ratios remain relatively constant in freshwater environments, typically hovering at approximately Y/Ho  $\sim 26$  (Lawrence *et al.* 2006, Bolhar and Van Kranendonk 2007). Intermediate ratios are commonly associated with inland waters or mixed systems (Webb and Kamber 2000, Van Kranendonk *et al.* 2003, Bolhar *et al.* 2004, Shields and Webb 2004, Lawrence and Kamber 2006). However, it has been frequently reported that marine carbonates may exhibit distinct REE + Y patterns from those of seawater, primarily due to the input of freshwater into shallow seawater (Frimmel 2009, Zhao *et al.* 2009, Bolhar *et al.* 2015). In addition to Ce, the typical marine REE features can thus be attributed to estuarine or mixing water processes (Lawrence and Kamber 2006).

The cap dolostone has Y/Ho ratios ranging from 24.50 to 76.67 (Fig. 5.10). Our Y/Ho values in the Tangará and Terconi sections are consistent with a mixture of waters leading to intermediate salinity, for example, in the basal microbialites (stratiform doloboundstones with gypsum pseudomorphs), with an average value of  $32 \pm 10$ ,  $n = 32$ .



However, intermittently elevated ratios (up to 70) of typical seawater are observed, implying sporadic episodes of increased salinity (Lawrence and Kamber 2006). The domical dolostones stromatolites with tubestone have Y/Ho ratios between 26 and 33 (average =  $29 \pm 1$ ), suggesting waters of intermediate salinity (Bolhar and Van Kranendonk 2007). The wave-dominated dolostone facies (e.g., Peloidal dolopackstone with quasi-planar lamination) occur with Y/Ho values ranging from 32 to 34 (average =  $33.5 \pm 0.6$ ), close to coastal marine values. These ratios are common in glacial meltwater and seawater and are generally characterized by low Y/Ho values relative to terrigenous REE + Y patterns (Frimmel 2009, Zhao and Zheng 2010). In addition, as discussed in section 6.1, our data suggest an absence of interference from siliciclastic components at lower Y/Ho values. Thus, these patterns are widely documented in cap dolostone deposits. These fluctuations are commonly interpreted as reflections of the dilution of seawater signals in shallow marine environments due to the influx of meltwater derived from ice caps (Hohl *et al.* 2017, Ren and Li 2023).

The Puga cap carbonate exhibits mostly weakly negative Eu anomalies throughout both successions. However, elevated values are documented at the base of the cap dolostone at the microbialites level. Positive Eu/Eu\* anomalies are not characteristic of the general marine carbonates (Lawrence *et al.* 2006) and are typically considered strong indicators of high temperature-reducing fluids (Bau, 1991, Klinkhammer *et al.* 1994, Barrat *et al.* 2000, Alexander *et al.* 2008, Parsapoor *et al.* 2009). REE-depleted patterns with positive Eu anomalies indicate the contribution of hydrothermal fluids (Cui *et al.* 2019). Our data are consistent with the positive Eu/Eu\* anomalies generally considered indicative of hydrothermal components in previous studies of post-Marinoan cap dolostones (Font *et al.* 2006, Nédélec *et al.* 2007, Huang *et al.* 2011, Meyer *et al.* 2012, Wang *et al.* 2014, Rodler *et al.* 2016, Hohl *et al.* 2017). Hydrothermal exchange reactions presumably strongly influenced the residual brine from the Marinoan glaciation due to the reduction in continental inputs for millions of years. This environment was previously proposed as a possible refuge for life (Schrage and Hoffman 2001). For example, the clade represented by *Trichodesmium* may have survived Cryogenian Snowball Earth in marine hydrothermal environments (Hoffman *et al.* 2017). Hydrothermal activity along mid-ocean ridges is a viable dissolved Fe(II) source within anoxic subglacial oceans. This proposition is supported by various studies (Martin 1964, Kirschvink 1992, Klein and Beukes 1993). High Fe/Al ratios but deficient concentrations of extractable pyrites suggest ferruginous rather than

euxinic conditions (Huang *et al.* 2011). In addition, REE absorption by Fe oxides is typically associated with submarine hydrothermal plume activity (German *et al.* 1991, Ling *et al.* 2013).

We tested the hydrothermal influence on Puga cap carbonates using Fe/Ti vs. Al/(Al + Fe + Mn) (Fig. 5.13C) (Bostrom 1973, Barrett 1981). Deposits with strong hydrothermal influence do not typically occur with high concentrations of Al, resulting in high Al/Ti ratios (Marchig *et al.* 1982). The contamination of these deposits by pelagic and terrigenous seabed sediments enriches them in components such as Ti and Al, resulting in a drastic reduction of Fe/Ti ratios and an increase in the Al/(Al + Fe + Mn) ratio. Our data suggest a significant influence of hydrothermal activity on siliciclastic contamination (Fig. 5.13A-B). The Eu/Eu\* anomalies correlate strongly with the Fe/Al ratios (Fig. 5.13 D). This relationship between the increase in Fe and strong Eu anomalies reinforces the interpretation of a hydrothermal contribution to the Puga cap carbonate, similar to that described by Huang *et al.* (2011), which suggests a hydrothermal origin of elevated iron and manganese for the Doushantou cap carbonate from China. Furthermore, we assessed the hydrothermal impact by applying conservative mixing lines (see Fig. 5. 13E-F).

This approach aligns with the model proposed by Alexander *et al.* (2008), which considers the interaction of high-T hydrothermal fluids with seawater during sediment deposition, utilizing middle rare earth element (MREE)/HREE ratios. To achieve this goal, we integrated data from high T-hydrothermal sources (> 350°C, Bau and Dulski, 1999) and shallow seawater components (Alibo and Nozaki 1999). Conservative mixing calculations between endmembers based on Sm/Yb vs. Eu/Sm (Fig. 5. 10 D) indicate that a high-T hydrothermal fluid contribution of less than 1% could have been responsible for the anomalies recorded in the cap dolostone (Alexander *et al.* 2009). The studied samples are significantly displaced from the mixing line, suggesting a minimal influence of hydrothermal fluids (up to 1%). This scenario suggests that there was no influence of high-temperature fluids, and that the depositional environment of carbonate rocks was distant from that of fumaroles. However, it is worth noting that positive Eu anomalies obtained from Archean and Paleoproterozoic chemical sediments are interpreted as mixtures of

seawater and hydrothermal fluids (Kamber and Webb 2001, Frei *et al.* 2008, Hodgskiss *et al.* 2021).

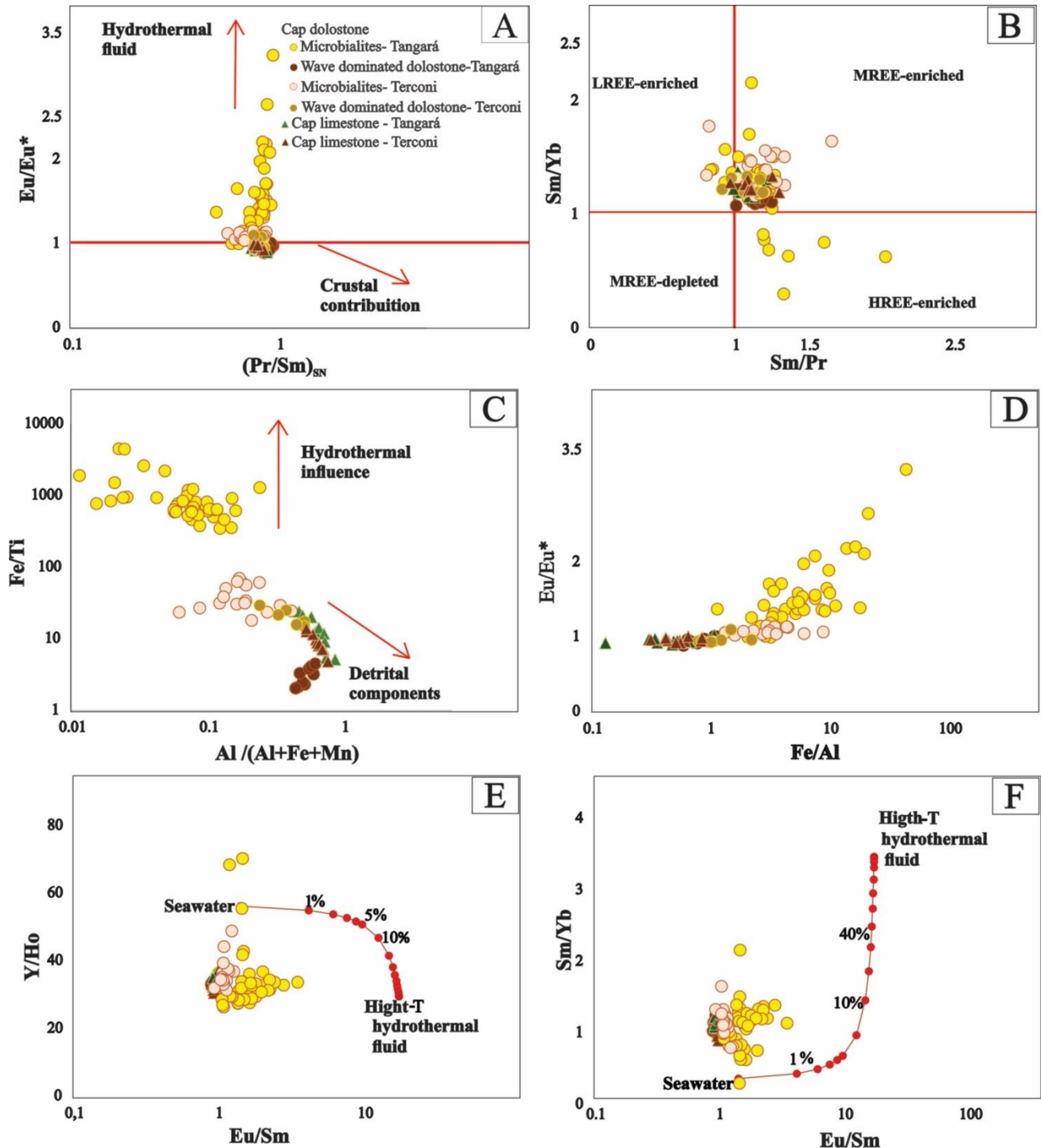


Figure 5.13- A) Plots showing the relationships between  $\text{Eu}/\text{Eu}^*$  anomalies and  $(\text{Pr}/\text{Sm})_{\text{SN}}$ . B) The bivariate graph of  $(\text{Sm}/\text{Yb})_{\text{SN}}$  versus  $(\text{Sm}/\text{Pr})_{\text{SN}}$  shows that the majority of samples were enriched in the MREE. C) Ratios of  $\text{Fe}/\text{Ti}$  vs.  $\text{Al}/(\text{Al} + \text{Fe} + \text{Mn})$ . D) Plots showing the relationship between  $\text{Eu}/\text{Eu}^*$  anomalies and  $\text{Fe}/\text{Al}$  ratios. E) and F) Elemental ratio plots for data with two-component conservative mixing lines for  $\text{Eu}/\text{Sm}$ ,  $\text{Sm}/\text{Yb}$ , and  $\text{Y}/\text{Ho}$  (symbols for all plots defined in A): (E)  $\text{Y}/\text{Ho}$  versus  $\text{Eu}/\text{Sm}$ , showing that up to 1% high-T hydrothermal ( $>350^\circ\text{C}$ , Bau and Dulski, 1999) fluid contributed to waters with shallow ( $<500\text{ m}$ ) seawater REY distributions (Alibo and Nozaki, 1999) (F)  $\text{Sm}/\text{Yb}$  as a function of  $\text{Eu}/\text{Sm}$ , demonstrating relatively small (up to 1%) contributions.

For the Ediacaran period, positive Eu anomalies are commonly associated with deep anoxic ocean (Kamber and Webb 2011, Bolhar *et al.* 2005, Allwood *et al.* 2010, Rödler *et al.* 2016). In addition, our interpretations align with recent interpretations of the origin of the Doushantou cap carbonates, which are mainly based on  $\delta^{13}\text{C}$ ,  $\delta^{34}\text{S}_{\text{CAS}}$ ,  $\delta^{17}\text{O}_{\text{CAS}}$ ,  $\delta^{44}\text{Ca}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ , rare earth elements, and trace metal elements. These data suggest that they may have formed under the influence of deglacial meltwater, hydrothermal fluids, and upwelling processes (Huang *et al.* 2009, 2011, Huang *et al.* 2013, Wang *et al.* 2014, Hohl *et al.* 2017, Zhao *et al.* 2018, Wei *et al.* 2019a, Peng *et al.* 2022). Carbonates associated with deep ocean brine are characterized by Fe and trace metal enrichments along positive Eu anomalies (Meyer *et al.* 2012). Liu *et al.* (2013) extensively discussed the potential origin of radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  in Marinoan cap carbonates of the Nuccaleena Formation, South Australia. They indicated that the interaction of carbonates with brine or hydrothermal fluids could better explain these values, or these interactions may reflect the mixing of glacial meltwater with seawater (Fig. 5.16 A-C). This evidence reinforces previous interpretations that the Marinoan cap carbonate precipitated in a mixture of coastal meltwater with saline Mg-rich deeper waters through upwelling processes (Ridgwell *et al.* 2003, Shields 2006, Yang *et al.* 2017, Liu *et al.* 2014, 2018, Hoffman *et al.* 2017, Santos *et al.* 2021, Rame and Marotzke 2022). Through modeling, glacial hydrothermal flow during the Marinoan Snowball glaciation was demonstrated using a binary mixture of Ge/Si and Eu/Eu\* values (Cui *et al.* 2019). Marinoan deposits accumulated during the drifting stage of post-rift subsidence (Hoffman *et al.* 2017), and this hydrothermal flow during Snowball Earth events could have enriched the oceans with certain elements in the aftermath of the Marinoan glaciation.

The syndepositional hydrothermal events were unlikely, and these observations align with our interpretations of rapid precipitation of the Marinoan cap carbonate (Hoffman *et al.* 1998, Nogueira *et al.* 2003, 2019, Crockford *et al.* 2016, 2021b, Yang *et al.* 2017, Zhou *et al.* 2017, Cui *et al.* 2019, Santos *et al.* 2021). Our data support that some samples have typical seawater values (Y/Ho up to 70), and others strongly indicate hydrothermal fluid interactions (Eu/Eu\* up to 3.2). Nevertheless, most of our samples exhibit Y/Ho ratios typical of mixwater of about ~33 (a combination of glacial meltwater and seawater). These findings are consistent with interpretations of upwelling events during the precipitation of the cap dolostone. It is suggested that deep Cryogenian waters would have interacted with high-temperature hydrothermal fluids responsible for element enrichment

(e.g., Eu, Fe, Mn). This evidence is consistent with the diachronous precipitation model proposed for the Marinoan cap dolostone from the meltwater layer during syn-deglacial transgression (Hoffman *et al.* 2017). This upwelling interaction may also have contributed to the lowered Y/Ho values of the dolostone samples in the basal succession, as hydrothermal fluids tend to possess low Y/Ho ratios. Fluctuations in Y/Ho values and high Eu anomalies observed at the base of the cap dolostone suggest that hydrothermal sources of REE+Y strongly influenced the cap dolostone on the southeastern margin of the Amazon Craton.

### 5.7.5 Paleoredox indications

Ce/Ce\* anomalies in the Puga cap carbonate indicate oxygen deficiency throughout the section (Fig. 5.10 and Fig. 5.14), but these anomalies are weaker in the microbialites interval. In modern seawater, REE+Y can record the evolution of seawater redox reactions, and a negative Ce anomaly marks oxidized conditions (Byrne and Sholkovitz 1996, Webb and Kamber 2000, Ling *et al.* 2013), while the absence of anomalies is indicative of anoxic conditions (Lawrence *et al.* 2006). Furthermore, soluble Ce<sup>3+</sup> is easily oxidized to Ce<sup>4+</sup>, which is relatively insoluble in oxic seawater (McLennan 1989, Alibo and Nozaki 1999, Pattan *et al.* 2005, Frimmel 2009). Therefore, the Ce anomaly in marine sediments distinguishes oxic from anoxic depositional environments throughout the sedimentary record (Bau *et al.* 1996, de Baar *et al.* 2018).

However, the scenario presented thus far demonstrates the influence of water mixing, particularly the strong influence of meltwater. The Y/Ho ratio (Fig. 5.14B) exhibited similar behavior to estuarine dynamics (freshwater and saltwater). In addition to Ce, typical marine REE features can be attributed to estuarine or mixing water processes since Ce anomalies only form at salinities greater than 2‰ (the ocean average is 3.5‰) (Lawrence and Kamber 2006). Therefore, only samples with a Y/Ho ratio  $\geq 36$  were considered for interpretation (Fig. 5.14 B). Three samples fell into the oxygenated category, but most of these eligible samples exhibited values suggesting dysoxic conditions. Our results have been extensively tested for post-depositional changes, at least, the samples with high Y/Ho ratios may reflect the redox conditions of our post-Marinoan scenario.

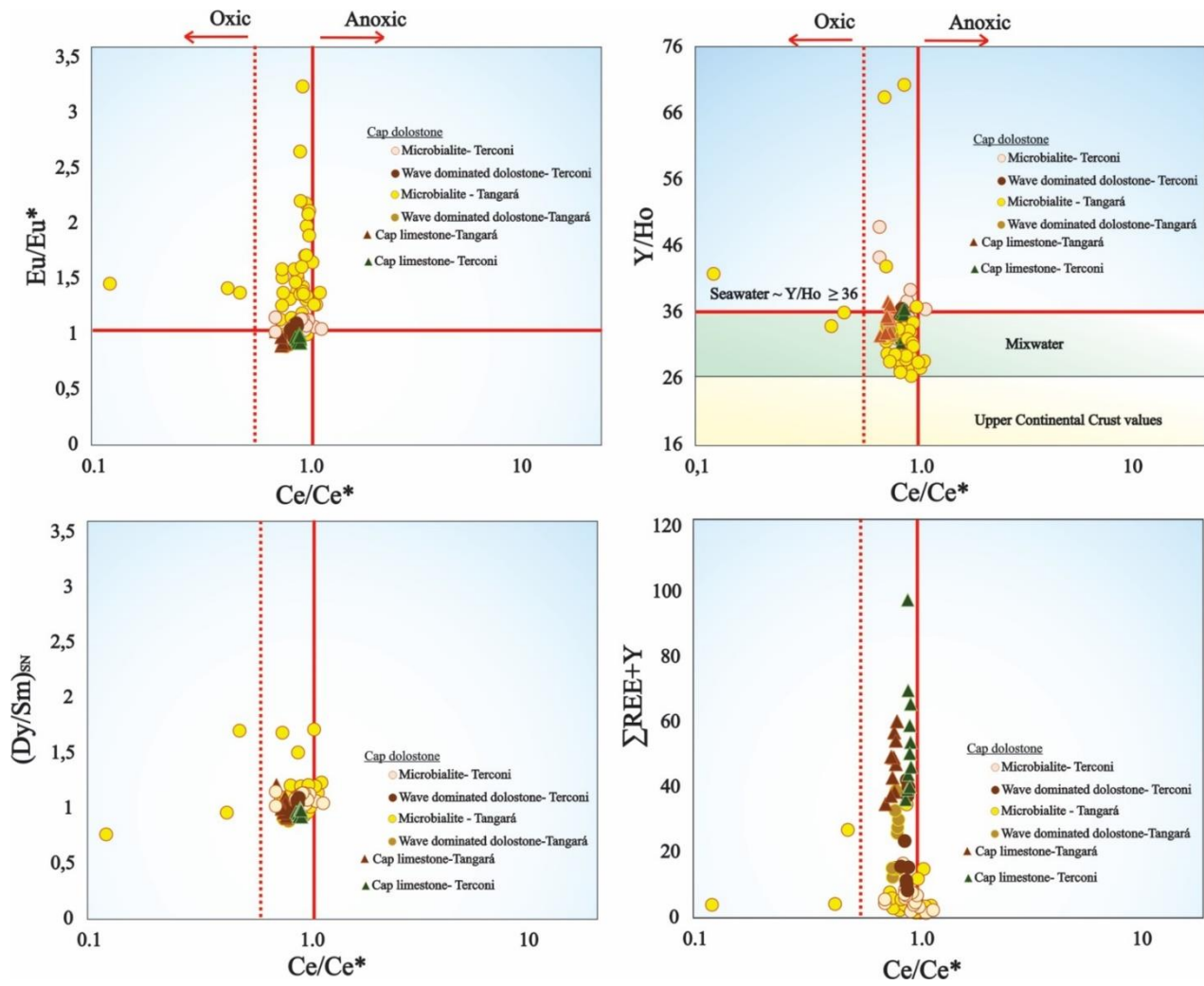


Figure 5. 14- A) Crossplot of  $Ce/Ce^*_{PAAS}$  vs.  $Eu/Eu_{PAAS}$ . B) Crossplot of Ce anomalies against Y/Ho ratios. The threshold of  $Y/Ho > 36$  represents samples with seawater signatures. C) Crossplot of  $Ce/Ce^*$  anomalies vs.  $(Dy/Sm)_{SN}$  ratios. D)  $Ce/Ce^*$  anomalies vs.  $\Sigma REE+Y$ .

The interpretation of a dysoxic to anoxic environment in the Puga cap carbonate is consistent with other post-Marinoan deposits (Huang *et al.* 2009, 2011, Wang *et al.* 2014, Lang *et al.* 2016, Rodler *et al.* 2016, Hohl *et al.* 2017, Caxito *et al.* 2018, Wu *et al.* 2019, Ren and Li 2023). In this sense, the results could reflect the biochemical conditions of this anomalous environment, as Ce anomalies are known to be affected by environmental parameters such as pH, alkalinity, and microbial activity (de Baar *et al.* 1985a, German and Elderfield 1990, Byrne and Kim 1993, Pourret *et al.* 2008, Zhao *et al.* 2022). The rate of biological  $O_2$  production is strongly affected by surface temperature (Harada *et al.* 2015, Middelburg 2019). Therefore, surface ocean warming to 50-60°C after the snowball would likely have reduced the dissolved  $O_2$  concentration at saturation.

The Ce/Ce\* values of the studied samples (0.70–1.05, mostly below 0.95) could indicate a small amount of oxygen deficiency in the water column (Fig. 5.8 and Fig. 5.9). Dysoxic waters would likely provide even more stressful conditions for microbial life after the Marinoan glaciation. Generally, previous studies suggest oxidizing conditions prevailed in the atmosphere and shallow seawater during the post-Marinoan phase (Fike *et al.* 2006, Sahoo *et al.* 2012, Sansjofre *et al.* 2014, Hohl *et al.* 2015, 2017, Ader *et al.* 2014). Sansjofre *et al.* (2014). These inferences are not supported by our new trace metal data which suggests that cap dolostones precipitated from a dysoxic water column with anoxia occurring only sporadically reaching the sediment-water column interface in the deepest parts of the platform on the Amazon craton. Therefore, our findings depart from previous works across certain intervals of cap dolostone deposition. However, other proxies must be applied to understand the role of microbial communities and evaluate reservoir effects due to water mixing. This observation associated with meltwater mixing with the upper layer evidence is consistent with the plume would hypothesis of Shields (2005), which states that a high alkalinity oxic meltwater lens overlays anoxic deeper waters.

### 5.7.6 Cap carbonate precipitation model and global correlation

The influence of meltwaters causing ocean stratification is important in understanding paleoceanographic dynamics and the geochemical record captured within post-Marinoan deposits. During this period, the thickness of glaciers has been estimated at 0.7–1.4 km for continental ice sheets (Liu and Peltier, 2010, Benn *et al.* 2015), while sea glaciers reached up to ~1 km (Tziperman *et al.* 2012). The meltwater volume was dependent on the water state in glaciers, for example, the oceans were composed partially of marine ice (frozen seawater) and meteoric ice (compressed snow) (Li and Pierrehumbert 2011, Yang *et al.* 2017, Hoffman *et al.* 2017, Wu *et al.* 2021). In contrast, the deglaciation of continental ice sheets (Liu and Peltier, 2010, Tziperman *et al.* 2012, Benn *et al.* 2015) was probably the main source of meltwater for the ocean (Wu *et al.* 2021). The complete ablation of thick marine ice is estimated to occur within at most ~300 to 1500 years (Liu and Di, 2022). Rapid deglaciation and warming caused a stable density stratification (Fig. 5.16 A) with complex geochemical conditions that evolved brine precipitation in deep waters accompanied by a superficial meltwater layer (Shields, 2005, Yang *et al.* 2017, Hoffman *et al.* 2017, 2021, Wei *et al.* 2019). The stable stratification was also induced by a salinity three times greater than the modern ocean, commonly found in the post-



Marinoan oceans (Shields, 2005, Gidding and Wallace, 2009, Liu *et al.* 2014, 2018, Wei *et al.* 2019, Yang *et al.* 2017, Hoffman *et al.* 2017). The timescale for ocean destratification varies from tens of thousands (Yang *et al.* 2017) to thousands of years (Rame and Marotzke 2022).

Oceanic circulation was a critical factor for destratification during the post-melting stage (Fig. 5.16 B) (Rame and Marotzke 2022). The stratification conditions putatively lasted for approximately  $\sim 8$  ka (Liu *et al.* 2014) or have been included on a scale of  $10^4$  and  $10^5$  years following a unidirectional mixing model (Yang *et al.* 2017). Another recent model by Rame and Marotzke (2022) considered a few thousand years for mixing water based on a three-dimensional model linked to oceanic circulation during the end of seawater stratification. The contrasting destratification timescales obtained by Yang *et al.* (2017) and Rame and Marotzke (2022) are partly due to the respective 1-D vs 3-D treatments as well as major differences in starting conditions. Yang *et al.* (2017) assumed a 2 km-thick sea glacier whose melt will produce a greater water volume than that continental ice sheets generated. In contrast, the Rame and Marotzke (2022) model considered only a few meters of thick marine ice cover due to thermodynamic limitations. Although glacial-isostatic adjustment (GIA) could be the driving force influencing the mixing of the waters and paleoceanography, the time spent on this event depends on the ice cap thickness and melting velocity.

Furthermore, Trindade *et al.* (2003) proposed a low paleolatitude ( $22 \pm 6/5^\circ$ ) for the Amazon block during the precipitation of the Puga cap carbonate. Integrating coastal configurations into the paleoceanographic models presented here (Fig. 5.15) may clarify the significant influence of continental sources on lower average Y/Ho values. Our data indicate a more pronounced impact of continental melting. However, the contribution of superchondritic values, particularly at the base, is noteworthy, yet distinguishing the effects of melting from the marine ice cap and the signature of brine deep-water upwelling poses a challenge. For example, many cap dolostone record enigmatic barite horizons ( $\text{BaSO}_4$ ) (e.g., Bao *et al.* 2008, Crockford *et al.* 2016, 2018, Okubo *et al.* 2018). In contrast, the correlate horizon in Puga cap carbonate is gypsum pseudomorphs ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (Santos *et al.* 2021, 2023). The  $\text{SO}_4^{2-}$  in the initial gypsum has been considered sourced from intense continental weathering (e.g., Crockford *et al.* 2016) or deeper waters with upwelling processes (Santos *et al.* 2023). However, paleoceanographic dynamics in the region precipitating the Puga cap dolostone may represent a local factor compared with

other locations where barium isotope data suggest that upwelled  $\text{Ba}^{2+}$  reacting with surface water  $\text{SO}_4^{2-}$  ultimately drove barite precipitation in several locations (Crockford *et al.* 2019). Such hypotheses may be explored in the future through additional isotopic studies. Nevertheless, our mineralogical and geochemical data, high Y/Ho values (up to 71), and gypsum precipitation in the fenestral porosities of basal dolostone support the interpretation of sporadic increases in salinity during water mixing. This salinity increase could be associated with episodic upwelling hypersaline deep water reaching shallow areas (Fig. 5.16 B-C). As previously discussed, the Eu/Eu\* anomalies correlate strongly with the Fe/Al ratio values, suggesting hydrothermal fluids in deeper brine water. Our evidence supports cap dolostone precipitation during ocean destratification (Hoffman *et al.* 2017, 2021, Rame and Marotzke 2022).

Throughout this deglacial period, the local decline in sea level might have momentarily surpassed the global (eustatic) sea-level rise rate (Fig. 5.16). Local sea-level rise caused by ice retreat and uplift of coastal zones promoting the sea-level fall resulting from ice loading reduction and gravitational decrease (Creveling and Mitrovica, 2014). This process led to the continuous uplift of the continental area, maintaining a shallow shelf isolated from direct oceanic processes (Fig. 5.16 A-C). Barrier-inland facies were not observed in the studied succession, indicating that irregular diamicton morphologies may have created protected areas against waves, promoting stratiform microbial proliferation and inducing dolomite precipitation (Fig. 5.3A-F) (Nogueira *et al.* 2003, 2019). This scenario resulted in a consistently shallow water column (Fig. 5.15). The eustatic contribution from the melting of far-field ice sheets was more significant than the local sea-level fall driven by near-field effects (Creveling and Mitrovica 2014) following a significant landward shoreline migration depositional pattern with high potential preservation found along the southern margin of the Amazon Craton (Fig. 5.16).

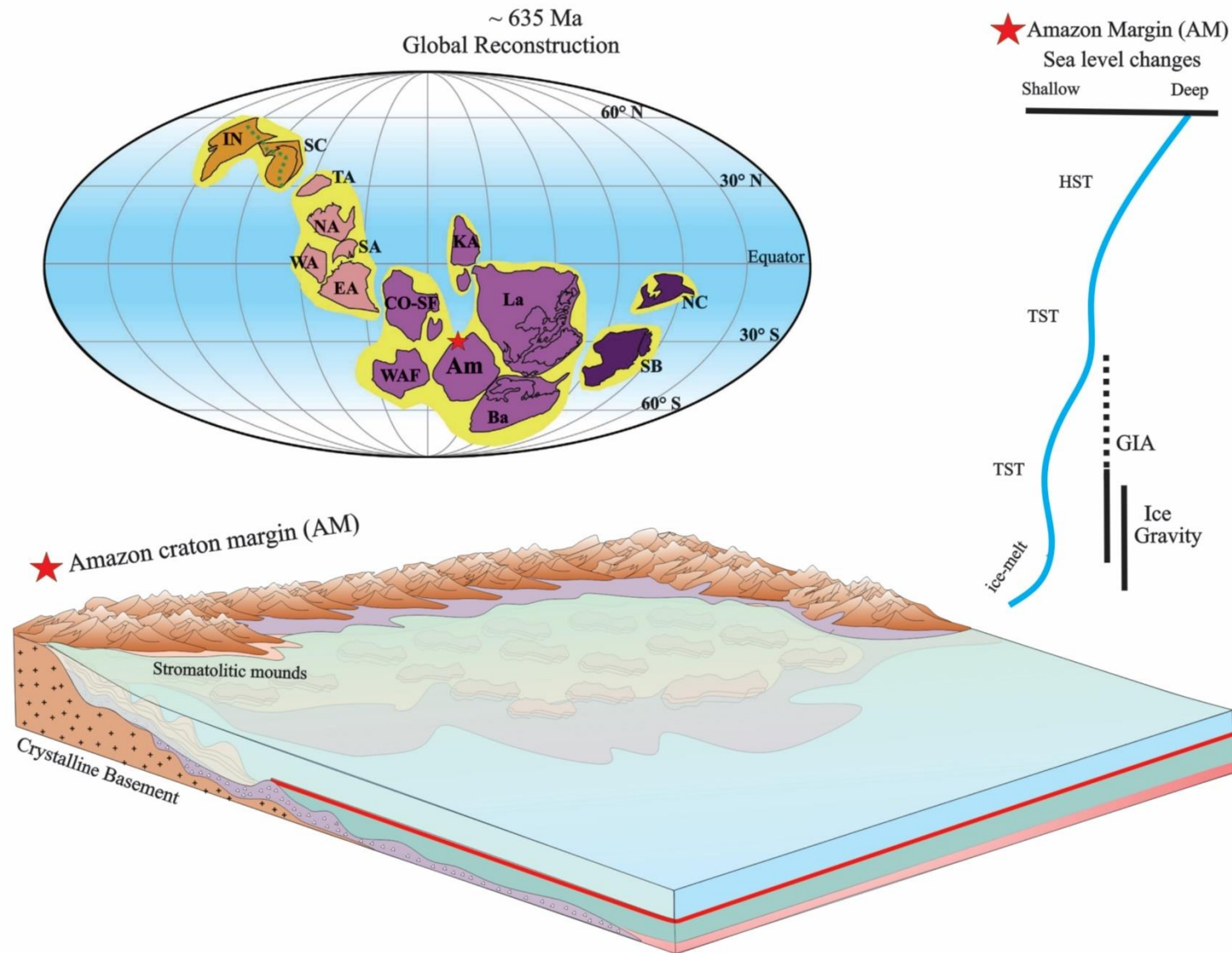


Figure 5.15- Paleomagnetically and geologically constrained global paleogeographic maps for ~ 635 Ma, according to Zhang *et al.* (2013). Am, Amazonia, BA, Baltica, CO- Congo, SF- São Francisco, EA-East Antarctica, IN-Greater India, KA-Kalahari, NA-North Australian, NC- North China, SA-South Australian, SC- South China, SB-Siberia, TA-Tarim, WAF-West Africa, WA-West Australian. LA- Laurentia. The position of the Amazon craton is constrained by a paleomagnetic pole ( $22 \pm 6/5^\circ$ ), indicating a low paleolatitude during the precipitation of Puga cap carbonate (Trindade *et al.* 2003). Model showing the envisaged paleoenvironmental reconstruction of the Amazon craton margin, aftermath Marinoan glaciation ~635 Ma. Ice gravity and GIA (glacioisostatic adjustment) primarily influenced the accommodation space during this period. The Puga carbonate cap is in a semi-restricted coastal environment with persistent shallow waters. Microbialites dominated precipitation during the synde-glacial transgression.

The deformed dolomite-diamictite contact indicates rapid accumulation of dolomite deposited over a still plastic diamicton linked to a regional scale event compatible with glacial isostatic adjustments/ice gravity in the coastal zone (Fig. 5.15 and Fig. 5.16). The diamicton substrate was colonized by microbial communities in stratified and shallow water (Fig. 5.16 C), following high organic productivity due to the maximum nutrient input from mixed water culminating in the giant stromatolites on the Amazon coastal (Santos *et al.*2021). In this context, our data highlight an early relative sea-level fall attributed to the loss of ice gravity (local ice sheet recession), evidenced by base deformation as well as the shallow-water characteristics of the cap dolostone. Subsequently, the landward migration of the shoreline could have a glacioeustatic origin (Fig. 5. 5 and Fig. 5.16).

During deglaciation, continental ice sheets trapped detrital materials (Spence *et al.*2016, Hoffman *et al.*2017). We previously demonstrated the purity of cap dolostone, which was between 1 and 5% contamination, based on Y/Ho vs. Zr and Al. In modern starved shelves, siliciclastic components trapping can occur at the terrestrial limit with the saline wedge, producing maximum estuarine turbidity (Swift 1968, Kidwell 1991, Geyer *et al.*2004, McHugh *et al.*2010). The generation of hyperpycnal flows to transport fine sediments distributed in surficial plumes that occur only in very shallow waters can extend for thousands of kilometers (Geyer *et al.*2004, Dowdeswell *et al.*2015). These conditions of high salinity density, according to the model by Yang *et al.*2017, may have controlled the sediment inflow to the shallow carbonate platform, as indicated by the low content of detrital components in the cap dolostone (Fig. 5.6 and Fig. 5.7). The density difference between meltwater and seawater or even sediment starvation can explain the low content of detrital constituents.

The siliciclastic starvation model indicates precipitation of the cap dolostone over  $\sim 10^5$ – $10^6$  years (Spence *et al.*2016, Wallace *et al.*2019). A larger landward shoreline migration in the siliciclastic starvation model during cap deposition is not directly associated with the final Snowball Earth conditions (Nordsvan *et al.*2019). However, our geochemical data and sedimentological evidence are consistent with other models of rapid precipitation (on the order of  $\sim 10^3$ – $10^4$  years) for cap dolostones. These models include factors such as enhanced continental weathering alkalinity and a persistent freshwater surface layer (Shields 2005, Hoffman *et al.*2017, Crockford *et al.*2021). It is impossible to

estimate how long the sediments were trapped in the ice sheets in the distal zone before they reached the coastal area (Fig. 5.15). However, the rapid precipitation of cap dolostones is consistent with our sedimentological evidence. Our data demonstrate that the transitions from cap dolostone to cap limestone accompany paleoenvironmental changes, primarily related to platform deepening during long-term transgression. Furthermore, our findings are consistent with the plume world model proposed by Shields (2005), which involves mixing water, as well as siliciclastic starvation described by Spence *et al.* (2016) for pure carbonates (Fig. 5.6, Fig. 5.7, and Fig. 5.11), and indicate intense microbial activity, evidenced by the presence of giant stromatolites. Nevertheless, a single model does not explain the precipitation of the Puga cap carbonate despite the similarity between different successions of this cap. One reason for this heterogeneity is that there is endemic distinct preservation between locations. Another possible explanation for siliciclastic starvation is the restrictive conditions with persistently shallow waters in the coastal zone, in this scenario, ice gravity and glacial isostatic adjustment strongly influenced the deposition of the first meters of cap dolostone (GIA). The lack of terrigenous components in cap dolostone may be evidence of rapid precipitation (keep-up) occurring before the main detritic flow on the coast of the Amazon Craton or lasted at least as long as the stratified oceans (Fig. 5.16 A-D).

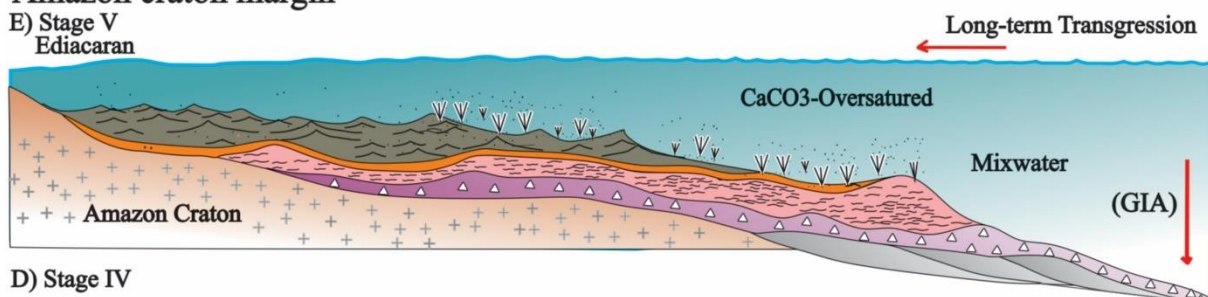
Water turbidity increases partially inhibit carbonate precipitation, causing marl deposition and suppressing microbial life, a prelude to decline of the marine stratification and thermal expansion (Fig. 5.16 D) (Romero *et al.* 2020, Santos *et al.* 2021, 2023, Nogueira *et al.* 2022). The mixing of water masses and massive detritic flow generated a geochemical change, causing  $\text{CaCO}_3$  oversaturation (Fig. 5.16 E), which contributed to the precipitation of peloidal limestones with calcite crystal fans (pseudomorphs after aragonite) (Higgins and Schag 2003, Nogueira *et al.* 2003, 2007, 2019, Hoffman *et al.* 2017, 2021, Soares *et al.* 2020, Santos *et al.* 2021, 2023). The cap limestone presents an abrupt increase in the Sr concentration that accompanies a rise in Zr, Al, and Th in covariance with REE+Y), indicating a direct relationship between the siliciclastic input and the platform deepening and, consequently, a change in the dolomitic-aragonitic features triggered by  $\text{CaCO}_3$  oversaturation (Nogueira *et al.* 2019). The concentration of Mg remained constant during the restriction of paleoenvironmental conditions on dolomitic platforms. Rapid sea-level rise facilitated the dispersion of Mg ions, leading to the definitive interruption of dolomite precipitation, which was abruptly replaced by  $\text{CaCO}_3$ -supersaturated

seas with massive aragonite precipitation influenced by long-term transgression (Fig. 5.16 E).

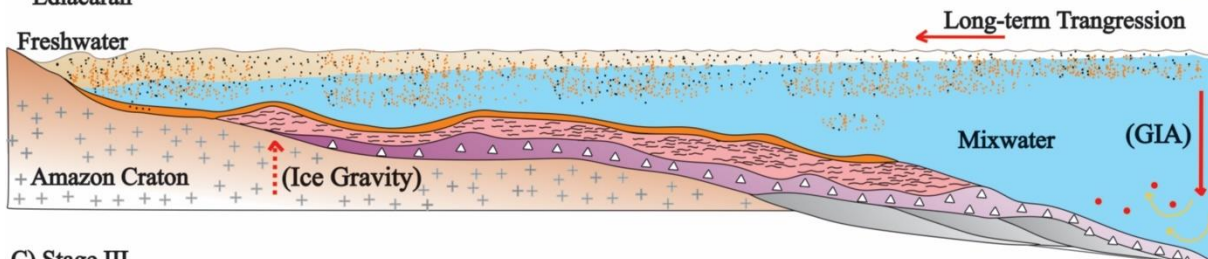
These dramatic changes are assumed to have resulted from the rapid recovery of primary productivity during deglaciation (Hu *et al.* 2021). The influx of detrital inputs in nutrient-rich freshwater inflows increases concomitantly with primary productivity. The negative  $\delta^{13}\text{C}$  isotopic signatures (Fig. 5.10) can result from microbial activity, which produces  $\delta^{13}\text{C}$  depleted bicarbonate reduced from the dissolved inorganic carbon reservoir (Nédélec *et al.* 2007). These interpretations are consistent with our  $\delta^{13}\text{C}$  data, which range from  $-8.2$  to  $-4.1\text{‰}$  (average =  $-4.9\text{‰}$ ). As discussed earlier, our new data, as well as previous data for Puga cap carbonate (Nogueira *et al.* 2003, 2019, Font *et al.* 2006, Sansjofre *et al.* 2011), displays similares trends to Marinoan cap dolostone successions worldwide (Nédélec *et al.* 2007, Hoffman *et al.* 2021, Peng *et al.* 2022). Additionally, in a global compilation, He *et al.* (2021) demonstrated a clear shift between shallow and deep-water environments in terms of  $\delta^{13}\text{C}$ . They attributed lighter values in deeper environments to increased remobilization of organic carbon in the water column. Therefore, the well-preserved  $\delta^{13}\text{C}$  values in the Puga cap carbonate may reflect temporal evolution and deepening caused by long-term transgression. These events were recorded in extensive carbonate platforms with restricted oceanic connection, marking the appearance of epicontinental seas, the primordial scenario from the initial phase of Western Gondwana.

# Amazon craton margin

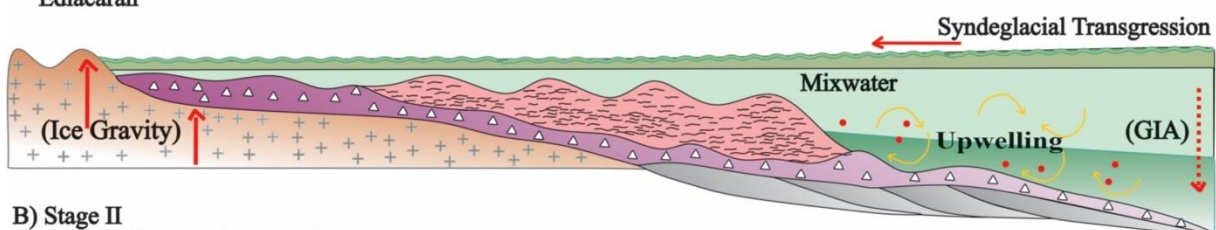
E) Stage V  
Ediacaran



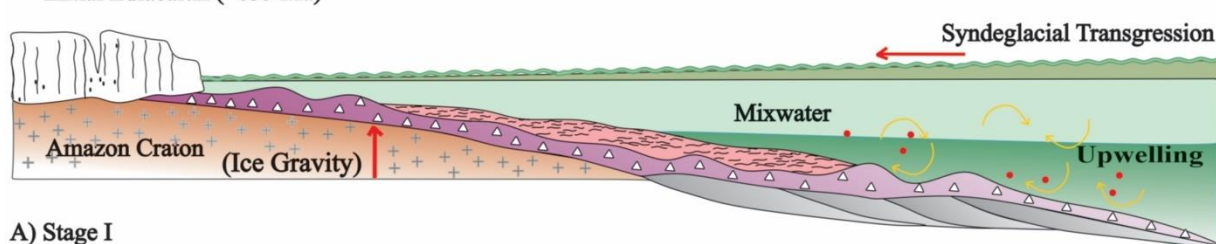
D) Stage IV  
Ediacaran



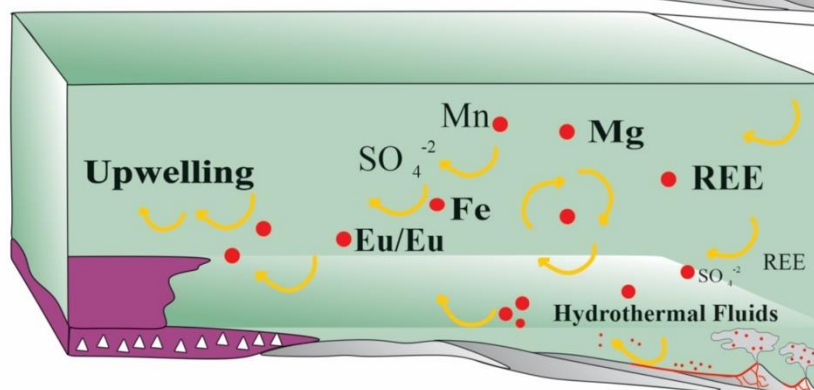
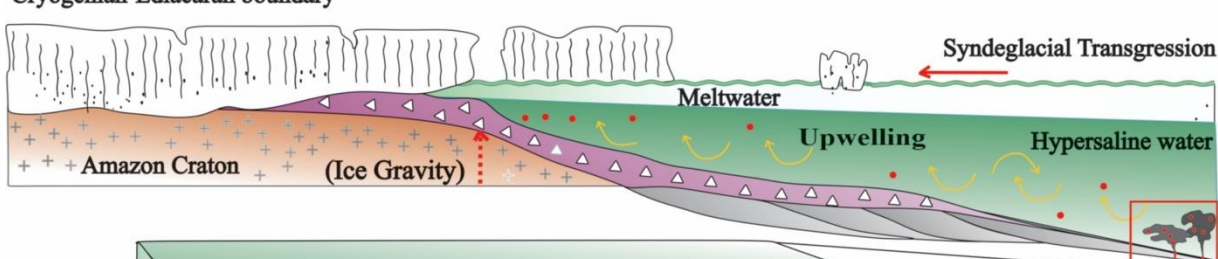
C) Stage III  
Ediacaran



B) Stage II  
Initial Ediacaran (~635 Ma)



A) Stage I  
Cryogenian-Ediacaran boundary



Caption on next page



Figure 5.16- Model for Puga cap precipitation on the southern Amazon Craton. A) Stage I- During the advance of the syn-deglacial transgression, meltwater production, and surface warming created stable density stratification, with hydrothermal fluids influencing deep water. Hydrothermal fluids are the principal sources of trace elements (rare earth elements) for the paleocoast. B) Stage II, A local sea-level decline may have temporarily exceeded the global (eustatic) sea-level rise rate. The early relative sea-level fall is attributed to the reduction in ice gravity due to local ice sheet recession, initiating the continuous uplift of the continental area. During the syn-deglacial transgression, the microbial community colonized the diamicton substrate in mixed water (seawater and meltwater) without the influence of hydrodynamic processes, producing stratiform stromatolites with gypsum cementation as a product of resurgences. During these events, hypersaline deep water reaches shallow water, causing increased salinity in the paleocoast. The detritus supply is reduced at the beginning of precipitation, consistent with the siliciclastic starvation model. C) Stage III- Increased accommodation of space and water mixing due to glacial isostatic adjustment (GIA) with postglacial transgression allows for the abundant growth of microbial communities in giant biostromes. D) Stage IV- The subsequent transgression appears to have been notably influenced by glacioisostatic adjustment (GIA), leading to the prevalence of deeper water facies and a consequential decline in microbial communities along the paleocoast. Initially, the microbial mats were reworked through hydrodynamic processes, wave action, and currents, marking the end of the restricted conditions. However, the total decline of the stromatolites from the Puga cap was caused by the massive influx of siliciclastic materials, which generated intense turbidity and burial of the communities. E) Stage V- Sea-level rise facilitated a dispersion of Mg ions, leading to the definitive interruption of dolomicrite precipitation, which was abruptly replaced by CaCO<sub>3</sub>-supersaturated seas with massive aragonite precipitation influenced by long-term transgression during the greenhouse climax.

## 5.8 CONCLUSION

The REE+Y patterns observed in the Puga cap carbonate provide valuable insights into post-snowball Earth marine conditions. The low Y/Ho ratios in the cap dolostones suggest a dilution of seawater composition due to meltwater influx from continents. Conversely, superchondritic Y/Ho ratios and positive Eu anomalies in the basal cap dolostones indicate upwelling towards the hypersaline seawater's coastal zone influenced by hydrothermal fluids. These findings imply that ocean destratification is associated with ocean circulation and glacial isostatic adjustment (GIA), with reduced siliciclastic inflow supporting a siliciclastic starvation model. The recurrence of shallow-water conditions, attributed to early evidence of relative sea-level decline, is linked to local ice sheet recession (ice gravity). This led to the continuous uplift of the coastal zone, the creation of an isolated shelf protected by ocean dynamics, and the deformation in diamictite, resulting in irregular substrate relief morphologies. After this post-glaciation scenario, a significant landward shoreline migration glacioeustatic was accompanied by the rapid recovery of primary productivity. This phase witnessed the flourishing of extensive microbial communities, inducing dolomite precipitation in the depositional environment within an estuarine plume. These observations contribute to a comprehensive understanding of the complex interplay between glaciation and ocean dynamics during the Cryogenian-Ediacaran boundary.

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## 5.9 SUPPLEMENTARY MATERIAL: RARE EARTH ELEMENTS AS INDICATORS FOR THE PALEOCEANOGRAPHIC CHANGES OF THE POST-MARINOAN SNOWBALL EARTH FROM THE AMAZON CRATON

**Supplementary Table 5.1.** Result of the concentration of rare earth elements Yttrium of the Puga cap carbonate- Terconi Section

Supplementary Table 5.2 Major and Minor Elements Concentration of the Puga cap carbonate- Tangará Section

**Supplementary Table 5.3.** Result of the concentration of rare earth elements Yttrium of the Puga cap carbonate- Terconi Section

**Supplementary Table 5.4** Major and Minor Elements Concentration of the Puga cap carbonate- Terconi Section

**Supplementary Table 5.5** Carbon and oxygen isotopes of the Puga cap carbonate- Tangará Section.

. Supplementary table 5.1 Result of the concentration of rare earth elements Yttrium of the Puga cap carbonate- Terconi Section

| Samples | Depth(m)<br>Meter (m) | Tangará Section |           |           |           |           |           |           |           |           |           |           |           |           |           |          |        | ΣREE+Y<br>ppm |             | Method |
|---------|-----------------------|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|--------|---------------|-------------|--------|
|         |                       | La<br>ppm       | Ce<br>ppm | Pr<br>ppm | Nd<br>ppm | Sm<br>ppm | Eu<br>ppm | Gd<br>ppm | Tb<br>ppm | Dy<br>ppm | Ho<br>ppm | Er<br>ppm | Tm<br>ppm | Yb<br>ppm | Lu<br>ppm | Y<br>ppm |        |               |             |        |
| JOR 1   | 0,2                   | 1,509           | 2,288     | 0,738     | 3,952     | 0,940     | 0,296     | 1,146     | 0,201     | 1,353     | 0,338     | 0,999     | 0,141     | 0,754     | 0,133     | 12,248   | 27,038 | Dolostone     | Acetic acid |        |
| JOR 2   | 0,4                   | 1,249           | 3,460     | 0,420     | 1,828     | 0,424     | 0,165     | 0,543     | 0,097     | 0,614     | 0,143     | 0,401     | 0,054     | 0,284     | 0,048     | 5,265    | 14,996 | Dolostone     | Acetic acid |        |
| JOR 5   | 1                     | 0,939           | 1,933     | 0,232     | 0,879     | 0,168     | 0,091     | 0,195     | 0,027     | 0,146     | 0,030     | 0,081     | 0,012     | 0,061     | 0,011     | 0,984    | 5,788  | Dolostone     | Acetic acid |        |
| JOR 7   | 1,4                   | 0,764           | 1,727     | 0,197     | 0,747     | 0,144     | 0,063     | 0,159     | 0,022     | 0,118     | 0,024     | 0,067     | 0,010     | 0,053     | 0,009     | 0,760    | 4,865  | Dolostone     | Acetic acid |        |
| JOR 8   | 1,6                   | 0,424           | 0,985     | 0,118     | 0,475     | 0,093     | 0,037     | 0,113     | 0,014     | 0,078     | 0,015     | 0,042     | 0,007     | 0,035     | 0,006     | 0,512    | 2,955  | Dolostone     | Acetic acid |        |
| JOR 9   | 1,8                   | 0,433           | 0,876     | 0,102     | 0,380     | 0,069     | 0,047     | 0,089     | 0,012     | 0,069     | 0,014     | 0,041     | 0,006     | 0,031     | 0,005     | 0,482    | 2,655  | Dolostone     | Acetic acid |        |
| JOR 10  | 2                     | 0,314           | 0,686     | 0,086     | 0,336     | 0,065     | 0,031     | 0,083     | 0,012     | 0,065     | 0,014     | 0,038     | 0,005     | 0,027     | 0,005     | 0,460    | 2,226  | Dolostone     | Acetic acid |        |
| JOR 11  | 2,2                   | 0,688           | 0,747     | 0,212     | 0,876     | 0,167     | 0,047     | 0,170     | 0,025     | 0,136     | 0,028     | 0,073     | 0,010     | 0,056     | 0,009     | 0,936    | 4,181  | Dolostone     | Acetic acid |        |
| JOR 13  | 2,6                   | 0,685           | 1,509     | 0,194     | 0,755     | 0,145     | 0,045     | 0,169     | 0,028     | 0,185     | 0,041     | 0,118     | 0,017     | 0,094     | 0,016     | 1,202    | 5,203  | Dolostone     | Acetic acid |        |
| JOR 15  | 3                     | 0,229           | 0,524     | 0,060     | 0,237     | 0,045     | 0,020     | 0,054     | 0,007     | 0,042     | 0,009     | 0,023     | 0,004     | 0,017     | 0,003     | 0,298    | 1,571  | Dolostone     | Acetic acid |        |
| JOR 16  | 3,4                   | 0,323           | 0,679     | 0,095     | 0,375     | 0,073     | 0,020     | 0,087     | 0,013     | 0,074     | 0,016     | 0,044     | 0,006     | 0,031     | 0,005     | 0,545    | 2,388  | Dolostone     | Acetic acid |        |
| JOR 19  | 3,8                   | 0,388           | 0,682     | 0,110     | 0,456     | 0,094     | 0,027     | 0,128     | 0,020     | 0,134     | 0,033     | 0,095     | 0,014     | 0,075     | 0,012     | 1,404    | 3,671  | Dolostone     | Acetic acid |        |
| JOR 20  | 4                     | 0,621           | 1,410     | 0,199     | 0,816     | 0,167     | 0,047     | 0,269     | 0,052     | 0,413     | 0,117     | 0,357     | 0,050     | 0,278     | 0,047     | 6,487    | 11,329 | Dolostone     | Acetic acid |        |
| JOR 22  | 4,4                   | 1,010           | 1,704     | 0,259     | 1,001     | 0,193     | 0,045     | 0,205     | 0,030     | 0,178     | 0,042     | 0,133     | 0,020     | 0,119     | 0,021     | 2,866    | 7,827  | Dolostone     | Acetic acid |        |
| JOR 23  | 4,6                   | 0,352           | 0,793     | 0,097     | 0,382     | 0,077     | 0,022     | 0,080     | 0,011     | 0,061     | 0,012     | 0,033     | 0,005     | 0,029     | 0,005     | 0,351    | 2,310  | Dolostone     | Acetic acid |        |
| JOR 25  | 5                     | 0,245           | 0,529     | 0,061     | 0,236     | 0,045     | 0,016     | 0,054     | 0,007     | 0,041     | 0,009     | 0,024     | 0,004     | 0,019     | 0,004     | 0,290    | 1,583  | Dolostone     | Acetic acid |        |
| JOR 29  | 5,8                   | 0,478           | 1,165     | 0,132     | 0,501     | 0,100     | 0,026     | 0,102     | 0,015     | 0,084     | 0,018     | 0,050     | 0,007     | 0,043     | 0,007     | 0,488    | 3,217  | Dolostone     | Acetic acid |        |
| JOR 33  | 6,6                   | 0,620           | 1,322     | 0,164     | 0,635     | 0,126     | 0,036     | 0,131     | 0,021     | 0,128     | 0,033     | 0,105     | 0,016     | 0,093     | 0,017     | 2,299    | 5,744  | Dolostone     | Acetic acid |        |
| JOR 37  | 7,4                   | 0,496           | 1,144     | 0,136     | 0,522     | 0,103     | 0,028     | 0,109     | 0,015     | 0,085     | 0,017     | 0,047     | 0,008     | 0,041     | 0,007     | 0,499    | 3,256  | Dolostone     | Acetic acid |        |
| JOR 38  | 7,6                   | 0,763           | 1,326     | 0,196     | 0,751     | 0,143     | 0,044     | 0,154     | 0,022     | 0,125     | 0,026     | 0,072     | 0,011     | 0,060     | 0,010     | 0,828    | 4,532  | Dolostone     | Acetic acid |        |
| JOR 39  | 7,8                   | 0,508           | 0,871     | 0,128     | 0,491     | 0,099     | 0,027     | 0,101     | 0,014     | 0,083     | 0,018     | 0,049     | 0,007     | 0,041     | 0,007     | 0,528    | 2,972  | Dolostone     | Acetic acid |        |
| JOR 41  | 8,2                   | 0,492           | 1,036     | 0,131     | 0,509     | 0,100     | 0,031     | 0,106     | 0,016     | 0,091     | 0,020     | 0,055     | 0,008     | 0,046     | 0,008     | 0,563    | 3,213  | Dolostone     | Acetic acid |        |

Continue

Continuation

|                |      |       |        |       |       |       |       |       |       |       |       |       |       |       |       |       |        |           |             |
|----------------|------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|-----------|-------------|
| <b>JOR 42</b>  | 8,4  | 0,706 | 1,522  | 0,195 | 0,756 | 0,153 | 0,049 | 0,156 | 0,024 | 0,140 | 0,029 | 0,085 | 0,013 | 0,073 | 0,012 | 0,814 | 4,727  | Dolostone | Acetic acid |
| <b>JOR 52</b>  | 10,4 | 0,979 | 1,693  | 0,253 | 0,976 | 0,191 | 0,062 | 0,202 | 0,030 | 0,170 | 0,036 | 0,097 | 0,015 | 0,081 | 0,014 | 1,148 | 5,948  | Dolostone | Acetic acid |
| <b>JOR 53</b>  | 10,6 | 0,463 | 1,032  | 0,119 | 0,459 | 0,089 | 0,024 | 0,095 | 0,013 | 0,073 | 0,015 | 0,041 | 0,006 | 0,032 | 0,006 | 0,468 | 2,934  | Dolostone | Acetic acid |
| <b>JOR 54</b>  | 10,8 | 0,907 | 2,141  | 0,258 | 1,009 | 0,198 | 0,055 | 0,210 | 0,031 | 0,178 | 0,037 | 0,102 | 0,015 | 0,086 | 0,015 | 1,179 | 6,421  | Dolostone | Acetic acid |
| <b>JOR 59</b>  | 11,8 | 1,266 | 0,240  | 0,222 | 0,862 | 0,155 | 0,044 | 0,162 | 0,021 | 0,100 | 0,020 | 0,049 | 0,007 | 0,036 | 0,006 | 0,817 | 4,008  | Dolostone | Acetic acid |
| <b>JOR 66</b>  | 13,2 | 0,989 | 1,977  | 0,253 | 0,982 | 0,192 | 0,060 | 0,208 | 0,031 | 0,172 | 0,037 | 0,098 | 0,015 | 0,085 | 0,014 | 1,086 | 6,199  | Dolostone | Acetic acid |
| <b>JOR 67</b>  | 13,4 | 0,607 | 1,347  | 0,149 | 0,566 | 0,105 | 0,045 | 0,121 | 0,017 | 0,092 | 0,020 | 0,053 | 0,008 | 0,045 | 0,008 | 0,621 | 3,804  | Dolostone | Acetic acid |
| <b>JOR 68</b>  | 13,6 | 0,623 | 1,181  | 0,162 | 0,655 | 0,128 | 0,041 | 0,141 | 0,020 | 0,110 | 0,023 | 0,062 | 0,009 | 0,051 | 0,009 | 0,769 | 3,984  | Dolostone | Acetic acid |
| <b>JOR 77</b>  | 15,4 | 0,564 | 1,298  | 0,149 | 0,573 | 0,110 | 0,038 | 0,123 | 0,017 | 0,094 | 0,019 | 0,053 | 0,009 | 0,045 | 0,008 | 0,572 | 3,672  | Dolostone | Acetic acid |
| <b>JOR 90</b>  | 18   | 0,573 | 1,299  | 0,144 | 0,550 | 0,108 | 0,041 | 0,116 | 0,017 | 0,093 | 0,019 | 0,053 | 0,008 | 0,045 | 0,008 | 0,587 | 3,662  | Dolostone | Acetic acid |
| <b>JOR 93</b>  | 18,6 | 0,938 | 1,966  | 0,254 | 0,983 | 0,191 | 0,057 | 0,203 | 0,030 | 0,166 | 0,035 | 0,096 | 0,015 | 0,084 | 0,015 | 0,994 | 6,028  | Dolostone | Acetic acid |
| <b>JOR 101</b> | 20,2 | 0,440 | 0,960  | 0,118 | 0,463 | 0,098 | 0,032 | 0,107 | 0,015 | 0,091 | 0,019 | 0,054 | 0,008 | 0,045 | 0,008 | 0,547 | 3,006  | Dolostone | Acetic acid |
| <b>JOR 117</b> | 23,4 | 0,429 | 1,214  | 0,130 | 0,521 | 0,105 | 0,028 | 0,114 | 0,018 | 0,102 | 0,022 | 0,063 | 0,010 | 0,058 | 0,010 | 0,607 | 3,430  | Dolostone | Acetic acid |
| <b>JOR 122</b> | 24,4 | 0,449 | 1,240  | 0,130 | 0,523 | 0,114 | 0,033 | 0,130 | 0,020 | 0,119 | 0,026 | 0,074 | 0,012 | 0,069 | 0,012 | 0,738 | 3,687  | Dolostone | Acetic acid |
| <b>JOR 138</b> | 27,6 | 0,387 | 1,144  | 0,128 | 0,517 | 0,112 | 0,030 | 0,122 | 0,019 | 0,114 | 0,025 | 0,075 | 0,012 | 0,069 | 0,012 | 0,713 | 3,477  | Dolostone | Acetic acid |
| <b>JOR 148</b> | 29,6 | 0,395 | 0,999  | 0,126 | 0,507 | 0,108 | 0,026 | 0,114 | 0,017 | 0,099 | 0,021 | 0,062 | 0,010 | 0,057 | 0,010 | 0,628 | 3,177  | Dolostone | Acetic acid |
| <b>JOR 151</b> | 30,2 | 0,696 | 1,521  | 0,222 | 0,926 | 0,211 | 0,049 | 0,222 | 0,033 | 0,193 | 0,041 | 0,117 | 0,018 | 0,105 | 0,018 | 1,201 | 5,574  | Dolostone | Acetic acid |
| <b>JOR 169</b> | 33,8 | 1,604 | 3,771  | 0,613 | 2,687 | 0,659 | 0,135 | 0,664 | 0,106 | 0,615 | 0,128 | 0,361 | 0,053 | 0,306 | 0,051 | 3,664 | 15,417 | Dolostone | Acetic acid |
| <b>JOR 170</b> | 34   | 1,206 | 3,599  | 0,445 | 1,864 | 0,442 | 0,093 | 0,456 | 0,076 | 0,452 | 0,097 | 0,278 | 0,042 | 0,242 | 0,041 | 2,568 | 11,902 | Dolostone | Acetic acid |
| <b>JOR 184</b> | 36,8 | 4,639 | 11,281 | 1,459 | 5,683 | 1,153 | 0,239 | 1,185 | 0,184 | 1,077 | 0,231 | 0,662 | 0,100 | 0,587 | 0,099 | 6,223 | 34,803 | Dolostone | Acetic acid |

Continue

## Continuation

|              |       |       |        |       |       |       |       |       |       |       |       |       |       |       |       |        |        |           |           |
|--------------|-------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------|-----------|-----------|
| <b>TS001</b> | 37    | 2,748 | 4,915  | 0,632 | 2,242 | 0,430 | 0,082 | 0,388 | 0,061 | 0,371 | 0,073 | 0,211 | 0,030 | 0,218 | 0,034 | 2,430  | 14,865 | Dolostone | Bulk rock |
| <b>TS003</b> | 37,4  | 2,274 | 4,072  | 0,543 | 1,896 | 0,381 | 0,073 | 0,337 | 0,050 | 0,291 | 0,060 | 0,168 | 0,026 | 0,174 | 0,027 | 2,016  | 12,388 | Dolostone | Bulk rock |
| <b>TS006</b> | 38    | 2,671 | 4,866  | 0,663 | 2,408 | 0,464 | 0,084 | 0,424 | 0,062 | 0,374 | 0,071 | 0,198 | 0,030 | 0,189 | 0,031 | 2,384  | 14,919 | Dolostone | Bulk rock |
| <b>TS009</b> | 39,83 | 2,701 | 5,026  | 0,675 | 2,358 | 0,466 | 0,088 | 0,396 | 0,064 | 0,372 | 0,073 | 0,213 | 0,032 | 0,209 | 0,033 | 2,483  | 15,189 | Dolostone | Bulk rock |
| <b>TS015</b> | 40    | 4,719 | 8,613  | 1,161 | 4,291 | 0,810 | 0,156 | 0,715 | 0,107 | 0,627 | 0,120 | 0,347 | 0,049 | 0,352 | 0,051 | 3,910  | 26,028 | Dolostone | Bulk rock |
| <b>TS017</b> | 40,2  | 4,960 | 9,208  | 1,228 | 4,511 | 0,887 | 0,162 | 0,761 | 0,114 | 0,664 | 0,129 | 0,373 | 0,055 | 0,379 | 0,058 | 4,286  | 27,775 | Dolostone | Bulk rock |
| <b>TS019</b> | 40,6  | 5,429 | 10,030 | 1,327 | 4,869 | 0,946 | 0,165 | 0,815 | 0,121 | 0,746 | 0,143 | 0,414 | 0,060 | 0,418 | 0,065 | 4,637  | 30,185 | Dolostone | Bulk rock |
| <b>TS021</b> | 41    | 5,700 | 10,750 | 1,451 | 5,246 | 1,073 | 0,190 | 0,918 | 0,139 | 0,837 | 0,158 | 0,470 | 0,072 | 0,473 | 0,074 | 5,364  | 32,915 | Dolostone | Bulk rock |
| <b>TS023</b> | 41,4  | 6,563 | 12,410 | 1,661 | 6,025 | 1,252 | 0,216 | 1,122 | 0,172 | 1,019 | 0,210 | 0,587 | 0,093 | 0,617 | 0,096 | 6,977  | 39,020 | Dolostone | Bulk rock |
| <b>TS029</b> | 44,8  | 9,215 | 16,460 | 2,296 | 8,480 | 1,770 | 0,333 | 1,733 | 0,274 | 1,646 | 0,345 | 0,985 | 0,141 | 0,913 | 0,140 | 12,270 | 57,001 | Dolostone | Bulk rock |
| <b>TS033</b> | 45,6  | 7,239 | 13,910 | 1,957 | 7,431 | 1,545 | 0,297 | 1,498 | 0,228 | 1,342 | 0,275 | 0,781 | 0,114 | 0,717 | 0,106 | 9,785  | 47,225 | Dolostone | Bulk rock |
| <b>TS035</b> | 46    | 8,724 | 18,830 | 2,623 | 9,952 | 2,263 | 0,412 | 1,942 | 0,302 | 1,756 | 0,336 | 0,948 | 0,138 | 0,927 | 0,143 | 11,110 | 60,406 | Limestone | Bulk rock |
| <b>TS036</b> | 46,2  | 7,201 | 14,380 | 2,059 | 7,786 | 1,714 | 0,322 | 1,616 | 0,247 | 1,491 | 0,293 | 0,847 | 0,121 | 0,806 | 0,121 | 10,240 | 49,244 | Limestone | Bulk rock |
| <b>TS039</b> | 46,8  | 5,256 | 8,297  | 1,316 | 5,073 | 1,144 | 0,242 | 1,251 | 0,185 | 1,171 | 0,247 | 0,673 | 0,089 | 0,573 | 0,084 | 9,294  | 34,895 | Limestone | Bulk rock |
| <b>TS042</b> | 47,4  | 8,257 | 17,020 | 2,390 | 9,030 | 1,975 | 0,350 | 1,701 | 0,266 | 1,554 | 0,296 | 0,843 | 0,121 | 0,819 | 0,123 | 9,621  | 54,366 | Limestone | Bulk rock |
| <b>TS044</b> | 47,8  | 6,004 | 11,110 | 1,573 | 5,927 | 1,266 | 0,243 | 1,230 | 0,187 | 1,129 | 0,227 | 0,636 | 0,090 | 0,588 | 0,085 | 8,430  | 38,725 | Limestone | Bulk rock |
| <b>TS046</b> | 48,2  | 7,888 | 15,330 | 2,162 | 7,840 | 1,577 | 0,279 | 1,442 | 0,227 | 1,360 | 0,267 | 0,773 | 0,111 | 0,735 | 0,110 | 9,354  | 49,455 | Limestone | Bulk rock |
| <b>TS050</b> | 51    | 7,065 | 13,750 | 1,915 | 6,951 | 1,391 | 0,250 | 1,209 | 0,193 | 1,133 | 0,228 | 0,644 | 0,095 | 0,625 | 0,093 | 7,493  | 43,035 | Limestone | Bulk rock |
| <b>TS058</b> | 52,6  | 5,970 | 11,130 | 1,593 | 5,844 | 1,244 | 0,240 | 1,154 | 0,180 | 1,052 | 0,214 | 0,606 | 0,086 | 0,531 | 0,077 | 7,585  | 37,506 | Limestone | Bulk rock |



Table 5.2 Major and Minor elements concentration of the Puga cap carbonate- Tangará Section

| Sam-<br>ples | De-<br>pth(m)<br>Meter<br>(m) | Tangará Section |        |       |         |       |          |        |            |            |       |          |       |         | Me-<br>thod    |             |
|--------------|-------------------------------|-----------------|--------|-------|---------|-------|----------|--------|------------|------------|-------|----------|-------|---------|----------------|-------------|
|              |                               | Ni              | Pb     | Th    | Al      | Zr    | Mn       | Sr     | Mg         | Ca         | Ti    | Fe       | Rb    | Ba      |                |             |
|              |                               | ppm             | ppm    | ppm   | ppm     | ppm   | ppm      | ppm    | ppm        | ppm        | ppm   | ppm      | ppm   | ppm     |                |             |
| JOR 1        | 0,2                           | 19,212          | 1,260  | 0,085 | 176,857 | 0,017 | 6946,128 | 38,602 | 100375,822 | 126615,046 | 0,167 | 749,702  | 0,072 | 85,994  | Dolos-<br>tone | Acetic acid |
| JOR 2        | 0,4                           | 4,128           | 32,448 | 0,115 | 149,946 | 0,019 | 4533,847 | 51,221 | 98797,029  | 106170,343 | 0,317 | 1413,608 | 0,087 | 110,711 | Dolos-<br>tone | Acetic acid |
| JOR 5        | 1                             | 4,919           | 78,711 | 0,109 | 94,173  | 0,064 | 2736,415 | 48,683 | 99184,583  | 114884,546 | 2,365 | 1985,541 | 0,060 | 132,278 | Dolos-<br>tone | Acetic acid |
| JOR 7        | 1,4                           | 5,314           | 57,667 | 0,137 | 87,133  | 0,068 | 2083,616 | 43,182 | 95320,940  | 101884,927 | 1,268 | 1212,495 | 0,052 | 80,042  | Dolos-<br>tone | Acetic acid |
| JOR 8        | 1,6                           | 3,988           | 10,168 | 0,063 | 101,925 | 0,133 | 615,664  | 58,605 | 117720,561 | 139009,284 | 1,327 | 614,292  | 0,093 | 35,090  | Dolos-<br>tone | Acetic acid |
| JOR 9        | 1,8                           | 7,118           | 21,157 | 0,018 | 39,374  | 0,060 | 1631,579 | 53,608 | 116796,664 | 129263,519 | 0,904 | 1723,605 | 0,043 | 78,295  | Dolos-<br>tone | Acetic acid |
| JOR 10       | 2                             | 9,913           | 13,383 | 0,020 | 42,813  | 0,064 | 1025,414 | 58,032 | 126094,112 | 146608,083 | 0,758 | 705,893  | 0,030 | 35,729  | Dolos-<br>tone | Acetic acid |
| JOR 11       | 2,2                           | 4,938           | 0,356  | 0,012 | 28,229  | 0,029 | 484,268  | 36,496 | 64980,944  | 133023,622 | 0,122 | 315,815  | 0,031 | 14,179  | Dolos-<br>tone | Acetic acid |
| JOR 13       | 2,6                           | 6,420           | 2,117  | 0,041 | 47,264  | 0,042 | 2172,772 | 42,774 | 97351,588  | 132196,931 | 1,106 | 850,131  | 0,044 | 31,494  | Dolos-<br>tone | Acetic acid |
| JOR 15       | 3                             | 5,667           | 6,262  | 0     | 31,108  | 0,085 | 853,558  | 39,889 | 79272,690  | 87185,999  | 0,402 | 606,511  | 0,029 | 21,870  | Dolos-<br>tone | Acetic acid |
| JOR 16       | 3,4                           | 2,578           | 0,685  | 0,012 | 44,755  | 0,101 | 545,442  | 31,905 | 68529,053  | 83904,438  | 0,196 | 151,381  | 0,025 | 8,083   | Dolos-<br>tone | Acetic acid |
| JOR 19       | 3,8                           | 2,972           | 1,594  | 0,017 | 74,261  | 0,139 | 368,449  | 46,643 | 93682,823  | 100911,829 | 0,472 | 163,776  | 0,032 | 11,739  | Dolos-<br>tone | Acetic acid |
| JOR 20       | 4                             | 3,083           | 0,308  | 0,027 | 45,219  | 0,069 | 884,203  | 33,277 | 65745,671  | 86613,228  | 0,145 | 135,404  | 0,042 | 12,246  | Dolos-<br>tone | Acetic acid |
| JOR 22       | 4,4                           | 2,487           | 0,112  | 0,091 | 41,545  | 0,066 | 269,686  | 21,734 | 39468,418  | 145147,884 | 0,432 | 163,605  | 0,042 | 9,100   | Dolos-<br>tone | Acetic acid |

|                   |      |       |        |       |         |       |          |        |            |            |       |          |       |        |                |             |
|-------------------|------|-------|--------|-------|---------|-------|----------|--------|------------|------------|-------|----------|-------|--------|----------------|-------------|
| <b>JOR<br/>23</b> | 4,6  | 2,746 | 9,388  | 0,059 | 100,072 | 0,092 | 294,264  | 52,703 | 98453,495  | 102457,066 | 0,789 | 281,095  | 0,054 | 13,842 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>25</b> | 5    | 3,854 | 1,999  | 0,016 | 68,607  | 0,156 | 345,421  | 46,915 | 92725,224  | 110609,234 | 0,425 | 212,423  | 0,040 | 11,705 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>29</b> | 5,8  | 2,895 | 9,371  | 0,127 | 100,653 | 0,178 | 385,787  | 49,517 | 88231,392  | 104010,961 | 0,856 | 521,591  | 0,049 | 18,636 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>33</b> | 6,6  | 4,058 | 12,176 | 0,130 | 73,138  | 0,093 | 583,353  | 53,200 | 97588,788  | 122203,046 | 1,064 | 627,451  | 0,059 | 24,064 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>37</b> | 7,4  | 2,183 | 9,046  | 0,095 | 117,762 | 0,092 | 396,677  | 63,476 | 117286,285 | 137989,263 | 0,978 | 699,224  | 0,056 | 17,631 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>38</b> | 7,6  | 2,343 | 8,798  | 0,074 | 89,243  | 0,070 | 763,605  | 62,269 | 97495,112  | 135603,517 | 0,961 | 672,184  | 0,043 | 33,246 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>39</b> | 7,8  | 3,503 | 4,076  | 0,045 | 60,489  | 0,099 | 420,125  | 47,170 | 81552,660  | 126212,780 | 0,468 | 325,863  | 0,035 | 15,573 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>41</b> | 8,2  | 2,412 | 9,832  | 0,061 | 80,563  | 0,112 | 417,807  | 50,406 | 99233,147  | 121433,960 | 0,836 | 448,346  | 0,053 | 22,826 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>42</b> | 8,4  | 4,617 | 19,796 | 0,137 | 96,543  | 0,072 | 882,684  | 59,027 | 103882,186 | 125178,239 | 1,154 | 729,793  | 0,071 | 45,839 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>52</b> | 10,4 | 2,882 | 46,776 | 0,169 | 188,240 | 0,088 | 1109,181 | 65,543 | 97735,131  | 128240,302 | 1,255 | 1024,182 | 0,128 | 49,657 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>53</b> | 10,6 | 2,379 | 8,762  | 0,070 | 103,386 | 0,132 | 401,051  | 64,021 | 102984,905 | 113586,270 | 0,789 | 941,167  | 0,057 | 13,554 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>54</b> | 10,8 | 2,177 | 20,156 | 0,139 | 167,343 | 0,119 | 953,651  | 86,799 | 130892,321 | 144715,414 | 1,485 | 1020,426 | 0,086 | 31,751 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>59</b> | 11,8 | 0,490 | 1,017  | 0     | 16,910  | 0,025 | 189,183  | 79,255 | 14768,278  | 248303,308 | 0,139 | 82,295   | 0     | 6,870  | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>66</b> | 13,2 | 4,716 | 30,423 | 0,162 | 125,161 | 0,075 | 782,075  | 64,680 | 88617,992  | 133024,707 | 1,228 | 735,815  | 0,102 | 45,780 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>67</b> | 13,4 | 2,780 | 41,240 | 0,085 | 135,431 | 0,135 | 781,892  | 71,448 | 104922,934 | 113556,375 | 1,033 | 1018,290 | 0,066 | 53,854 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>68</b> | 13,6 | 3,679 | 23,578 | 0,084 | 118,348 | 0,039 | 1130,451 | 39,016 | 78520,160  | 98337,239  | 0,538 | 1181,654 | 0,087 | 27,136 | Dolos-<br>tone | Acetic acid |
| <b>JOR<br/>77</b> | 15,4 | 3,394 | 31,235 | 0,090 | 135,729 | 0,059 | 551,114  | 49,064 | 98514,460  | 105499,447 | 0,843 | 532,986  | 0,077 | 37,499 | Dolos-<br>tone | Acetic acid |

|                |       |        |         |       |         |        |          |        |            |            |          |          |        |         |           |             |
|----------------|-------|--------|---------|-------|---------|--------|----------|--------|------------|------------|----------|----------|--------|---------|-----------|-------------|
| <b>JOR 90</b>  | 18    | 2,391  | 33,726  | 0,067 | 111,404 | 0,147  | 488,461  | 55,500 | 80806,212  | 110730,205 | 1,306    | 1093,897 | 0,057  | 45,550  | Dolostone | Acetic acid |
| <b>JOR 93</b>  | 18,6  | 3,111  | 53,962  | 0,220 | 149,419 | 0,060  | 1121,014 | 60,664 | 81428,664  | 106865,941 | 1,567    | 819,121  | 0,106  | 38,981  | Dolostone | Acetic acid |
| <b>JOR 101</b> | 20,2  | 3,401  | 10,530  | 0,056 | 99,427  | 0,058  | 838,714  | 37,731 | 67226,938  | 84147,491  | 0,276    | 337,056  | 0,060  | 23,193  | Dolostone | Acetic acid |
| <b>JOR 117</b> | 23,4  | 3,068  | 23,670  | 0,112 | 87,637  | 0,028  | 714,162  | 36,249 | 70203,523  | 75575,620  | 0,590    | 347,381  | 0,056  | 12,799  | Dolostone | Acetic acid |
| <b>JOR 122</b> | 24,4  | 2,444  | 32,843  | 0,466 | 231,171 | 0,058  | 474,724  | 33,223 | 65341,808  | 73790,727  | 0,204    | 262,358  | 0,162  | 13,836  | Dolostone | Acetic acid |
| <b>JOR 138</b> | 27,6  | 3,597  | 32,647  | 0,119 | 125,676 | 0,043  | 735,417  | 45,850 | 93045,211  | 103865,121 | 0,509    | 416,099  | 0,063  | 14,732  | Dolostone | Acetic acid |
| <b>JOR 148</b> | 29,6  | 2,387  | 20,965  | 0,088 | 95,189  | 0,034  | 531,680  | 39,570 | 74189,961  | 81031,110  | 0,468    | 302,978  | 0,046  | 12,494  | Dolostone | Acetic acid |
| <b>JOR 151</b> | 30,2  | 3,486  | 31,176  | 0,138 | 148,874 | 0,056  | 592,379  | 62,061 | 88674,984  | 122135,330 | 0,855    | 392,813  | 0,080  | 12,698  | Dolostone | Acetic acid |
| <b>JOR 169</b> | 33,8  | 1,732  | 33,904  | 0,294 | 219,732 | 0,033  | 707,909  | 55,883 | 63867,020  | 112208,021 | 0,735    | 451,361  | 0,215  | 21,009  | Dolostone | Acetic acid |
| <b>JOR 170</b> | 34    | 1,589  | 43,996  | 0,327 | 162,418 | 0,024  | 711,527  | 44,133 | 67908,044  | 84870,617  | 0,809    | 517,878  | 0,166  | 19,076  | Dolostone | Acetic acid |
| <b>JOR 184</b> | 36,8  | 2,346  | 108,134 | 1,171 | 509,246 | 0,054  | 1413,161 | 79,945 | 109855,272 | 116757,364 | 1,600    | 1465,942 | 0,555  | 72,270  | Dolostone | Acetic acid |
| <b>TS001</b>   | 37    | 11,210 | 78,469  | 0,972 | 20,091  | 12,000 | 1548,660 | 68,280 | 123308,933 | 211150,446 | 1548,902 | 2253,488 | 4,947  | 101,700 | Dolostone | Bulk rock   |
| <b>TS003</b>   | 37,4  | 7,921  | 56,266  | 0,581 | 12,335  | 7,000  | 1316,361 | 64,410 | 126685,608 | 217726,560 | 1316,567 | 1767,442 | 3,183  | 63,480  | Dolostone | Bulk rock   |
| <b>TS006</b>   | 38    | 9,102  | 62,531  | 0,714 | 18,000  | 7,000  | 1393,794 | 62,540 | 123489,826 | 212079,679 | 1394,012 | 2165,116 | 5,095  | 62,750  | Dolostone | Bulk rock   |
| <b>TS009</b>   | 39,83 | 8,732  | 76,196  | 0,722 | 15,644  | 7,000  | 1858,392 | 72,490 | 121861,787 | 216082,531 | 1858,682 | 2386,047 | 4,911  | 173,100 | Dolostone | Bulk rock   |
| <b>TS015</b>   | 40    | 9,953  | 99,838  | 1,383 | 29,753  | 14,000 | 1935,825 | 86,680 | 117158,561 | 208362,745 | 1936,127 | 4020,930 | 9,963  | 91,590  | Dolostone | Bulk rock   |
| <b>TS017</b>   | 40,2  | 9,104  | 67,068  | 1,530 | 32,929  | 16,000 | 1316,361 | 85,200 | 118545,409 | 209149,020 | 1316,567 | 2651,163 | 10,530 | 86,400  | Dolostone | Bulk rock   |

|       |      |       |        |       |        |        |          |          |            |            |          |          |        |         |                |           |
|-------|------|-------|--------|-------|--------|--------|----------|----------|------------|------------|----------|----------|--------|---------|----------------|-----------|
| TS019 | 40,6 | 8,686 | 74,151 | 1,583 | 34,438 | 16,000 | 1393,794 | 81,590   | 117701,241 | 206003,922 | 1394,012 | 3358,140 | 10,660 | 77,580  | Dolos-<br>tone | Bulk rock |
| TS021 | 41   | 8,338 | 53,308 | 1,768 | 37,853 | 20,000 | 1316,361 | 81,860   | 116193,797 | 204216,934 | 1316,567 | 3402,326 | 12,010 | 69,570  | Dolos-<br>tone | Bulk rock |
| TS023 | 41,4 | 8,534 | 26,959 | 2,017 | 40,738 | 24,000 | 1084,062 | 76,880   | 116193,797 | 206432,799 | 1084,231 | 3048,837 | 12,970 | 103,800 | Dolos-<br>tone | Bulk rock |
| TS029 | 44,8 | 8,702 | 17,846 | 2,683 | 45,424 | 48,000 | 309,732  | 689,600  | 3075,186   | 352250,980 | 309,780  | 3932,558 | 16,610 | 81,320  | Dolos-<br>tone | Bulk rock |
| TS033 | 45,6 | 6,701 | 6,662  | 1,634 | 27,741 | 20,000 | 309,732  | 548,800  | 3316,377   | 366832,799 | 309,780  | 1060,465 | 9,779  | 44,100  | Dolos-<br>tone | Bulk rock |
| TS035 | 46   | 7,147 | 6,883  | 2,408 | 42,988 | 39,000 | 309,732  | 468,000  | 4220,844   | 356182,353 | 309,780  | 2651,163 | 15,720 | 67,190  | Limes-<br>tone | Bulk rock |
| TS036 | 46,2 | 7,450 | 6,847  | 1,858 | 25,888 | 34,000 | 232,299  | 479,000  | 4220,844   | 367762,032 | 232,335  | 1811,628 | 9,800  | 46,380  | Limes-<br>tone | Bulk rock |
| TS039 | 46,8 | 7,951 | 6,285  | 1,139 | 17,153 | 18,000 | 154,866  | 1115,000 | 2411,911   | 378198,039 | 154,890  | 2341,860 | 6,520  | 30,040  | Limes-<br>tone | Bulk rock |
| TS042 | 47,4 | 7,011 | 2,890  | 2,396 | 45,185 | 29,000 | 232,299  | 563,800  | 1989,826   | 356825,668 | 232,335  | 751,163  | 16,660 | 57,330  | Limes-<br>tone | Bulk rock |
| TS044 | 47,8 | 6,769 | 7,681  | 1,604 | 25,438 | 28,000 | 232,299  | 624,500  | 3557,568   | 368691,266 | 232,335  | 3093,023 | 9,842  | 42,800  | Limes-<br>tone | Bulk rock |
| TS046 | 48,2 | 7,546 | 4,611  | 2,447 | 34,279 | 43,000 | 232,299  | 950,700  | 2231,017   | 366260,963 | 232,335  | 2076,744 | 13,350 | 55,240  | Limes-<br>tone | Bulk rock |
| TS050 | 51   | 6,458 | 42,950 | 1,859 | 38,091 | 26,000 | 232,299  | 715,100  | 2050,124   | 365045,811 | 232,335  | 1723,256 | 13,590 | 54,800  | Limes-<br>tone | Bulk rock |
| TS058 | 52,6 | 7,231 | 3,947  | 1,472 | 30,679 | 19,000 | 232,299  | 644,300  | 2411,911   | 371979,323 | 232,335  | 1325,581 | 11,610 | 42,540  | Limes-<br>tone | Bulk rock |

Table 5.3 Results of the concentration of rare earth elements Yttrium of the Puga cap carbonate- Terconi Section

| Sam-<br>ples | Depth<br>(m)<br>Meter<br>(m) | Terconi Section |       |       |       |       |       |       |       |        |       |       |       |       |       |       |        | ΣREE+Y<br>ppm | dolos-<br>tone | bulk<br>rock |
|--------------|------------------------------|-----------------|-------|-------|-------|-------|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|--------|---------------|----------------|--------------|
|              |                              | La              | Ce    | Pr    | Nd    | Sm    | Eu    | Gd    | Tb    | Dy     | Ho    | Er    | Tm    | Yb    | Lu    | Y     |        |               |                |              |
|              |                              | ppm             | ppm   | ppm   | ppm   | ppm   | ppm   | ppm   | ppm   | ppm    | ppm   | ppm   | ppm   | ppm   | ppm   | ppm   |        |               |                |              |
| Tes 1        | 0,1                          | 0,639           | 1,721 | 0,232 | 1,02  | 0,26  | 0,064 | 0,305 | 0,05  | 0,312  | 0,067 | 0,188 | 0,025 | 0,162 | 0,025 | 2,478 | 7,548  |               |                |              |
| TR1 F        | 2,06                         | 0,544           | 1,43  | 0,192 | 0,856 | 0,199 | 0,04  | 0,187 | 0,026 | 0,0142 | 0,028 | 0,073 | 0,01  | 0,061 | 0,009 | 0,98  | 4,6492 |               |                |              |
| Tes 3        | 2,42                         | 0,218           | 0,569 | 0,067 | 0,289 | 0,065 | 0,014 | 0,058 | 0,01  | 0,052  | 0,011 | 0,03  |       | 0,026 | 0,005 |       | 1,414  |               |                |              |
| Tes 5        | 4,2                          | 0,257           | 0,709 | 0,082 | 0,373 | 0,078 | 0,016 | 0,077 | 0,011 | 0,073  | 0,014 | 0,036 | 0,005 | 0,032 | 0,005 | 0,511 | 2,279  |               |                |              |
| TR2 E        | 4,56                         | 0,799           | 1,7   | 0,243 | 1,03  | 0,231 | 0,048 | 0,229 | 0,033 | 0,0193 | 0,039 | 0,099 | 0,014 | 0,088 | 0,013 | 1,37  | 5,9553 |               |                |              |
| Tes 7        | 5,2                          | 0,228           | 0,551 | 0,073 | 0,304 | 0,066 | 0,015 | 0,057 | 0,01  | 0,056  | 0,012 | 0,035 | 0,005 | 0,031 | 0,005 | 0,444 | 1,892  |               |                |              |
| TR3 C        | 5,9                          | 0,388           | 0,981 | 0,125 | 0,545 | 0,123 | 0,027 | 0,112 | 0,017 | 0,104  | 0,021 | 0,061 | 0,008 | 0,052 | 0,008 | 0,72  | 3,292  |               |                |              |
| Tes 9        | 6,2                          | 0,486           | 1,175 | 0,157 | 0,679 | 0,138 | 0,031 | 0,139 | 0,02  | 0,124  | 0,024 | 0,063 | 0,009 | 0,058 | 0,009 | 0,905 | 4,017  |               |                |              |
| TR4Q         | 6,21                         | 0,637           | 1,43  | 0,178 | 0,728 | 0,166 | 0,034 | 0,158 | 0,024 | 0,149  | 0,029 | 0,08  | 0,011 | 0,077 | 0,012 | 1,02  | 4,733  |               |                |              |
| Tes 11       | 7,2                          | 0,879           | 2,066 | 0,254 | 1,046 | 0,235 | 0,049 | 0,221 | 0,032 | 0,197  | 0,041 | 0,119 | 0,017 | 0,108 | 0,018 | 1,616 | 6,898  |               |                |              |
| TeS12        | 7,7                          | 0,562           | 1,123 | 0,176 | 0,667 | 0,147 | 0,031 | 0,141 | 0,024 | 0,136  | 0,028 | 0,083 | 0,012 | 0,074 | 0,012 | 1,24  | 4,456  |               |                |              |
| Tes 13       | 8,2                          | 0,549           | 1,034 | 0,178 | 0,74  | 0,151 | 0,036 | 0,152 | 0,025 | 0,163  | 0,034 | 0,105 | 0,697 | 0,096 | 0,016 | 1,663 | 5,639  |               |                |              |
| Tes 15       | 9,2                          | 1,247           | 2,458 | 0,292 | 1,105 | 0,214 | 0,047 | 0,189 | 0,029 | 0,167  | 0,036 | 0,093 | 0,63  | 0,096 | 0,015 | 1,131 | 7,749  |               |                |              |
| TR5E         | 9,6                          | 1,203           | 2,327 | 0,289 | 1,078 | 0,215 | 0,045 | 0,182 | 0,029 | 0,167  | 0,032 | 0,096 | 0,014 | 0,094 | 0,015 | 1,07  | 6,856  |               |                |              |
| Tes16        | 9,7                          | 1,279           | 2,567 | 0,329 | 1,253 | 0,248 | 0,051 | 0,218 | 0,034 | 0,191  | 0,037 | 0,111 | 0,94  | 0,105 | 0,016 | 1,28  | 8,659  |               |                |              |

|        |      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |        |                |              |
|--------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|----------------|--------------|
| TR5I   | 10,5 | 1,235 | 2,403 | 0,312 | 1,197 | 0,239 | 0,05  | 0,204 | 0,032 | 0,187 | 0,036 | 0,104 | 0,015 | 0,105 | 0,015 | 1,19  | 7,324  | dolos-<br>tone | bulk<br>rock |
| Tes 18 | 10,7 | 2,833 | 5,099 | 0,675 | 2,598 | 0,536 | 0,097 | 0,454 | 0,07  | 0,403 | 0,077 | 0,216 | 0,842 | 0,204 | 0,03  | 2,468 | 16,602 | dolos-<br>tone | bulk<br>rock |
| TR5J   | 10,7 | 1,681 | 3,298 | 0,429 | 1,683 | 0,332 | 0,069 | 0,307 | 0,045 | 0,268 | 0,053 | 0,149 | 0,022 | 0,151 | 0,022 | 1,82  | 10,329 | dolos-<br>tone | bulk<br>rock |
| TR5L   | 11,1 | 1,323 | 2,759 | 0,349 | 1,343 | 0,284 | 0,057 | 0,235 | 0,038 | 0,217 | 0,042 | 0,118 | 0,018 | 0,113 | 0,018 | 1,45  | 8,364  | dolos-<br>tone | bulk<br>rock |
| Tes 20 | 11,7 | 2,63  | 4,784 | 0,641 | 2,441 | 0,483 | 0,09  | 0,419 | 0,067 | 0,394 | 0,076 | 0,225 | 0,696 | 0,213 | 0,036 | 2,496 | 15,691 | dolos-<br>tone | bulk<br>rock |
| TR5Q   | 12,6 | 1,818 | 3,527 | 0,46  | 1,804 | 0,386 | 0,073 | 0,347 | 0,055 | 0,329 | 0,062 | 0,175 | 0,025 | 0,168 | 0,027 | 2,17  | 11,426 | dolos-<br>tone | bulk<br>rock |
| Tes 22 | 12,7 | 3,915 | 7,56  | 0,978 | 3,739 | 0,737 | 0,133 | 0,612 | 0,096 | 0,554 | 0,109 | 0,326 | 0,888 | 0,316 | 0,047 | 3,52  | 23,53  | dolos-<br>tone | bulk<br>rock |
| TR5W   | 13,6 | 2,476 | 4,906 | 0,633 | 2,506 | 0,533 | 0,113 | 0,48  | 0,072 | 0,425 | 0,085 | 0,236 | 0,036 | 0,251 | 0,039 | 2,7   | 15,491 | dolos-<br>tone | bulk<br>rock |
| Tes 24 | 13,7 | 7,259 | 13,09 | 1,635 | 6,171 | 1,262 | 0,239 | 1,197 | 0,191 | 1,137 | 0,24  | 0,705 | 0,106 | 0,708 | 0,114 | 8,207 | 42,261 | dolos-<br>tone | bulk<br>rock |
| Tes 26 | 14,7 | 6,498 | 11,55 | 1,475 | 5,768 | 1,229 | 0,236 | 1,244 | 0,2   | 1,214 | 0,246 | 0,713 | 0,101 | 0,644 | 0,096 | 8,987 | 40,201 | dolos-<br>tone | bulk<br>rock |
| Tes 28 | 15,7 | 6,428 | 11,92 | 1,46  | 5,437 | 1,102 | 0,208 | 1,077 | 0,165 | 1,014 | 0,205 | 0,581 | 0,082 | 0,529 | 0,081 | 7,224 | 37,513 | dolos-<br>tone | bulk<br>rock |
| Tes 30 | 16,4 | 13,89 | 32,52 | 4,25  | 16,91 | 3,509 | 0,637 | 2,858 | 0,449 | 2,698 | 0,518 | 1,504 | 0,225 | 1,532 | 0,241 | 15,87 | 97,611 | limes-<br>tone | bulk<br>rock |
| Tes 32 | 17,2 | 7,071 | 13,43 | 1,707 | 6,621 | 1,361 | 0,255 | 1,293 | 0,201 | 1,257 | 0,249 | 0,724 | 0,103 | 0,639 | 0,097 | 9,01  | 44,018 | limes-<br>tone | bulk<br>rock |
| Tes 34 | 18,2 | 5,385 | 11,74 | 1,492 | 5,647 | 1,141 | 0,218 | 1,048 | 0,163 | 0,991 | 0,205 | 0,576 | 0,084 | 0,545 | 0,08  | 7,042 | 36,357 | limes-<br>tone | bulk<br>rock |
| Tes 36 | 19,2 | 6,274 | 12,22 | 1,552 | 5,972 | 1,207 | 0,229 | 1,165 | 0,178 | 1,09  | 0,225 | 0,633 | 0,09  | 0,566 | 0,086 | 7,882 | 39,369 | limes-<br>tone | bulk<br>rock |
| Tes 38 | 20,7 | 6,267 | 12,39 | 1,558 | 6,083 | 1,259 | 0,24  | 1,184 | 0,19  | 1,151 | 0,232 | 0,652 | 0,091 | 0,578 | 0,088 | 8,285 | 40,248 | limes-<br>tone | bulk<br>rock |
| Tes 40 | 21,7 | 7,487 | 14,4  | 1,786 | 6,963 | 1,366 | 0,263 | 1,319 | 0,205 | 1,261 | 0,255 | 0,747 | 0,109 | 0,721 | 0,107 | 9,317 | 46,306 | limes-<br>tone | bulk<br>rock |

|           |      |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |        |                |              |
|-----------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|----------------|--------------|
| Tes 42    | 27,2 | 10,75 | 23,33 | 2,941 | 11,33 | 2,26  | 0,406 | 1,988 | 0,311 | 1,877 | 0,375 | 1,078 | 0,157 | 1,056 | 0,162 | 11,82 | 69,841 | limes-<br>tone | bulk<br>rock |
| Tes 44    | 28,2 | 8,524 | 18,46 | 2,239 | 8,519 | 1,687 | 0,304 | 1,498 | 0,234 | 1,367 | 0,276 | 0,778 | 0,116 | 0,775 | 0,117 | 8,996 | 53,89  | limes-<br>tone | bulk<br>rock |
| Tes 46    | 30,7 | 8,194 | 19,01 | 2,484 | 10,08 | 2,082 | 0,408 | 1,868 | 0,287 | 1,687 | 0,325 | 0,895 | 0,128 | 0,815 | 0,12  | 10,71 | 59,093 | limes-<br>tone | bulk<br>rock |
| TeS<br>48 | 31,7 | 7,097 | 16,24 | 2,098 | 8,408 | 1,766 | 0,34  | 1,57  | 0,245 | 1,442 | 0,283 | 0,79  | 0,111 | 0,718 | 0,107 | 9,235 | 50,45  | limes-<br>tone | bulk<br>rock |
| TeS<br>50 | 32,7 | 9,834 | 21,95 | 2,795 | 11,13 | 2,256 | 0,427 | 1,943 | 0,302 | 1,744 | 0,338 | 0,941 | 0,138 | 0,917 | 0,133 | 10,88 | 65,728 | limes-<br>tone | bulk<br>rock |

Table 5.4 Major and Minor Elements Concentration of the Puga cap carbonate- Terconi Section.

| Sam-<br>ples | Depth<br>(m)<br>Meter<br>(m) | Terconi Section |          |       |          |       |          |       |          |          |          |          |       |       |                |              |
|--------------|------------------------------|-----------------|----------|-------|----------|-------|----------|-------|----------|----------|----------|----------|-------|-------|----------------|--------------|
|              |                              | Ni              | Pb       | Th    | Al       | Zr    | Mn       | Sr    | Mg       | Ca       | Ti       | Fe       | Rb    | Ba    |                |              |
|              |                              | ppm             | ppm      | ppm   | ppm      | ppm   | ppm      | ppm   | ppm      | ppm      | ppm      | ppm      | ppm   | ppm   |                |              |
| Tes 1        | 0,1                          | 8,285           | 6,249    | 0,194 | 10,21765 | 3,561 | 3407,052 | 49,13 | 125986,2 | 213185,7 | 59,93339 | 3007,496 |       | 18,19 | dolos-<br>tone | bulk<br>rock |
| TR1 F        | 2,06                         | 12,7            | 14,5     | 0,14  | 6,352941 | 4,02  | 1471,227 | 43,1  | 132233   | 215285,7 | 59,93339 | 1818,486 |       | 30,4  | dolos-<br>tone | bulk<br>rock |
| Tes 3        | 2,42                         | 9,186           | 8,4477   | 0,045 | 1,694118 | 1,71  | 1006,629 | 47,12 | 127680,5 | 215700   | 59,93339 | 1398,835 |       | 19,06 | dolos-<br>tone | bulk<br>rock |
| Tes 5        | 4,2                          | 8,724           | 8,8094   | 0,039 | 2,858824 | 1,73  | 1161,495 | 50,11 | 128838,2 | 217621,4 | 59,93339 | 1608,661 |       | 20,76 | dolos-<br>tone | bulk<br>rock |
| TR2 E        | 4,56                         | 15,4            | 15,1     | 0,24  | 13,23529 | 4,63  | 851,763  | 51,6  | 127107,7 | 223714,3 | 59,93339 | 1748,544 | 0,54  | 20,4  | dolos-<br>tone | bulk<br>rock |
| Tes 7        | 5,2                          | 7,538           | 6,8224   | 0,032 | 0        | 1,535 | 851,763  | 48,93 | 127222,3 | 222435,7 | 0        | 1398,835 |       | 12,04 | dolos-<br>tone | bulk<br>rock |
| TR3 C        | 5,9                          | 9,9             | 8,09     | 0,09  | 4,235294 | 12,6  | 1161,495 | 39,6  | 104013,6 | 271500   | 59,93339 | 1888,428 |       | 33,6  | dolos-<br>tone | bulk<br>rock |
| Tes 9        | 6,2                          | 8,154           | 9,8275   | 0,119 | 5,135294 | 2,152 | 1238,928 | 41,64 | 122018,6 | 228078,6 | 59,93339 | 2308,078 |       | 25,53 | dolos-<br>tone | bulk<br>rock |
| TR4Q         | 6,21                         | 8,84            | 9,07     | 0,22  | 7,941176 | 9,75  | 851,763  | 45,26 | 126745,9 | 223000   | 119,8668 | 2168,195 | 0,59  | 19,05 | dolos-<br>tone | bulk<br>rock |
| Tes 11       | 7,2                          | 11,19           | 13,7614  | 0,277 | 11,01176 | 4,515 | 1471,227 | 45,85 | 126456,5 | 216000   | 59,93339 | 3776,855 | 0,452 | 50    | dolos-<br>tone | bulk<br>rock |
| TeS12        | 7,7                          | 10,35           | 12,1308  | 0,177 | 0        | 3,346 | 1006,629 | 41,63 | 118364,5 | 227464,3 | 0        | 2447,962 | 0,342 | 13,97 | dolos-<br>tone | bulk<br>rock |
| Tes 13       | 8,2                          | 8,992           | 8,248    | 0,16  | 6,988235 | 2,467 | 929,1961 | 47,32 | 121976,4 | 229842,9 | 59,93339 | 2028,311 |       | 19,21 | dolos-<br>tone | bulk<br>rock |
| Tes 15       | 9,2                          | 8,668           | 90,0266  | 0,218 | 12,17647 | 3,126 | 1780,959 | 54,48 | 122983,3 | 217428,6 | 59,93339 | 4196,506 | 0,764 | 26,36 | dolos-<br>tone | bulk<br>rock |
| TR5E         | 9,6                          | 6,42            | 147,65   | 0,32  | 12,17647 | 3,95  | 1548,66  | 60,12 | 119811,7 | 228500   | 119,8668 | 3776,855 | 1,13  | 15,71 | dolos-<br>tone | bulk<br>rock |
| Tes16        | 9,7                          | 9,49            | 128,1337 | 0,308 | 11,17059 | 3,755 | 1393,794 | 60,08 | 120909,1 | 223314,3 | 59,93339 | 3357,205 | 0,762 | 3,95  | dolos-<br>tone | bulk<br>rock |



|        |      |       |          |       |          |       |          |       |          |          |          |          |       |       |                |              |
|--------|------|-------|----------|-------|----------|-------|----------|-------|----------|----------|----------|----------|-------|-------|----------------|--------------|
| TR5I   | 10,5 | 6,56  | 109,27   | 0,32  | 15,88235 | 3,42  | 1471,227 | 53,87 | 123972,2 | 215785,7 | 59,93339 | 3636,972 | 1,12  | 16,67 | dolos-<br>tone | bulk<br>rock |
| Tes 18 | 10,7 | 9,05  | 50,87    | 0,749 | 42,3     | 8,54  | 1780,959 | 58,26 | 120559,4 | 214950   | 179,8002 | 4406,331 | 1,704 | 7,14  | dolos-<br>tone | bulk<br>rock |
| TR5J   | 10,7 | 6,76  | 125,95   | 0,56  | 22,23529 | 6,74  | 1780,959 | 52,02 | 131268,2 | 227785,7 | 179,8002 | 4196,506 | 1,75  | 6,668 | dolos-<br>tone | bulk<br>rock |
| TR5L   | 11,1 | 6,35  | 68,67    | 0,24  | 10,58824 | 3,14  | 1626,093 | 50,79 | 123791,3 | 218071,4 | 59,93339 | 3776,855 | 0,95  | 9,042 | dolos-<br>tone | bulk<br>rock |
| Tes 20 | 11,7 | 6,753 | 174,5919 | 0,616 | 36,58235 | 8,149 | 1703,526 | 62,85 | 117737,4 | 214757,1 | 179,8002 | 4476,273 | 2,714 | 7,336 | dolos-<br>tone | bulk<br>rock |
| TR5Q   | 12,6 | 6,711 | 27,4761  | 0,41  | 15,88235 | 4,65  | 1548,66  | 54,65 | 126263,5 | 221642,9 | 119,8668 | 3497,088 | 1,72  | 10,18 | dolos-<br>tone | bulk<br>rock |
| Tes 22 | 12,7 | 5,992 | 14,2848  | 0,954 | 52,25294 | 10,5  | 1006,629 | 76,42 | 120185,5 | 208450   | 239,7336 | 4126,564 | 5,856 | 15,24 | dolos-<br>tone | bulk<br>rock |
| TR5W   | 13,6 | 6,59  | 127,37   | 0,92  | 34,94118 | 10,9  | 2013,258 | 59,14 | 123308,9 | 211642,9 | 239,7336 | 5175,69  | 2,9   | 9,255 | dolos-<br>tone | bulk<br>rock |
| Tes 24 | 13,7 | 7,696 | 6,6125   | 1,681 | 83,64706 | 23,65 | 1161,495 | 69,84 | 114867,2 | 202542,9 | 479,4671 | 7064,118 | 10,99 | 42,19 | dolos-<br>tone | bulk<br>rock |
| Tes 26 | 14,7 | 5,885 | 3,9488   | 1,549 | 56,11765 | 27,13 | 1393,794 | 60,43 | 117978,6 | 204871,4 | 359,6003 | 5665,283 | 10,58 | 37,44 | dolos-<br>tone | bulk<br>rock |
| Tes 28 | 15,7 | 6,336 | 3,7688   | 1,598 | 63,84706 | 27    | 542,031  | 56,83 | 117188,7 | 205878,6 | 419,5337 | 5315,574 | 10,57 | 40,99 | dolos-<br>tone | bulk<br>rock |
| Tes 30 | 16,4 | 10,9  | 5,4287   | 3,826 | 194,7176 | 77,17 | 387,165  | 315,2 | 24788,41 | 275857,1 | 1138,734 | 7973,361 | 43,67 | 146,8 | limes-<br>tone | bulk<br>rock |
| Tes 32 | 17,2 | 8,094 | 4,5474   | 1,801 | 66,28235 | 35,14 | 154,866  | 1080  | 3412,854 | 365007,1 | 419,5337 | 4056,622 | 13,33 | 52,91 | limes-<br>tone | bulk<br>rock |
| Tes 34 | 18,2 | 7,729 | 7,4157   | 1,553 | 68,92941 | 24,99 | 309,732  | 479,4 | 14947,82 | 344750   | 419,5337 | 2937,554 | 6,801 | 26,38 | limes-<br>tone | bulk<br>rock |
| Tes 36 | 19,2 | 8,935 | 3,3707   | 1,621 | 68,13529 | 29,71 | 154,866  | 1030  | 7308,089 | 356507,1 | 419,5337 | 3007,496 | 8,427 | 35,28 | limes-<br>tone | bulk<br>rock |
| Tes 38 | 20,7 | 8,13  | 3,5529   | 1,501 | 63,79412 | 25,82 | 232,299  | 827,8 | 13193,15 | 351428,6 | 419,5337 | 3357,205 | 11,07 | 52,45 | limes-<br>tone | bulk<br>rock |
| Tes 40 | 21,7 | 8,301 | 2,9175   | 2,144 | 91,21765 | 48,66 | 154,866  | 1263  | 3629,926 | 348228,6 | 599,3339 | 2867,612 | 18,52 | 74,14 | limes-<br>tone | bulk<br>rock |

|           |      |       |        |       |          |       |         |       |          |          |          |          |       |       |                |              |
|-----------|------|-------|--------|-------|----------|-------|---------|-------|----------|----------|----------|----------|-------|-------|----------------|--------------|
| Tes 42    | 27,2 | 9,093 | 3,5389 | 2,905 | 132,6706 | 64,88 | 464,598 | 233,3 | 17245,16 | 306000   | 839,0674 | 7413,827 | 24,64 | 108,9 | limes-<br>tone | bulk<br>rock |
| Tes 44    | 28,2 | 11,52 | 3,4278 | 2,3   | 109,6941 | 41,95 | 387,165 | 378,4 | 3443,002 | 343778,6 | 659,2673 | 5595,341 | 22,91 | 123,2 | limes-<br>tone | bulk<br>rock |
| Tes 46    | 30,7 | 8,683 | 2,3856 | 1,794 | 74,01176 | 26,86 | 464,598 | 388,1 | 9261,737 | 350957,1 | 419,5337 | 4825,982 | 15,09 | 80,71 | limes-<br>tone | bulk<br>rock |
| TeS<br>48 | 31,7 | 7,149 | 2,0303 | 1,512 | 68,77059 | 24,81 | 464,598 | 345,6 | 10847,57 | 349857,1 | 419,5337 | 5805,166 | 12,89 | 226,3 | limes-<br>tone | bulk<br>rock |
| TeS<br>50 | 32,7 | 9,893 | 3,5269 | 2,379 | 111,1235 | 37,95 | 464,598 | 427   | 3895,236 | 344628,6 | 659,2673 | 4686,098 | 24,85 | 90,65 | limes-<br>tone | bulk<br>rock |

Table 5.5 Carbon and oxygen isotopes of the Puga cap carbonate- Tangará Section.

| Depth | Identifier 1 | Weight (mg) | $\delta^{13}\text{C}/^{12}\text{C}$<br>Corr. | $\delta^{18}\text{O}/^{16}\text{O}$ | Corr. | [CaCO <sub>3</sub> %] | Cap carbonate |
|-------|--------------|-------------|----------------------------------------------|-------------------------------------|-------|-----------------------|---------------|
| 0,2   | JOR001       | 80          | -7,956625                                    | -4,121875                           | 0,2   | 89%                   | cap dolostone |
| 0,4   | JOR002       | 94          | -8,200625                                    | -4,087875                           | 0,4   | 83%                   | cap dolostone |
| 1     | JOR005       | 92          | -5,017625                                    | -5,469875                           | 1     | 90%                   | cap dolostone |
| 1,4   | JOR007       | 80          | -4,694625                                    | -5,398875                           | 1,4   | 91%                   | cap dolostone |
| 1,6   | JOR008       | 98          | -4,168625                                    | -5,295875                           | 1,6   | 94%                   | cap dolostone |
| 1,8   | JOR009       | 65          | -4,1982                                      | -5,6453                             | 1,8   | 87%                   | cap dolostone |
| 2     | JOR010       | 75          | -4,4932                                      | -5,9153                             | 2     | 91%                   | cap dolostone |
| 2,2   | JOR011       | 75          | -5,0002                                      | -5,5633                             | 2,2   | 87%                   | cap dolostone |
| 2,6   | JOR013       | 72          | -5,3532                                      | -5,9573                             | 2,6   | 89%                   | cap dolostone |
| 3     | JOR015       | 74          | -4,2612                                      | -5,5343                             | 3     | 91%                   | cap dolostone |
| 3,2   | JOR016       | 70          | -5,0472                                      | -5,4903                             | 3,2   | 75%                   | cap dolostone |
| 3,8   | JOR019       | 80          | -5,4572                                      | -4,9903                             | 3,8   | 89%                   | cap dolostone |
| 4     | JOR020       | 81          | -6,5092                                      | -6,3993                             | 4     | 53%                   | cap dolostone |
| 4,4   | JOR022       | 83          | -7,3832                                      | -7,3323                             | 4,4   | 79%                   | cap dolostone |
| 4,6   | JOR023       | 83          | -4,7602                                      | -4,7873                             | 4,6   | 85%                   | cap dolostone |
| 5     | JOR025       | 73          | -4,4862                                      | -5,2533                             | 5     | 93%                   | cap dolostone |
| 5,8   | JOR029       | 81          | -4,8892                                      | -4,8763                             | 5,8   | 93%                   | cap dolostone |
| 6,6   | JOR033       | 71          | -4,2892                                      | -5,5433                             | 6,6   | 92%                   | cap dolostone |
| 7,4   | JOR037       | 96          | -4,350625                                    | -4,792875                           | 7,4   | 94%                   | cap dolostone |
| 7,6   | JOR038       | 92          | -4,708625                                    | -4,897875                           | 7,6   | 94%                   | cap dolostone |
| 7,8   | JOR039       | 69          | -4,9672                                      | -5,3453                             | 7,8   | 94%                   | cap dolostone |
| 8,2   | JOR041       | 80          | -4,4952                                      | -5,1623                             | 8,2   | 90%                   | cap dolostone |
| 8,4   | JOR042       | 71          | -4,66825                                     | -5,131125                           | 8,4   | 86%                   | cap dolostone |
| 8,4   | JOR042       | 70          | -4,64325                                     | -5,115125                           | 8,4   | 75%                   | cap dolostone |
| 10,4  | JOR052       | 70          | -6,635875                                    | -4,784125                           | 10,4  | 95%                   | cap dolostone |
| 10,6  | JOR053       | 54          | -4,14725                                     | -4,596125                           | 10,6  | 98%                   | cap dolostone |
| 10,8  | JOR054       | 63          | -4,34925                                     | -4,694125                           | 10,8  | 98%                   | cap dolostone |
| 11,8  | JOR059       | 60          | -6,68225                                     | -4,095125                           | 11,8  | 96%                   | cap dolostone |
| 11,8  | JOR059       | 57          | -6,73425                                     | -4,103125                           | 11,8  | 100%                  | cap dolostone |
| 13,2  | JOR066       | 99          | -4,533625                                    | -4,671875                           | 13,2  | 93%                   | cap dolostone |
| 13,4  | JOR067       | 96          | -5,444625                                    | -4,294875                           | 13,4  | 93%                   | cap dolostone |
| 13,6  | JOR068       | 92          | -5,223625                                    | -4,367875                           | 13,6  | 94%                   | cap dolostone |
| 15,4  | JOR077       | 71          | -4,15025                                     | -5,184125                           | 15,4  | 85%                   | cap dolostone |
| 18    | JOR090       | 76          | -4,83025                                     | -4,888125                           | 18    | 93%                   | cap dolostone |
| 18,6  | JOR093       | 66          | -4,88325                                     | -4,919125                           | 18,6  | 87%                   | cap dolostone |
| 20,2  | JOR101       | 69          | -5,04525                                     | -4,882125                           | 20,2  | 86%                   | cap dolostone |
| 23,4  | JOR117       | 62          | -5,23225                                     | -4,886125                           | 23,4  | 63%                   | cap dolostone |
| 24,4  | JOR122       | 59          | -5,24225                                     | -4,839125                           | 24,4  | 73%                   | cap dolostone |
| 27,6  | JOR138       | 65          | -4,79725                                     | -4,766125                           | 27,6  | 72%                   | cap dolostone |
| 27,6  | JOR138       | 65          | -4,76525                                     | -4,674125                           | 27,6  | 81%                   | cap dolostone |
| 29,6  | JOR148       | 65          | -4,96925                                     | -4,566125                           | 29,6  | 67%                   | cap dolostone |
| 30,2  | JOR151       | 63          | -4,94725                                     | -4,475125                           | 30,2  | 83%                   | cap dolostone |
| 33,8  | JOR169       | 74          | -5,36425                                     | -3,935125                           | 33,8  | 88%                   | cap dolostone |
| 34    | JOR170       | 71          | -5,65225                                     | -3,749125                           | 34    | 75%                   | cap dolostone |
| 36,8  | JOR184       | 60          | -5,16925                                     | -5,065125                           | 36,8  | 94%                   | cap dolostone |

## **CAPÍTULO 6: UNRAVELING POST-MARINOAN SEAWATER EVOLUTION IN THE AMAZON CRATON**

Renan F. dos Santos<sup>1</sup>, Afonso C. R. Nogueira<sup>1,7</sup>, Davi F. de Carvalho<sup>1</sup>, Peter W. Crockford<sup>2</sup>, Juliana C. Marques<sup>3</sup>, Egberto Pereira<sup>4</sup>, Lucieth C. Viera<sup>5</sup>, Pierre Sansjofre<sup>6</sup>

*1Programa de Pós-Graduação em Geologia e Geoquímica, Faculdade de Geologia, Instituto de Geociências, Universidade Federal do Pará, Rua Augusto Corrêa s/n, CEP 66075-110, Belém-PA, Brasil*

*2Department of Earth Sciences, Carleton University, Ottawa ON, Canada, K1S 5B6*

*3Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Porto Alegre, 90040-060, Brazil*

*4Departamento de Estratigrafia e Paleontologia da Faculdade de Geologia da Universidade do Estado do Rio de Janeiro–UERJ, Rua São Francisco Xavier, 524. 4º andar/ bloco A. Maracanã. CEP: 20.550-013, Rio de Janeiro, RJ, Brazil*

*5Instituto de Geociências, Universidade de Brasília, Campus Universitario ´ Darcy Ribeiro, Ala Central, Brasília, DF 70910-900, Brazil*

*6Muséum National d'Histoire Naturelle, Institut de Physique des Matériaux et de Cosmochimie, Sorbonne Université, Paris, France*

*7Research Productivity of CNPq*

À ser submetido em *Precambrian Research*

## 6 UNRAVELING POST-MARINOAN SEAWATER EVOLUTION IN THE AMAZON CRATON

Renan F. dos Santos<sup>1</sup>, Afonso C. R. Nogueira<sup>1,7</sup>, Davi F. de Carvalho<sup>1</sup>, Peter W. Crockford<sup>2</sup>, Juliana C. Marques<sup>3</sup>, Egberto Pereira<sup>4</sup>, Lucieth C. Viera<sup>5</sup>, Pierre Sansjofre<sup>6</sup>

*1Programa de Pós-Graduação em Geologia e Geoquímica, Faculdade de Geologia, Instituto de Geociências, Universidade Federal do Pará, Rua Augusto Corrêa s/n, CEP 66075-110, Belém-PA, Brasil*

*2Department of Earth Sciences, Carleton University, Ottawa ON, Canada, K1S 5B6*

*3Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Porto Alegre, 90040-060, Brazil*

*4Departamento de Estratigrafia e Paleontologia da Faculdade de Geologia da Universidade do Estado do Rio de Janeiro—UERJ, Rua São Francisco Xavier, 524. 4º andar/ bloco A. Maracanã. CEP: 20.550-013, Rio de Janeiro, RJ, Brazil*

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*6Muséum National d'Histoire Naturelle, Institut de Physique des Matériaux et de Cosmochimie, Sorbonne Université, Paris, France*

*7Research Productivity of CNPq*

### ABSTRACT

The aftermath of the Marinoan glaciation (~635 Ma) recorded in cap carbonate sequences worldwide documents the continuous generation of accommodation space linked to the eustatic balance during post-glacial marine transgression. Basinward meltwater, devoid of siliciclastics, would have created density-stable stratified seawater, forming an anomalous scenario for the Puga cap carbonate precipitation on the Amazon margin. The duration of the post-glacial events and the transition from the syndeglacial stage to the long-term transgression are still controversial. Understanding how these Ediacaran stratified oceans were formed can be unraveled by a detailed reading of the chemical isotopic behavior throughout the cap carbonate record. Our research, which uses isotopic ( $\epsilon\text{Nd}$ ) compositions combined with  $\delta^{13}\text{C}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopes, has practical implications in tracing weathering sources and oceanic circulation during Puga cap carbonate precipitation along the Amazon margin. Our data shows similar Nd model ages (TDM) for the glacial diamictite (1.6 to 1.8 Ga) and cap dolostone (1.8-2.9 Ga), suggesting dominant Paleoproterozoic to Mesoproterozoic continental sources, with less radiogenic ( $-14$ )  $\epsilon\text{Nd}$  (635Ma) values and, variable and higher  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7264 to 0.7084). This isotopic composition demonstrates a strong influence of meltwater in cap dolostone precipitation. The intense chemical weathering of diamicton regoliths could homogenize the precipitation of Nd

seawater signatures of the cap dolomuds during syn-deglacial transgression. High  $^{87}\text{Sr}/^{86}\text{Sr}$  is also consistent with freshly exposed source rocks, as weathering leads to the preferential release of high  $^{87}\text{Sr}/^{86}\text{Sr}$  solutions, leaving a residual with low  $^{87}\text{Sr}/^{86}\text{Sr}$ . The association of more radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  values with the most negative  $\epsilon\text{Nd}(t)$  values reinforces the connection to the contribution of continental weathering in meltwater, which is associated with deglaciation processes and the rapid precipitation model. Contrastingly, the upsection is characterized by predominantly radiogenic (-6.3)  $\epsilon\text{Nd}$  values. The Nd isotope system exhibits a short residence time and is a reliable indicator of local environmental conditions. In this context, these Nd isotope changes, coupled with lower radiogenic values of  $^{87}\text{Sr}/^{86}\text{Sr}$ , delineate the geochemical response to the mingling of two distinct signatures and density water masses associated with upwelling events. The weathering contributes to increased biogeochemical cycles and abundant flourishing and growth of microbial communities in the Marinoan aftermath.  $\delta^{13}\text{C}$  values of -7. to -4‰ for the cap dolostone, are related to the recovery of paleoproductivity and Ediacaran paleoceanographic changes. The cap limestone in the upper portion occurs with the typical early Ediacaran seawater signature (0.7071-0.7073) and more radiogenic  $\epsilon\text{Nd}(t)$ . The geochemical trends explain the demise of stratified oceans associated with water mixing and a predominance of marine waters associated with long-term transgression.

**Keywords:** syndeglacial transgression; weathering; mixwater; upwelling events

## 6.1 INTRODUCTION

The termination of the Marinoan Snowball Earth glaciation also marks the end of the Cryogenian and the beginning of the Ediacaran period (~635Ma). A panglacial climate would have significantly limited biogeochemical cycling which would then have been restored and possibly transiently accelerated upon deglaciation (Kirschvink 1992, Hoffman and Schrag 2002, Corsetti and Lorentz 2006, Fairchild and Kennedy 2007, Rooney *et al.* 2015, Hoffman *et al.* 2017, 2021, Peng *et al.* 2022). Post-glacial cap carbonate sequences offer a critical window into the evolution of shallow water platform environments during this crucial time (Hoffman *et al.* 2017, Yu *et al.* 2020). One mode of observation of these environments is the isotopic compositions of various elements (e.g.,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$ , and  $\delta^{13}\text{C}$ ) and element concentrations (e.g., Sr, Fe, Mn, rare earth elements) within carbonate sequences (Nogueira *et al.* 2003, 2007, Font *et al.* 2006, Sansjofre *et al.* 2011, 2014, Hohl *et al.* 2017, 2022, Ren and Li 2023, Santos *et al.*

unpublished). One such sequence is the Puga cap carbonate, located on the southern margin of the Amazon Craton (Fig. 6. 1). This sequence is interpreted as formed via rapid precipitation within a shallow coastal marine environment (Santos *et al.* unpublished). Synsedimentary deformations at the base of the sequence, reinforce interpretations of rapid precipitation (Nogueira *et al.* 2003, Santos *et al.* 2023), and geochemical evidence supports that this occurred initially during the mixing of shallow and deep waters (Santos *et al.* unpublished). The plume-world model proposed by Shields (2005) suggests that rapid deglaciation resulted in cap carbonates forming on a  $10^3$  to  $10^4$  yr time scale, placing these units at the end of the fastest carbonate accumulation rates ever recorded (Nogueira *et al.* 2003, 2022, Santos *et al.* 2021, unpublished).

Modeling studies along with geochemical evidence have predicted that the interaction between meltwater and marine waters during deglaciation created a density-stable stratification with low-salinity surface waters sitting atop higher salinity deeper waters (Shield 2005, Liu *et al.* 2014, 2018, Yang *et al.* 2017, Hoffman *et al.* 2017). This regime has been estimated to have lasted  $10^4$ – $10^5$  yrs (Yang *et al.* 2017, Hoffman *et al.* 2017), has recently been reevaluated by Ramme and Marotzke (2022), and shortened to only thousands of years. This reassessment considered not only glacioisostatic adjustments but also intrinsic upwelling processes. Geochemical changes in the marine environment accompanying this destratification remain challenging to reconstruct due to the local and heterogeneous nature of how these events are mapped onto depositional environments. However, geochemical measurements applied to well-studied stratigraphy may provide such insight (Nogueira *et al.* 2003, Font *et al.* 2006, Hoffman *et al.* 2017).

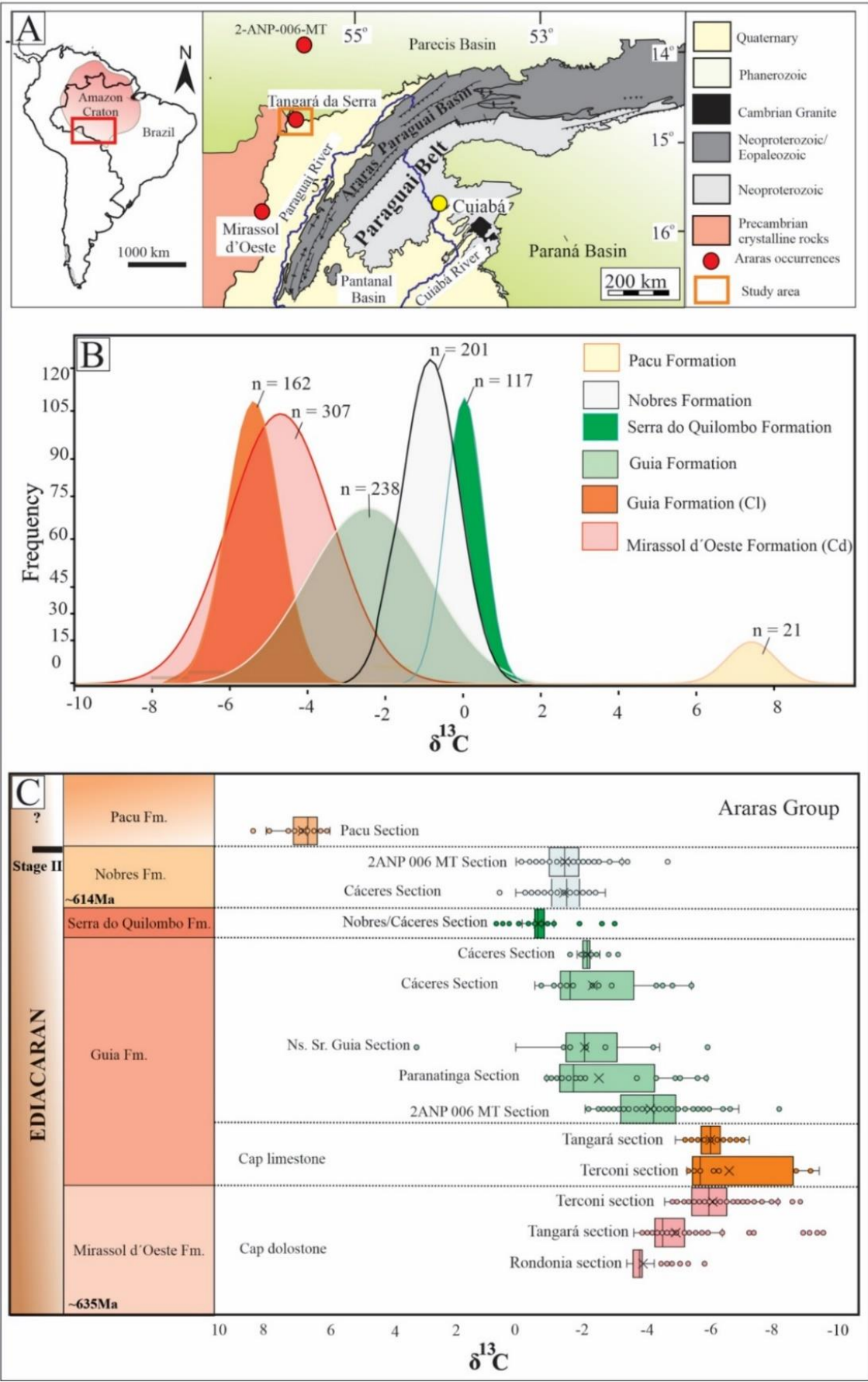
Two such systems can provide important insights into the exit from the Marinoan Snowball Earth Sr and Nd isotopes. Compared to  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, the Nd isotope system has a shorter residence time (~600 years) relative to the mixing time scales of the global ocean. Moreover, it is also less susceptible to early diagenetic exchange, and thus being an excellent marker of local environmental conditions (Banner *et al.* 1988, Burton and Vance 2000, Wei *et al.* 2019, Hohl *et al.* 2022). In addition, Nd isotopes can decipher weathering sources making it an informative tracer on the level of mass exchange between deglacial water masses and open ocean waters. That is, in conjunction with other isotopes such as  $\delta^{13}\text{C}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ , the Nd isotope could trace the mixtures of water masses, meltwater, and hypersaline water associated with the upwelling process. Our research, which

uses isotopic ( $\epsilon\text{Nd}$ ) compositions combined with  $\delta^{13}\text{C}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopes, has practical implications in tracing weathering sources and oceanic circulation. The shorter residence time and excellent preservation of the  $\epsilon\text{Nd}$  demonstrated that part of the Sr data is related to local trends on the Amazon margin along the Cryogenian-Ediacaran transition

## 6.2 GEOLOGIC BACKGROUND

The Araras Group encompasses a predominantly carbonate succession deposited in the intracratonic Araras Alto-Paraguai Basin on the Amazon Craton (Fig. 6.1) (Nogueira *et al.* 2019, 2022). The development of platforms during the extensional events of Gondwana's early stages, following the Brasiliano-Pan African orogeny (Alvarenga and Trompette, 1992, Trindade *et al.* 2003, Tohver *et al.* 2010), may have provided nearly complete exposure and minimal structural deformation across hundreds of square kilometers (Santos *et al.* 2020). Early sedimentation of these basins is associated with the Marinoan glaciation (~ 650-635 Ma) which is recorded in the glaciomarine deposits of the Puga Formation. Diamictites and dropstones characterize the base of the Puga Formation, which are then conformably overlain by cap carbonate in the WNW area and deepwater limestones of the Guia Formation to the distal portions (SSE and NE) of the basin (Alvarenga *et al.* 2004, 2010, Nogueira *et al.* 2007, 2022). The whole cap carbonate sequence (Araras Group, Fig. 6.1B), is divided from base to top into four formations (Fig. 6.1 C): 1) Mirassol d'Oeste (cap dolostone), composed of dolomitic layers interpreted as a shallow platform environment, 2) Guia (cap limestone), composed of carbonates and shales, interpreted as a moderately deep platform, 3) Serra do Quilombo, composed of shallow to moderately deep dolomitic platforms, and 4) Nobres, consisting of tidally influenced dolomites (Nogueira and Riccomini, 2006, Nogueira *et al.* 2003, 2007, 2019, 2022, Milhomen *et al.* 2013, Rudnitzki *et al.* 2016, Romero *et al.* 2020, 2022, Soares *et al.* 2013, 2020, Santos *et al.* 2021, 2023).





Caption on next page

Figure 6.1)- Location and simplified geologic map of the southwestern Amazon Craton with Neoproterozoic cap carbonate occurrences. The Cryogenian-Ediacaran boundary is exposed in the primary Araras carbonate succession overlying crystalline and metasedimentary rocks of the Precambrian basement in the southwestern and occurrence portions of the Amazon Craton. B) Density curves of the  $\delta^{13}\text{C}$  data of Araras Group following the proposed stratigraphy of Nogueira and Riccomini, 2006: Mirassol d'Oeste Formation (cap dolostone) this work and compiled from Nogueira *et al.* 2003, 2019, Alvarenga *et al.* 2004, 2008, Font *et al.* 2006, Sansjofre *et al.* 2011, Gaia *et al.* 2017, Santos *et al.* 2024). Guia Formation (cap limestone) is compiled from Nogueira *et al.* 2003, 2019, Alvarenga *et al.* 2004, 2008, Sansjofre *et al.* 2011). Guia Formation (Alvarenga *et al.* 2004, 2008, Nogueira *et al.* 2007, Alencar, 2017, Lamoso *et al.* 2023). Serra do Quilombo Formation is compiled by (Nogueira *et al.* 2007, Milhomen, 2012). Nobres Formation is compiled from (Nogueira *et al.* 2007, Rudninski 2015, Lamoso *et al.* 2023). And Pacu Formation? Are compiled by Souza (2015). C) Box-plot distribution of  $\delta^{13}\text{C}$  values for the Araras Group, comparing the mean values of the main occurrences across the Araras-Alto Paraguai Basin.

The Puga cap carbonate succession is part of the early sedimentation phases of the Araras Alto Paraguai intracratonic basin, located on the southern Amazon (Fig. 6.1A) (Nogueira *et al.* 2019, 2022, Santos *et al.* 2021, 2023). Outcrops are located in the Terconi and Tangará quarries which were deposited along the southern margin of the Amazon Craton (Nogueira *et al.* 2003, Soares *et al.* 2020, Santos *et al.* 2021). The base of the succession comprises massive, stratified, polymictic diamictite and dropstones of the Puga Formation, which overlies the Cuiabá Group (Paraguai belt) with an erosional and angular unconformity (Nogueira *et al.* 2003, 2019, Alvarenga *et al.* 2011). Clasts are dispersed in a grey-green to reddish-grey, fine siliciclastic matrix, with diameters ranging from a few centimeters to up to one meter. Clasts mainly consist of basement rocks (e.g., granite, gneiss, quartzite, quartz, schists), some of which deflect underlying laminae and display facets and striations as well as abundant detrital mica. Although variations in the relative proportions of the matrix (muddy sand) and clasts (Alvarenga and Trompette, 1992, Nogueira *et al.* 2003, Dantas *et al.* 2009, Alvarenga *et al.* 2011, Gaia *et al.* 2014, Santos *et al.* 2023) is displayed in the mostly massive diamictite, crude stratification is occasionally observed. Stratified diamictite includes centimeter-thick beds of massive diamictite associated with mudstone which exhibits graded bedding and outsized clasts that deflect underlying laminae (Nogueira *et al.* 2003, Alvarenga *et al.* 2011). The silty/sandy matrix occurs with millimeter to centimeter-sized dropstones and varies in composition (e.g., sandstone, gneiss, granite, volcanic) (Alvarenga and Trompette 1992, Nogueira *et al.* 2003, Santos *et al.* 2023). Together these observations describe the Puga Formation as a glacio-marine deposit associated with the Marinoan glaciation events (~ 650 - 635 Ma) and the establishment of the intracratonic Araras Alto-Paraguai basin in the Amazon Craton (Nogueira *et al.* 2003, 2019, Alvarenga *et al.* 2011, Santos *et al.* 2020, Santos *et al.* 2021, 2023). Detrital zircon maximum depositional ages for the diamictite Puga Formation are reported as  $< 706 \pm 9$  Ma by Babinski *et al.* (2013) and  $< 686 \pm 10$  Ma by McGee *et al.*

(2018). The Puga diamictite-cap dolostone contact also displays soft-sediment deformation possibly representing tectonic activity at the very early stages of the Marinoan glaciation aftermath or rapid deposition (Nogueira *et al.* 2003, 2007, 2019, 2022, Sansjofre *et al.* 2011, 2014, Crockford *et al.* 2021, Santos *et al.* 2021, 2023).

The carbonate platform establishment during the glacial aftermath was likely promoted by increasing accommodation space in response to the combination of glacial isostatic adjustment (GIA), long-term transgression, and local factors. In the Southern Amazon craton, subsidence rates allowed the development of the extensive post-glacial carbonate cover of the Araras Group. In this location, the Marinoan cap carbonate succession comprises dolomitic deposits (Mirassol d'Oeste Formation) and limestones (Guia Formation) in direct contact with the diamictites of the underlying Puga Formation (Nogueira *et al.* 2003, 2007, 2019, Soares *et al.* 2013, 2020, Romero *et al.* 2020, Santos *et al.* 2021). To date, this cap carbonate has been predominantly studied in four locations: Amazon Craton, around the regions of Mirassol d'Oeste and Tangará da Serra in Mato Grosso, Espigão d'Oeste, and Chupinguaia in Rondônia. The facies between locations are similar and laterally correlatable for hundreds of kilometers (Nogueira *et al.* 2003, 2019, Gaia *et al.* 2017, Soares *et al.* 2020). The base of the cap dolostone is composed of stratiform stromatolites with gypsum pseudomorphs, giant domical stromatolites with associated tubular structures, peloidal dolomudstone with parallel lamination, peloidal dolograstones with quasi-planar lamination, and peloidal dolopackstone with megaripples (Nogueira *et al.* 2003, Soares *et al.* 2020, Romero *et al.* 2020, Santos *et al.* 2021, 2023).

The cap limestone is commonly associated with the base of the Guia Formation, with a thickness of ~ 40m. It presents two primary microfacies, cement (crystal fans) and mudstone, which form distinct and closely associated layers. In addition, dolomitic marlstone, bituminous shales, and breccias are subordinate lithotypes in the Guia succession. The shale is predominantly calcitic (microcrystalline calcite) with well-developed fissility and is thus considered to belong to the calcareous mudstone facies. The dolomitic marlstone occurs at the contact between the Mirassol d'Oeste and Guia Formations. The mudstone microfacies are characterized by microcrystalline calcite interspersed with terrigenous grains. The cementstone microfacies are exclusively characterized by arborescent calcite crystals nucleated at the base of thin millimeter-scale cement crusts, forming fans with ascending radiation. Crystal fans occur in isolated and decimeter-scale arrays and are considered aragonite pseudomorphs. The facies association of the limestone cap indicates wave and storm-dominated shallow platforms transitioning into a CaCO<sub>3</sub>,

oversaturated moderately deep platform (Nogueira *et al.* 2003, 2007, 2019, Sansjofre *et al.* 2014, Soares *et al.* 2020, Carvalho *et al.* 2023). The diagenetic processes of the cap limestone were pyrite precipitation, calcite cementation, neomorphism of micrite and crystal fans, partial crystal fans dissolution, dolomitization, chemical compaction, fracturing, ferrous dolomite, and calcite precipitation (Soares *et al.* 2020, Santos *et al.* 2023).

In the cap dolostone deposits,  $\delta^{13}\text{C}$  values typically show a negative trend (Fig. 6.1 B), ranging from ca. -8 to -5 ‰, (mean =  $-4.46 \pm 1.25$  ‰,  $n = 307$ , with a poor correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ,  $R^2 = 0.23$ ) (Nogueira *et al.* 2003, 2007, 2019, Alvarenga *et al.* 2004, 2010, Font *et al.* 2006, Sansjofre *et al.* 2011, Santos *et al.* unpublished, and this work). These  $\delta^{13}\text{C}$  isotopic values (Fig. 6. 1B) confirm the previous interpretation of a post-glacial shallow marine paleoenvironment (Fig. 4) with favorable conditions for microbial colonization commonly found in the lower Ediacaran strata (REF). As the transgression continued, micrite precipitation occurred in an aragonitic sea, forming a moderately deep platform which is recorded in the cap limestone deposits (Fig. 6.1 C) (Lower Guia Formation) and show  $\delta^{13}\text{C}$  values from ca. -6 to -2‰ (mean =  $-5.4 \pm 0.65$ ‰,  $n = 168$ , and poor correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ,  $R^2 = 0.05$ ).

Advancements in carbonate radioisotopic dating provide a tentative age calibration of the Puga cap carbonate. Pb/Pb ages of  $633 \pm 30$ ,  $627 \pm 32$  (weighted mean ages of cap dolostone and limestone, Babinski *et al.* 2006, 2011),  $622 \pm 33$  and  $622 \pm 30$  Ma (cap limestone, Romero *et al.* 2013, Souza *et al.* 2024) indicate a Lower Ediacaran origin of this unit. The imprecision of these ages likely reflects the low spatial resolution of the Pb-Pb approach resulting in the homogenization of distinct depositional and diagenetic carbonate phases (Roberts *et al.* 2020, Soares *et al.* 2020, Carvalho *et al.* 2023). The U-Pb in situ age of  $622 \pm 3$  Ma obtained from seafloor crystal fans of the cap limestone (Carvalho *et al.*, 2023) was interpreted as a constraint on the transition from shallow to intermediate burial diagenesis (Carvalho *et al.* 2023) was interpreted as a constraint on the transition from shallow to intermediate burial diagenesis.  $^{87}\text{Sr}/^{86}\text{Sr}$  values of 0.7078 to 0.7098 for the cap dolostone, are much higher than expected for early Ediacaran seawater (ca. 0.7073). Such values may be attributed to a large inflow of continental waters (Romero *et al.* 2012) and enhanced weathering of platforms, exposed to moderate greenhouse conditions in the Marinoan aftermath (Sansjofre *et al.* 2011, Ramme *et al.* 2024).

### 6.3 MATERIALS AND METHODS

Samples in this study were collected from two drill cores and an outcrop (See supplementary material 1) at the Calcário Tangará quarry in the Tangará da Serra region of Mato Grosso, Central-Western Brazil (Fig. 6.1A). The JOR drill core is approximately 40m long (Fig. 6.5) and corresponds to the Ornamental open pit, and the JBN drill core (~ 32 m), of the Bananal open pit, both located in the same quarry (14° 45' 26" S, 57° 50' 02" W). The studied succession is approximately 90 meters thick in total (Fig. 6.2), with the initial 10 meters consisting of diamictites from the Puga Formation (Details of the facies are presented in supplementary material 1).

#### 6.3.1 Carbon and oxygen isotope analyses

Fifty samples were collected from a core (JBN-10) of approximately 20 m in depth and 5 cm in diameter at intervals of 40 cm, corresponding to the basal portion of the Mirassol d'Oeste Formation in the Tangará da Serra-MT section (Fig. 6.2). An agate mortar and pestle was used to pulverize approximately 3 g of homogeneous pinky dolomicrite domains from each sample. When greater precision was required to avoid recrystallized portions or those affected by diagenetic fluids, a diamond drill with approximately 1 mm diameter was employed. The samples were analyzed at the Laboratory of Chemostratigraphy and Organic Geochemistry (LGQM) at the State University of Rio de Janeiro (UERJ) using a Kiel IV Carbonate Device and a Delta V Plus - Isotope Ratio MS analyzer (Thermo Scientific). Procedures recommended by Craig (1957) were followed. Initially, the samples were placed in plastic containers, washed with distilled water and alcohol, and left to dry. Subsequently, they were reacted with 100% orthophosphoric acid at 25°C for 12 hours. The results are presented in  $\delta$  (‰) notation calibrated to V-PDB (Vienna Pee Dee Belemnite).

#### 6.3.2 Strontium-Neodymium isotope analyses

Whole-rock isotope analyses were conducted at the Laboratory of Isotopic Geology (LGI) at the Center for Petrology and Geochemistry Studies (CPGq) at the Federal University of Rio Grande do Sul (UFRGS) and at the Geochronology Laboratory of the Institute of Geosciences, University of Brasília (UNB). A total of 18 samples were analyzed at UFRGS, comprising ten diamictite samples and eight carbonate samples, while six carbonate samples were analyzed at UNB. For carbonate rocks analysis, approximately 10–20 ml of the acetic acid leachate stock solution was utilized for Sr and Nd isotopic composition measurements. The aliquots were dried, treated three times with 1 ml of

concentrated  $\text{HNO}_3$  at  $110^\circ\text{C}$ , and equilibrated in 2.5 M HCl. For diamictite rocks analysis, aliquots containing approximately 100 mg of sample were weighed on a high-precision balance and dissolved in stages, including the use of a concentrated acid mixture of  $\text{HNO}_3$  and HF in Savillex® PFA vials and a hot plate, followed by treatment with concentrated HCl. For the Sm/Nd analyses of the diamictites, approximately 100  $\mu\text{g}$  of sample powder was mixed with a  $^{149}\text{Sm}/^{150}\text{Nd}$  spike solution in Savillex vials. Any residues were dissolved with aqua regia until the solution became clear. After drying, the material was diluted in 2.5 M HCl to generate a stock solution. Reagents were purified by sub-boiling distillation, and dilutions were carried out with ultrapure Milli-Q water. Sr and REE extraction were performed using acid washes in Teflon columns with Biorad AG® 50W-X8 cation exchange resin. From the concentrated REE fraction, Sm and Nd were separated using quartz columns packed with Eichron Ln Spec resin. Sr, Sm and Nd concentrates were collected in Savillex® vials and dried on a hot plate for subsequent mass spectrometry analysis.

#### 6.3.2.1 Analytical Procedures

For analysis, Sr and Nd salts were dissolved in 2  $\mu\text{L}$  of phosphoric acid ( $\text{H}_3\text{PO}_4$ , 0.25M) and 2  $\mu\text{L}$  of nitric acid ( $\text{HNO}_3$ , 0.25M), respectively. Pre-degassed rhenium double filaments were utilized. Analyses were performed utilizing the Thermo Scientific™ TRITON multi-collector thermal ionization mass spectrometer (TIMS) at UFRGS. ICP-MS (Neptune Series High-Resolution Multicollector ICP-MS) equipped with 9 Faraday cup detectors, a central electron multiplier, and 5 MIC (multi-ion channel) ion counters was utilized at UNB. For Sr, 150 isotopic ratios were obtained for each sample, integrated, and normalized to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ . For Nd, 210 isotopic ratios were obtained for each sample whenever possible, and integrated. The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio was normalized to the  $^{146}\text{Nd}/^{144}\text{Nd}$  ratio of 0.7219. Analysis of the NBS-987 (Sr) and JNdi (Nd) reference materials are routinely used for instrumental variation monitoring and all results obtained for these batches were within the laboratory's historical range and are consistent with literature reports. No instrumental analytical deviation correction was necessary. Blank and reference material analyses (BHVO-2 and BCR-2) are routinely performed for quality control. After reduction, TDM values were calculated using the model De Paolo (1981).

## 6.4 RESULTS

### 6.4.1 Isotopic Signatures of the Puga Cap Carbonate Sequence

The Nd results, including  $\epsilon\text{Nd}$  and model ages (Nd-TDM), are shown in Table 6.2. The  $^{143}\text{Nd}/^{144}\text{Nd}$  values vary from 0.50844 to 0.51209 for diamictite samples and from 0.5115908 to 0.512093 for cap dolostone samples. The analyzed diamictite pebbles, e.g., gneissic, mafic, ultramafic, and granitic rocks (See supplementary material 1), exhibit variable TDM values (1.6–1.8). Ga)  $\epsilon\text{Nd}(635)$  around -4 to -11 (Fig. 6.4 B). On the other hand, the matrix of the diamictite displays variable TDM values (1.5–3.7 Ga) and  $\epsilon\text{Nd}(635)$  around -5 to -30. Cap dolostones in the Tangará section exhibit lower  $\epsilon\text{Nd}(t)$  values ranging from -14.9 to -6.34, with high Nd concentrations ranging from 1.45 ppm to 5.67 ppm (Fig. 6. 2 and Fig. 6. 4). They also present lower  $\epsilon\text{Nd}(635)$  values, closer to those reported for the matrix of the diamictite with variable TDM values (1.8–2.9 Ga) (Table 6.1).

The  $\delta^{13}\text{C}$  analyses of the basal 20 m cap dolostone resulted in values ranging from ca. - 7 to -4 ‰ (Fig. 6.3). The basal seven m-thick stratiform stromatolites with pseudomorph evaporite cement and fenestral porosity displayed the most negative and variable values, with shifts between ca. -7 and -4 ‰, which stabilize (ca. -5 ‰) in the next three meters. In the intermediate portion of the section (ca. 10-20 m), corresponding to the horizon with giant domal stromatolites,  $\delta^{13}\text{C}$  values show a smooth decrease from ca. -4 to -7 ‰ (See Supplementary Table 6.1). Then values recover to ca. -5‰ along the grainstone/peloidal dolomudstone, partly coinciding with the interval shown by Sansjofre *et al.* (2011), Nogueira *et al.* (2019) and Santos *et al.* (2024). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in cap dolostones range from 0.72637 to 0.70842 (Fig. 6. 2). The new data presented are predominantly associated with microbialites and complement the  $^{87}\text{Sr}/^{86}\text{Sr}$  chemostratigraphy of the profile previously presented by Romero *et al.* 2013 and Souza *et al.* 2024, which covers the reworked facies of cap dolostone (0.7077 -0.70975) and cap limestone (0.70709-0.70729) (Fig. 6.2 and Table 6.1).



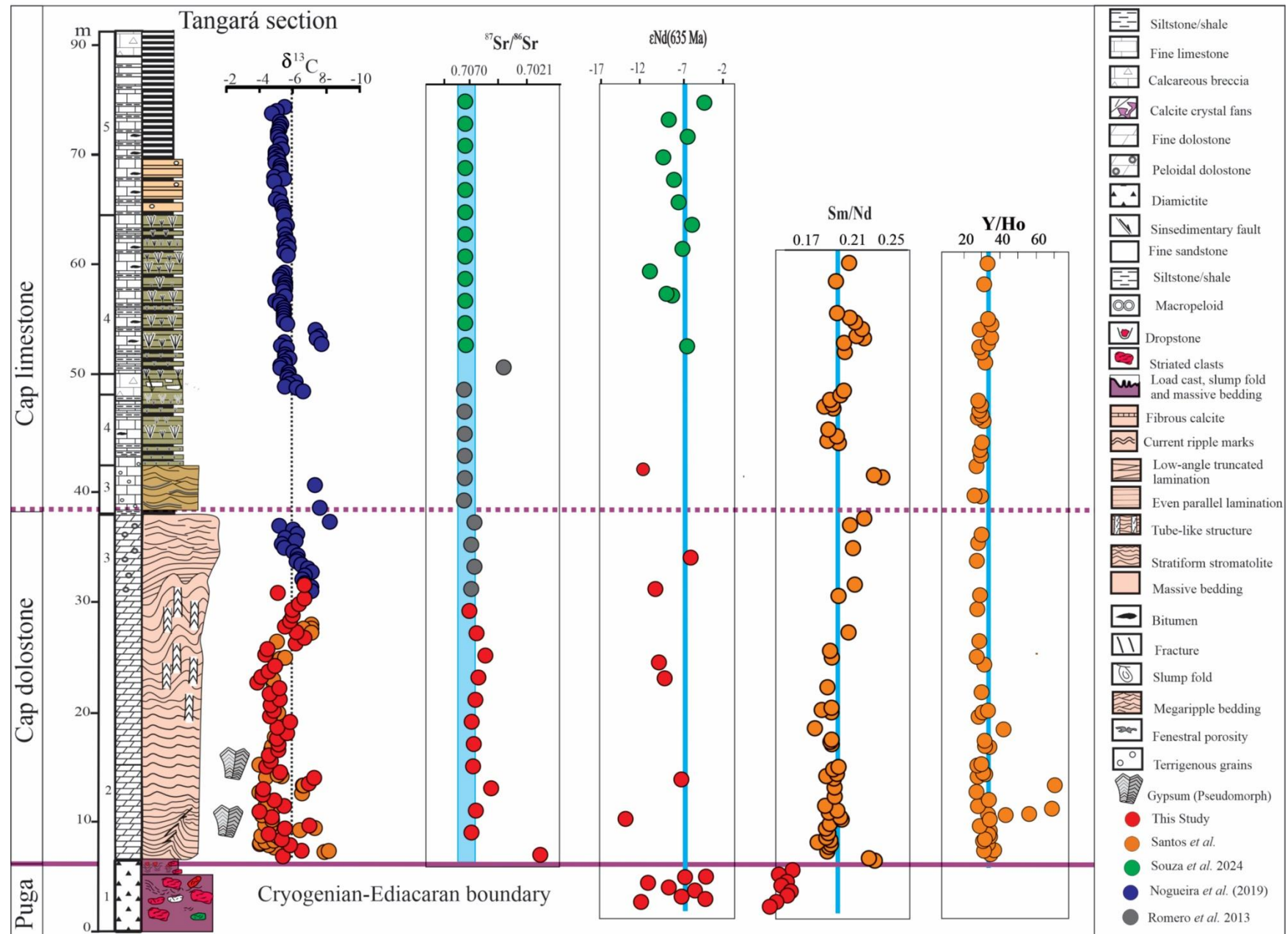


Figure 6.2- Stratigraphic and chemostratigraphic data of the Puga cap carbonate at the Tangará section.  $\delta^{13}\text{C}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ , and  $\epsilon\text{Nd}(t)$  isotopic compositions were obtained from the Puga cap carbonate. Neodymium isotope compositions are plotted as initial epsilon values (i.e., radiogenic decay corrected), assuming a depositional age of 635 Ma. The data were obtained in this study and compiled from previous studies to complete the succession:  $\delta^{13}\text{C}$  (Sansjofre *et al.* 2011, Nogueira *et al.* 2019, Santos *et al.* unpublished),  $^{87}\text{Sr}/^{86}\text{Sr}$  (Romero *et al.* 2013, Souza *et al.* 2024), and  $\epsilon\text{Nd}(t)$  (Souza *et al.* 2024).



Table 6.1- Sr isotopic analyses for carbonate samples by sequential leaching steps (JOR) from cap dolostone (this work) and cap limestone (CT3-11) by Romero *et al.* (2013) and (L1–L9) by Souza *et al.* (2024) for the Puga cap carbonate succession in the Tangará section.

| Samples  | $^{87}\text{Sr}/^{86}\text{Sr}$ | error (abs,) 2SE |               |                           |
|----------|---------------------------------|------------------|---------------|---------------------------|
| JBN-10T  | 0,81195                         | 0,00001          | Diamicite     | This study                |
| JBN-10BT | 0,86674                         | 0,00005          | Diamicite     | This study                |
| JBN-10BM | 0,84952                         | 0,00007          | Diamicite     | This study                |
| JBN-10BC | 0,91072                         | 0,00005          | Diamicite     | This study                |
| JOR 1    | 0,72637                         | 0,000008         | Cap dolostone | This study                |
| JOR-2    | 0,70898                         | 0,00018          | Cap dolostone | This study                |
| JOR-33   | 0,70802                         | 0,00002          | Cap dolostone | This study                |
| Jor-42   | 0,71011                         | 0,00007          | Cap dolostone | This study                |
| JOR 58   | 0,71393                         | 0,000003         | Cap dolostone | This study                |
| Jor-93   | 0,70940                         | 0,00004          | Cap dolostone | This study                |
| Jor-101  | 0,70953                         | 0,00025          | Cap dolostone | This study                |
| JOR 124  | 0,70904                         | 0,000003         | Cap dolostone | This study                |
| Jor-138  | 0,70999                         | 0,00005          | Cap dolostone | This study                |
| Jor-170  | 0,71073                         | 0,00004          | Cap dolostone | This study                |
| Giant 1  | 0,70951                         | 0,000002         | Cap dolostone | This study                |
| Giant 2  | 0,71246                         | 0,000015         | Cap dolostone | This study                |
| Jor-184  | 0,71026                         | 0,00002          | Cap dolostone | This study                |
| JOR 189  | 0,70842                         | 0,000002         | Cap dolostone | This study                |
| CT1-10   | 0,70891                         | 0.000222         | Cap dolostone | Romero <i>et al.</i> 2013 |
| CT1-9    | 0,70973                         | 0.000141         | Cap dolostone | Romero <i>et al.</i> 2013 |
| CT1-8    | 0,70894                         | 0.000386         | Cap dolostone | Romero <i>et al.</i> 2013 |
| CT1-6    | 0,70975                         | 0.000337         | Cap dolostone | Romero <i>et al.</i> 2013 |
| CT3-11   | 0.707098                        | 0.000026         | Cap limestone | Romero <i>et al.</i> 2013 |
| CT3-9    | 0.707260                        | 0.000015         | Cap limestone | Romero <i>et al.</i> 2013 |
| CT3-7    | 0.707250                        | 0.000036         | Cap limestone | Romero <i>et al.</i> 2013 |
| CT3-6    | 0.707274                        | 0.000028         | Cap limestone | Romero <i>et al.</i> 2013 |
| CT3-3    | 0.707232                        | 0.000013         | Cap limestone | Romero <i>et al.</i> 2013 |
| CT3-1    | 0.707101                        | 0.000012         | Cap limestone | Romero <i>et al.</i> 2013 |
| CT2-2    | 0.717139                        | 0.001597         | Cap limestone | Romero <i>et al.</i> 2013 |
| TS-125   | 0.707548                        | 0,000069         | Cap limestone | Souza <i>et al.</i> 2024  |
| TS-121   | 0.707366                        | 0,000042         | Cap limestone | Souza <i>et al.</i> 2024  |
| TS-114   | 0.707696                        | 0,000012         | Cap limestone | Souza <i>et al.</i> 2024  |
| TS-107   | 0.707595                        | 0,000024         | Cap limestone | Souza <i>et al.</i> 2024  |
| TS-093   | 0.707224                        | 0,000015         | Cap limestone | Souza <i>et al.</i> 2024  |
| TS-080   | 0.707362                        | 0,000057         | Cap limestone | Souza <i>et al.</i> 2024  |
| TS-073   | 0.707192                        | 0,000041         | Cap limestone | Souza <i>et al.</i> 2024  |
| TS-069   | 0.707534                        | 0,000077         | Cap limestone | Souza <i>et al.</i> 2024  |
| TS-060   | 0.707251                        | 0,000031         | Cap limestone | Souza <i>et al.</i> 2024  |
| TS-056   | 0.707075                        | 0,000049         | Cap limestone | Souza <i>et al.</i> 2024  |
| TS-050   | 0.707051                        | 0,000011         | Cap limestone | Souza <i>et al.</i> 2024  |
| CT3-11   | 0.707088                        | 0,000031         | Cap limestone | Souza <i>et al.</i> 2024  |

Table 6.2- Sm-Nd isotopic data for the Puga cap carbonate, Puga diamictite, and cap dolostone (Mirassol d'Oeste Formation) (this work) and cap limestone (Guia Formation) by Souza *et al.* (2024) at the Calcário Tangará Quarry. The data from the Terconi section by Dantas *et al.* (2009).

|                        |                                               |                                               |           |                        |           |               | continue                  |
|------------------------|-----------------------------------------------|-----------------------------------------------|-----------|------------------------|-----------|---------------|---------------------------|
| Samples                | $^{143}\text{Nd}/^{144}\text{Nd}_{\text{am}}$ | $^{147}\text{Sm}/^{144}\text{Nd}_{\text{am}}$ | f (Sm-Nd) | $\epsilon\text{Nd}(t)$ | T DM (Ga) |               | Author                    |
| Bulk rock-10T          | 0,51164                                       | 0,1051                                        | -0,466    | -12,21                 | 2,0       | Diamictite    | This study                |
| Bulk rock-10TB         | 0,51073                                       | 0,1165                                        | -0,408    | -30,75                 | 3,7       | Diamictite    | This study                |
| Matrix-10-BM           | 0,51205                                       | 0,1157                                        | -0,412    | -4,97                  | 1,5       | Diamictite    | This study                |
| Pebble-10-BC           | 0,51192                                       | 0,1199                                        | -0,391    | -7,87                  | 1,8       | Diamictite    | This study                |
| Matrix-JBN             | 0,51197                                       | 0,1109                                        | -0,436    | -6,07                  | 1,6       | Diamictite    | This study                |
| Matrix-RJBN            | 0,51181                                       | 0,1115                                        | -0,433    | -9,29                  | 1,8       | Diamictite    | This study                |
| Gnaiss pebble-JBN      | 0,50844                                       | 0,2437                                        | 0,239     | -85,85                 | #NUM!     | Diamictite    | This study                |
| Rhyolite pebble-JBN    | 0,51163                                       | 0,0941                                        | -0,522    | -11,45                 | 1,8       | Diamictite    | This study                |
| Mafic pebble-JBN       | 0,51188                                       | 0,1052                                        | -0,465    | -7,42                  | 1,6       | Diamictite    | This study                |
| Ultramafic pebble- JBN | 0,51209                                       | 0,12062                                       | -0,387    | -4,54                  | 1,6       | Diamictite    | This study                |
| Mira 14                | 0,51198                                       | 0,1386                                        | -0,2954   | -8,1                   | 2,2       | Diamictite    | Dantas <i>et al.</i> 2009 |
| Araras 9               | 0,511939                                      | 0,1206                                        | -0,3871   | -7,5                   | 1,8       | Diamictite    | Dantas <i>et al.</i> 2009 |
| CAC 17                 | 0,511905                                      | 0,1205                                        | -0,3874   | -8,1                   | 1,9       | Diamictite    | Dantas <i>et al.</i> 2009 |
| FS 90                  | 0,511973                                      | 0,1226                                        | -0,3767   | -7,0                   | 1,8       | Diamictite    | Dantas <i>et al.</i> 2009 |
| Granite pebble         | 0,511855                                      | 0,1195                                        | -0,3925   | -9,0                   | 1,9       | Diamictite    | Dantas <i>et al.</i> 2009 |
| basic pebble           | 0,512046                                      | 0,1377                                        | -0,2999   | -6,8                   | 2,0       | Diamictite    | Dantas <i>et al.</i> 2009 |
| gneiss pebble          | 0,511958                                      | 0,1338                                        | -0,3198   | -8,2                   | 2,1       | Diamictite    | Dantas <i>et al.</i> 2009 |
| JOR-2                  | 0,5116691                                     | 0,1404                                        | -0,2864   | -14,3                  | 2,9       | Cap Dolostone | This study                |
| JOR-22                 | 0,5115908                                     | 0,1168                                        | -0,4060   | -14,0                  | 2,3       | Cap Dolostone | This study                |
| Jor-42                 | 0,5119505                                     | 0,1225                                        | -0,3773   | -7,4                   | 1,8       | Cap Dolostone | This study                |
| Jor-93                 | 0,5118293                                     | 0,1175                                        | -0,4025   | -9,4                   | 1,9       | Cap Dolostone | This study                |
| Jor-101                | 0,5118391                                     | 0,1284                                        | -0,3474   | -10,1                  | 2,2       | Cap Dolostone | This study                |
| Jor-138                | 0,5118291                                     | 0,1311                                        | -0,3335   | -10,5                  | 2,2       | Cap Dolostone | This study                |
| Jor-170                | 0,512093                                      | 0,1434                                        | -0,2712   | -6,3                   | 2,1       | Cap Dolostone | This study                |

conclusion

| Samples | $^{143}\text{Nd}/^{144}\text{Nd}_{\text{am}}$ | $^{147}\text{Sm}/^{144}\text{Nd}_{\text{am}}$ | f (Sm-Nd) | $\epsilon\text{Nd}(t)$ | T DM (Ga) |               | Author                    |
|---------|-----------------------------------------------|-----------------------------------------------|-----------|------------------------|-----------|---------------|---------------------------|
| MIRA 7  | 0,511905                                      | 0,1203                                        | -0,3885   | -8,1                   | 1,9       | Cap Dolostone | Dantas <i>et al.</i> 2009 |
| CAC 15B | 0,511905                                      | 0,1164                                        | -0,4080   | -7,8                   | 1,8       | Cap Dolostone | Dantas <i>et al.</i> 2009 |
| TS-125  | 0,512042                                      | 0,1365                                        | -0,3060   | -6,7                   | 2,0       | Cap Limestone | Souza <i>et al.</i> 2024  |
| TS-121  | 0,511935                                      | 0,1354                                        | -0,3116   | -8,8                   | 2,2       | Cap Limestone | Souza <i>et al.</i> 2024  |
| TS-114  | 0,511838                                      | 0,1408                                        | -0,2842   | -11,1                  | 2,5       | Cap Limestone | Souza <i>et al.</i> 2024  |
| TS-107  | 0,512055                                      | 0,1460                                        | -0,2578   | -7,3                   | 2,2       | Cap Limestone | Souza <i>et al.</i> 2024  |
| TS-093  | 0,511932                                      | 0,1364                                        | -0,3066   | -8,9                   | 2,2       | Cap Limestone | Souza <i>et al.</i> 2024  |
| TS-080  | 0,51206                                       | 0,1337                                        | -0,3203   | -6,2                   | 1,9       | Cap Limestone | Souza <i>et al.</i> 2024  |
| TS-073  | 0,511976                                      | 0,1328                                        | -0,3249   | -7,7                   | 2,0       | Cap Limestone | Souza <i>et al.</i> 2024  |
| TS-069  | 0,511965                                      | 0,1369                                        | -0,3040   | -8,3                   | 2,1       | Cap Limestone | Souza <i>et al.</i> 2024  |
| TS-060  | 0,511887                                      | 0,1334                                        | -0,3218   | -9,5                   | 2,2       | Cap Limestone | Souza <i>et al.</i> 2024  |
| TS-056  | 0,51206                                       | 0,1398                                        | -0,2893   | -6,7                   | 2,0       | Cap Limestone | Souza <i>et al.</i> 2024  |
| TS-050  | 0,511921                                      | 0,1339                                        | -0,3193   | -8,9                   | 2,1       | Cap Limestone | Souza <i>et al.</i> 2024  |
| CT3-11  | 0,512167                                      | 0,1416                                        | -0,2801   | -4,7                   | 1,8       | Cap Limestone | Souza <i>et al.</i> 2024  |

## 6.5 DISCUSSION

### 6.5.1 Evaluation of detrital silicate contamination and fluid overprints on the geochemical composition of cap dolostone

The geochemical behavior of the Puga diamictite and cap carbonate can be interpreted by tracking isotopic trends in multiproxies cross plots (Fig. 6.2). These cross plots were constructed from Nd ( $\epsilon\text{Nd}$  (635)),  $\delta^{13}\text{C}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios obtained here and in previous studies (including the underlying metasedimentary sequence) (Dantas *et al.* 2009, Sansjofre *et al.* 2011, Nogueira *et al.* 2019, Souza *et al.* 2024). Additionally, considering published minor and major element concentration data (Romero *et al.* 2012, Sansjofre *et al.* 2014, Santos *et al.* unpublished), rocks showed general preservation of depositional compositions with local diagenetic alteration. To have confidence in Sr-Nd-C-O trends throughout the Puga cap carbonates, it is essential to investigate how

diagenetic processes affect their isotopic compositions thoroughly. Additionally, it is crucial to consider the potential for contamination from non-carbonate minerals (e.g., aluminosilicates). Sequential leaching procedures were instrumental in identifying significant  $^{87}\text{Sr}/^{86}\text{Sr}$  variations in each sample which are challenging to explain through shifts in seawater chemistry. These isotopic fluctuations may result from external influences, such as the input of terrigenous grains from the continent during carbonate deposition (Romero *et al.* 2013, Souza *et al.* 2024). Zr, Th, and Al, concentrated in different detrital minerals, are generally used to test the influence of detrital contamination (Frimmel, 2009). Incorporating terrigenous silicate detrital components in geochemical sampling may affect the results of measured marine carbonates (Wei *et al.* 2019).

Our data shows a low correlation between  $^{87}\text{Sr}/^{86}\text{Sr}$  and Al ( $R^2 = 6 \times 10^{-5}$ ). This evidence suggests that there is no siliciclastic contamination influencing the samples' primary Sr and Nd isotopic signatures, which is consistent with the findings of Romero *et al.* (2013), who demonstrated  $R^2 = 0.0145$  for the cap dolostone and  $R^2 = 0.0329$  for the cap limestone from the same succession. Additionally, samples in this study, previously analyzed by Santos *et al.* (unpublished), show low Zr (mean = 0.1 ppm), Th (mean = 0.1 ppm), and Al (mean = 73 ppm). However, the values described here for the cap dolostone have a significant variation, characterized by radiogenic values. These elements present a low systematic correlation with  $\Sigma\text{REE}$ , suggesting a low impact of detrital contribution on the geochemical signatures of the cap dolostone.

These variations could be attributed to exotic Sr introduced through diagenetic processes involving interaction between rocks and fluids. The influence of diagenetic alteration on the isotopic compositions of fluid mobile  $\delta^{18}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  has been studied in detail for Proterozoic (Derry *et al.* 1989) and Phanerozoic samples (e.g., Brand and Veizer, 1980, 1981, Banner and Hanson, 1990, Jacobsen and Kaufman, 1999). The succession, as well as the samples studied here, have been extensively investigated in terms of mineralogical and diagenetic aspects, and it has been shown that the impact of post-depositional fluids has had little effect on the primary geochemistry of these units (Soares *et al.* 2020, Santos *et al.* 2023). The succession mainly comprises dolomicrite, pseudomorphs of gypsum, and ferrous calcite. The paragenetic relationships of the cap dolostone have revealed a predominance of early diagenetic process (Soares *et al.* 2020, Santos *et al.* 2023)

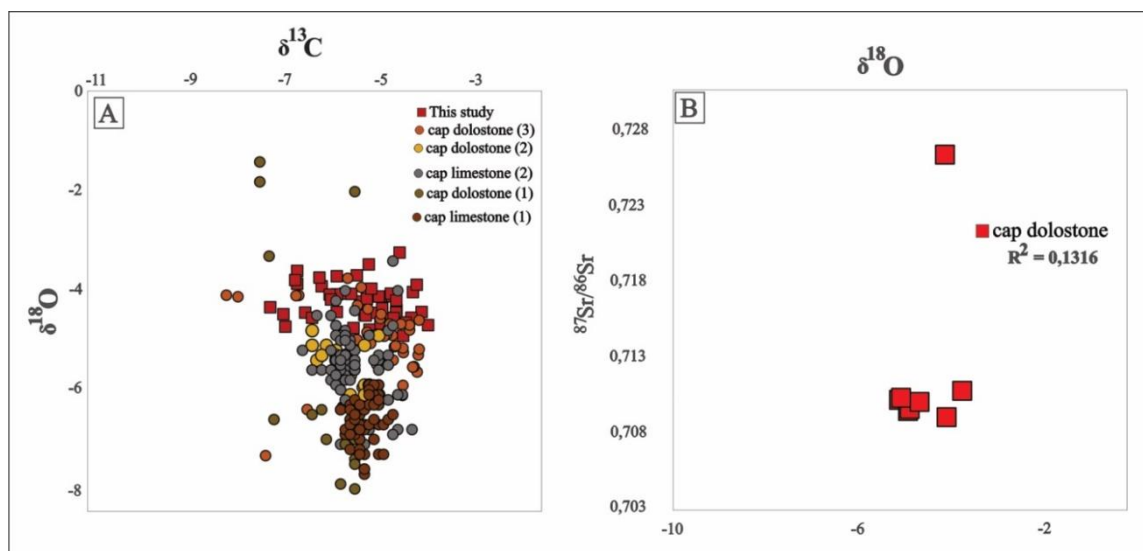


Figure 6.3- A) Cross-plots of  $\delta^{13}\text{C}$  vs.  $\delta^{18}\text{O}$  compositions of the carbonate fraction in the Puga cap carbonate from the southern Amazon Craton. New data from this study and compiled data from 1) Nogueira *et al.* 2019, 2) Sansjofre *et al.* 2011, and 3) Santos *et al.* unpublished. B) Cross-plots of  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $\delta^{18}\text{O}$ ,  $R^2 = 0.13$ .

Seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  composition is controlled by the influx of Sr from two main primary sources: continental weathering (fluvial) and hydrothermal activity (Palmer and Elderfield 1985, Palmer and Edmond 1989, Zachos *et al.* 1999, Antonelli *et al.* 2017, Peucker-Ehrenbrink and Fiske 2019) and seafloor weathering (hydrothermal systems increased rates of rock dissolution (Coogan and Dosso 2015)). Diagenetic alteration often results in the elevation of primordial  $^{87}\text{Sr}/^{86}\text{Sr}$  depositional ratios due to the contribution of radiogenic Sr derived from interaction with Rb-rich fluids (Cui *et al.* 2020). Early dolomitization may have enhanced the exceptional preservation of the Puga cap dolostone (Soares *et al.* 2020, Santos *et al.* 2023). Our data demonstrated a poor correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  ( $R^2 = 0.026$ , Fig. 6.3A) and poor correlations of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  with  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $R^2 = 0.32$  for  $\delta^{13}\text{C}$ ,  $R^2 = 0.13$  for  $\delta^{18}\text{O}$ , Fig. 6.3 B) which provides evidence for negligible diagenetic alteration. Mn/Sr vs.  $\delta^{18}\text{O}$  display an absence correlation ( $R^2 = 0.017$ ). On the other hand, a negligible correlation is observed for Sr/Ca ratios when plotted against  $\delta^{18}\text{O}$  ( $R^2 = 0.43$ ) and Mg/Ca ratios ( $R^2 = 0.40$ ). Despite the low correlation, our data have a more significant relationship with syndepositional dolomitization (Sr/Ca and Mg/Ca) than post-stabilization changes in dolomite (Santos *et al.* unpublished). Nevertheless, despite variable radiogenic values, Sr tests with O indicate a low influence of intermediate to deep burial diagenetic processes on the Puga cap dolostone (Fig. 6.3 B). Gypsum pseudomorphs suggest early dolomitization may have influenced Sr isotope compositions (Santos *et al.* 2021, 2023). In addition, compared with the  $^{87}\text{Sr}/^{86}\text{Sr}$  system,

which is sensitive to differential weathering of Rb-rich silicate minerals in the post-glaciation (Blum and Erel, 1995, Anderson *et al.* 1997), the  $^{143}\text{Nd}/^{144}\text{Nd}$  system is relatively less susceptible to incongruent weathering of different silicate minerals (Bayon *et al.* 2015).

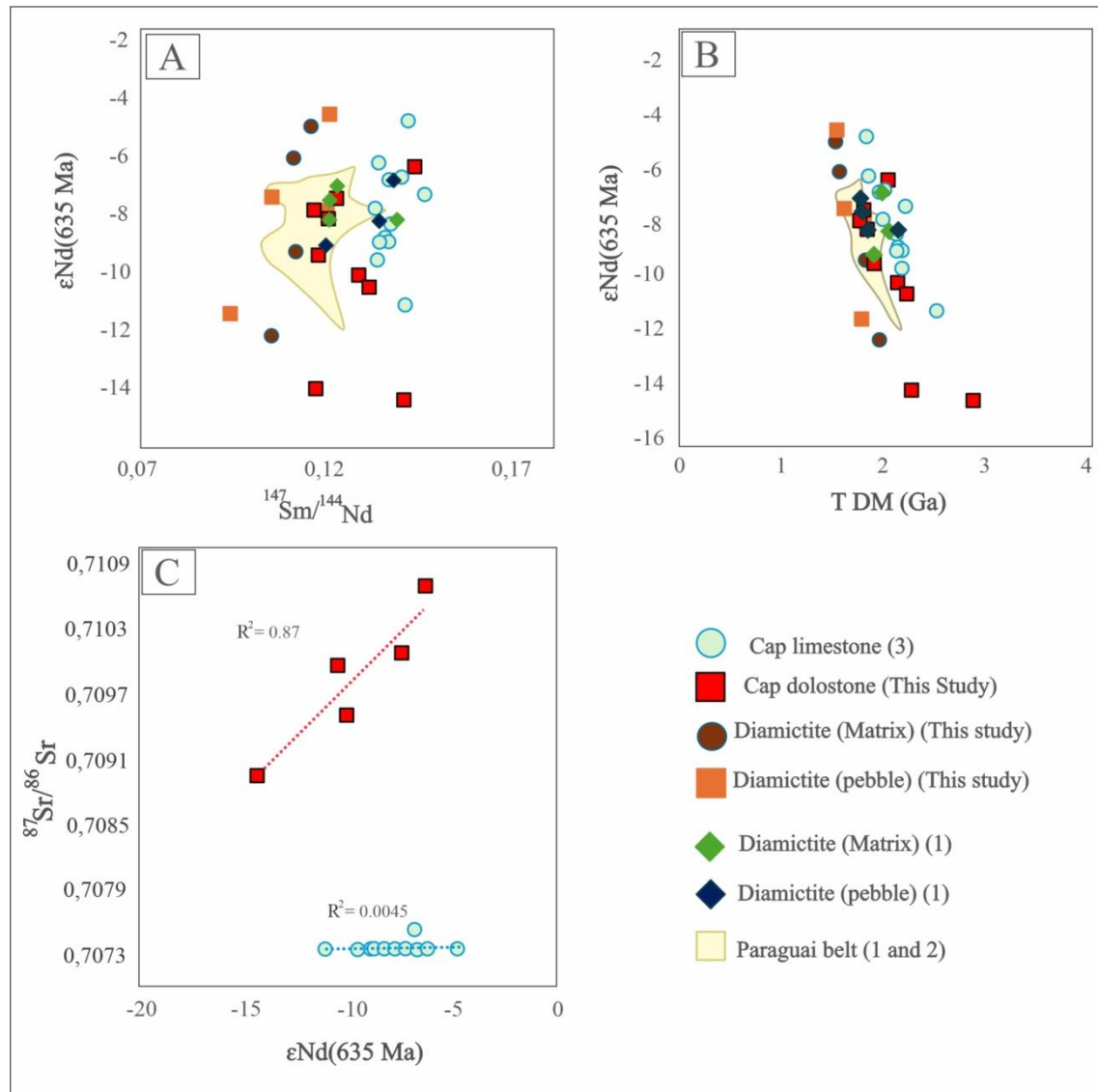


Figure 6.4- Cross-plots of  $\epsilon\text{Nd}(t)$  values vs A)  $^{147}\text{Sm}/^{144}\text{Nd}$  and B) TDM model age. Cross-plots of  $^{143}\text{Nd}/^{144}\text{Nd}$  vs. C)  $^{87}\text{Sr}/^{86}\text{Sr}$ . Data of the Puga cap carbonate sequence, including cap dolostone and Puga diamictite (this study), and cap limestone data (Souza *et al.* 2024) from the Tangará da Serra region, compared with the Paraguai Fold Belt (Dantas *et al.* 2006, Babinski *et al.* 2008) and Puga diamictite from the Terconi section (Dantas *et al.* 2006).

These observations suggest that our samples have preserved their original Sr and Nd isotopic compositions with minimal influence from detrital contamination or diagenetic alteration. This evidence is corroborated by the trace element analysis conducted by Santos *et al.* unpublished, which supports the notion that REE + Y and  $\delta^{13}\text{C}$  in the cap dolostone serve as pristine geochemical indicators. Importantly, the well-preserved isotopic compositions of Nd, Sr, and  $\delta^{13}\text{C}$  isotopes within the Puga cap carbonate, allow for the reconstruction of environmental conditions following the Marinoan Glaciation along the Amazon Craton.

### 6.5.2 $\delta^{13}\text{C}$ Chemostratigraphy of the cap dolostone

The  $\delta^{13}\text{C}_{\text{carb}}$  profile of the Marinoan cap dolostones studied here, shows only a minor scatter (mean =  $-5.23 \pm 0.84$  ‰,  $n = 48$ ), closely resembling those presented previously by Santos *et al.* for the same section (Fig. 6.2). The minimal sample-to-sample variation, weak correlation with  $\delta^{18}\text{O}$  isotopes (Fig. 6.3A), and weak correlation with Mg/Ca values suggests that dolomitization was syndepositional (Santos *et al.* unpublished). The Puga cap carbonate microfabrics and geochemistry indicate that syndepositional to early diagenetic processes have exerted the primary influence on this unit (Romero *et al.* 2013, Sansjofre *et al.* 2011, 2014, Soares *et al.* 2020, Carvalho *et al.* 2023, Santos *et al.* 2023, 2024). Negative  $\delta^{13}\text{C}$  values in Marinoan cap dolostone were initially interpreted as a product of post-glacial upwelling from a deep ocean enriched with  $\delta^{12}\text{C}$ , leading to a low  $\delta^{13}\text{C}$  value (Kaufman *et al.* 1991, Grotzinger and Knoll 1995). Other proposed explanations include the release of isotopically light gas hydrates associated with methanogenesis (Kennedy *et al.* 2001, Jiang *et al.* 2003), a catastrophic temperature increase, and a kinetic isotopic effect related to the rapid sedimentation of carbonates (Higgins and Schrag, 2003). Additionally, Rayleigh distillation from a large atmospheric reservoir of  $\text{CO}_2$  has been considered (Hoffman *et al.* 1998). More recently, the idea that meltwater plumes, characterized by equally negative  $\delta^{13}\text{C}$  values, could have influenced the negative values of cap carbonate could have influenced the negative values of cap carbonate has been proposed (He *et al.* 2021). On the other hand, early diagenesis under the influence of deeper waters may have caused heavier  $\delta^{13}\text{C}$  compositions in cap carbonate successions (approximately -3 to -1‰, Ahm *et al.* 2019).

According to geochemical models, at the end of glaciations, carbonate precipitated from glacial oceans would have an isotopic composition of approximately 1‰ (Le Hir *et al.* 2008, Ahm *et al.* 2019). The influence of high atmospheric  $\text{pCO}_2$  and

temperatures on the surface meltwater may have affected carbonate precipitation kinetics, resulting in negative  $\delta^{13}\text{C}$  values (approximately - 6‰) and high variability in  $^{87}\text{Sr}/^{86}\text{Sr}$  in dolomitic caps (Higgins and Schrag, 2003, Halverson *et al.* 2010, Romero *et al.* 2012). The respiration of organic matter (either aerobically or anaerobically) through microbial activity during cap dolostone precipitation may have led to even more negative values (Gammon 2012, Font *et al.* 2006, Nedeléc *et al.* 2007, Santos *et al.*). This interpretation is consistent with our data, as microbialites dominate cap dolostone units in our study area (Nogueira *et al.* 2003, 2022, Font *et al.* 2006, Romero *et al.* 2020, Santos *et al.* 2021, 2023).

However, the persistence of negative  $\delta^{13}\text{C}$  values in the cap limestone, with its strong inorganic influence, isotopically homogeneous, and local variations, must be considered primarily related to changes in relative sea level and the time required for the mixing process of glacial meltwater and seawater. Previous studies have interpreted this geochemical behavior as resulting from kinetic effects linked to  $\text{CaCO}_3$  peak supersaturation in thermally expanded, well-mixed waters during the long-term transgression following glaciation (Nogueira *et al.* 2003, 2022, Sansjofre *et al.* 2011, 2014, Yang *et al.* 2017, Soares *et al.* 2020). Despite a decline in microbial production, biomarker evidence has been presented which reveals a predominance of planktonic activities during cap limestone deposition in the Puga cap carbonate sequence (van Maldegem *et al.* 2018). Average values shift from - 8 to - 5 ‰ in cap dolostone to - 6 to - 2‰ in cap limestone, and the reasons for these changes could be related to rapid sea-level changes. This interpretation agrees with recent work by He *et al.* (2021), which, in a global compilation, demonstrated a clear shift between shallow and deep-water environments in terms of  $\delta^{13}\text{C}$ . They attributed lighter values in deeper environments to increased remobilization of organic carbon in the water column. Thus, the decline in  $\delta^{13}\text{C}$  values from - 3 to - 5‰ would reflect temporal evolution and sea level changes associated with long-term transgression during early Ediacaran (He *et al.* 2021).

Despite uncertainties regarding the origin of  $\delta^{13}\text{C}$  signals or their use in chemostratigraphy correlation, data from the cap dolostone and the entire Araras Group exhibit well-preserved signals, displaying distinct trends for each unit (Fig. 6.1 B). Ediacaran carbonates commonly exhibit isotopic carbon excursions ( $\delta^{13}\text{C}$ ) characterized by distinct negative and positive deviations, in agreement with stratigraphic trends and sea-level changes (Hayes *et al.* 1999, Jacobsen and Kaufman 1999, Hoffman and Schrag 2002, Nogueira *et al.* 2007, Ader *et al.* 2009, Halverson *et al.* 2010, Sansjofre *et al.* 2011, Lyons *et al.* 2014, He *et al.* 2021). The  $\delta^{13}\text{C}$  from the Araras carbonate succession is interpreted



as representative of the original ocean water chemistry (Fig. 6.2), displaying a trend with strongly depleted  $\delta^{13}\text{C}$  values at the base and enriched compositions upsection (Fig. 6.1 B). The enrichment trend observed in the Araras carbonates is indicative of a return to typical seawater compositions, likely associated with the re-establishment of biological activity (Nogueira *et al.* 2007). During the sea level rise, the platform surface rapidly expanded, promoting abundant organic productivity and increasing the  $\delta^{12}\text{C}$  retention by organisms (Mitchell *et al.* 1996, Nédélec *et al.* 2007, Santos *et al.* unpublished).

### 6.5.3 Decreased $\epsilon\text{Nd}(t)$ values and radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ in continental shelf seawater:

The Puga Formation is intricately linked to the sequence of events of the Marinoan glaciation ( $\sim 650$ -635 Ma). Diamictites and dropstones, interpreted as glaciomarine, predominantly exhibit magmatic and metamorphic source rocks from the Amazon craton (Dantas *et al.* 2009, Alvarenga *et al.* 2011). Our  $^{143}\text{Nd}/^{144}\text{Nd}$  data in diamictites from the Tangará section display TDM model ages ranging from 1.6 to 2.0 Ga, with one sample showing values of 3.7 Ga, considerably older than those found in this study. However, most of our data are consistent with the TDM model ages ranging from 1.5 to 2.2 Ga described by Dantas *et al.* (2009) in the Terconi section. These results, particularly for the diamictite matrix, indicate primarily cratonic sources for the matrix and clasts, supporting this interpretation (Fig. 6. 4 B-C and Fig. 6.5). This homogenization of Nd isotopes has been attributed to factors such as the deposition of excellent material without tractional currents and sorting mechanisms (Dantas *et al.* 2009). The Marinoan cap dolostones in this study exhibit relatively high  $\epsilon\text{Nd}(t)$  values ranging between -14.9 to -6.34 (average  $\epsilon\text{Nd}(t) = -10.05$ ). Conversely,  $\epsilon\text{Nd}(t)$  values of the cap dolostone are notably lower at the base of the section ( $\sim 4\text{m}$ , ranging from -14 to -14.3) and higher (-10.51 to -6.34) further upsection (Fig. 6.5). Dantas *et al.* (2009) also reported higher values (-8.16 to -7.85) for the cap dolostone in the Mirassol d'Oeste. Furthermore, Souza *et al.* (2024) observed an average  $\epsilon\text{Nd}(t) = -8.01$  values on its upper portion and overlying cap limestone. The average  $\epsilon\text{Nd}(t)$  value of Puga cap carbonate differs from that of the modern Pacific Ocean  $\epsilon\text{Nd}(t) = -4$  (Goldstein and Hemming 2014). However, these values are very close to those found for glaciomarine deposits of the Puga Formation (average  $\epsilon\text{Nd}(t) = -7.9$ ), suggesting a more significant continental influence on seawater chemistry during succession precipitation. In addition, the decreased  $\epsilon\text{Nd}(t)$  values of shallow marine carbonates generally may have resulted from enhanced continental weathering of old continental

crust (Wei *et al.* 2019). Abrupt changes in seawater  $\epsilon\text{Nd}(t)$  values are primarily associated with continental weathering input and ocean circulation (Goldstein and Hemming, 2014, Dera *et al.* 2015).

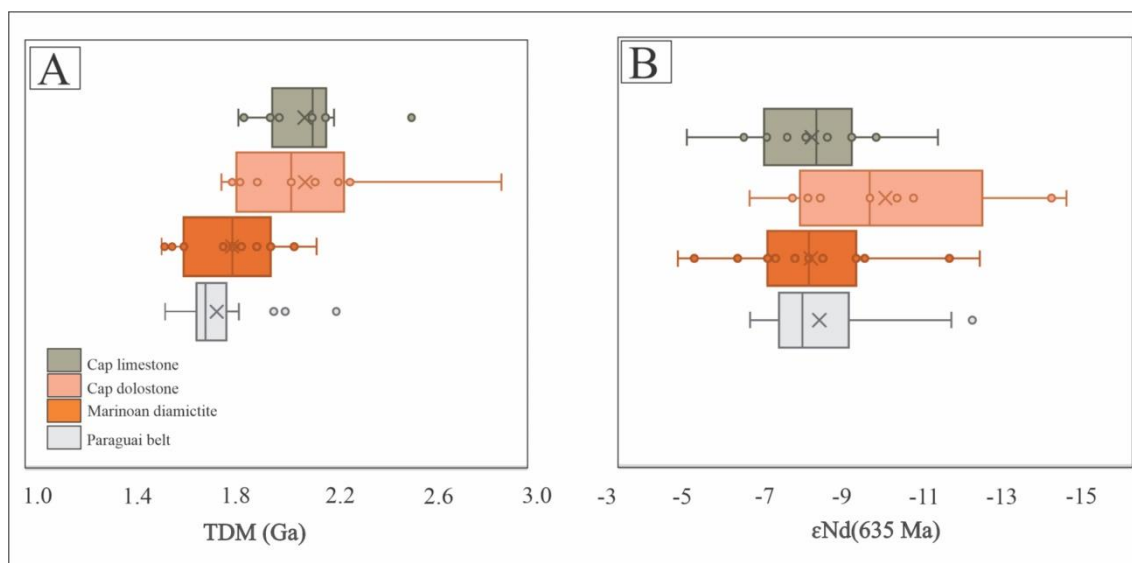


Fig. 6.5- Box-plot distribution of TDM values for the Puga cap carbonate and the Paraguai fold belt (Cuiabá Group), compared to the average values for the cap carbonate in Tangará da Serra occurrence. B) Box-plot distribution of  $\epsilon\text{Nd}(t)$  values for the Puga cap carbonate and the Paraguai fold belt (Cuiabá Group), compared to the average values for the cap carbonate in Tangará da Serra section.

The negative  $\epsilon\text{Nd}(t)$  values suggest that the Rare Earth Elements (REE) in seawater originated from continental crust sources, likely transported by alluvial-fluvial streams formed over the recently exposed platform affected by greenhouse weathering. The sudden influx of fresh meltwater from rivers and groundwater into coastal areas may have rapidly decreased carbonate  $\epsilon\text{Nd}(t)$  values. Freshwater typically contains significantly higher Nd concentrations, with less radiogenic Nd, than open oceans (Goldstein and Jacobsen, 1987). The similarity in Nd isotopic composition between rocks affected by glaciation and cap carbonate can be attributed to two simultaneous mechanisms linked to deglaciation: i) the rapid precipitation of cap carbonates and ii) the high influx of continental suggesting a more significant continental influence of the enhanced weathering of Amazon Craton on seawater chemistry during succession precipitation. The abrupt change in  $\epsilon\text{Nd}(t)$  could also have been influenced by the mixing of isotopically distinct water bodies following the Marinoan glaciation. In this scenario,  $\epsilon\text{Nd}(t)$  values likely reflect the mixing between higher seawater and lower meltwater ratios. An alternative explanation for similar Nd values will be the alkalinity model proposed by Fabre and Berger (2012), which considers the predominance of long-term regolith weathering, triggering

efficient atmospheric CO<sub>2</sub> removal during post-Marinoan events. Thus, the intense post-glacial chemical weathering could homogenize Nd seawater signatures of the cap dolostones during syn-deglacial transgression along the Amazon craton. Considering the short duration for cap dolostone deposition, the initial centimeters showing older model ages indicate a more substantial influence of meltwater. Indeed, the cap dolostone precipitation model suggests mixing between meltwater and seawater.

The cap dolostone would have precipitated during this mixing process under the influence of Glacial Isostatic Adjustment (GIA), reflected in the Nd isotopic variation. Additionally, the REE data obtained for the succession exhibit a continental crust pattern ( $Y/Ho > 36$ ), indicating a significant meltwater contribution. Although this seems contradictory to lower siliciclastic content, it can be explained by the siliciclastic starvation model proposed by Santos *et al.* (unpublished). The decrease in marine carbonate  $\epsilon Nd(t)$  values from the Puga carbonate coincides with an increase in silicate residue in the upper section (Santos *et al.* unpublished), suggesting enhanced denudation of old continental rock related to post-Marinoan continental weathering. The  $\epsilon Nd(t)$  values in the cap limestone (Souza *et al.* 2024) suggest continental weathering. However, compared to the cap dolostone, the Nd values demonstrate a progressively higher radiogenic Nd contribution. These  $\epsilon Nd(t)$  values indicate a more significant mixing of water masses related to the destratification of the oceans, associated with upwelling events and glacioisostatic adjustments during the greenhouse climax (Hoffman *et al.* 2017, Yang *et al.* 2017, Santos *et al.* 2021, 2024, Ramme and Marotzke 2022).

New  $^{87}Sr/^{86}Sr$  data in cap dolostones range from 0.7264 to 0.7084, and these values are higher than pre- and post-glacial  $^{87}Sr/^{86}Sr$  values of seawater (Kennedy *et al.* 1998, Halverson *et al.* 2007), indicating a significant input of continental silicate weathering (Gaillardet *et al.* 1999, Vance *et al.* 2009, Allegre *et al.* 2010). High  $^{87}Sr/^{86}Sr$  is also consistent with freshly exposed source rocks, as weathering leads to the preferential release of high  $^{87}Sr/^{86}Sr$  solutions, leaving residual material with low  $^{87}Sr/^{86}Sr$  (Blum and Erel, 1995). More radiogenic values at the base are consistent with those found in recent glacial hydrographic basins, such as Rhone meltwaters (0.7251–0.7258) and Oberaar meltwaters (0.7137–0.7174) in the Swiss Alps (Arn *et al.* 2003). Glaciers and glacial periods can significantly shift the balance between physical and chemical weathering processes. This is due to the extensive contact between diluted meltwater and fine-grained sediments, potentially hastening weathering processes (Anderson *et al.* 2000, Sharp *et al.* 2002, Arn *et*

*et al.* 2003, Hagedorn and Hasholt, 2004). Blun and Erel (1995) illustrated that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio released during the initial weathering phases markedly exceeds that in subsequent stages. Glacial activity could impact marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios through alterations in worldwide riverine Sr fluxes (i.e., rates of rock weathering) and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (i.e., proportions of mineral weathering). The association of more radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  values with the most negative  $\epsilon\text{Nd}(t)$  values reinforces the connection to the contribution of continental weathering in meltwater. It has potential implications for post-glacial weathering. This distinction suggests a significant influence of continental sources dissolved in the meltwater, from which the cap dolostone precipitated, exhibiting a much higher radiogenic Sr content than expected for the Ediacaran period (Liu *et al.* 2014). In contrast, the  $^{87}\text{Sr}/^{86}\text{Sr}$  compositions (0.7070–0.70975) for the cap limestone found in the upper portion of the section studied by Romero *et al.* (2013) and Souza *et al.* (2024), are consistent with well-preserved Ediacaran limestones. These typically display  $^{87}\text{Sr}/^{86}\text{Sr}$  compositions ranging from 0.7080 to 0.7090, close to the global seawater strontium isotope curve (Jacobsen and Kaufman, 1999, Halverson *et al.* 2007a, 2007b, 2010, Narbonne *et al.* 2012, Macdonald *et al.* 2013, Bold *et al.* 2016, Xiao *et al.* 2016, Kuznetsov *et al.* 2018, Zhou *et al.* 2020).

Our data reveals a significant stratigraphic variation, with a clear trend of more radiogenic values at the base of the cap carbonate succession (Fig. 6.6), which is also observed in other cap carbonate occurrences (Hohl *et al.* 2017). The cap limestone exhibits less radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  values (Romero *et al.* 2013, Souza *et al.* 2024) similar to Marinoan cap carbonate worldwide (e.g., Liu *et al.* 2013, Hohl *et al.* 2017, Rodler *et al.* 2017, Wei *et al.* 2019). These deposits have been considered a subsiding platform record associated with long-term transgression (Nogueira *et al.* 2003, 2022, Soares *et al.* 2020). The generally low and consistent  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, as well as the high Sr concentration observed in cap limestone, can be indicative of the mixing of deep-sea water and carbonate precipitation triggered during complete deglaciation, accompanied by oceanic upwelling and warming (Hoffman *et al.* 2017). Despite the complexities in the Sr isotopic signatures, the Nd isotope compositions of all samples maintain a provenance linkage and support the predicted paleoceanographic changes proposed by the Plumeworld hypothesis (Shields 2005) and the existence of ‘Glacial Lake Harland’ (Hoffman *et al.*, 2017). They are also corroborated by the paleoceanographic evolution proposed for the cap carbonate sequence based on REE patterns presented by Santos *et al.* (unpublished). The radiogenic (Nd-, and Sr-) isotopic composition of Puga cap carbonate succession strongly indicates

meltwater with sediments produced by erosion of crystalline rocks (Amazon craton) and secondarily the glaciogenic diamicton. Thus, cap dolostones deposited in the coastal environment in a semi-restricted setting would have been more strongly influenced by the meltwater plume (Fig. 6.6 A-C) and have higher  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon\text{Nd}(t)$  values than those in deeper water settings (cap limestone) where hypersaline seawater had greater influence associated with the upwelling process during mixwater (Fig. 6.6 C-D).

#### 6.5.4 Syndeglacial evolution

A super greenhouse climate was moderate and possibly short-lived after the global glaciation. Marinoan cap dolostones could have formed just a few thousand years after the start of deglaciation, concurrent with rapid warming and recovery of biological activity (Ramme *et al.* 2024). These factors enhance biogeochemical cycles and promote flourishing and growth of microbial communities, leading to noticeable organomineralization in a shallow-water environment induced by ice gravity, leading to continuous uplift of the coastal zone along the Amazon margin (Fig. 6.6) (Santos *et al.* 2021). Coastal uplift induced by ice gravity can have triggered the syn-sedimentary deformation in the cap carbonate (Nogueira *et al.* 2003, 2022, Santos *et al.* 2023). The deformed dolomite-diamictite contact indicates rapid accumulation of dolomicrite over unlithified and plastic diamictite (Nogueira *et al.* 2003, 2019, Soares *et al.* 2013, Santos *et al.* 2023). These deformations formed under fast precipitation rates during syn-deglacial transgression (Kennedy *et al.* 2001, Hoffman *et al.* 1988, 2017, Nogueira *et al.* 2003, 2019, Crockford *et al.* 2021, Santos *et al.* 2023). The continuity of these processes led to the implantation of an isolated shelf protected by ocean dynamics. The irregular diamicton morphologies generated the undulated substrate. The retreat of low a supersaturated environment allowed the flourishing of extensive microbial communities (Nogueira *et al.* 2003, Font *et al.* 2006, Romero *et al.* 2020, Santos *et al.* 2021, 2023).

The rapid deglaciation resulted in cap carbonates forming rapidly ( $10^3$ – $10^4$  yr) and the plume-world model proposed by an interaction between meltwater and marine water, persistent ocean stratification followed deglaciation due to water density contrast (Fig. 6.6): i) an upper warmer, less dense deglacial meltwater, and ii) a lower hypersaline and dense seawater. Dolomite precipitation and water mixing processes in this scenario were probably diachronous (Hoffman *et al.* 2017, Santos *et al.* unpublished). Upwelling and glacioisostatic processes might have gradually mixed waters, causing ocean destratification (Hoffman *et al.* 2017, Ramme and Marotzke 2022). The cap carbonate immediately

precipitated over the Puga diamictite in a coastal-marine environment influenced by microbial mat proliferation during the transition from icehouse to greenhouse conditions (Fig. 6.6) (Nogueira *et al.* 2003, 2019, 2019, Font *et al.* 2006, 2010, Sansjofre *et al.* 2014, Romero *et al.* 2020, Santos *et al.* 2021, 2023).

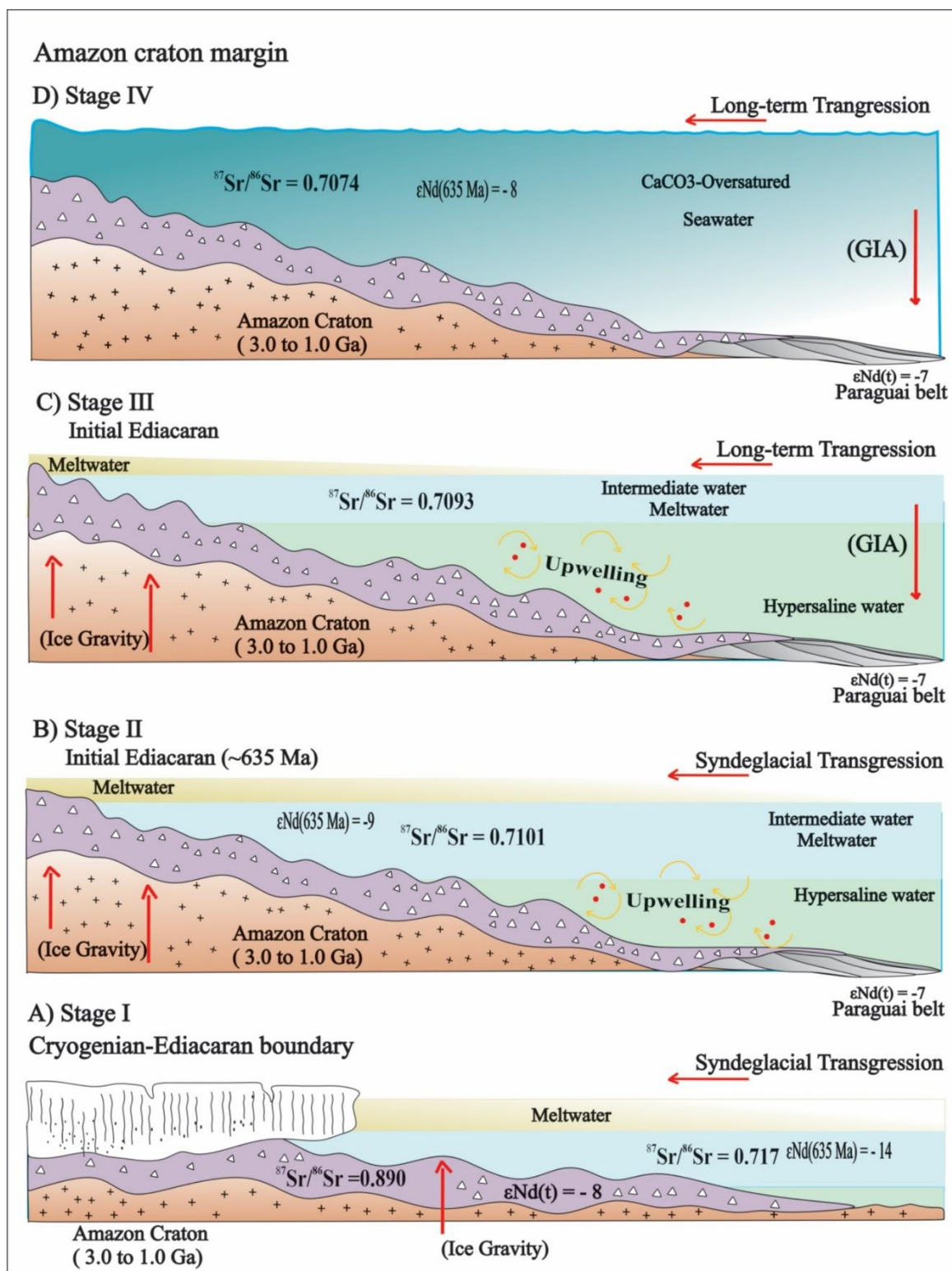
The cap dolostone showed an Nd isotope composition similar to that of the southeastern glaciomarine section (Fig. 6.5). Given Nd's relatively short residence time (Tachikawa *et al.* 1999), assuming the high precipitation rates for these deposits, the Nd isotopic composition can be interpreted as an instantaneous and local record in seawater (Banner *et al.* 1988, Burton and Vance 2000, Dantas *et al.* 2009, Tachikawa *et al.* 2017, Wei *et al.* 2019, Hohl *et al.* 2022). We interpret these signatures as indicative of a rapid precipitation rate, close to previous interpretations by Dantas *et al.* (2009). In addition, the  $\epsilon\text{Nd}(t)$  values (-14 to -6) in the cap dolostone are significantly negative and exhibit radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.7264 to 0.7084) (Fig. 6.3 C). Wei *et al.* (2019) describe lower  $\epsilon\text{Nd}(t)$  values accompanied by increasing  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in rocks from the Ediacaran to early Cambrian periods, the authors suggest that these changes may indicate enhanced weathering of ancient continental rocks during this time. Our isotopic data support these interpretations, as the more radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  values in the cap dolostone coincide with Nd values that exhibit isotopic signatures similar to those of glacially derived rocks. The precipitation of the cap dolostone occurs in mixed waters, but with a much more significant influence from meltwater enriched by the weathering of rocks from the Amazon craton, which could have rapidly decreased the carbonate  $\epsilon\text{Nd}(t)$  values, this interpretation agrees with the interpretation of TDM model ages between 1.8 and 2.9 Ga. Similarly, the constant water mixing processes associated with the end of ocean stratification would have increased the Nd values and brought the Sr values closer to those of Ediacaran marine deposits. The modifications in signals follow the paleoceanographic changes and indicate mixtures of water masses associated with mixwater processes during the syn-deglacial transgression.

This interpretation corroborates the interpretations of Santos *et al.* (unpublished), which consider REE+Y in the cap dolostone are linked with mixwater settings and upwelling towards the coastal zone with hypersaline seawater mixed with some hydrothermal fluids (Fig. 6.6). The  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures of the cap limestone are accompanied by the contribution of continental-derived material following deglaciation (Romero *et al.* 2013, Souza *et al.* 2024). In addition, Souza *et al.* (2024) provided Nd-TDM model ages

for cap limestone, ranging from 1.84 to 2.54 Ga, similar to those observed for the Puga diamictite and cap dolostone (Fig. 6.5). These ages are comparable to those found for the Paleoproterozoic continental crust, constituting the Araras-Alto Paraguai basin substrate. The progressive mixing between seawater and meltwater changes the major radiogenic Nd values and  $^{87}\text{Sr}/^{86}\text{Sr}$  values for less radiogenic, compatible with a seawater signature (Fig. 6.6). The interpretation of rapid cap precipitation seems more acceptable with the rare Earth elements analysis favoring the short-lived destratification during the final stages of deglaciation (Fig. 6.6). These conditions were the anomalous scenario for the cap carbonate precipitation in a freshwater environment with inherited high alkalinity from the weathered basement rocks and glaciogenic diamicton combined with the increase of microbial activity.

## 6.6 CONCLUSION

Our new high-resolution radiogenic Nd isotope data combined with  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{13}\text{C}$  isotopes sheds light on the changes in shallow seawater sources during the deposition of cap dolostone on the continental shelf margin at the Cryogenian-Ediacaran boundary.  $\delta^{13}\text{C}$  isotopes, these findings allow us to discern patterns in weathering sources, oceanic circulation, and paleoproductivity along the Amazon margin during this crucial period. Notably, cap dolostone Puga exhibits a consistent increase in  $\epsilon\text{Nd}(t)$  values from approximately -14 to -6 and less radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$ , indicative of diminishing terrestrial influences and a strengthening export of seawater via upwelling processes. These variations in weathering sources and water mass exchange with the open ocean are key factors influencing the temporal fluctuations in  $\epsilon\text{Nd}(t)$  values and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios observed in continental shelf waters and mixtures of water masses, meltwater, and hypersaline water associated with the upwelling process. Such insights deepen our understanding of paleoenvironmental dynamics during the transition from the Cryogenian to the Ediacaran, highlighting the complex interplay between terrestrial weathering, oceanic circulation, and biogeochemical processes along continental margins in the aftermath of Marinoan glaciation.



*Caption on next page*



Figure 6.6- Post-glacial evolution to long-term transgression of the southern margin of the Amazon Craton. A) Cap dolostone begins to precipitate during the syn-deglacial transgression, evidenced by  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon\text{Nd}(t)$  values indicating a more significant influence of continental weathering. B) Microbialites develop from the early stages and dominate part of the cap dolostone precipitation environment. The mixture of hypersaline deep water begins to occur through upwelling processes, enhanced by glacial-isostatic adjustment and local gravity, keeping the environment shallow and conducive to microbial community proliferation.  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon\text{Nd}(t)$  values evidenced the continuo influence of continental weathering. C) Wave action starts to dominate the environment, leading to reworking, macropeloids formation, and a gradual decline of microbial communities. D) Increased water depth and siliciclastic input from continental weathering enhance the  $\text{CaCO}_3$  supersaturation event. The  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon\text{Nd}(t)$  values indicate well-mixed water with a more significant influence of hypersaline deep water, typical of the Ediacaran period

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## 6.7 SUPPLEMENTARY MATERIAL: UNRAVELING POST-MARINOAN SEA-WATER EVOLUTION IN THE AMAZON CRATON

**Supplementary Material 1-** Stratigraphic aspects of the Puga cap carbonate sequence

**Supplementary Table 6.1-** Carbon and oxygen isotopes of the Puga cap carbonate from the JBN drill core in the Tangará section.

### Stratigraphic aspects

The first twelve meters of the examined drill cores (Fig. 6. 1) consist of glacio-genic diamictite and dropstones beds from the Puga Formation (Fig. 6.2). Directly above these deposits, the Mirassol d'Oeste Formation dolomites form approximately 40-meter-thick cap dolostone layers (Fig. 6. 3). The contact between the cap dolostone and glacial diamictite is sharp and shows synsedimentary deformation, including deformed laminations, micro-faults, massive bedding, and incipient breccias. The Puga Formation consists of diamictites and dropstones. A polymictic matrix-supported conglomerate characterizes the Foliated Diamictite. This conglomerate has a mixture of poorly sorted clasts, including sandstone, gneiss, granite, and volcanic rocks. These clasts range from coarse sand to pebble-grained and exhibit faceted and striated features. The matrix surrounding these clasts is clay-rich and shows incipient foliation (Fig. 6. 2). The Massive dropstones is observed within a siltite/sandy matrix. These dropstones vary in size from millimeters to centimeters and are composed of different materials such as sandstone, gneiss, granite, and volcanic rocks.

The cap dolostone can be subdivided from base to top into four microfacies. Microbialites facies are characterized by stratiform doloboundstones with gypsum pseudomorph and domical doloboundstones with tubestone. Wave-rippled dolostone, comprising two microfacies: dolograinstone/peloidal dolomudstone with quasi-planar to low-angle lamination and peloidal dolomudstone/dolopackstone with megaripple Bedding (Fig. 6.3). The cap limestone, which forms the top of the cap carbonate, corresponds to the 50 basal meters of the Guia Formation consisting of discontinuous layers of dolomitic marlstone (ca. 10m) and limestone (ca. 40m) that conformably overlies the cap dolostone. The intermediate ~25m of the cap limestone contains abundant seafloor precipitates, including decimetre-thick clusters of pseudomorph aragonite crystal fans. The crystal fans are draped by cm-thick micritic laminae with megaripple bedding alternated with mm-thick limestone shale, characterizing an anomalous  $\text{CaCO}_3$  oversaturation state in intermediate to deep platform environments. For more details, see Nogueira *et al.* (2003, 2019), Soares *et al.* (2020), and Santos *et al.* (2021, 2023).



Figure 6.1 Photograph of the drill core JOR (Ornamental mining front) showing the contact between glaciogenic diamictites Puga and cap dolostone (Mirassol d'Oeste Formation).



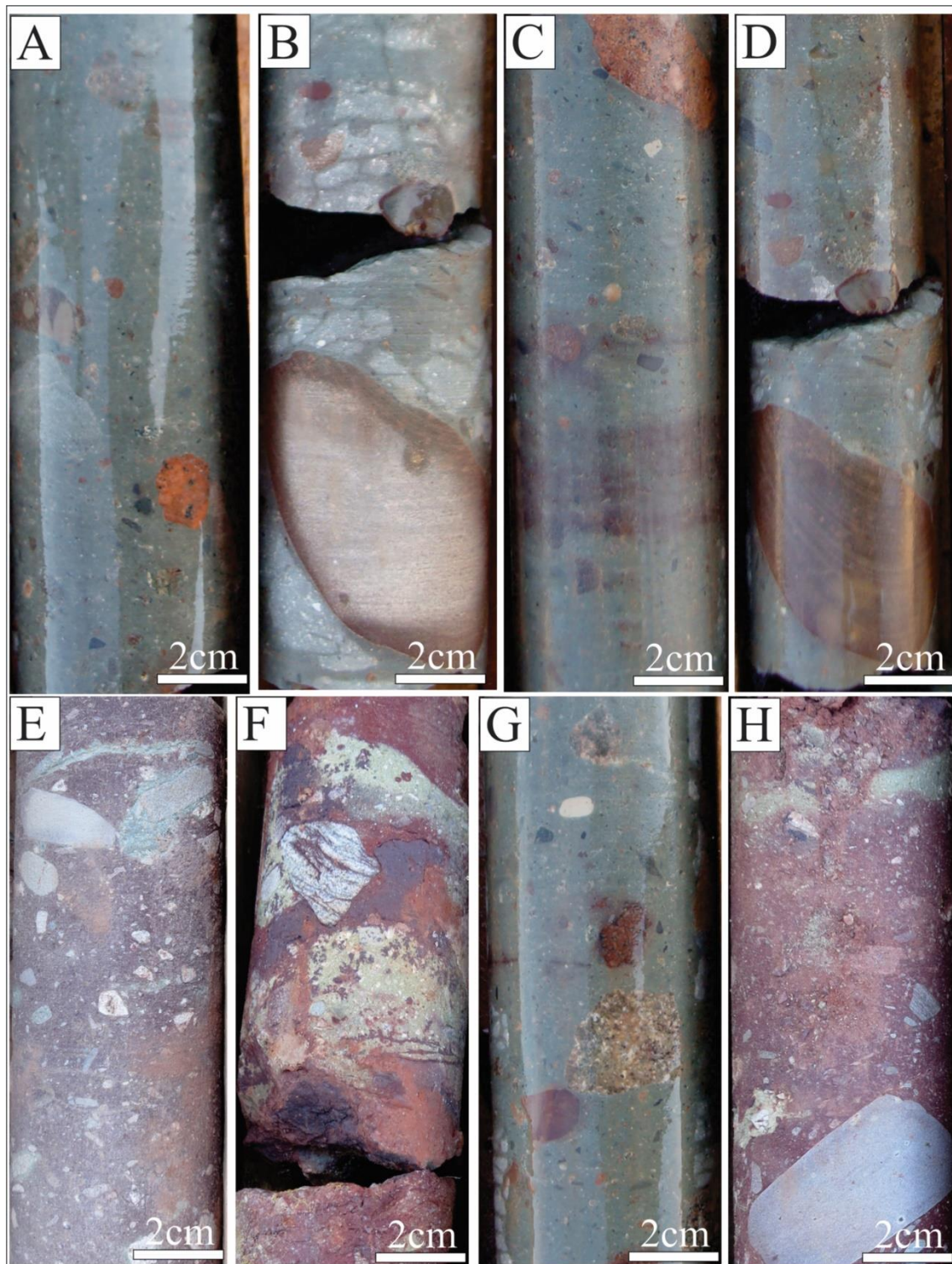


Figure 6. 2. Details of the main characteristics observed in the Puga Formation glacial diamictites (related to the marine glacial environment). Highlighting the compositional diversity of clasts that exhibit (e.g., sandstone, gneiss granite volcanic, etc.) varying sizes until 10 cm.



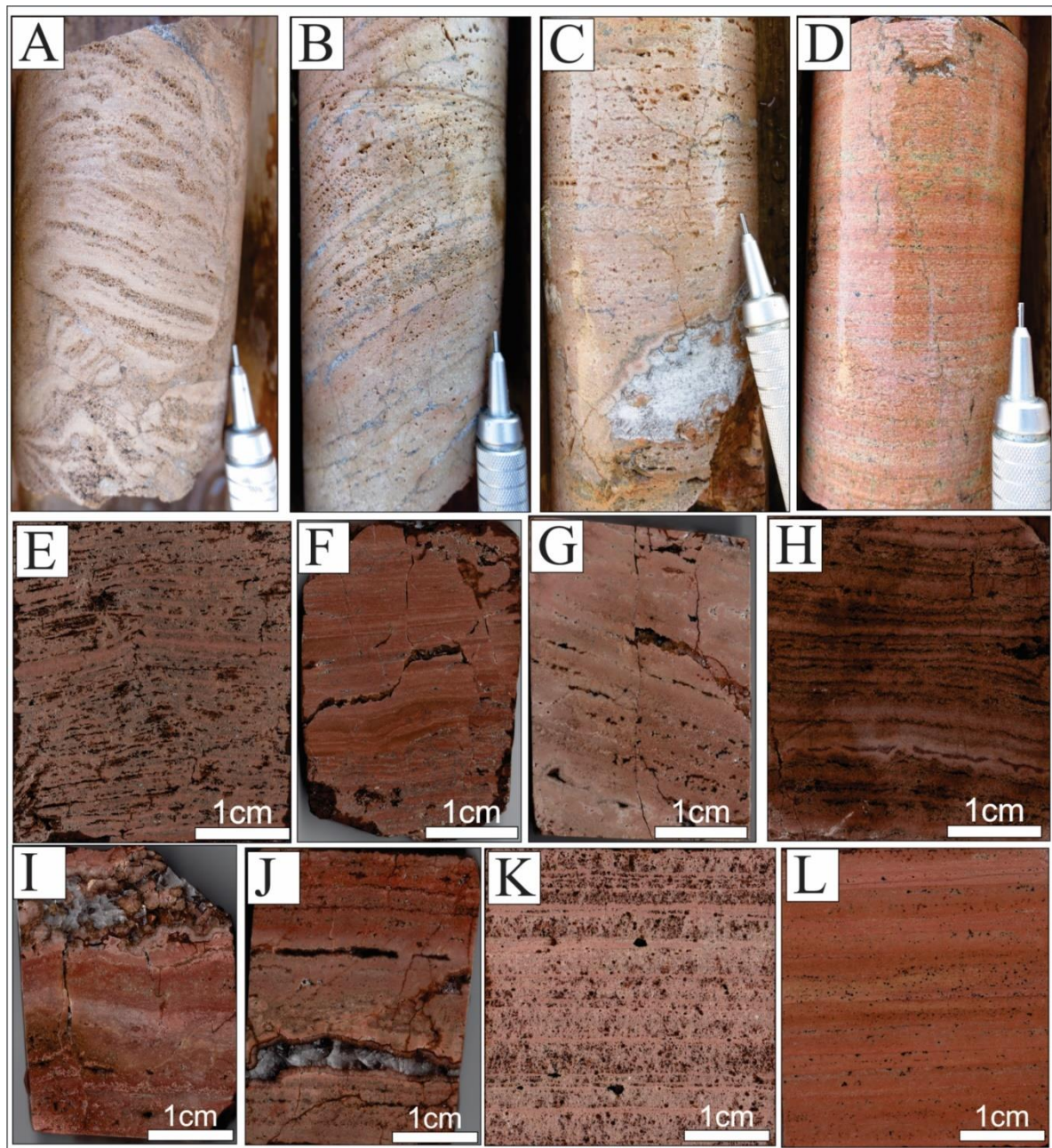


Figure 6. 3. Details of the main characteristics observed in the cap dolostone (Mirassol d'Oeste Formation). A), B), and C) correspond to microbialite facies, with C) highlighting the dissolution and calcite cementation processes. D) Quasi-planar laminations. E-L) Polished blocks showcasing the primary features of the laminations. E-F) Synsedimentary deformation of the microbialites (base of the cap dolostone). E-H) Alternating laminar sequences of the microbialites. I-J) Highlighting the processes of cementation and dissolution in fenestral pores. K-L) Quasi-planar laminations.

Supplementary Table 6.1- Carbon and oxygen isotopes of the Puga cap carbonate from the JBN drill core in the Tangará section.

| Depth | Samples | $\delta^{13}\text{C}/^{12}\text{C}$ (‰) | $\delta^{18}\text{O}/^{16}\text{O}$ (‰) |
|-------|---------|-----------------------------------------|-----------------------------------------|
| 0,2   | BN-1    | -5,457                                  | -3,69                                   |
| 0,6   | BN-3    | -6,546                                  | -4,441                                  |
| 1     | BN-5    | -5,88                                   | -3,705                                  |
| 1,4   | BN-7    | -5,389                                  | -4,216                                  |
| 1,8   | BN-9    | -4,628                                  | -4,393                                  |
| 2,2   | BN-11   | -5,573                                  | -4,942                                  |
| 2,4   | BN-12   | -7,003                                  | -4,472                                  |
| 3     | BN-15   | -4,808                                  | -4,545                                  |
| 3,4   | BN-17   | -4,096                                  | -4,429                                  |
| 3,8   | BN-19   | -5,528                                  | -4,752                                  |
| 4,2   | BN-21   | -4,964                                  | -4,665                                  |
| 4,6   | BN-23   | -4,282                                  | -4,028                                  |
| 5     | BN-25   | -4,313                                  | -4,543                                  |
| 5,4   | BN-27   | -6,962                                  | -4,723                                  |
| 5,8   | BN-29   | -7,279                                  | -4,333                                  |
| 6,2   | BN-31   | -5,298                                  | -4,487                                  |
| 6,6   | BN-33   | -4,488                                  | -4,911                                  |
| 7     | BN-35   | -4,756                                  | -4,111                                  |
| 7,4   | BN-37   | -4,635                                  | -4,435                                  |
| 7,8   | BN-39   | -5,193                                  | -4,783                                  |
| 8,2   | BN-41   | -5,205                                  | -3,468                                  |
| 8,6   | BN-43   | -5,108                                  | -4,908                                  |
| 9     | BN-45   | -5,701                                  | -4,059                                  |
| 9,4   | BN-47   | -5,139                                  | -4,446                                  |
| 9,8   | BN-49   | -5,882                                  | -4,425                                  |
| 10,2  | BN-51   | -4,713                                  | -4,106                                  |
| 10,6  | BN-53   | -4,928                                  | -4,353                                  |
| 11    | BN-55   | -4,744                                  | -4,056                                  |
| 11,4  | BN-57   | -5,273                                  | -4,497                                  |
| 11,8  | BN-59   | -4,685                                  | -4,549                                  |
| 12,2  | BN-61   | -5,25                                   | -4,16                                   |
| 12,6  | BN-63   | -3,964                                  | -4,691                                  |
| 13    | BN-65   | -4,201                                  | -3,876                                  |
| 13,4  | BN-67   | -4,632                                  | -4,193                                  |
| 13,8  | BN-69   | -4,994                                  | -4,118                                  |
| 14,6  | BN-73   | -4,43                                   | -4,637                                  |
| 15    | BN-75   | -4,563                                  | -3,23                                   |
| 15,4  | BN-77   | -6,196                                  | -3,91                                   |
| 15,8  | BN-79   | -6,714                                  | -3,598                                  |
| 16,2  | BN-81   | -6,247                                  | -3,731                                  |
| 16,6  | BN-83   | -5,574                                  | -4,064                                  |
| 17    | BN-85   | -5,874                                  | -4,069                                  |
| 17,4  | BN-87   | -6,029                                  | -4,075                                  |



|      |       |        |        |
|------|-------|--------|--------|
| 17,8 | BN-89 | -6     | -4,173 |
| 18,2 | BN-91 | -6,399 | -4,545 |
| 18,6 | BN-93 | -6,711 | -3,859 |
| 19   | BN-95 | -5,157 | -3,96  |
| 19,4 | BN-97 | -6,757 | -3,784 |

## CAPÍTULO 7: POST-MARINOAN PALEOREDOX AND PALEOPRODUCTIVITY RECORD IN PUGA CAP CARBONATE: IMPLICATION FOR COASTAL LIFE COLONIZATION AT THE AMAZON CRATON MARGINAL SEA

Renan F. dos Santos<sup>1</sup>, Pierre Sansjofre<sup>2</sup>, Afonso C. R. Nogueira<sup>1,7</sup>, Simon Hohl<sup>3</sup>, Marlone H. H. Bom<sup>4</sup>, Ailton Brito<sup>1</sup>, Flávia Callefo<sup>5</sup>, Stefan Lalonde<sup>6</sup>

*1Programa de Pós-Graduação em Geologia e Geoquímica, Faculdade de Geologia, Instituto de Geociências, Universidade Federal do Pará, Rua Augusto Corrêa s/n, CEP 66075-110, Belém-PA, Brasil*

*2 Muséum National d'Histoire Naturelle, Institut de Physique des Matériaux et de Cosmochimie, Sorbonne Université, Paris, France*

*3State Key Laboratory of Marine Geology, Tongji University, Siping Road 1239, Shanghai 200092, PR China*

*4Instituto Tecnológico de Micropaleontologia (itt Fossil), Universidade do Vale do Rio dos Sinos, Av. UNISINOS, 950, 93022-750 Sao ~ Leopoldo, RS, Brazil*  
*5Brazilian Synchrotron*  
*5Light Laboratory, Brazilian Center for Research in Energy and Materials – Campinas (SP), Brazil*

*6Institut Universitaire Européen de la Mer, Technopôle Brest-Iroise, France*

*7Research Productivity of CNPq*

Submetido em ***Palaeogeography, Palaeoclimatology, Palaeoecology***

### HIGHLIGHTS

- 1) Complex environmental and biogeochemical cycles interplay in post-Marinoan (~635 Ma)
- 2) Climatic extreme scenarios shed critical light on the life proliferation
- 3) Microbial mat flourishing occurred under oxic conditions in coastal environments
- 4) Microbial communities could be self-sufficient under shallow marine conditions
- 5) Sequential redox transition marked the shift towards greenhouse conditions.

| Palaeogeography, Palaeoclimatology, Palaeoecology                                                                             |                   |                                                                                                                                                      |                        |              |                |
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## 7 POST-MARINOAN PALEOREDOX AND PALEOPRODUCTIVITY RECORD IN PUGA CAP CARBONATE: IMPLICATION FOR COASTAL LIFE COLONIZATION AT THE AMAZON CRATON MARGINAL SEA

Renan F. dos Santos<sup>1</sup>, Pierre Sansjofre<sup>2</sup>, Afonso C. R. Nogueira<sup>1,7</sup>, Simon Hohl<sup>3</sup>, Marlone H. H. Bom<sup>4</sup>, Ailton Brito<sup>1</sup>, Flávia Callefo<sup>5</sup>, Stefan Lalonde<sup>6</sup>

*1Programa de Pós-Graduação em Geologia e Geoquímica, Faculdade de Geologia, Instituto de Geociências, Universidade Federal do Pará, Rua Augusto Corrêa s/n, CEP 66075-110, Belém-PA, Brasil*

*2 Muséum National d'Histoire Naturelle, Institut de Physique des Matériaux et de Cosmochimie, Sorbonne Université, Paris, France*

*3State Key Laboratory of Marine Geology, Tongji University, Siping Road 1239, Shanghai 200092, PR China*

*4Instituto Tecnológico de Micropaleontologia (itt Fossil), Universidade do Vale do Rio dos Sinos, Av. UNISINOS, 950, 93022-750 São Leopoldo, RS, Brazil*

*5Light Laboratory, Brazilian Center for Research in Energy and Materials – Campinas (SP), Brazil*

*6Institut Universitaire Européen de la Mer, Technopôle Brest-Iroise, France*

*7Research Productivity of CNPq*

### ABSTRACT

Snowball Earth represent one of the extremely global paleoclimatic disturbances, causing paleoenvironmental and paleoceanographic changes that dramatically impact life evolution. Cryogenian ocean's chemical activity and dynamics were strongly affected by the glacial-interglacial transitions, and some of these modifications can be found in postglacial cap carbonates through the analysis of major and redox-sensitive trace elements. A geochemical study of the Marinoan (~ 635Ma) Puga cap carbonate from marine Ediacaran strata on the Amazon Craton, Brazil, revealed an changing redox state during the postglacial transgression. Mo, U, V, Cr, Ni, and Co proxies indicate that microbialites in the basal cap dolostone were deposited under oxic conditions, while the upper mega-ripple bedded dolostone indicates predominantly dysoxic conditions. During the development of microbialites, a nutrient-rich water surface resulted in elevated primary productivity, as evidenced by the flourishing of microbial mats in a semi-restricted marine environment along the cratonic margin. The continuous rise in sea level led to the drowning of coastal regions and caused rapid modification of biogeochemical cycling during the early precipitation of cap limestone. There was a direct link between microbial communities and initial oxygen production shortly after the Marinoan glaciation. The persistence of ecological stress is primarily associated with hydrodynamics, wave action, and sea-level rise during long-term transgression. The revision and reinterpretation of the redox background for the Puga cap carbonate improved the high-resolution analyses of redox proxies across the main

sections of this deposit, allowing for the identification of transitions between each redox zone. The prolonged and recurrent sequential redox transition marks the passage between icehouse and greenhouse conditions in the Amazon Craton during the Marinoan glaciation.

**Keywords:** trace elements; redox zone; environmental change; microbialites; cap dolostone

## 7.1 INTRODUCTION

The Cryogenian records catastrophic climatic and environmental disturbances. During this period, two global-scaled glaciations, also known as snowball Earth events, occurred, the Sturtian (~717-660 Ma) and the Marinoan glaciation (~650-635 Ma) (Kirschvink 1992, Hoffman and Schrag 2002, Corsetti and Lorentz 2006, Fairchild and Kennedy 2007, Rooney *et al.* 2015, Hoffman *et al.* 2017, 2021), and their impacts on marine biogeochemical cycles have been linked directly to the following evolution of metazoans in the Ediacaran (Li *et al.* 2010, Sansjofre *et al.* 2016, Brocks *et al.* 2018, Van Maldegem *et al.* 2018). During the Marinoan glaciation, low atmospheric  $p\text{CO}_2$  conditions presumably led to nearly complete coverage of continents and seas by ice caps, which significantly limited the availability of sunlight and nutrients to primitive (i.e., single-celled) yet diverse marine life (Sansjofre *et al.* 2014). Consequently, a considerable decline in primary production limits oxygen release from planktonic photosynthesis, resulting in decreased  $p\text{O}_2$  levels in the surface ocean and strong dysoxia and anoxia in deep-sea environments (Hoffman *et al.* 2017). However, primary production presumably persisted in cracks, polynyas, or larger open ice-free areas, potentially sustained by local geothermal heat sources (Hoffman *et al.* 2017). Earth's environment gradually moved from icehouse to greenhouse conditions during the Ediacaran Period, leading to deglaciation. The release of a vast meltwater plume from waning glaciers introduced substantial freshwater influxes into the ocean, creating density stratification that restricted adequate water mass mixing (Shields 2005, Liu *et al.* 2014, 2018, Hoffman *et al.* 2017, Santos *et al.* 2021, 2023). The freshwater influx also led to a chemocline between two redox zones: an upper oxic zone and a lower anoxic zone. This stratification further influences nutrient availability and distribution throughout the water column (Shields 2005, Liu *et al.* 2014, Hohl *et al.* 2017, Hoffman *et al.* 2017, Yang *et al.* 2017, Santos *et al.* 2021, 2023). Post-Cryogenian carbonate deposits, presumably precipitated directly from two endmember seawater mixes rich in dissolved inorganic carbon (DIC) and high alkalinity meltwater, are widespread and well known as cap carbonates. These archives serve as prime observations recording marine environmental perturbations of the late Neoproterozoic (Hoffman *et al.* 2017, Hohl *et al.* 2017, 2022, Liu *et al.* 2018, Sansjofre *et al.* 2014, Santos *et al.* 2021, 2023).

Many proxies are now available for reconstructing past redox environments. After evaluating the impact of diagenesis on geochemical signals, at least two major problems arose when reconstructing the past redox environment. First, do we record the seawater signal or sedimentary pore-water signals? The second is called "the reservoir effect" and was presented by Algeo (2005). Redox sensitive trace elements (RSTEs), e.g., Mo, U, and V, have been widely used as independent proxies for the reconstruction of past ocean redox conditions (Li *et al.* 2010, Poulton and Canfield, 2011, Planavsky *et al.* 2011, Sansjofre *et al.* 2014, Gilleaudeau and Kah 2015, Sperling *et al.* 2015, Hohl *et al.* 2017, Wang *et al.* 2022). Molybdenum, U, and V enrichments have been applied as paleoredox proxies because they exhibit conservative geochemical behavior under oxic conditions with little sedimentary uptake but tend to accumulate under anoxic/euxinic conditions (e.g., Tribovillard *et al.* 2006, Algeo and Tribovillard, 2009, Tribovillard *et al.* 2012, Algeo *et al.* 2012, Scott and Lyons 2012). The authigenic enrichment of these metals in sediments is driven by their different solubilities and affinities for particulates under varying redox conditions during sediment deposition or early diagenesis (Thomson *et al.* 1990, 1996, Tribovillard *et al.* 2006).

Here, we focused on the Marinoan cap carbonates of the Araras Group in Brazil to constrain the late Neoproterozoic environmental and climatic perturbations (Fig. 7.1A). We used the classification scheme for the geochemical environment proposed by Canfield and Thamdrup (2009) to trace the redox transitional zones. We analyzed the microbialites of the Mirassol d'Oeste Fm. (Fig. 7.1A and Fig. 7.1B) and present high-resolution concentrations of redox-sensitive elements and reconstructions of  $pO_2$  (e.g., V, Mo, and U) and paleoproductivity indicators (e.g., B, Zn, P, and Cr). In addition, compilations encompass a dataset comprising the redox framework of the Puga cap carbonate, which assisted us in refining the transitional redox zones as well as Fe speciation together with previously published major and trace elements (Sansjofre, 2011, Sansjofre *et al.* 2014), biomarkers (Elie *et al.* 2007, Souza Jr., 2017, van Mandegem *et al.* 2019), and  $\delta^{13}C$ ,  $\delta^{18}O$  and  $\delta^{15}N$  isotopes (Nogueira *et al.* 2003, Font *et al.* 2006, Ader *et al.* 2010, 2014, Sansjofre *et al.* 2011, Santos *et al.* unpublished). Our study delves into the effects of upwelling in biogeochemical metal cycling during early Ediacaran cap carbonate precipitation on the Amazon Craton. These results demonstrate an unequivocal synchronous relationship between the initial oxygenation of the Amazon margin and the local flourishing shortly after the Marinoan glaciation.

## 7.2 GEOLOGIC BACKGROUNDS

The post-Marinoan Puga cap carbonate sequence was deposited in the intracratonic Araras-Alto Paraguai Basin, southern Amazon Craton (Fig. 7.1A), during the early Ediacaran (Nogueira *et al.* 2019, 2022, Santos *et al.* 2020). The basal fill of this basin is composed of glacial diamictites from the Puga Formation, containing abundant dropstones. (Fig. 7.1B). The Ediacaran Araras Group consists of four formations: 1) the Mirassol d'Oeste Formation, 2) the Guia Formation, 3) the Serra do Quilombo Formation, and 4) the Nobres Formation (Nogueira and Riccomini 2006, Nogueira *et al.* 2003, 2007, 2019, 2022, Rudnitzki *et al.* 2016, Romero *et al.* 2020, 2022, Soares *et al.* 2013, 2020, Santos *et al.* 2021).

These Puga cap carbonate sequence ages are correlated with the Marinoan global glaciation (~650-635 Ma) (Nogueira *et al.* 2003, 2019, 2022, Font *et al.* 2006, Sansjofre *et al.* 2011, 2014, Soares *et al.* 2020, Santos *et al.* 2021, 2023). The cap dolostone (Mirassol d'Oeste Fm.) overlies discordantly on the marine glacial deposits of the Puga Fm. Its approximately 40 m thick cap dolostones (Fig. 7.1B) comprise fine pink dolomites, stratiform stromatolites, and giant domal stromatolites with abundant tubestones, as well as micro/macropeloidal dolomites (Nogueira *et al.* 2003, 2019, 2022, Font *et al.* 2006, Sansjofre *et al.* 2014, Soares *et al.* 2020, Romero *et al.* 2020, Santos *et al.* 2021, 2023). Abrupt, laterally irregular, and undulating plastic deformations at the base of the Mirassol d'Oeste Fm. have been interpreted as glacial isostatic rebounding due to a rapid shift from glacial to greenhouse conditions (Nogueira *et al.* 2003, 2019, Nogueira and Riccomini 2006, Santos *et al.* 2023).

The overlying Guia Fm., approximately 200 m thick, consists of laminated fine bituminous limestones, bituminous shales, red pelites, and limestone with calcite crystal fans (aragonite pseudomorphs), locally interrupted by breccias and deformational structures. The base of the Guia Fm. is the limestone portion of the Puga cap carbonate at ~50 m (Fig. 7.1B) (Nogueira *et al.* 2003, 2007, Sansjofre *et al.* 2011, 2014, Soares *et al.* 2020). The Serra do Quilombo Fm., with a thickness of 100 m, is predominantly composed of breccias with dolomitic cement and matrix intercalated with fine dolomites and sandy dolomites with hummocky cross-stratification and interpreted as deposits from a moderately shallow to deep platform affected by seismic activity and storms (Nogueira and Riccomini 2006, Nogueira *et al.* 2007).

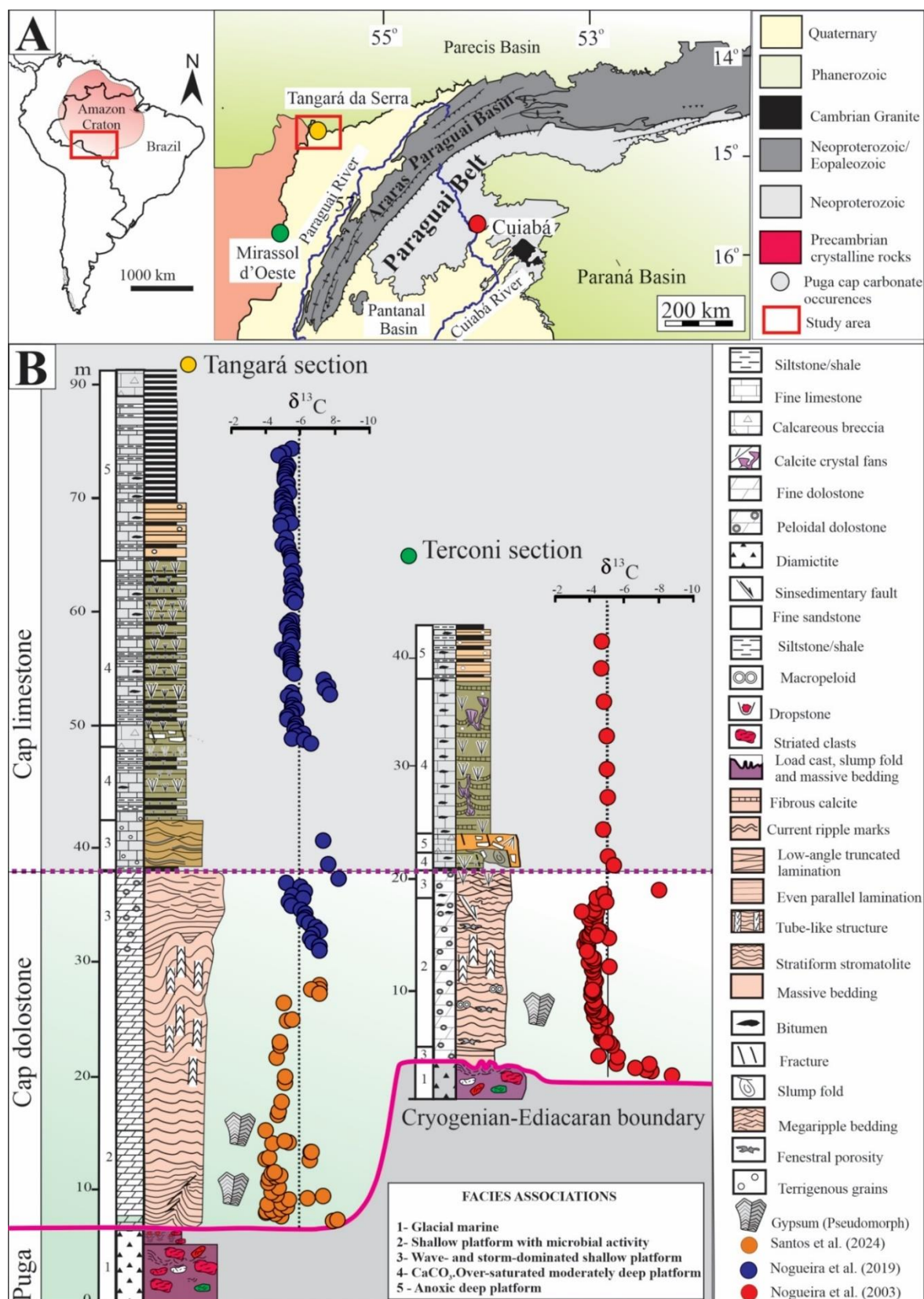


Figure 7.1- A) Location and simplified geologic map of the southwestern Amazon Craton with Neoproterozoic cap carbonate occurrences. The Cryogenian-Ediacaran boundary is exposed in the primary cap carbonate succession overlying crystalline and metasedimentary rocks of the Precambrian basement in the southwestern and southern portions of the Amazon Craton. Puga cap carbonate (PCC) occurrences are within the study area (Tangará section) in the Tangará da Serra- and Terconi section, in Mirassol d'Oeste- Mato Grosso, Central-Western Brazil. B) Stratigraphic sections of the Marinoan Puga cap carbonate in the southern Amazon Craton, perfil composta e quimioestratigrafia da Puga cap carbonate Tangará and Terconi section. The  $\delta^{13}\text{C}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  curves with values in ‰ were obtained by 1) Nogueira *et al.* (2019) and Santos *et al.* (2024), 6) Romero *et al.* (2013), 7) Nogueira *et al.* 2007. Paleoenvironmental interpretation (facies association) of the Puga cap carbonate (Nogueira *et al.* 2003, 2007, 2019).

The Nobres Fm. consists of fine dolomites, subordinate oolitic dolomites, stromatolites, sandy dolomites, breccias, sand/mud rhythmites, and sandstones interpreted as deposits from a tidal flat/sabkha environment (Rudnitzki *et al.* 2017, Romero *et al.* 2022). The Araras Group deposits record a post-glacial transgression characterized by microbial colonization on shallow platforms—as evidenced by microbialites in the Mirassol d'Oeste Formation (Fig. 7.1B). The ongoing transgression and glacioisostatic adjustments led to moderately deep environments associated with the Guia and lower Serra do Quilombo Fms. Subsequently, a gradual decrease in sea level led to establishing coastal environments within greenhouse conditions, featuring tidal flats and sabkha settings in the Nobres Fm. (Rudnitzki *et al.* 2017, Soares *et al.*, 2020, Romero *et al.* 2020, 2022, Santos *et al.* 2021, 2023, Nogueira *et al.* 2022). The ages of the cap dolostone and cap limestone were determined to be  $627 \pm 32$  Ma and  $622 \pm 33$  Ma, respectively, using carbonate Pb–Pb dating (Babinski *et al.* 2006, Romero *et al.* 2013). A recent study by Carvalho *et al.* (2023) determined an age of  $623 \pm 3$  million years using U–Pb via LA–ICP–MS on crystal fans (cap limestone), interpreted as a constraint on the transition from shallow to intermediate burial diagenesis of the Puga cap carbonate.

### 7.2.1 Sedimentology and Stratigraphic Aspect of the Puga Cap Carbonate

The samples utilized in this study were extracted from the ~40 m long drill core JOR (Ornamental open pit) from the Tangará Section at Calcário Tangará quarry in the Tangará da Serra region, Mato Grosso state ( $14^{\circ} 45' 26''$  S,  $57^{\circ} 50' 02''$  W) (Fig. 7.1 A). In the Tangará section, the lower ~10 m consists of diamictites from the Puga Formation, and the upper ~30 m comprises cap dolostones from the Mirassol d'Oeste Formation. The outcrop samples further complement the composite profile of the Tangará da Serra region, with ~5 m corresponding to cap dolostone and ~50 m comprising cap limestone of the overlying Guia Formation. In addition, we compiled data previously published by Sansjofre, 2011, Sansjofre *et al.* 2014 Ader *et al.* 2014, from outcrops in the Terconi section at Terconi quarry in the Mirassol d'Oeste region, Mato Grosso state ( $15^{\circ}40'42''$  S,  $58^{\circ}04'32''$  W) (Fig. 7.1 A).

This study follows the sedimentological and stratigraphic framework previously proposed by Santos *et al.* (2021). The Tangará da Serra succession has a thickness of approximately 90 m (Fig. 7.1B), with the initial dozen meters of the studied cores comprising glaciomarine diamictites and dropstone beds from the Puga Fm cap dolomites of the Mirassol d'Oeste Fm. directly overlie these deposits, which form a ~40 m-thick cap dolostone layer. The cap dolostone is in sharp contact with glacial diamictite and exhibits synsedimentary deformation (e.g., deformed laminations, micro-faults, massive bedding, and incipient breccias). The cap



dolostone was subdivided from base to top in microfacies: 1) microbialite facies comprises stratiform doloboundstones with gypsum pseudomorph and domal doloboundstones with tubestone; 2) wave-rippled dolostone consists of two microfacies, the peloidal dolograinstones/dolomudstone with quasi-planar to low-angle lamination and the peloidal dolograinstones with mega-ripple bedding. The cap limestone (50 m thick in the Guia Formation) (Fig. 7.1B) is the top of the succession and is composed of discontinuous layers of dolomitic marlstone that are concordantly superimposed on the cap dolostone and limestone with calcite crystal fans interbedded with mega-rippled limestone (see Soares *et al.* 2020 and Santos *et al.* 2021, 2023 for more details).

### 7.3 GEOCHEMICAL METHODS

#### 7.3.1 Major and trace elements

In total, 42 samples of the drill core JOR, comprising the cap dolostone from the Tangará section, were prepared for major and trace element concentration determination using carbonate leaching to avoid detrital silicate and oxide contamination following the digestion protocol of Rongemaille *et al.* (2011): Approximately 20 mg of powder was weighed into acid-cleaned 2.5 mL microcentrifuge tubes, and 0.5 mL of 0.85 N (i.e., 5%) trace-metal grade acetic acid was added and left to dissolve the samples overnight at room temperature. The samples were centrifuged, and 0.25 mL aliquots of the supernatant were diluted in 4.75 mL of 0.45 N (i.e., 2%) PFA-distilled HNO<sub>3</sub> with 10 ppb In as an internal standard to control instrumental drift. Analyses were conducted on a Thermo Scientific ELEMENT XR high-resolution inductively coupled plasma mass spectrometer (HR ICP-MS) from the PôleSpectrométrie Océan (PSO) at the Institut Universitaire Européen de la Mer, Université de Bretagne Occidentale, France. Using low-, medium-, and high-resolution modes allowed major/minor/trace/REE + Y concentrations to be measured at a constant dilution factor during a single analytical session. Concentrations were determined by external calibration with a synthetic, matrix-matched calibration solution. Repeated analyses of the standard reference material CAL-S (N = 15) showed a 1 SE precision of 7–9%, with results within 10% of published values.

##### 7.3.1.1 Quantification of authigenic trace metal concentrations

For the precise assessment of trace metal concentrations in predominantly carbonate samples, we used an alternative normalization method that circumvents the limitations associated with aluminum normalization in samples with low aluminum content (e.g., Calvert and Petersen 1993, Tribovillar *et al.* 2006, Sansjofre *et al.* 2014). Rather than resorting to

conventional aluminum normalization, which may be biased due to potential aluminum enrichment in oxide phases (e.g., Van der Weijden 2002), we calculate a given element's authigenic fraction ( $X_{auth}$ ). This calculation involves subtracting the expected detrital fraction ( $X_{detrital}$ ) from the total concentration of the element (equation 1). The detrital fraction is determined by multiplying the aluminum content of the sample by the element-to-aluminum ratio of the standard used by McLennan (1989) for post-Archean shale (PAAS). These reference numbers are preferred to the bibliographic reference values (Paul *et al.* 2023).

$$X_{auth} = X_{total} - X_{det}$$

$$X_{det} = \left( \frac{X}{Al} \right) PAAS \times Al_{samples}$$

This approach provides a more accurate interpretation of temporal and spatial variations in trace metal concentrations, allowing a more direct correlation with relative changes in the redox environment (Sansjofre *et al.* 2014).

## 7.4 RESULTS

### 7.4.1 Trace Elements

The trace element data are listed in Supplementary Table 1 and described below. The concentrations of immobile elements commonly used to assess detrital contamination in leachates include Al, Zr, Sc, Rb, and Th. The Al concentrations range from 28.23 to 509.25 ppm, the Zr concentrations range from 0.02 to 0.18, the Sc concentrations range from 0.07 to 2.25, the Rb concentrations range from 0.03 to 0.55, and the Th concentrations range from 0.01 to 1.17 ppm. The aluminum concentrations correlated with the Rb ( $R^2 = 0.85$ ) and Th ( $R^2 = 0.69$ ) concentrations.

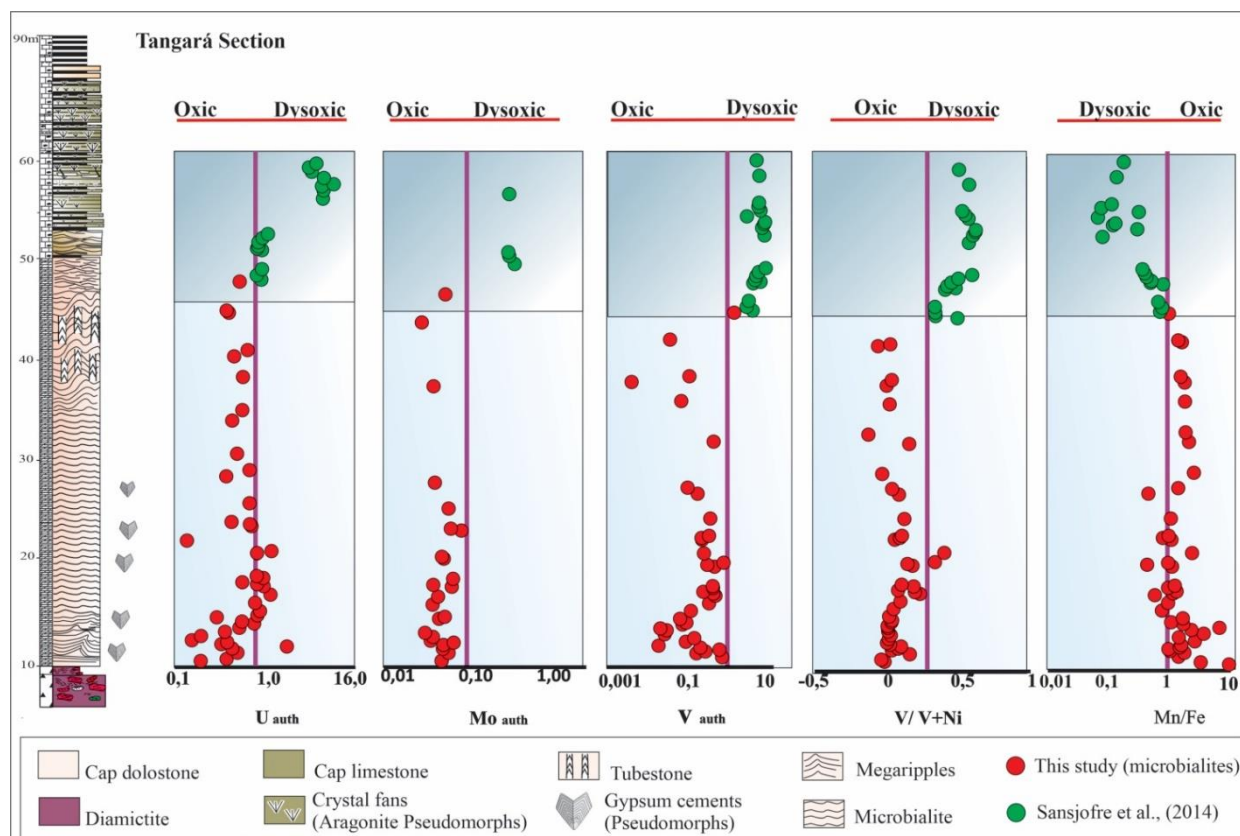


Figure 7.2- Stratigraphic distribution of redox elements sensitive,  $U_{auth}$ ,  $Mo_{auth}$ ,  $V_{auth}$ ,  $V/(V+Ni)$  ratio,  $Fe/Mn$  ratio in Tangará Section. The new data are microbialites level and the lower and upper Tangará sections by Sansjofre *et al.* (2014).

#### 7.4.1.1 Redox-sensitive and bioavailable trace elements

Authigenic redox-sensitive and bioavailable trace metal concentrations (V, Cr, Co, Ni, Cu, Cd, Zn, Pb, U, and Mo) in microbialites of the Puga cap carbonate from the Tangará section. Cap dolostones exhibit low trace element concentrations, particularly for redox-sensitive trace elements (RSEs), Mo, U, and V.  $Mo_{auth}$  concentrations range from 0.02 to 0.08 ppm (average =  $0.03 \pm 0.02$  ppm,  $n = 43$ ). The  $U_{auth}$  concentrations range from 0.1 to 1.2 ppm (average =  $0.5 \pm 0.4$  ppm,  $n = 43$ ), and the  $V_{auth}$  concentrations range from 0.02 to 1.05 ppm (average =  $0.21 \pm 0.3$  ppm,  $n = 43$ ) (Fig. 7.2). The concentrations of redox-sensitive elements in the cap dolostones are similar to those in Sansjofre *et al.* (2014) (Fig. 7.2 and Fig. 7.6). The bioessential trace elements in the microbialites ranged from 0.47 to 19.8 ppm (average =  $3.0 \pm 2.9$ ,  $n = 43$ ) for Ni, 0.15 to 6.10 ppm (average =  $0.9 \pm 1.2$ ,  $n = 43$ ) for Cr, 8.33 to 101.25 ppm (average =  $32 \pm 18$ ,  $n = 43$ ) for P, 0.5 to 15.84 ppm (average =  $1.97 \pm 2.67$ ,  $n = 43$ ) for Cu, and 9.36 to 237 ppm (average =  $52.1 \pm 41.5$ ,  $n = 43$ ) for Zn (Fig. 7.3).

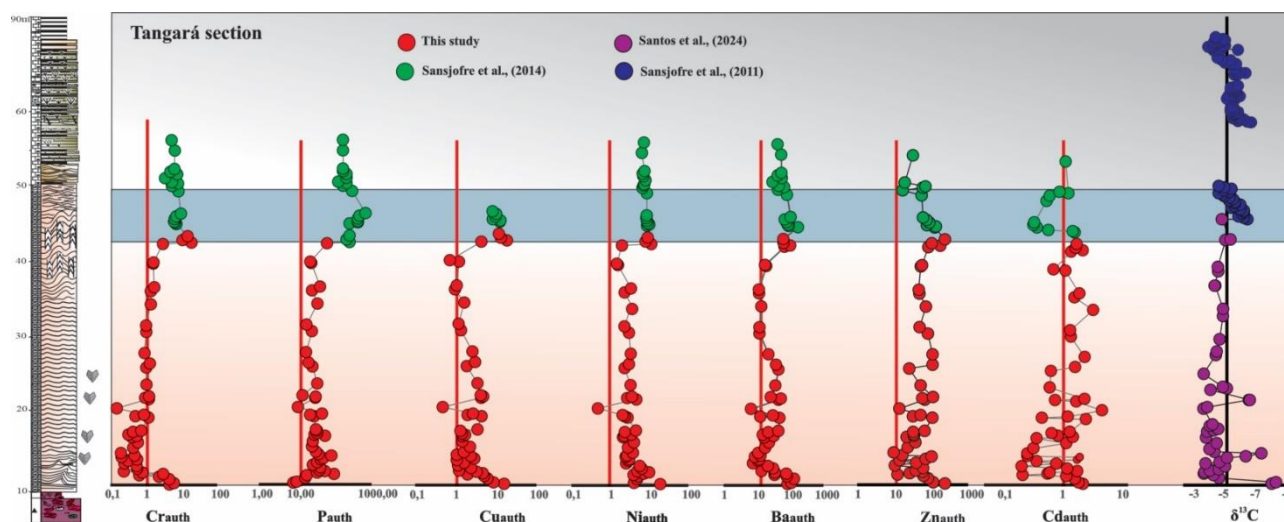


Figure 7.3- Stratigraphic distribution of reconstructed paleoproductivity,  $Cr_{auth}$ ,  $P_{auth}$ ,  $Cu_{auth}$ ,  $Ni_{auth}$ ,  $Ba_{auth}$ ,  $Zn_{auth}$ , and  $Cd_{auth}$  in Tangará Section. The new data are microbialites level and the lower and upper Tangará sections by Sansjofre *et al.* (2014). The  $\delta^{13}C$  values in ‰ were obtained by 1) Sansjofre *et al.* (2011) and Santos *et al.* (2024).

## 7.5 DISCUSSION

### 7.5.1 Assessment of sample purity and potential contamination via silicate input and diagenetic overprinting

To reliably interpret the trace element composition of carbonates for paleoenvironmental reconstruction, it is crucial to screen for detrital aluminosilicate contamination as well as evaluate potential diagenetic overprinting and post-depositional alteration (i.e., via diagenetic, meteoric, or metamorphic fluid-rock interactions) (Kamber and Webb 2001, Kamber *et al.* 2005, Bolhar and Van Kranendonk 2007, 2014, Schier *et al.* 2018, Viehmann *et al.* 2019, 2020, 2023, Sansjofre *et al.* 2014, Hohl *et al.* 2017). We monitored the concentration of a geochemical proxy of interest relative to an almost immobile element (e.g., Al, Zr, Th) commonly associated with detrital aluminosilicates. The aluminum concentrations in carbonate leachates of the Puga carbonate layer succession are < 1 %. The stromatolitic dolomite content shows no correlation with the Al content ( $R^2 = 0.04$ ), suggesting that these samples most closely represent the pristine geochemical composition. No dilution effect by the clastic fraction is observed, which is expected for the carbonate sample and low Al concentration. Ni, V, U, Zn, Pb, and Cu do not correlate with Al and can be used as paleoredox indicators

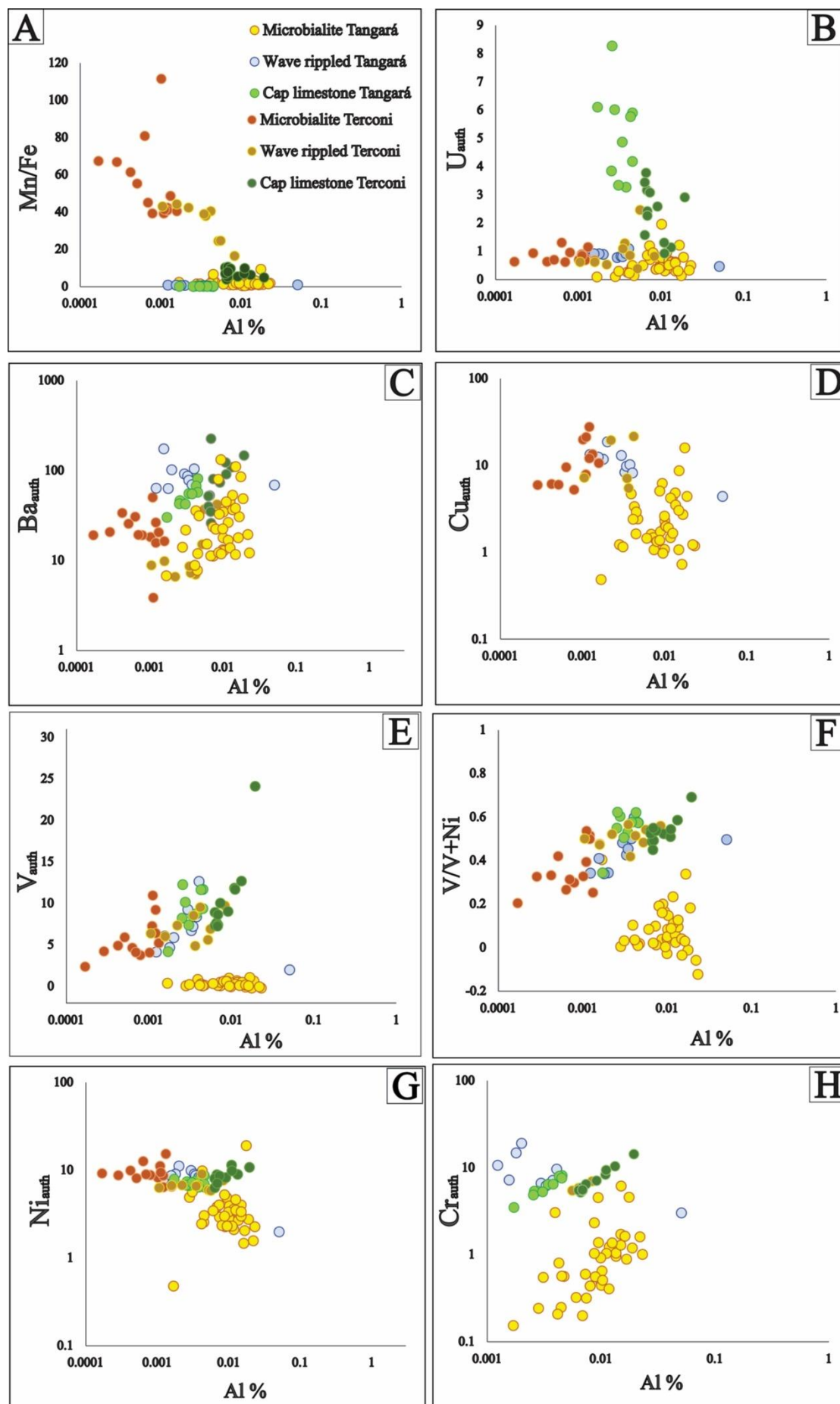


Figure 7.4- Crosplot of metal trace vs. Al concentrations of the Puga cap carbonate. Sansjofre *et al.* (2014) presented new data on microbialites in the lower and upper Tangará sections and Terconi sections.

Metal trace element concentrations (e.g., Mn/Fe vs. Sr =  $R^2 < 0,132$ ) were not shown to exhibit any significant correlations with fluid-mobile concentrations. Despite the low correlation with mobile elements, trace elements may have been mobilized at different times and through various physicochemical processes during separate post-depositional events (Viehmann *et al.* 2023). Therefore, the potential for multistage elemental mobilization processes must be partially ruled out. Nevertheless, several studies have shown that the paragenetic relationships of the Puga cap carbonate demonstrate consistent evidence of early diagenetic processes, with less influence from late diagenetic events (Soares *et al.* 2020, Santos *et al.* 2023). The cap dolostone shows increased syndepositional cementation, which may have enhanced its preservation (Santos *et al.* 2021, 2023). This exceptional preservation is observed in both the well-preserved primary texture (e.g., grumous textures and shrubs facies) and the preserved  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  signals from previously published data (Nogueira *et al.* 2003, 2007, 2019, Font *et al.* 2006, Sansjofre *et al.* 2011, Soares *et al.* 2020, Santos *et al.* 2021, 2023, 2024).

### 7.5.2 The environmental scenario of the Araras platform paleomargin

The Snowball Earth hypothesis implies that thick ice caps isolate oceanic and atmospheric reservoirs from one another, promoting the development of anoxic conditions in the deeper ocean (Hoffman *et al.* 2017) and significantly influencing the input, mixing, and upwelling of redox-sensitive elements and their recording in authigenic biochemical sediments (Hoffman *et al.* 2017, Font *et al.* 2006, Sansjofre *et al.* 2014). During deglaciation, oxidative weathering would give rise to a chemocline separating the sea into two redox zones, the upper oxic zone and the lower anoxic zone, and oxidative weathering would give rise to a chemocline dividing the ocean into two redox zones, the upper oxic zone, and the lower anoxic zone. (Hoffman and Schrag 2002, Li *et al.* 2010, Ader *et al.* 2009).

Epicontinental seas were the primordial scenario from the initial phase of Western Gondwana, with the development of extensive carbonate platforms with restricted oceanic connections under post-snowball conditions (Nogueira *et al.* 2022). Transgression following a low sea-level stand period related to the Marinoan glaciation led to an enlargement of the platforms landward, covering cratonic regions (Hoffman *et al.* 2017). These conditions were crucial for the potential preservation of almost one km-thick carbonate hundreds of kilometers long along the southern margin of the Amazon Craton (Nogueira *et al.* 2003, 2007, 2019, 2022, Font *et al.* 2006, Sansjofre *et al.* 2014, Romero *et al.* 2020, Santos *et al.* 2021, 2023).

Carbonate precipitation on the southern margin of the Amazon craton is characterized by the recurrence of shallow water influenced by ice gravity and glacioisostatic adjustments (Nogueira *et al.* 2003, Santos *et al.* 2023, 2024). These conditions favor the persistence of a semi-restricted marine environment, creating an ideal setting for the flourishing of microbial communities along the craton margin (Nogueira *et al.* 2003, 2022, Font *et al.* 2006, Romero *et al.* 2020, Santos *et al.* 2021, 2024). The microbial communities primordially colonized the diamictite substrate, forming stratiform bioconstructions on a shallow platform under calm water conditions. The transition from stratiform to domal morphology reflects the progressive deepening of the platform, concomitant with increases in microbial activity (Santos *et al.* 2021). Similarly, the shallow environmental conditions allowed for the retention of dissolved Mg, promoting the development of dolomitic platforms. Gypsum pseudomorphs in fenestral porosity indicate sporadic supersaturation during upwelling events related to water mixing events (Santos *et al.* 2021, 2023). In upwelling systems, concentrations of Co and Mn are kept at low levels due to the depletion of these dissolved elements in the deep waters of the ocean, followed by their remobilization and transport to open ocean areas under oxygen-deficient conditions (Calvert and Pedersen 1993, Sweere *et al.* 2016, Tribovillard *et al.* 2006). The upwelling process receives nutrients from deeper oceanic waters, which typically have lower Co and Mn concentrations (due to their lower solubility in modern fully oxygenated oceanic basins and the formation of Mn oxyhydroxides), limiting authigenic enrichments in sediments beneath upwelling zones (Sweere *et al.* 2016). In contrast, hydrographically restricted basins receive Co and Mn from riverine input, making authigenic enrichments less likely to be limited by supply (Calvert and Pedersen 1993, Tribovillard *et al.* 2006, Sweere *et al.* 2016, Hippert *et al.* 2019).

To assess the impact of upwelling on the post-Marinoan cap carbonates of the Araras platform, we calculated the Co and Mn enrichment factors in carbonate leachates by adopting the methodology proposed by Sweere *et al.* (2016). Organic-rich sediments deposited in upwelling-influenced areas exhibit low  $\text{Co} \times \text{Mn}$  ( $< 0.4$ ) values, whereas restricted settings typically display high  $\text{Co} \times \text{Mn}$  values ( $> 0.4$ ), indicating seasonal upwelling currents (Sweere *et al.* 2016).

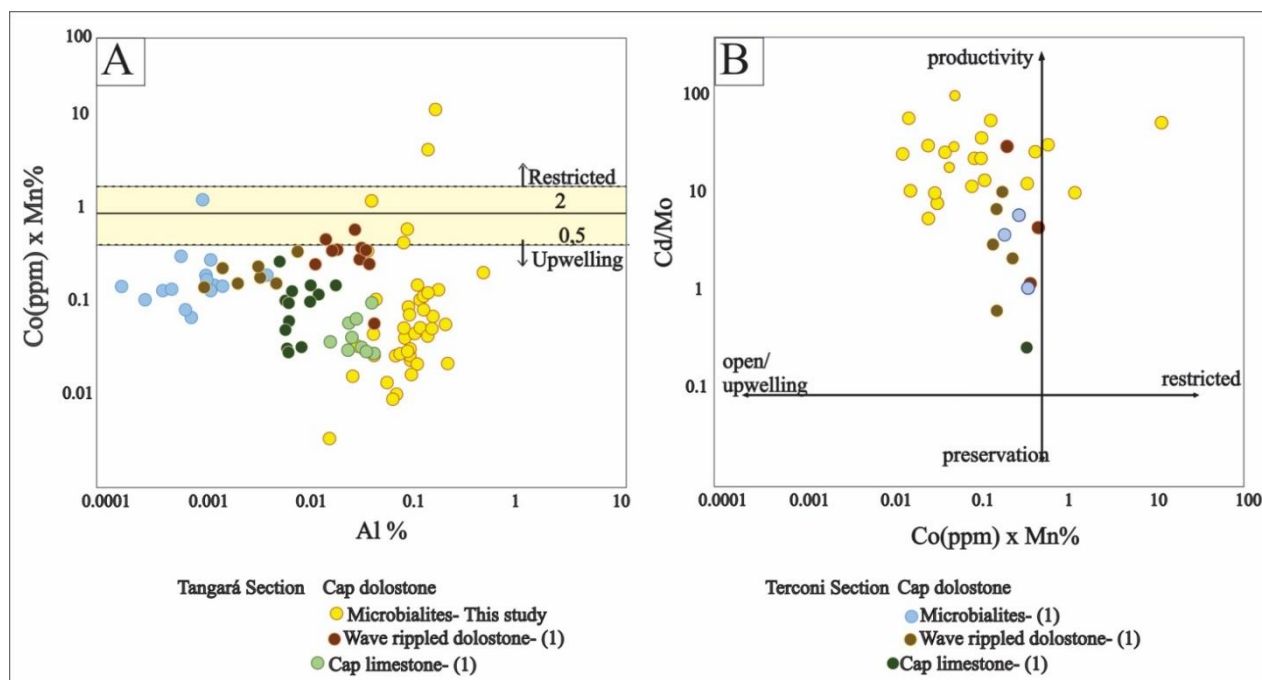


Figure 7.5- A) Co x Mn vs Al % covariation plots from Sweere *et al.* (2016). B) Cd/Mo x (Co x Mn) covariation plots from Sweere *et al.* (2016). The new data on microbialites was presented in the lower and upper Tangará sections and Terconi sections by Sansjofre *et al.* 2014.

In the microbialites facies of the cap dolostone, the Co x Mn values range from 0.1 to 11.66, with an average of  $0.5 \pm 1.87$  ( $n = 43$ ) (Fig. 7.5). In addition, we calculated the values previously presented by Sansjofre *et al.* in 2014. The wave-dominated dolostone facies exhibit Co x Mn values ranging from 0.21 to 0.60, with an average of  $0.36 \pm 0.11$  ( $n = 10$ ) (Fig. 7.5). Strongly influenced upwelling is observed throughout the cap limestone, where Co x Mn varies from 0.03 to 0.1, with an average of  $0.04 \pm 0.02$  ( $n = 10$ ). Additionally, the Co x Mn values in the Terconi section are similar to those in the Tangará section, with averages of  $0.15 \pm 0.27$  ( $n = 17$ ) in the microbialites,  $0.18 \pm 0.06$  ( $n = 7$ ) in the wave-dominated dolostone, and  $0.10 \pm 0.06$  ( $n = 13$ ) in the cap limestone (Fig. 7.5). The Puga cap carbonate succession precipitated under similar marine conditions, as demonstrated by the Co x Mn values, with discrepancies occurring only in the basal portions of the two strata. In the Tangará quarry, the values at the base range from 0.43 to 11.66. Our data demonstrate that oceanic circulation constantly influenced ongoing upwelling throughout the precipitation of the Puga cap carbonate succession (Fig. 7.5).

The high Co x Mn values at the base of the cap dolostone indicate precipitation in a restricted environment with low oceanic circulation. This scenario appears to become more dynamic toward the top, where values are predominantly less than 0.4. Upwelling events are invoked to explain ocean destratification dynamics following the Marinoan event (Rame and Marotzke 2022, Santos *et al.* 2021, 2023). Our evidence demonstrated the more significant influence of upwelling events as a source of bioessential elements than continental detrital components during microbial proliferation. The upwelling model is appealing because it aligns with



carbonate precipitation in shallow-water conditions with light  $\delta^{13}\text{C}$  values (Nogueira *et al.* 2003, Font *et al.* 2006, Sansjofre *et al.* 2011). Moreover, biochar could provide a significant supply of nutrients, reduce trace metals in shallow-water platforms, and promote microbial development (Sansjofre *et al.* 2014, Romero *et al.* 2020, Santos *et al.* 2021). The upwelling has been suggested to explain the short destratification timescale found in this study, implying that Marinoan cap dolostones accumulated during the deglacial period under the influence of a freshwater environment (Rame and Marotzke 2022). The rapid cementation facilitated by post-Marinoan supersaturation increases the potential for preserving large mounds. The formation of giant stromatolites results from a combination of specific factors, including 1) coastal shallow and clear waters, 2) warm temperatures, 3) enhanced carbonate production, and 4) the continuous generation of accommodation space induced by glacial isostatic adjustment (GIA) (Santos *et al.* 2021). The microbialites of the shallow platforms offer an excellent window of opportunity for understanding the recovery of biogeochemical cycles and paleo-redox reconstruction of the Amazon paleo-margin during the fast post-Marinoan transgression (Fig. 7.7).

## 7.6 PALEOREDOX CONDITIONS DURING POST-MARINOAN CAP CARBONATE PRECIPITATION ON THE AMAZON CRATON MARGIN

The Snowball Earth model postulates the occurrence of an extreme icehouse with low latitude and altitude glaciations followed by abrupt deglaciation under hot greenhouse conditions (Hoffman *et al.* 2017). In this context, there is an anticipation of widespread, massive, and rapid precipitation of cap carbonates during deglaciation, coupled with stabilizing preexisting anoxia in deeper waters (Hoffman and Schrag 2002, Nogueira *et al.* 2003, Font *et al.* 2006, Hoffman *et al.* 2017, 2021). Redox-sensitive elements (RSEs) (e.g., U, Mo, V, and Mn) and Fe speciation have been established as geochemical proxies for inferring the paleoredox conditions of marine sediments (Algeo *et al.* 2012, Algeo and Rowe 2012, Brumsack, 2006, Lyons *et al.* 2003, McManus *et al.* 2006, Tribovillard *et al.* 2006, Piper *et al.* 2007, Scott and Lyons, 2012) and have been widely applied as proxies in post-Snowball Earth sedimentary successions (Sansjofre *et al.* 2014, Hohl *et al.* 2017).

Our data encompass the primary interval of microbialites from the Puga cap carbonate (Fig. 7.2). The microbialites, including stratiform and giant domal stromatolites, in the cap dolostone consistently showed depletion in the  $V_{\text{auth}}$ ,  $\text{Mo}_{\text{auth}}$ , and  $\text{U}_{\text{auth}}$  sections compared to the upper section. However, there is an enrichment in the Mn/Fe ratios (Fig. 7.2). Mo, U, and V behave conservatively in oxic waters with limited sediment uptake but are highly reactive under anoxic conditions (U and V) and sulfidic conditions (Mo), leading to significant authigenic

sedimentary enrichments under reducing conditions (Brumsack 2006, Algeo and Maynard 2004, Tribovillard *et al.* 2006, Algeo and Tribovillard 2009, Algeo and Rowe 2012, Sahoo *et al.* 2012, Reinhard *et al.* 2013, Partin *et al.* 2013, Sansjofre *et al.* 2014). Authigenic Mn enrichment in marine sediments is a reliable indicator of oxic bottom water conditions (e.g., Calvert and Petersen 1993, 2007). Excess dissolved Mn is linked to Mn oxyhydroxide accumulation at the sediment-water interface, occurring only beneath oxygenated bottom waters (Calvert and Pederson, 1993, Ferreira *et al.* 2020).

The depletion of U, Mo, V, and enrichment of Mn/Fe across the microbialites level are best interpreted as precipitated in an oxygenated water column. These new data complement the redox profile previously presented by Sansjofre *et al.* (2014), focusing mainly on the wave-dominated dolostone facies and cap limestone in the Tangará da Serra region. It is characterized by the presence of iron (Fe) and manganese (Mn) oxides, the absence of pyrite (Sansjofre *et al.* 2014, Santos *et al.* 2023), and deficient total organic carbon (TOC) contents (Sousa *et al.* 2016, van Maldegem *et al.* 2018), indicating deposition under oxic conditions. After the Marinoan glaciation, the water column on the Araras platform likely transitioned to predominantly oxic conditions, with anoxia restricted to the sediment porewater and sediment-water column interface in the deeper regions of the platform (Font *et al.* 2006, Sansjofre *et al.* 2014). In the wave-dominated dolostone facies occurs an increase in the concentrations of U, Mo, and V in both the Tangará and Terconi quarries sections (Fig. 7.2 and Fig. 7.6). Enrichment of these elements is characteristic of suboxic-anoxic (euxinic) depositional settings, where authigenic molybdenum is taken up as particle-reactive thiomolybdate (Tribovillard *et al.* 2012). Dysoxic conditions promoted an increase in the burial rate of organic matter, which likely activated the process of trapping trace metals (Sansjofre *et al.* 2014). These dysoxic conditions persist in the deposits associated with the cap limestone (Fig. 7.2 and Fig. 7.6). At this level, there is an accumulation of trace metals, pyrite, and preserved organic matter. These conditions are associated with a deepening of the water column and a long-term transgression, as discussed by Nogueira *et al.* (2003, 2022) and Sansjofre *et al.* (2014). The ensuing interpretations, drawn from the data amalgamated from Elie *et al.* (2016), Sousa *et al.* (2016), and van Maldegem *et al.* (2018), refine our understanding of redox conditions and productivity brought forth by trace elements. The organic matter was deposited under anoxic conditions (Pr/Ph ratio <1), consistent with our paleo redox data indicating dysoxic conditions (Sousa *et al.* 2016, van Maldegem *et al.* 2018).

Other redox indicators for the Terconi section (Sansjofre 2011), such as iron speciation data, are predominantly present in a highly reactive state, with FeHr/FeT ratios averaging 0.82

for the cap dolostones and 0.74 for the limestones (Fig. 7.6). These findings further complement our understanding of redox conditions. This reactive iron is abundant in oxidized and carbonate forms ( $\text{Fe}_{\text{ox}}$ ) ( $\text{Fe}_{\text{carb}}$ ). At the base of the cap limestones, iron is predominantly in the form of pyrite ( $\text{Fe}_{\text{pyr}}$ ), resulting in a mixture of the three phases,  $\text{Fe}_{\text{ox}}$ ,  $\text{Fe}_{\text{carb}}$ , and  $\text{Fe}_{\text{pyr}}$ , in the upper section, with concentrations of 0.35%, 0.55%, and 0.10%, respectively (Fig. 7.6) (Sansjofre 2011). Pyrite is absent in the dolostone matrix and is recognized as a diagenetic phase associated with calcitic cement generated by mesodiagenesis (Santos *et al.* 2023). However, sulfur is frequently found in the limestone matrix and is interpreted as sulfur in water, indicating the presence of large amounts of preserved organic matter in anoxic environments (Soares *et al.* 2020). In addition, these conditions coincide with an increase in organic matter content (Sansjofre *et al.* 2014). Pyrite and sulfur isotope analyses detect euxinic conditions, referred to as the sulfidic zone (Sansjofre *et al.* 2014, 2016, Soares *et al.* 2020). In this zone, sulfate serves as an oxidant and undergoes reduction. Intense sulfate-reduction metabolism produces  $\text{H}_2\text{S}$ , which is typically enriched in  $^{32}\text{S}$  compared to the sulfate pool. This  $\text{H}_2\text{S}$  reacts with free iron in ferruginous water, forming pyrite (Sansjofre *et al.* 2016). Using multiple sulfur isotopes ( $^{33}\text{S}/^{32}\text{S}$ ,  $^{34}\text{S}/^{32}\text{S}$ , and  $^{36}\text{S}/^{32}\text{S}$  ratios) of carbonate-associated sulfate, Sansjofre *et al.* 2016 instead demonstrated the most impressive event of oceanic sulfate drawdown in Earth's history, driven by increased pyrite burial, which may have contributed to the Ediacaran oxygenation of the oceans and atmosphere. Ader *et al.* (2014) illustrated that the Araras Group exhibits  $\delta^{15}\text{N}$  values ranging between +2.2 and +10.5‰. (Fig. 7.6).  $\delta^{15}\text{N}$  shows a good correlation between TOC and N, attributing a major contribution of organic matter to the nitrogen pool. The values vary between 2.4 and 9.9‰. The basal part of the cap dolostone first shows a decrease from 4.2 to 2.4‰ and quickly rises to a nadir of 9.9‰ in the upper part of the cap dolostone. The upper parts of the cap dolostone and limestone exhibit a constant  $\delta^{15}\text{N}$  value of approximately 5‰, except for the last value of 2.5‰. The most plausible hypothesis suggests a nitrogen cycle akin to that of the contemporary ocean, where nitrate remains stable throughout the sea, except in anoxic oxygen minimum zones and specific locally confined anoxic basins. This inference implies the presence of sufficient dissolved  $\text{O}_2$  to stabilize nitrate in most late Neoproterozoic oceans. Consistent with the interpretations of Sansjofre *et al.* (2014), these conditions directly imply the preservation of organic matter (OM) in cap dolostone (Fig. 7.6), as previously demonstrated by Elie *et al.* (2008), Souza *et al.* (2016), and van Maldegem *et al.* (2018). However, anoxic conditions begin at the sediment-water interface in limestone deposits, increasing the potential for preserving organic matter (OM) (Sansjofre *et al.* 2014).

In summary, an apparent stratigraphic/faciological alignment between the microbialites

and the development of an interface water-sediment system oxygenated during shallow marine deposition may suggest a cause-and-effect relationship between them, notably since widespread dysoxia coincided with the decline of microbialites in the Puga cap carbonate (Fig. 7.2 and Fig. 7.6). This upper step of the chemocline coupled to the transgressive tract of the sequence is more appropriate for rapid sedimentation flux. The complex interplay between trace metals and organic compounds, in addition to their integration within organomineralization mechanisms, has played a pivotal role in shaping the unique geochemical profiles discernible with stromatolitic carbonates (Robbins *et al.* 2016)

### 7.6.1 Paleoproductivity indicators

Microbialites are authigenic carbonate deposits that can record the chemistry of the ambient fluid at the time of their growth (Burne and Moore 1987, Grotzinger and Knoll 1999, Hohl and Viehmann 2021). Trace metals are incorporated into sediments in association with organic matter, mainly in depositional processes with low oxygenation (Tribovillard *et al.* 2006, Algeo *et al.* 2012, Algeo and Rowe 2012, Brumsack 2006, Lyons *et al.* 2003, McManus *et al.* 2006, Piper *et al.* 2007, Scott and Lyons 2012, Robbins *et al.* 2016). In the water column, where the chemocline is near or below the sea floor, most adsorbed metals are liberated and recycled due to oxidative degradation of organic matter during settling. As the chemical line rises in the water column, more surface-adsorbed metals are retained and delivered to the sea floor (Ripley *et al.* 1990).

The new data presented here predominantly encompasses stromatolitic facies (Fig. 7.2 and Fig. 7.3). In this context, these biochemical sediments can act as geochemical archives to aid in reconstructing paleoenvironmental changes in post-Snowball Earth shallow water environments. The concentrations of bio-essential trace metals in carbonate can be used as indicators of paleoproductivity. Within the succession, composed of stratiform stromatolites showing higher enrichments of Zn, Cd, Cu, Ba, and Cr compared to the giant stromatolite level, there is a trend of depletion in paleoredox and bioessential elements (Fig. 7.3).

In oxic marine environments, Nickel (Ni), Zinc (Zn), Cadmium (Cd), and Copper (Cu) all function as micronutrients. When complexed with organic matter, Nickel enhances scavenging in the water column, contributing to sediment enrichment. Zinc predominantly forms complexes with humic/fulvic acids, while Cadmium consistently exhibits nutrient-like behavior, associating mainly with organic matter in sediments. Copper, prevalent as organometallic ligands in oxic environments, partially behaves as a micronutrient, and its removal from solution in deep waters is influenced by complex interactions with organic matter and Fe–Mn

oxyhydroxides (Tribovillard *et al.* 2006). Additionally, a high concentration of Ni and Cu in the sediments indicates a substantial input of organic matter, leading to the abundant deposition of these elements. Reducing conditions further facilitated the fixation of Ni and Cu within the sedimentary environment. However, recent studies have demonstrated that the concentrations and systematic behavior of bioessential elements have negligible or limited nutritional value but can act as cofactors in microbiota metabolism, including element cycling in modern and marine oceans (e.g., Morel and Price 2003, Robbins *et al.* 2016, Facey *et al.* 2019). Fe, Ni, and Co are recognized as crucial cofactors in anaerobic methanogenesis. In this process, iron (Fe) plays a pivotal role. At the same time, copper (Cu) and molybdenum (Mo) are essential for aerobic methane oxidation and nitrous oxide cycling, as highlighted by studies such as those conducted by Glass and Orphan (2012). Moreover, in oxygenic photosynthesis, another vital biological process, iron (Fe), manganese (Mn), magnesium (Mg), and copper (Cu), are essential cofactors, as evidenced by Shcolnick and Keren (2006). This underscores these elements' diverse roles in supporting fundamental biological processes across different environmental conditions. Our study observed systematic enrichment in the first few centimeters of the stratiform dolostones for the metals Zn, Cu, Ba, Cd, Cr, Mn, and Fe. It records a trend of accumulation fluctuations, whereas this accumulation was insignificant at the stromatolitic level (Fig. 7.3 and Fig. 7.6).

Our data do not show significant trace metal accumulation associated with increased productivity, as one would expect, at the giant stromatolite level (see  $\delta^{13}\text{C}$  in Fig. 7.3 and Fig. 7.6). The negative  $\delta^{13}\text{C}$  isotopic signatures (Fig. 7.10) can result from microbial activity, which produces  $\delta^{13}\text{C}$  depleted bicarbonate reduced from the dissolved inorganic carbon reservoir (Nédélec *et al.* 2007, Santos *et al.* unpublished). In contrast, as the microbial activity decreases (wave-rippled dolostone), greater accumulation is observed, extending to the cap limestone (Fig. 7.3). Despite the conditions of high carbonate production mediated by microbial mats, the intense oxygenation maintained by these microorganisms affects the preservation of organic matter, as observed in Puga cap carbonate biomarker studies (see Elie *et al.* 2007, Sousa *et al.* 2016, van Maldegem *et al.* 2018). There is evidence of siliciclastic starvation during the flourishing of microbial mats on the Amazon craton margin (Santos *et al.* unpublished). However, this scarcity probably did not directly influence micronutrient supplies, and microbial communities could be self-sufficient under shallow marine conditions or, more likely, they adapted to the stressful condition, as occurs today in modern microbial mats (i.e. Höhn *et al.* 1986, Vasconcelos *et al.* 2006). Active photosynthesis within the microbial mat could have maintained the superoxygenated water-sediment interface (van Maldegem *et al.* 2018). Biogeochemical

reactions in microenvironments with diverse microbiota can unfold as cascades, with interconnections and interdependencies (Des Marais 1990, van Gernerden 1993, Dupraz and Visscher 2005, Saghai *et al.* 2017). Such phenomena are anticipated in the context of complex microbial mat development, as observed in Lagoa Vermelha, RJ (Vasconcelos *et al.* 2006). In environments conducive to stromatolite growth, particularly to a significant extent, geochemical conditions are expected to favor the predominance of aerobic photosynthesis, while the favorable thermodynamic for carbonate precipitation is constant, maintaining stability over prolonged periods (Dupraz and Visscher 2005, Bosak *et al.* 2013, Awramik and Buchheim 2015, Callefo *et al.* 2018, Santos *et al.* 2021, Antunes *et al.* 2022). Therefore, the absence of traces of the mentioned metals throughout the stromatolitic session is plausible, suggesting insignificant accumulation of these elements due to prevailing environmental conditions. This understanding underscores the complex interaction between geochemical and microbiological conditions, influencing the distribution and concentration of these metals during microbial mat flourishing.

### 7.6.2 Paleoenvironmental control

The persisting shallow water environment created by ice gravity and glacioisostatic adjustment during sin-deglacial transgression facilitated intense production mediated by microbial communities in the southern Amazon craton. (Santos *et al.* 2021, 2023, unpublished). This is because the carbonate precipitation rate (productivity) exceeded the accommodation space creation, resulting in a shallowing upward trend. The flourishing and growth of microbial communities in shallow water support the interpretation of laterally extensive microbialites, creating a narrow and broad photic zone along this margin in the aftermath of the Marinoan glaciation (Nogueira *et al.* 2003, 2022, Font *et al.* 2006, Romero *et al.* 2020, Santos *et al.* 2021). Given the widespread occurrence of microbialites in the Puga cap dolostone, we speculate that oxygenic photosynthesis by microbial communities may have induced super oxygenated conditions in the seafloor, playing a role in the modification of biogeochemical cycles post-Snowball Earth.

The persistence of ecological stress is primarily related to hydrodynamics and wave action, and the Amazon margin deepened as the sea level continued to rise and the degree of deep-water restriction became weaker. The decline in microbial communities is attributed to burial resulting from the detrital debris influx, likely associated with deglaciation (Romero *et al.* 2020, Santos *et al.* 2021, 2023). This process increases water turbidity, reducing benthic photosynthesis due to decreased light availability, the influx of detrital material leads to burial and potential water column eutrophication, indicated by the increase in  $P_{auth}$  alongside markers of

detrital components (e.g., Al, Zr, Th). Elevated phosphorus concentrations are detected in sediments resulting from recent upwelling, indicating increased nutrient availability and subsequent heightened productivity (Schoepfer *et al.* 2015). These findings suggest the potential use of phosphorus as a proxy for productivity in contemporary sediments and ancient ones, as demonstrated by studies such as Arning *et al.* (2009) and Hetzel *et al.* (2011). Other Ediacaran successions worldwide invoke similar processes (Gaucher *et al.* 2004, Elie *et al.* 2007, Nagy *et al.* 2009, Frei *et al.* 2013, Spangenberg *et al.* 2013), and an increase in primary productivity is more evident, and most likely caused by basin eutrophication, enhancing water-column stratification, as indicated by even higher excess metal trace concentrations (e.g., Ba, Zn, Cr, P, Fig. 7.3 and Fig. 7.6), then in the wave ripples dolostone and cap limestone (Fig. 7.3). The massive input of nutrients leads to a decrease in the ideal conditions for oxygenic photosynthesis, as demonstrated in the systematic enrichment of trace metals such as  $V_{auth}$ ,  $Mo_{auth}$ , and  $U_{auth}$  (Fig. 7.2 and Fig. 7.6). This scenario has enabled the diversification of other microbial niches in the water column, as recorded in biomarkers by van Maldegem *et al.* (2018), which showed a positive correlation with our data (Fig. 7.6).

The accumulation of organic matter played a crucial role in the sequestration of trace metals in the sediment. These dysoxic conditions are characterized by a more significant collection of bioessential elements and the preservation of organic matter, as indicated by the presence of typical sedimentary organic matter biomarkers (e.g., n-alkanes, hopanes, and steranes), marking the initial record of enhanced organic production and biological diversity (Elie *et al.* 2007, Sousa *et al.* 2016, van Maldegem *et al.* 2018). The transition from cap dolostone to limestone signifies a shift to dysoxic conditions. Studies of organic fossils in the Puga cap carbonate show that benthic to planktonic communities transition as the carbonate factory changes (Sousa *et al.* 2016, van Maldegem *et al.* 2019). The decline in BNG abundance at the dolostone–carbonate contact suggests a potential link between early post-glacial ecosystem biological activity and the mineralogy of deposited carbonates (van Maldegem *et al.* 2018). The cap limestone marks the onset of high production by phototrophic organisms and a considerable increase in eukaryotic organisms over bacterial communities, as well as the prevalence of red algae as the primary organic matter (Elie *et al.* 2007, Souza *et al.* 2017, van Maldegem *et al.* 2018).

Although organic matter (OM) is not preserved, this does not imply that it was not deposited since oxic respiration causes most organic carbon under oxic conditions to be respired as  $CO_2$  instead of preserved (van Maldegem *et al.* 2018). Ambient oxygen akin to benthic  $O_2$  environments could have facilitated oxidative weathering of organic matter, fostering widespread degradation of organic material at the microbialites level, as extensively discussed by

Elie *et al.* (2007), Sousa *et al.* (2016), and van Maldegem *et al.* (2018), corroborating with the interpretations of the redox elements in this study (Fig. 7.2 and Fig. 7.6). Several researchers (e.g., Beveridge and Murray 1976, 1980, Brumsack 1980, Bruland 1983, Wangersky 1986, Tribouillard *et al.* 2006) have noted that many metals reaching the sea floor are adsorbed on the surface of organic matter. During the sin-deglacial transgression, the shallow water environment along the margin of the Amazon craton facilitated the liberation and recycling of most adsorbed metals. This occurred in the water column where the chemocline approached or descended below the seafloor, primarily due to the oxidative degradation of organic matter during settling. The long-term transgression advancement resulted in a rise in sea level. Consequently, as the chemocline ascended within the water column, more surface-adsorbed metals were retained and transported to the seafloor (Ripley *et al.* 1990, Hatch and Leventhal 1992).

### 7.6.3 Biogeochemical Zone

These biogeochemical zones exhibit variations in oxygen availability, nutrient availability, pH, and different forms of organic and inorganic compounds. These environmental variations allow for the coexistence of microbial communities within shallow environments. With significant oxygen availability, various metabolic processes can occur among the present organisms. The significant metabolic pathways inferred from microbial communities include photosynthesis, aerobic respiration, aerobic decomposition, inorganic compound oxidation, nitrogen fixation, and anaerobic respiration (Riding 2000, Noffke *et al.* 2001, D'Hondt *et al.* 2009, Bosak *et al.* 2009, 2013, Roy *et al.* 2012, Starnawski *et al.* 2017, Dupraz *et al.* 2009, Baumgäther *et al.* 2006). This metabolic zonation can help identify a precise oxidation vertical zonation with two extreme poles, oxic and anoxic (Froelick *et al.* 1979, D'Hondt *et al.* 2009).



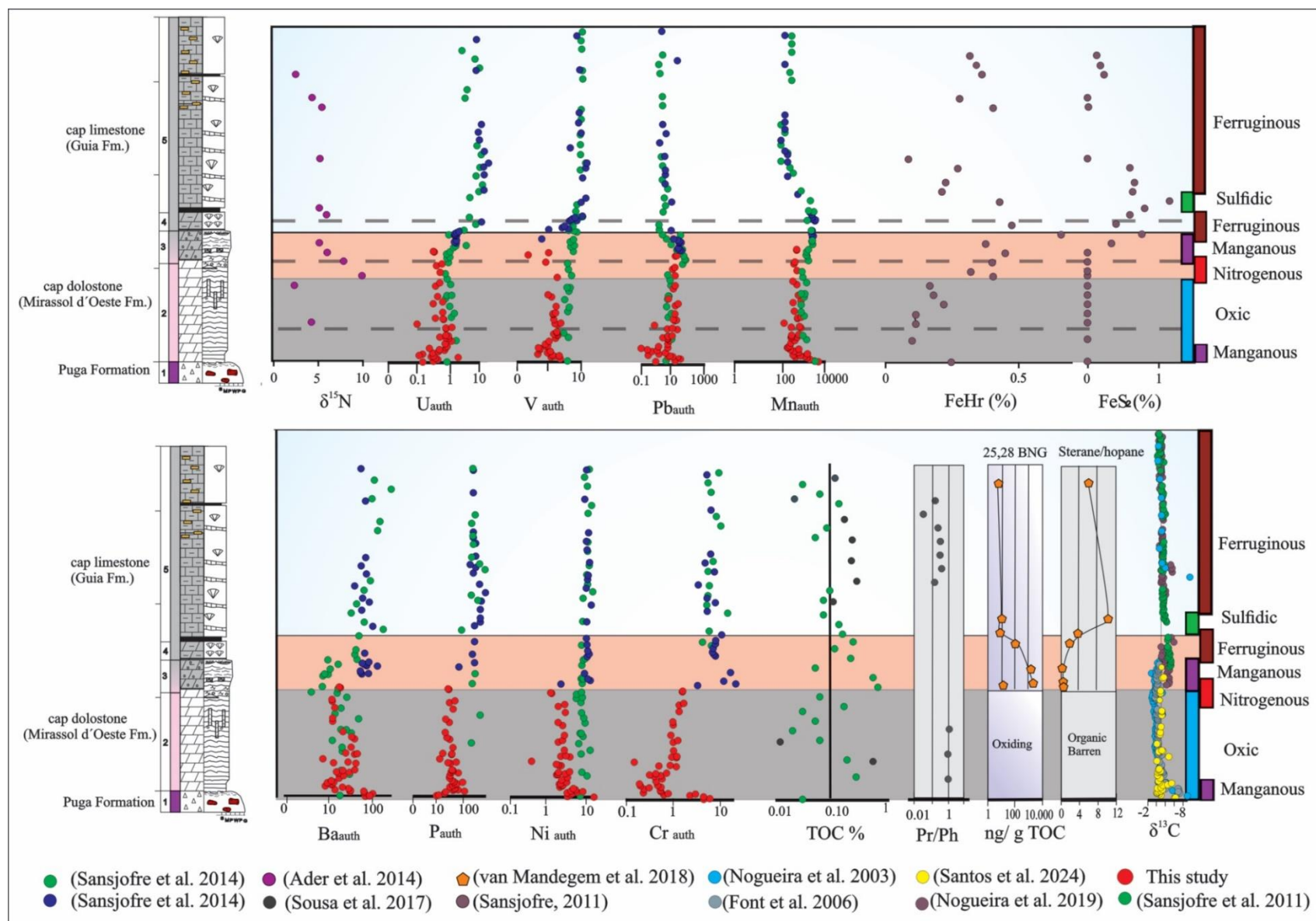
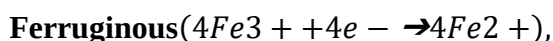
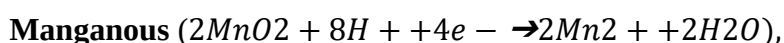
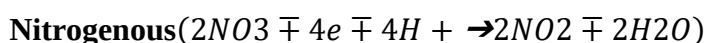
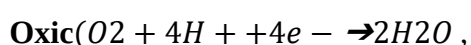


Figure 7.6- The stratigraphic and chemostratigraphic background of the Puga cap carbonate succession offers insights into biogeochemical zones. The inclusion of new data on microbialites from the Tangará section, along with iron speciation, is complemented by previously published major and trace elements (Sansjofre, 2011, Sansjofre *et al.* 2014), biomarkers (Elie *et al.* 2007, Souza Jr., 2017, van Mandegem *et al.* 2019),  $\delta^{15}\text{N}$  isotopes (Ader *et al.* 2010, 2014), and  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  isotopes (Nogueira *et al.* 2003, Font *et al.* 2006, Sansjofre *et al.* 2011, Santos *et al.* 2024). The delineation of biogeochemical zones follows the proposed redox sequence by Canfield and Thamdrup (2009).

It is evident that our dataset precisely aligns with the redox sequence by Canfield and Thamdrup (2009). In the following sections, we discuss the biogeochemical zones based on the new data presented in this study and utilize the redox background of the Puga cap carbonate (Fig. 7.6) (e.g., Font *et al.* 2006, Ader *et al.* 2014, Sansjofre *et al.* 2014 and this study). The sequence here shows a decrease in oxygen content from the dolostone to the limestone sediment, which agrees with the Snowball Earth hypothesis. However, this decrease is small and stops with a quick excursion to the sulfidic zone. Interpreting this sequence as a perfect reflection of the water column redox state described in Canfield and Thamdrup, 2009 is very attractive. However, because of these samples' age and diagenetic history, the direct attribution of this redox zone to the sediment had to be carefully examined.

Redox environments can be divided into 2 or 3 zones, anoxic, suboxic, and oxic, with clearly defined O<sub>2</sub> contents in each zone of 2 mg/L, 0.2 mg/L, and <0.2 mg/L, respectively (Tyson and Pearson 1991, Algeo and Li 2020). Canfield and Thamdrup (2009) highlighted the complexity of redox zones (following the work of Froelich *et al.* (1979) and proposed a zonation for the water column redox state that can be translated to sediments. This zonation follows the energetic pathways organisms use during organic matter oxidation, where N, Mn, and Fe reduction are predominant in the so-called "suboxic" zone and change to the nitrogenous, manganous, and ferruginous zones. Furthermore, sulfate reduction and methanogenesis dominate most anoxic water (Canfield and Thamdrup 2009). Here, we trace each of these zones across a sediment redox transition in the rock record of the Puga cap carbonates (Fig. 7.7). Nitrate, Mn, and Fe reduction are predominant in the so-called "suboxic" zone, which recently changed to nitrogenous, manganous, and ferruginous zones. As a final point, sulfate reduction and methanogenesis became predominant in the most anoxic water (Canfield and Thamdrup 2009). In the water column, this metabolic cascade is concentrated a few meters thick and reflects a progressive decrease in the oxygen concentration with depth.

Redox zones are determined by the most abundant redox-active species, which in turn reflects the dominant electron-accepting processes supporting microbial organic carbon oxidation (Canfield and Thamdrup 2009, Tostevin and Poulton 2019, Swanner *et al.* 2020) (e.g.,  $\text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$ ) and follow the general sequence:



**Sulfidic or euxinic** ( $0.5SO_4^{2-} + 5H + 4e^- \rightarrow 0.5H_2S + 2H_2O$ ),

and **Methanic** ( $0.5CO_2 + 4H + 4e^- \rightarrow 0.5CH_4 + H_2O$ .)

The order of this sequence reflects thermodynamics, precisely the decreasing amount of free energy available to microbes, coupling each electron acceptance reaction to the oxidation of organic carbon (Froelich *et al.* 1979). This thermodynamic ordering can vary depending on the environmental activity of the species in the redox couple, pH, and temperature. Kinetics can also control which process predominates (Swanner *et al.* 2020). The metabolic zones within benthic communities, localized areas of higher oxygenation in aquatic environments, can exhibit distinct biogeochemical characteristics and microbial activities. These zones can be categorized based on the prevailing redox conditions and metabolic processes. The following are several metabolic zones commonly observed in Puga cap carbonate:

**Oxic Zone:** This zone predominates throughout the precipitation of the cap dolostone and has direct control over the shallow environment and microbial communities at the margin of the Amazon Craton. Aerobic respiration is restricted to the oxic zone. Oxygenic photosynthesis by organisms such as cyanobacteria or algae can also contribute to the oxygen supply in this zone (Canfield and Thamdrup 2009). The colonization of microbial communities shortly after the ice retreat created a predominantly oxygenated microenvironment at the water-sediment interface. The oxic zone prevailed, leaving a solid signature of interactions between oxygenated and paleoredox trace metals (e.g., U, Mo, V), resulting in organic matter depletion (Fig. 7. 6).

**Nitrogenous Zone:** This zone is less developed than other zones but is inferred mainly based on data from Ader *et al.* (2014), which predominantly plots the upper facies of the dolostone cap. The  $\delta^{15}N$  values show a good correlation with TOC, attributing a major contribution of organic matter to the nitrogen pool. The values vary between 2.4 and 9.9‰ (Fig. 7.6). Deeper within benthic communities where oxygen concentrations are lower, nitrate ( $NO_3^-$ ) can serve as an alternative electron acceptor for microbial respiration and is often associated with the reduction of nitrate to nitrite ( $NO_2^-$ ) or further to nitrous oxide ( $N_2O$ ) or dinitrogen gas ( $N_2$ ) by denitrifying bacteria (Canfield and Thamdrup 2009, Galbraith *et al.* 2008).

**Ferruginous Zone:** Ferruginous conditions are more common in the cap limestone and are directly related to predominantly dysoxic conditions that prevail with long-term transgression (Fig. 7. 6). Iron speciation strongly influenced the ferruginous zone despite the primary source of highly reactive iron being upwelling (Sansjofre 2011).  $Fe^{2+}$  precipitates under supersaturated conditions, binding to carbonate minerals. Reactive Fe enrichment in marine sediments and sedimentary rocks is generally considered a paleoindicator of anoxic conditions in

the water column at deposition (Raiswell and Canfield, 1998, Poulton and Canfield, 2011, Scholz, 2018). Additionally, there is an increase in the proportion of pyrite and organic matter in this zone (Sansjofre *et al.* 2014). A high proportion of pyrite is a paleoindicator of euxinic/feruginous conditions (Poulton and Canfield 2011).

**Sulfidic Zone:** The available data for the Puga sequence (Fig. 7.6) indicate that the sulfidic zone is the least developed (Sansjofre *et al.* 2014, 2016). Nevertheless, alternative methods can contribute to refining these interpretations. The sulfidic zone in water columns is characterized by sulfide accumulation, typically hydrogen sulfide (H<sub>2</sub>S). This compound is a byproduct of microbial activities occurring in anaerobic conditions, where oxygen is limited or absent. The formation of the sulfidic zone is influenced by various biotic and abiotic reactions, encompassing the interaction of sulfide with different electron acceptors, such as oxygen (O<sub>2</sub>), nitrate (NO<sub>3</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), manganese dioxide (MnO<sub>2</sub>), and iron oxides (Fe oxides) (Canfield *et al.* 2005, Canfield and Thamdrup 2009).

**Manganous Zone:** Manganese enrichment occurs across the entire cap dolostone succession, with notable increases occurring at the base and top (Fig. 7.6). This suggests the existence of two distinct Mn-enriched zones in these specific areas. This Mn enrichment is most likely the result of deposition under dysoxic to oxic conditions or deposition in a closed system where dissolved Mn cannot be removed and alkalinity is high enough to form Mn<sup>2+</sup> carbonate (Hetzel *et al.* 2006). A reducing environment or diagenesis produces soluble Mn<sup>2+</sup> (Morford *et al.* 2001). Mn<sup>2+</sup> can be reprecipitated in the presence of O<sub>2</sub> or form Mn carbonate where alkalinity is high. In the water column, the manganous zone is defined by the level at which organisms use oxide manganese as an electron acceptor. Below the chemocline, the reductive dissolution of oxyhydroxide particles releases soluble Mn<sup>2+</sup>, which is recorded by decreased Mn content in the sediment (Calvert and Pedersen 1996, Tribovillard *et al.* 2006).

Characteristic chemical by-products accompany most metabolic processes, as shown in Fig. 7.7. Despite recognizing that biogeochemical zones may overlap and that the concentrations of paleoredox and paleoproductivity elements may not accurately reflect the depth distribution of respiratory processes, we have attempted to delineate the distribution of crucial metabolic and biogeochemical zones occurring during the precipitation of the Puga cap dolostone. The widespread development of microbialites provides valuable insights into microbial activity, environmental conditions, and aquatic chemistry. Regardless of its location, sediment, or water column, the oxic to anoxic transition in the modern environment is a gradual and progressive transition that can occur in the non-well-mixed water column or even in sediments. This redox zonation is partly due to organic matter oxidation during sedimentation. In surface

water, oxygenic photosynthesis is the most competitive metabolic process. Bacterial sulfate reduction at the sediment-water column interface has been suggested to lead to the microbially mediated formation of primary dolomite (Font *et al.* 2006). However, van Maldegem *et al.* (2018) demonstrated that the presence of 25,28-BNG suggests a cyanobacterial-dominated ecosystem (Fig. 7.6). Bacteria use light energy (phototrophy), CO<sub>2</sub> is the carbon source for organic matter (autotrophy) and releases O<sub>2</sub>. Both respiration and oxidation of organic matter consume O<sub>2</sub>. This photoautotrophic metabolism becomes less competitive with decreasing O<sub>2</sub> concentration and sunlight wavelength with increasing water column depth. It is replaced by other bacterial communities that use dead organisms for carbon sources (heterotrophy) and new electron acceptors. The presence of biomarkers indicating green and purple sulfur bacteria is evidence for euxinia and euxinia in the photic zone because green and sulfur bacteria that oxidize H<sub>2</sub>S without oxygen are phototrophic (Sansjofre *et al.* 2016, van Maldegem *et al.* 2018). Analogous modern purple sulfur bacteria demand high amounts of light and typically thrive within the upper 10-20 m of a water column. These organisms are best known today from studies of meromictic lakes (Overmann 1991).

In summary, the precipitation of cap dolostone occurs in the oxic zone and is enhanced by microbial community activity in shallow environments (Fig. 7.6 and Fig. 7.7). The characteristics of the zones change abruptly with facies variations, revealing paleoenvironmental control related to the post-Marinoan transgression (Fig. 7.7). These redox conditions, likely influenced by high carbonate precipitation rates, support the existence of such records. During the precipitation of the cap limestone, where the ferruginous zone predominates and there is a higher accumulation of organic matter and redox-sensitive trace metals, an increase in the chemocline is associated with post-Marinoan transgression (Fig. 7.7). In this context, each redox zone in the water column aligns with distinct sedimentary layers characterized by unique biogeochemical signal.

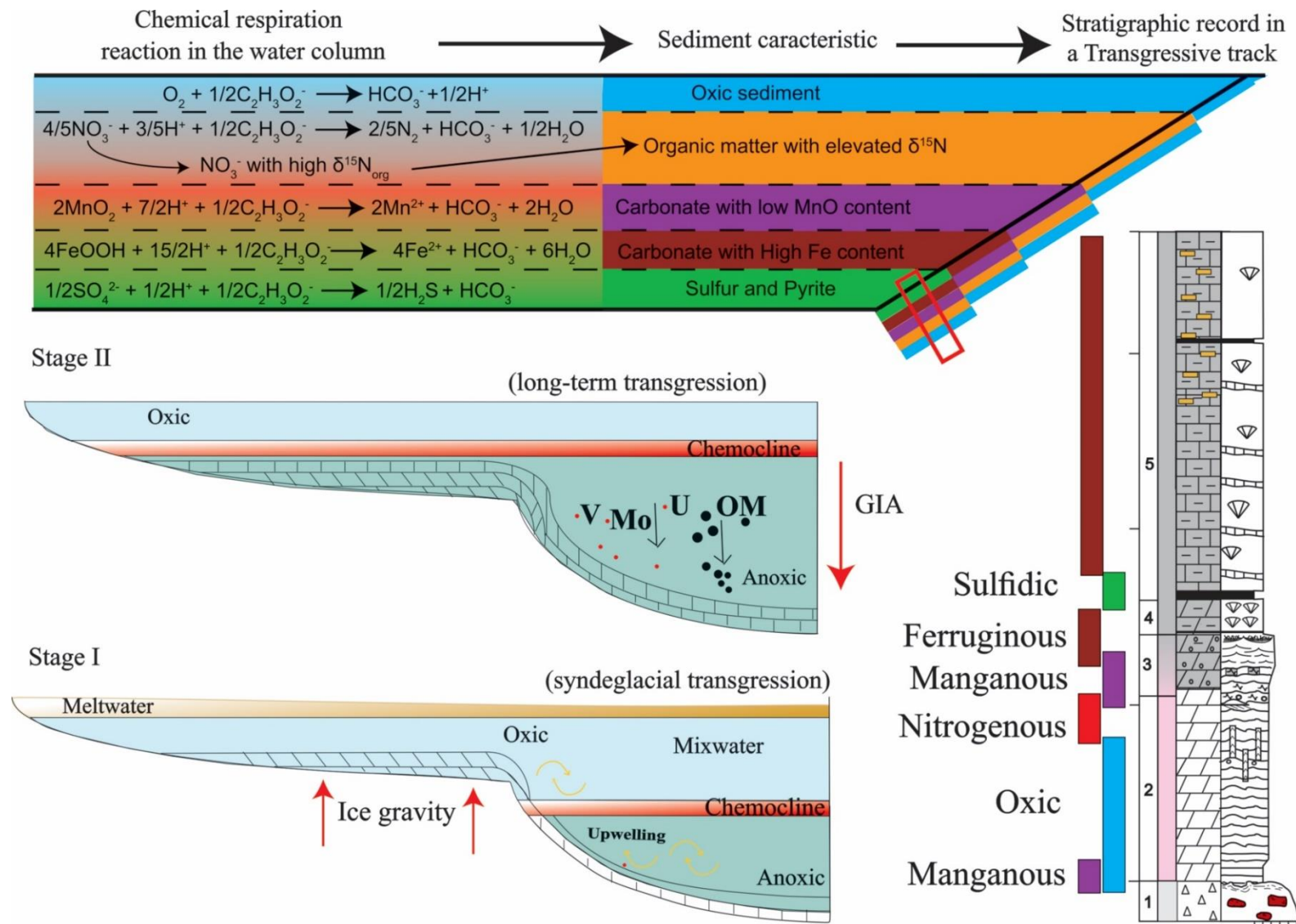


Figure 7.7- A) Schematic representation of the standard Gibbs free energy calculated for the principal respiratory pathways of organic matter mineralization in nature with acetate as an electron donor (Canfield and Thamdrup, 2009). B) Schematic representation of the evolution of restriction extent, redox conditions, nutrient cycling, and marine productivity in the Amazon Craton margin in response to sea-level changes linked to ice gravity and glacial isostatic adjustment. Stage I witnessed a major transgression following the Marinoan (~635 Ma) deglaciation. The shallow water environment, permanently created by ice gravity and glacioisostatic adjustment during post-deglacial transgression, facilitated intense production mediated by microbial communities in the southern Amazon Craton. Oxic conditions predominate throughout the fluorescence of microbial mats in the coastal zone. In Stage II, as the transgression progresses sea level rises, and oceanic circulation increases, dysoxic conditions and a ferruginous zone predominate, leading to a higher accumulation of organic matter and redox-sensitive trace metals. An increase in the chemocline is associated with post-Marinoan transgression.

## 7.7 CONCLUSIONS

The metal trace authigenic patterns observed in the Puga cap carbonate provide valuable insights into post-snowball earth redox marine conditions. Our study sheds light on the evolving redox conditions during the postglacial transgression of the Marinoan Puga cap carbonate from the Amazon Craton, Brazil. Microbialites in the basal cap dolostone formed under oxic conditions, while the upper mega-ripple bedded dolostone indicates predominantly dysoxic conditions. Despite the high productivity of microbial mats in a semi-restricted marine environment, subsequent sea-level rise submerged coastal regions, triggering rapid modifications in biogeochemical cycling during cap limestone precipitation. Our findings provide valuable insights into the complex interplay of environmental processes and biogeochemical cycling during this critical period in Earth's history, enhancing our understanding of past climatic fluctuations and environmental dynamics. In addition, analyzing climatic extreme geological scenarios sheds critical light on the proliferation of extremophile life and its implications for other planetary surfaces.

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7.9 SUPPLEMENTARY MATERIAL: POST-MARINOAN PALEOREDOX AND  
PALEOPRODUCTIVITY RECORD IN PUGA CAP CARBONATE: IMPLICATION  
FOR COASTAL LIFE COLONIZATION FROM THE AMAZON CRATON MAR-  
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**Supplementary Table 7.1** Trace Metal Concentration of the Puga Cap Carbonate, Tangará and  
Terconi Sections.

Supplementary Table 7. 1- Trace Metal Concentration of the Puga Cap Carbonate from the Tangará, and Terconi Sections.

| Tangará Section |       |       |       |        |      |      |      |      |      |        |       |       |        |         |         |        |            |
|-----------------|-------|-------|-------|--------|------|------|------|------|------|--------|-------|-------|--------|---------|---------|--------|------------|
| De-<br>pth      | Co    | Ni    | Cu    | Zn     | V    | Cr   | U    | Mo   | Cd   | Ba     | Sr    | Pb    | Al     | Mn      | Fe      | P      |            |
| m               | ppm   | ppm   | ppm   | ppm    | ppm  | ppm  | ppm  | ppm  | ppm  | ppm    | ppm   | ppm   | ppm    | ppm     | ppm     | ppm    |            |
| 0,2             | 16,84 | 19,21 | 16,00 | 237,29 | 0,06 | 4,53 | 0,14 | 0,04 | 2,28 | 85,99  | 38,60 | 1,26  | 176,86 | 6946,13 | 749,70  | 8,33   | This study |
| 0,4             | 9,58  | 4,13  | 8,84  | 113,68 | 0,11 | 6,10 | 0,31 | 0    | 1,93 | 110,71 | 51,22 | 32,45 | 149,95 | 4533,85 | 1413,61 | 10,28  | This study |
| 1               | 2,23  | 4,92  | 6,26  | 82,75  | 1,11 | 4,51 | 0,43 | 0,05 | 1,66 | 132,28 | 48,68 | 78,71 | 94,17  | 2736,41 | 1985,54 | 17,34  | This study |
| 1,4             | 2,10  | 5,31  | 5,16  | 62,21  | 0,35 | 2,32 | 0,36 | 0,05 | 1,20 | 80,04  | 43,18 | 57,67 | 87,13  | 2083,62 | 1212,50 | 19,28  | This study |
| 1,6             | 0,41  | 3,99  | 2,06  | 12,40  | 0,52 | 0,65 | 1,96 | 0    | 0,22 | 35,09  | 58,60 | 10,17 | 101,92 | 615,66  | 614,29  | 101,25 | This study |
| 1,8             | 2,17  | 7,12  | 4,74  | 26,28  | 0,87 | 3,03 | 0,26 | 0,05 | 0,58 | 78,29  | 53,61 | 21,16 | 39,37  | 1631,58 | 1723,60 | 36,07  | This study |
| 2               | 11,91 | 9,91  | 3,39  | 57,31  | 0,33 | 0,80 | 0,31 | 0,06 | 0,63 | 35,73  | 58,03 | 13,38 | 42,81  | 1025,41 | 705,89  | 57,38  | This study |
| 2,2             | 0,34  | 4,94  | 1,24  | 38,36  | 0,07 | 0,24 | 0,11 | 0,03 | 1,83 | 14,18  | 36,50 | 0,36  | 28,23  | 484,27  | 315,81  | 40,72  | This study |
| 2,6             | 0,50  | 6,42  | 2,46  | 60,79  | 0,19 | 0,56 | 0,14 | 0,03 | 1,24 | 31,49  | 42,77 | 2,12  | 47,26  | 2172,77 | 850,13  | 43,36  | This study |
| 3               | 0,40  | 5,67  | 1,18  | 10,47  | 0,23 | 0,55 | 0,29 | 0,03 | 0,21 | 21,87  | 39,89 | 6,26  | 31,11  | 853,56  | 606,51  | 27,58  | This study |
| 3,4             | 0,84  | 2,58  | 1,67  | 39,36  | 0,11 | 0,25 | 0,45 | 0    | 0,81 | 8,08   | 31,91 | 0,69  | 44,76  | 545,44  | 151,38  | 35,99  | This study |
| 3,8             | 0,30  | 2,97  | 1,14  | 14,02  | 0,16 | 0,32 | 0,71 | 0    | 0,38 | 11,74  | 46,64 | 1,59  | 74,26  | 368,45  | 163,78  | 45,02  | This study |
| 4               | 0,31  | 3,08  | 2,94  | 71,47  | 0,10 | 0,57 | 0,49 | 0    | 1,81 | 12,25  | 33,28 | 0,31  | 45,22  | 884,20  | 135,40  | 52,01  | This study |
| 4,4             | 0     | 2,49  | 2,43  | 102,89 | 0,16 | 0,21 | 0,23 | 0,04 | 2,03 | 9,10   | 21,73 | 0,11  | 41,54  | 269,69  | 163,61  | 86,28  | This study |
| 4,6             | 0,93  | 2,75  | 1,17  | 16,74  | 0,28 | 0,48 | 0,79 | 0,05 | 0,26 | 13,84  | 52,70 | 9,39  | 100,07 | 294,26  | 281,10  | 39,18  | This study |
| 5               | 0,28  | 3,85  | 1,68  | 9,75   | 0,19 | 0,20 | 0,86 | 0    | 0,26 | 11,70  | 46,91 | 2,00  | 68,61  | 345,42  | 212,42  | 33,42  | This study |
| 5,8             | 0,84  | 2,89  | 2,38  | 23,26  | 0,31 | 0,44 | 0,74 | 0,03 | 0,33 | 18,64  | 49,52 | 9,37  | 100,65 | 385,79  | 521,59  | 26,45  | This study |
| 6,6             | 0,47  | 4,06  | 1,54  | 37,80  | 0,56 | 0,59 | 1,19 | 0,04 | 1,20 | 24,06  | 53,20 | 12,18 | 73,14  | 583,35  | 627,45  | 27,58  | This study |
| 7,4             | 0,57  | 2,18  | 1,57  | 21,91  | 0,83 | 0,40 | 0,96 | 0    | 0,38 | 17,63  | 63,48 | 9,05  | 117,76 | 396,68  | 699,22  | 58,50  | This study |
| 7,6             | 0,56  | 2,34  | 1,80  | 34,31  | 0,71 | 0,55 | 0,78 | 0,06 | 1,55 | 33,25  | 62,27 | 8,80  | 89,24  | 763,60  | 672,18  | 30,47  | This study |
| 7,8             | 0,34  | 3,50  | 1,50  | 33,69  | 0,41 | 0,32 | 0,50 | 0,03 | 0,86 | 15,57  | 47,17 | 4,08  | 60,49  | 420,12  | 325,86  | 35,83  | This study |

|      |      |       |       |        |      |       |      |      |      |        |       |        |        |         |         |        |                              |
|------|------|-------|-------|--------|------|-------|------|------|------|--------|-------|--------|--------|---------|---------|--------|------------------------------|
| 8,2  | 0,68 | 2,41  | 1,40  | 32,91  | 0,69 | 0,44  | 0,95 | 0    | 0,67 | 22,83  | 50,41 | 9,83   | 80,56  | 417,81  | 448,35  | 35,67  | This study                   |
| 8,4  | 1,03 | 4,62  | 3,57  | 67,03  | 0,70 | 0,74  | 0,78 | 0,06 | 1,37 | 45,84  | 59,03 | 19,80  | 96,54  | 882,68  | 729,79  | 33,40  | This study                   |
| 10,4 | 1,26 | 2,88  | 4,55  | 108,07 | 0,92 | 1,18  | 0,79 | 0,05 | 2,57 | 49,66  | 65,54 | 46,78  | 188,24 | 1109,18 | 1024,18 | 29,67  | This study                   |
| 10,6 | 0,44 | 2,38  | 2,08  | 32,23  | 0,57 | 0,51  | 0,78 | 0,04 | 0,46 | 13,55  | 64,02 | 8,76   | 103,39 | 401,05  | 941,17  | 23,21  | This study                   |
| 10,8 | 0,77 | 2,18  | 2,87  | 52,47  | 1,32 | 0,88  | 1,22 | 0    | 1,27 | 31,75  | 86,80 | 20,16  | 167,34 | 953,65  | 1020,43 | 48,57  | This study                   |
| 11,8 | 0,19 | 0,49  | 0,50  | 13,76  | 0,35 | 0,15  | 0,09 | 0    | 4,81 | 6,87   | 79,26 | 1,02   | 16,91  | 189,18  | 82,30   | 11,14  | This study                   |
| 13,2 | 1,38 | 4,72  | 4,43  | 68,37  | 0,50 | 1,20  | 0,66 | 0,08 | 1,76 | 45,78  | 64,68 | 30,42  | 125,16 | 782,07  | 735,82  | 32,12  | This study                   |
| 13,4 | 1,51 | 2,78  | 4,93  | 57,59  | 0,50 | 0,95  | 0,63 | 0,06 | 0,77 | 53,85  | 71,45 | 41,24  | 135,43 | 781,89  | 1018,29 | 32,91  | This study                   |
| 13,6 | 1,37 | 3,68  | 4,31  | 112,69 | 0,64 | 1,23  | 0,36 | 0    | 2,43 | 27,14  | 39,02 | 23,58  | 118,35 | 1130,45 | 1181,65 | 14,66  | This study                   |
| 15,4 | 1,54 | 3,39  | 3,63  | 52,19  | 0,70 | 1,04  | 0,62 | 0,05 | 0,63 | 37,50  | 49,06 | 31,24  | 135,73 | 551,11  | 532,99  | 36,05  | This study                   |
| 18   | 0,97 | 2,39  | 2,00  | 25,65  | 0,41 | 1,03  | 0,30 | 0,04 | 0,65 | 45,55  | 55,50 | 33,73  | 111,40 | 488,46  | 1093,90 | 27,17  | This study                   |
| 18,6 | 1,16 | 3,11  | 3,17  | 109,55 | 0,37 | 1,28  | 0,62 | 0    | 1,69 | 38,98  | 60,66 | 53,96  | 149,42 | 1121,01 | 819,12  | 21,04  | This study                   |
| 20,2 | 0,90 | 3,40  | 2,69  | 110,13 | 0,07 | 0,91  | 0,42 | 0    | 2,44 | 23,19  | 37,73 | 10,53  | 99,43  | 838,71  | 337,06  | 18,18  | This study                   |
| 23,4 | 0,76 | 3,07  | 1,45  | 82,01  | 0,72 | 1,03  | 0,37 | 0    | 1,43 | 12,80  | 36,25 | 23,67  | 87,64  | 714,16  | 347,38  | 26,19  | This study                   |
| 24,4 | 0,52 | 2,44  | 1,39  | 48,98  | 0,13 | 1,01  | 0,50 | 0    | 1,39 | 13,84  | 33,22 | 32,84  | 231,17 | 474,72  | 262,36  | 18,82  | This study                   |
| 27,6 | 0,75 | 3,60  | 1,77  | 72,78  | 0,29 | 1,36  | 0,51 | 0,04 | 3,41 | 14,73  | 45,85 | 32,65  | 125,68 | 735,42  | 416,10  | 36,64  | This study                   |
| 29,6 | 0,58 | 2,39  | 1,06  | 48,24  | 0,16 | 1,37  | 0,39 | 0    | 1,65 | 12,49  | 39,57 | 20,97  | 95,19  | 531,68  | 302,98  | 26,41  | This study                   |
| 30,2 | 0,77 | 3,49  | 1,20  | 46,36  | 0,38 | 1,71  | 0,59 | 0    | 1,99 | 12,70  | 62,06 | 31,18  | 148,87 | 592,38  | 392,81  | 42,98  | This study                   |
| 33,8 | 0,86 | 1,73  | 1,42  | 52,62  | 0,28 | 1,60  | 0,33 | 0    | 1,15 | 21,01  | 55,88 | 33,90  | 219,73 | 707,91  | 451,36  | 25,06  | This study                   |
| 34   | 0,77 | 1,59  | 0,87  | 57,10  | 0,31 | 1,63  | 0,31 | 0,03 | 0,73 | 19,08  | 44,13 | 44,00  | 162,42 | 711,53  | 517,88  | 23,54  | This study                   |
| 36,8 | 1,59 | 2,35  | 4,83  | 84,16  | 2,79 | 3,01  | 0,46 | 0,05 | 1,45 | 72,27  | 79,95 | 108,13 | 509,25 | 1413,16 | 1465,94 | 65,44  | This study                   |
| 37   | 2,36 | 11,21 | 18,72 | 176,50 | 5,86 | 18,94 | 0,89 | bdl  | 2,27 | 101,70 | 68,28 | 78,47  | 20,09  | 1548,66 | 2253,49 | 261,83 | Sansjofre <i>et al.</i> 2014 |
| 37,4 | 1,93 | 7,92  | 13,31 | 103,70 | 4,12 | 10,61 | 0,78 | bdl  | 1,73 | 63,48  | 64,41 | 56,27  | 12,34  | 1316,36 | 1767,44 | 218,19 | Sansjofre <i>et al.</i> 2014 |
| 38   | 2,55 | 9,10  | 11,79 | 237,90 | 4,68 | 14,71 | 0,91 | bdl  | 1,80 | 62,75  | 62,54 | 62,53  | 18,00  | 1393,79 | 2165,12 | 261,83 | Sansjofre <i>et al.</i> 2014 |
| 39,8 | 2,54 | 8,73  | 12,46 | 125,00 | 6,07 | 7,15  | 0,91 | 0,37 | 1,66 | 173,10 | 72,49 | 76,20  | 15,64  | 1858,39 | 2386,05 | 261,83 | Sansjofre <i>et al.</i> 2014 |
| 40   | 3,09 | 9,95  | 13,00 | 133,70 | 9,27 | 6,58  | 0,78 | bdl  | 1,54 | 91,59  | 86,68 | 99,84  | 29,75  | 1935,83 | 4020,93 | 436,38 | Sansjofre <i>et al.</i> 2014 |

|      |      |      |       |       |       |      |      |      |      |        |         |       |       |         |         |        |                              |
|------|------|------|-------|-------|-------|------|------|------|------|--------|---------|-------|-------|---------|---------|--------|------------------------------|
| 40,2 | 2,20 | 9,10 | 8,35  | 77,45 | 6,75  | 6,16 | 0,82 | bdl  | 0,60 | 86,40  | 85,20   | 67,07 | 32,93 | 1316,36 | 2651,16 | 436,38 | Sansjofre <i>et al.</i> 2014 |
| 40,6 | 2,74 | 8,69 | 9,79  | 89,41 | 7,24  | 6,41 | 0,82 | 0,32 | 0,38 | 77,58  | 81,59   | 74,15 | 34,44 | 1393,79 | 3358,14 | 436,38 | Sansjofre <i>et al.</i> 2014 |
| 41   | 2,74 | 8,34 | 10,21 | 75,92 | 8,39  | 7,09 | 0,93 | 0,31 | 0,33 | 69,57  | 81,86   | 53,31 | 37,85 | 1316,36 | 3402,33 | 480,02 | Sansjofre <i>et al.</i> 2014 |
| 41,4 | 2,37 | 8,53 | 8,24  | 60,51 | 12,67 | 9,58 | 1,09 | bdl  | 0,34 | 103,80 | 76,88   | 26,96 | 40,74 | 1084,06 | 3048,84 | 698,21 | Sansjofre <i>et al.</i> 2014 |
| 44,8 | 1,91 | 8,70 | bdl   | 55,62 | 11,72 | 8,08 | 5,90 | bdl  | 0,56 | 81,32  | 689,60  | 17,85 | 45,42 | 309,73  | 3932,56 | 305,47 | Sansjofre <i>et al.</i> 2014 |
| 45,6 | 1,35 | 6,70 | bdl   | 17,02 | 10,16 | 5,33 | 6,01 | bdl  | 0,63 | 44,10  | 548,80  | 6,66  | 27,74 | 309,73  | 1060,47 | 174,55 | Sansjofre <i>et al.</i> 2014 |
| 46   | 3,18 | 7,15 | bdl   | 59,57 | 11,68 | 7,91 | 5,76 | bdl  | 1,30 | 67,19  | 468,00  | 6,88  | 42,99 | 309,73  | 2651,16 | 218,19 | Sansjofre <i>et al.</i> 2014 |
| 46,2 | 2,58 | 7,45 | bdl   | 70,91 | 12,25 | 5,32 | 8,26 | bdl  | 0,92 | 46,38  | 479,00  | 6,85  | 25,89 | 232,30  | 1811,63 | 130,91 | Sansjofre <i>et al.</i> 2014 |
| 46,8 | 2,41 | 7,95 | bdl   | 19,42 | 4,16  | 3,46 | 6,09 | 0,32 | bdl  | 30,04  | 1115,00 | 6,28  | 17,15 | 154,87  | 2341,86 | 218,19 | Sansjofre <i>et al.</i> 2014 |
| 47,4 | 1,22 | 7,01 | bdl   | bdl   | 9,42  | 7,57 | 4,18 | bdl  | bdl  | 57,33  | 563,80  | 2,89  | 45,19 | 232,30  | 751,16  | 218,19 | Sansjofre <i>et al.</i> 2014 |
| 47,8 | 1,32 | 6,77 | bdl   | bdl   | 8,22  | 4,83 | 3,84 | bdl  | bdl  | 42,80  | 624,50  | 7,68  | 25,44 | 232,30  | 3093,02 | 174,55 | Sansjofre <i>et al.</i> 2014 |
| 48,2 | 1,42 | 7,55 | bdl   | bdl   | 8,49  | 6,35 | 4,86 | bdl  | bdl  | 55,24  | 950,70  | 4,61  | 34,28 | 232,30  | 2076,74 | 174,55 | Sansjofre <i>et al.</i> 2014 |
| 51   | 1,28 | 6,46 | bdl   | 32,20 | 8,77  | 6,44 | 3,27 | bdl  | 1,17 | 54,80  | 715,10  | 42,95 | 38,09 | 232,30  | 1723,26 | 174,55 | Sansjofre <i>et al.</i> 2014 |
| 52,6 | 2,84 | 7,23 | bdl   | bdl   | 7,38  | 5,24 | 3,34 | bdl  | bdl  | 42,54  | 644,30  | 3,95  | 30,68 | 232,30  | 1325,58 | 174,55 | Sansjofre <i>et al.</i> 2014 |

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Terconi Section

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| De-<br>pth | Cd  | Co  | Cr  | Cu   | Ni   | Pb   | U   | V   | Zn   | Mo  | Al   | Ba   | Mn     | Fe      | P     | Sr   |                              |
|------------|-----|-----|-----|------|------|------|-----|-----|------|-----|------|------|--------|---------|-------|------|------------------------------|
| m          | ppm | ppm | ppm | ppm  | ppm  | ppm  | ppm | ppm | ppm  | ppm | ppm  | ppm  | ppm    | ppm     | ppm   | ppm  |                              |
| 0,1        | 0,2 | 3,7 | bdl | 19,9 | 8,3  | 6,2  | 0,7 | 4,0 | 16,3 | bdl | 10,2 | 18,2 | 3407,1 | 30,6    |       | 49,1 | Sansjofre <i>et al.</i> 2014 |
| 2,06       | 1,9 | 2,1 | bdl | 9,5  | 12,7 | 14,5 | 1,3 | 4,6 | 36,1 | bdl | 6,4  | 30,4 | 1471,2 | 18,2    |       | 43,1 | Sansjofre <i>et al.</i> 2014 |
| 2,42       | 0,6 | 1,5 | bdl | bdl  | 9,2  | 8,4  | 0,6 | 2,4 | 15,0 | bdl | 1,7  | 19,1 | 1006,6 | 14,9    |       | 47,1 | Sansjofre <i>et al.</i> 2014 |
| 4,2        | 0,8 | 0,9 | bdl | 5,9  | 8,7  | 8,8  | 0,9 | 4,2 | 19,6 | bdl | 2,9  | 20,8 | 1161,5 | 17,4    | 178,9 | 50,1 | Sansjofre <i>et al.</i> 2014 |
| 4,56       | 1,5 | 1,8 | bdl | 13,4 | 15,4 | 15,1 | 1,2 | 5,2 | 40,2 | bdl | 13,2 | 20,4 | 851,8  | 17,5    |       | 51,6 | Sansjofre <i>et al.</i> 2014 |
| 5,2        | 0,7 | 0,7 | bdl | bdl  | 7,5  | 6,8  | 0,8 | 2,7 | 16,6 | bdl | 0,0  | 12,0 | 851,8  | #DIV/0! |       | 48,9 | Sansjofre <i>et al.</i> 2014 |

|      |     |     |      |      |      |       |     |      |       |     |       |       |        |      |       |        |                              |
|------|-----|-----|------|------|------|-------|-----|------|-------|-----|-------|-------|--------|------|-------|--------|------------------------------|
| 5,9  | 1,7 | 1,1 | bdl  | 6,1  | 9,9  | 8,1   | 0,6 | 4,9  | 28,1  | bdl | 4,2   | 33,6  | 1161,5 | 18,9 |       | 39,6   | Sansjofre <i>et al.</i> 2014 |
| 6,2  | 1,6 | 1,1 | bdl  | 6,0  | 8,2  | 9,8   | 0,7 | 5,9  | 21,9  | bdl | 5,1   | 25,5  | 1238,9 | 22,4 |       | 41,6   | Sansjofre <i>et al.</i> 2014 |
| 6,21 | 0,5 | 0,8 | bdl  | 5,3  | 8,8  | 9,1   | 1,0 | 3,8  | 16,6  | bdl | 7,9   | 19,1  | 851,8  | 21,7 | 349,1 | 45,3   | Sansjofre <i>et al.</i> 2014 |
| 7,2  | 1,4 | 1,3 | bdl  | 7,8  | 11,2 | 13,8  | 0,9 | 7,2  | 23,3  | bdl | 11,0  | 50,0  | 1471,2 | 37,4 |       | 45,9   | Sansjofre <i>et al.</i> 2014 |
| 7,7  | 1,3 | 1,1 | bdl  | 5,8  | 10,4 | 12,1  | 0,7 | 4,6  | 22,4  | bdl | 0,0   | 14,0  | 1006,6 | 0,0  |       | 41,6   | Sansjofre <i>et al.</i> 2014 |
| 8,2  | 1,5 | 0,9 | bdl  | bdl  | 9,0  | 8,2   | 0,6 | 4,1  | 19,0  | bdl | 7,0   | 19,2  | 929,2  | 20,6 |       | 47,3   | Sansjofre <i>et al.</i> 2014 |
| 9,2  | 2,3 | 1,6 | bdl  | 27,7 | 8,7  | 90,0  | 0,8 | 9,2  | 253,1 | 0,4 | 12,2  | 26,4  | 1781,0 | 42,0 |       | 54,5   | Sansjofre <i>et al.</i> 2014 |
| 9,6  | 6,6 | 0,9 | bdl  | 12,0 | 6,4  | 147,7 | 0,7 | 6,4  | 197,0 | bdl | 12,2  | 15,7  | 1548,7 | 37,8 |       | 60,1   | Sansjofre <i>et al.</i> 2014 |
| 9,7  | 6,1 | 1,2 | bdl  | 21,1 | 9,5  | 128,1 | 0,8 | 10,9 | 313,9 | bdl | 11,2  | 4,0   | 1393,8 | 33,7 |       | 60,1   | Sansjofre <i>et al.</i> 2014 |
| 10   | 4,2 | 1,0 | bdl  | 10,7 | 6,6  | 109,3 | 0,7 | 6,0  | 267,4 | bdl | 15,9  | 16,7  | 1471,2 | 36,4 | 192,0 | 53,9   | Sansjofre <i>et al.</i> 2014 |
| 10,2 | 2,7 | 1,1 | bdl  | 21,6 | 9,1  | 50,9  | 0,9 | 9,6  | 546,8 | 0,7 | 42,3  | 7,1   | 1781,0 | 44,0 | 130,9 | 58,3   | Sansjofre <i>et al.</i> 2014 |
| 10,3 | 4,4 | 0,9 | bdl  | 19,5 | 6,8  | 126,0 | 0,5 | 7,3  | 592,2 | 0,6 | 22,2  | 6,7   | 1781,0 | 42,0 | 0,0   | 52,0   | Sansjofre <i>et al.</i> 2014 |
| 10,6 | 2,5 | 0,9 | bdl  | 7,2  | 6,4  | 68,7  | 0,6 | 6,3  | 201,5 | 0,8 | 10,6  | 9,0   | 1626,1 | 37,8 | 0,0   | 50,8   | Sansjofre <i>et al.</i> 2014 |
| 10,7 | 4,0 | 1,1 | bdl  | 5,5  | 6,8  | 174,6 | 1,3 | 4,9  | 199,4 | 0,4 | 36,6  | 7,3   | 1703,5 | 44,8 | 0,0   | 62,9   | Sansjofre <i>et al.</i> 2014 |
| 11,7 | 2,1 | 1,5 | bdl  | bdl  | 6,7  | 27,5  | 0,6 | 6,0  | 207,1 | bdl | 15,9  | 10,2  | 1548,7 | 35,0 | 261,8 | 54,7   | Sansjofre <i>et al.</i> 2014 |
| 12,7 | 0,4 | 1,6 | bdl  | bdl  | 6,0  | 14,3  | 0,4 | 5,6  | 181,8 | 0,7 | 52,3  | 15,2  | 1006,6 | 41,2 | 87,3  | 76,4   | Sansjofre <i>et al.</i> 2014 |
| 13,6 | 3,2 | 1,2 | bdl  | 7,1  | 6,6  | 127,4 | 1,1 | 8,6  | 144,8 | 1,5 | 34,9  | 9,3   | 2013,3 | 51,8 | 327,3 | 59,1   | Sansjofre <i>et al.</i> 2014 |
| 13,7 | 0,3 | 3,0 | 6,9  | bdl  | 7,7  | 6,6   | 0,8 | 9,8  | 18,8  | 1,0 | 83,6  | 42,2  | 1161,5 | 70,7 | 192,0 | 69,8   | Sansjofre <i>et al.</i> 2014 |
| 14,7 | bdl | 2,0 | 5,4  | bdl  | 5,9  | 3,9   | 2,5 | 7,0  | bdl   | bdl | 56,1  | 37,4  | 1393,8 | 56,7 | 362,2 | 60,4   | Sansjofre <i>et al.</i> 2014 |
| 15,7 | bdl | 1,9 | 5,8  | bdl  | 6,3  | 3,8   | 1,6 | 7,4  | bdl   | bdl | 63,8  | 41,0  | 542,0  | 53,0 | 240,0 | 56,8   | Sansjofre <i>et al.</i> 2014 |
| 16,4 | bdl | 4,0 | 14,2 | bdl  | 10,9 | 5,4   | 2,9 | 24,4 | 14,7  | bdl | 194,7 | 146,8 | 387,2  | 79,7 | 130,9 | 315,2  | Sansjofre <i>et al.</i> 2014 |
| 17,2 | bdl | 2,1 | 5,2  | bdl  | 8,1  | 4,5   | 3,8 | 7,7  | 11,3  | bdl | 66,3  | 52,9  | 154,9  | 40,6 | 148,4 | 1080,0 | Sansjofre <i>et al.</i> 2014 |
| 18,2 | bdl | 2,0 | 5,4  | bdl  | 7,7  | 7,4   | 2,4 | 7,5  | 21,7  | bdl | 68,9  | 26,4  | 309,7  | 29,4 | 144,0 | 479,4  | Sansjofre <i>et al.</i> 2014 |
| 19,2 | bdl | 1,9 | 5,9  | bdl  | 8,9  | 3,4   | 3,2 | 7,3  | bdl   | bdl | 68,1  | 35,3  | 154,9  | 30,0 | 130,9 | 1030,0 | Sansjofre <i>et al.</i> 2014 |
| 20,7 | bdl | 2,2 | 5,5  | bdl  | 8,1  | 3,6   | 3,4 | 9,0  | bdl   | bdl | 63,8  | 52,5  | 232,3  | 33,4 | 170,2 | 827,8  | Sansjofre <i>et al.</i> 2014 |
| 21,7 | bdl | 2,2 | 7,0  | bdl  | 8,3  | 2,9   | 2,6 | 9,1  | bdl   | bdl | 91,2  | 74,1  | 154,9  | 28,7 | 144,0 | 1263,0 | Sansjofre <i>et al.</i> 2014 |

|      |     |     |      |     |      |     |     |      |      |     |       |       |       |      |     |       |                              |
|------|-----|-----|------|-----|------|-----|-----|------|------|-----|-------|-------|-------|------|-----|-------|------------------------------|
| 27,2 | bdl | 2,6 | 10,3 | bdl | 9,1  | 3,5 | 1,1 | 12,9 | 16,6 | bdl | 132,7 | 108,9 | 464,6 | 74,0 | 0,0 | 233,3 | Sansjofre <i>et al.</i> 2014 |
| 28,2 | 0,2 | 2,6 | 8,3  | bdl | 11,5 | 3,4 | 1,3 | 12,0 | 65,4 | bdl | 109,7 | 123,2 | 387,2 | 56,0 | 0,0 | 378,4 | Sansjofre <i>et al.</i> 2014 |
| 30,7 | bdl | 2,8 | 6,4  | bdl | 8,7  | 2,4 | 3,1 | 10,1 | 12,7 | bdl | 74,0  | 80,7  | 464,6 | 48,2 | 0,0 | 388,1 | Sansjofre <i>et al.</i> 2014 |
| 31,7 | bdl | 2,1 | 5,5  | bdl | 7,1  | 2,0 | 2,3 | 8,7  | bdl  | bdl | 68,8  | 226,3 | 464,6 | 58,0 | 0,0 | 345,6 | Sansjofre <i>et al.</i> 2014 |
| 32,7 | bdl | 3,3 | 9,3  | bdl | 9,9  | 3,5 | 0,9 | 11,8 | 11,9 | bdl | 111,1 | 90,7  | 464,6 | 46,8 |     | 427,0 | Sansjofre <i>et al.</i> 2014 |

**CAPÍTULO 8: HIGH-RESOLUTION MAPPING AND CRYSTAL ARCHITECTURE OF A MARINOAN CAP DOLOSTONE (~635 MA): INSIGHTS INTO THE DOLOMITE PROBLEM AND ITS POTENTIAL AS AN ASTROBIOLOGICAL ANALOG**

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*1Programa de Pós-Graduação em Geologia e Geoquímica, Faculdade de Geologia, Instituto de Geociências, Universidade Federal do Pará, Rua Augusto Corrêa s/n, CEP 66075-110, Belém-PA, Brasil*

*2Laboratório de Paleobiologia e Astrobiologia, Departamento de Biologia, Universidade Federal de São Carlos, Sorocaba, São Paulo 13506-900, Brazil*

*3Departamento de Geologia, Universidade Estadual Paulista – UNESP, Rio Claro, SP 13506-900, Brasil*

*4Brazilian Synchrotron Light Laboratory, Brazilian Center for Research in Energy and Materials – Campinas (SP), Brazil*

*5Muséum National d'Histoire Naturelle, Institut de Physique des Matériaux et de Cosmochimie, Sorbonne Université, Paris, France*

*6Research Productivity of CNPq*

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***In Preparation***



## 8 HIGH-RESOLUTION MAPPING AND CRYSTAL ARCHITECTURE OF A MARINOAN CAP DOLOSTONE (~635 MA): INSIGHTS INTO THE DOLOMITE PROBLEM AND ITS POTENTIAL AS AN ASTROBIOLOGICAL ANALOG

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*1Programa de Pós-Graduação em Geologia e Geoquímica, Faculdade de Geologia, Instituto de Geociências, Universidade Federal do Pará, Rua Augusto Corrêa s/n, CEP 66075-110, Belém-PA, Brasil*

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*3Departamento de Geologia, Universidade Estadual Paulista – UNESP, Rio Claro, SP 13506-900, Brasil*

*4Brazilian Synchrotron Light Laboratory, Brazilian Center for Research in Energy and Materials – Campinas (SP), Brazil*

*5Muséum National d'Histoire Naturelle, Institut de Physique des Matériaux et de Cosmochimie, Sorbonne Université, Paris, France*

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### 8.1 INTRODUCTION

Dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] is a common and one of Earth's most abundant carbonate minerals. They can form as a primary precipitate, diagenetic replacement, or hydrothermal metamorphic phase, requiring permeability and an adequate supply of  $\text{Mg}^{2+}$  (Tucker 1982, Morrow 1982, Friedman 1995, Warren 2000, Ryb *et al.* 2018). Synsedimentary dolomite precipitation occurs in specific environments with relatively high temperatures, typically ranging from 35 to 40°C, high evaporation rates, and a high Mg/Ca ratio promoted by the precipitation of sulfates, (e.g., evaporites) (Sibley and Gray (1987) and Warren (2000), as well as low concentrations of the sulfate ion, one of the main inhibitors of dolomite precipitation (Baker and Kastner 1981, Van Lith *et al.*, 2003). Dolomites are usually more common in Precambrian than in the Phanerozoic record (Tucker 1982, Smith 1982, Friedman 1995, Ryb *et al.* 2018) and are commonly found in ancient marine carbonate rocks. Once their precipitation remains rare in Holocene sediments,

despite seawater being supersaturated with the mineral, dolomites pose a challenge for researchers seeking to use them as analogs for widespread dolomitization (Wright 1999, Warren 2000, Klein and Mizusaki 2007).

Thus, the renowned 'dolomite problem' (Fairbridge 1957) emerges from modern instances that fail to adequately represent ancient and profound times. This problem is compounded by the difficulty in experimentally reproducing both the formation and, particularly, the Mg–Ca ordering of dolomite. Some experiments, drawing comparisons with Phanerozoic records, suggest that dolomite cation ordering occurs through progressive dissolution–(re)crystallization, a process that unfolds long after sedimentation (i.e. on a geological scale of thousands or millions of years) (Manche and Kaczmarek 2021, Pina *et al.* 2020, 2022). Once "the Precambrian dolomite problem" is even more challenging, great effort is being made to study "cap dolostones" (Fairchild 1993, Hoffman *et al.* 1998, Kennedy *et al.* 1998, James *et al.* 2001, Jiang *et al.* 2003, Shields 2005, Fabre *et al.* 2012, 2013, Higgins *et al.* 2018, Ahm *et al.* 2019). They are pervasively dolomitized Neoproterozoic carbonates that directly overlie Marinoan glacial deposits worldwide.

The Ediacaran cap carbonate deposits of the Amazon Craton, for example, have dolomicrite in close association with microbial communities (sulfate-reducing bacteria) that thrive on open platforms (Nogueira *et al.* 2003 2019, Font *et al.* 2006, Romero *et al.* 2020, Santos *et al.*, 2021). Romero *et al.* (2020) and Santos *et al.* (2021) interpreted peloidal aggregates within the texture of these same stromatolites (e.g., grumous and shrub textures) as micritized forms of photosynthetic cyanobacteria, consistent with the presence of photosynthetic cyanobacterial biomarkers described by Elie *et al.* (2007), Souza *et al.* (2016), and van Maldegem *et al.* (2018). However, another enigma surrounding sedimentary dolomites is the nature of their precipitation and crystallization. Some studies have shown that room temperature synthesis (proto-)dolomite precipitation (and maybe crystallization) is closely related to microbial activities (Zhang *et al.* 2015). At the same time, abiotic carbonation experiments demonstrated the role of highly negatively charged clay minerals, such as montmorillonite, in proto-dolomite precipitation in environmental conditions (Liu *et al.* 2019).

It is even more challenging to distinguish between biosignatures or minerals of paleobiological relevance and those associated with inorganic precipitation. Separating these phases poses a geobiological effort, as diagenesis can overlap with the records

through carbonate remobilization, precipitation, or authigenic phases. In this study, we present the results of a comprehensive paleometric approach. This approach, which considers petrography, high-resolution mapping microprobe, and nano X-ray fluorescence (Synchrotron nano XRF), X-ray diffraction (XRD) crystallography, and micro-Raman spectroscopy, provides a detailed and multi-faceted understanding of the cap dolostones from the Amazon Craton. We aim to delineate and compare the properties of the cap dolostones from the Amazon Craton and determine their diagenetic processes and sequences. Additionally, we propose some insights into the "dolomite problem" during the Cryogenian-Ediacaran, contributing to understanding organic carbonate precipitation conditions during the recovery of oceans post-snowball Earth events. Finally, we emphasize that the different versions of the Earth (and related life signs) preserved in the geological record, such as the problematic cap dolostones from Amazon Craton, offer us an opportunity to comprehend and extrapolate our interpretations to generate more efficient protocols for exploring life on other rocky worlds

## 8.2 GEOLOGIC SETTING

The Mirassol d'Oeste Formation is linked to the base of the Araras Group in the Araras-Alto Paraguai basin (Fig. 8.1 A-B) (Nogueira *et al.* 2019, 2022). The Ediacaran Mirassol Formation (~635 Ma) in the South Amazon Craton is renowned as a cap dolostone, associated with the post-Marinoan context (Nogueira *et al.* 2003, 2019, Sansjofre *et al.* 2014, Santos *et al.* 2021, 2023). These dolomitic deposits are part of the Puga cap carbonate succession, approximately 90 meters thick, where the lower 10 meters consist of glaciomarine deposits of the Puga Formation (Fig. 8.1 C). Adjacent to these deposits is cap dolostone (Mirassol d'Oeste Formation), the focus of this study, overlain by cap limestone deposits associated with the Guia Formation (Fig. 8.1 C). The cap dolostone is subdivided from base to top into four microfacies: 1) microbialites facies, encompassing stratiform doloboundstones with gypsum pseudomorphs and domical doloboundstones with tubestone, 2) wave-rippled dolostone, comprising two microfacies: dolograins/peloidal dolomudstone with quasi-planar to low-angle lamination, and peloidal dolomudstone/dolopackstone with megaripple bedding (For more details, see Santos *et al.* 2023). Several studies have explored the petrography, isotopic, and geochemical aspects of its shallow water microbialites facies, attributing the dolomite origin to an early diagenetic process (Nogueira *et al.* 2003, Font *et al.* 2006, Sansjofre *et al.* 2014, Soares *et al.* 2020, Santos *et al.* 2021, 2023).

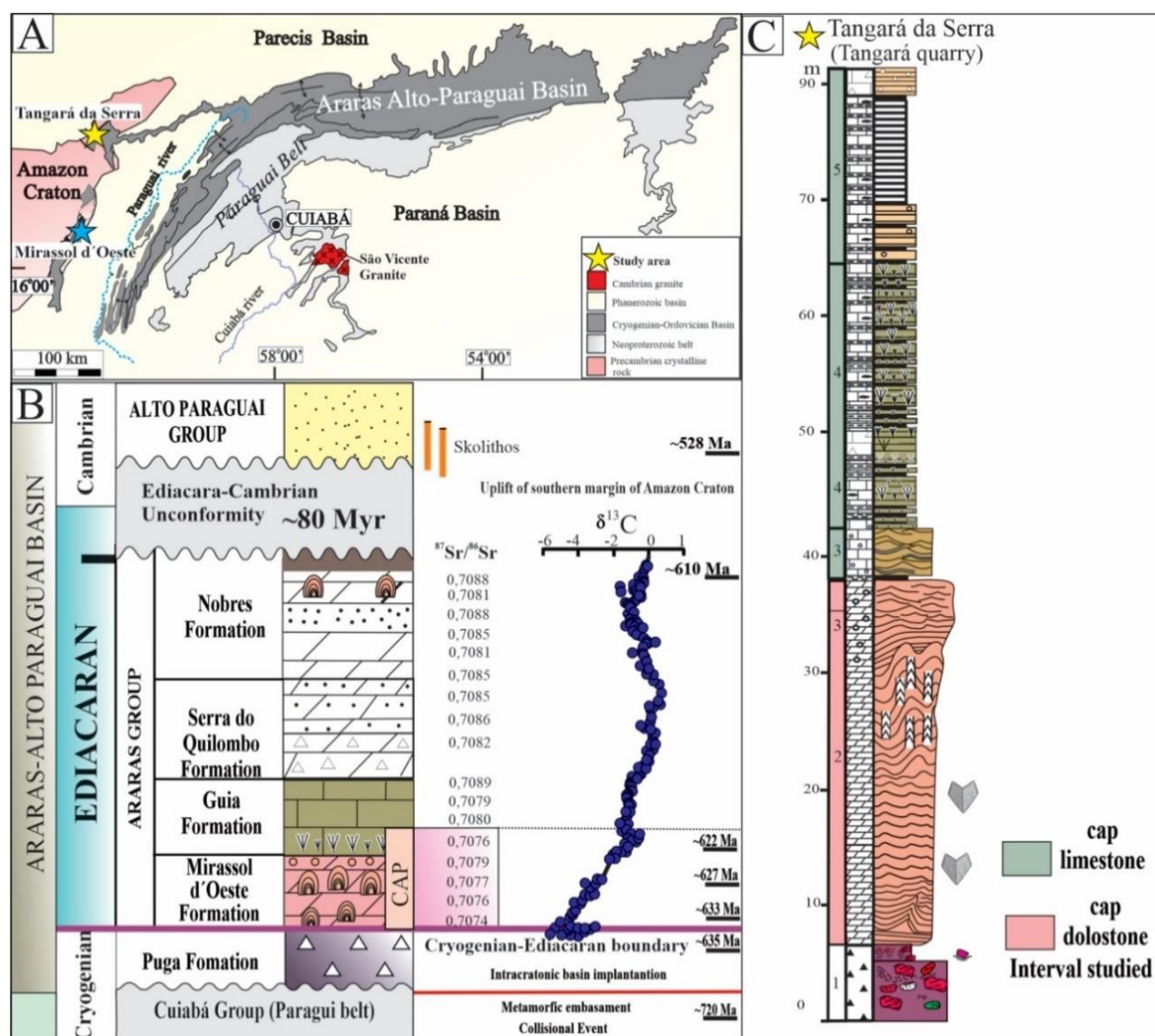


Figure 8.1- A) Geological context of the southern Amazon Craton, indicating the Araras-Alto Paraguai Basin, Paraguai Belt, and the occurrences of Puga cap carbonate (PCC) within the study area (the Calcário Tangará and Terconi quarries), highlighted by stars in the Tangará da Serra and Mirassol d'Oeste-Mato Grosso, Central-Western Brazil. B) Lithostratigraphy of the Neoproterozoic-Cambrian deposits of the Araras-Alto Paraguai basin (adapted from Nogueira and Riccomini 2006 and Nogueira et al. 2019). C) Stratigraphic sections of the Marinoan Puga cap carbonate in the southern Amazon Craton. Open pit of the Calcário Tangará quarry, Tangará da Serra region, Mato Grosso state

### 8.3 MATERIALS AND METHODS

#### 8.3.1 Optical Microscopy Analysis

We analyzed 93 polished thin sections of the cap dolostone (Mirassol d'Oeste Formation). The samples were obtained from two drill cores and an outcrop in the Tangará da Serra region of Mato Grosso (MT), Central-Western Brazil (Fig. 8.1 A). In addition, 10 thin sections of the cap dolostone from the Terconi section at the Mirassol d'Oeste region-MT. The modified Dunham classification (1962) was used for microfacies classification, with refinements based on the works of Wright (1992), Tucker (1993), and Flügel (2004). Approximately 300 points were counted following the Glagolev-Chayes

methods (Galehouse, 1971). The modified Dunham classification (1962) was used for microfacies classification, with refinements based on the works of Wright (1992), Tucker (1992), and Flügel (2004). Dolomite types were recognized and classified individually based on crystal size and shape of crystal boundaries, following the proposal by Sibley and Gregg (1987) and Mazzulo (1992), while the classification of porosity followed the proposal of Choquette and Pray (1970). Approximately 300 points were counted using a point counter to characterize the proportions of constituents following the Glagolev-Chayes methods (Galehouse, 1971).

### **8.3.2 Cathodoluminescence and Scanning Electron Microscopy Analyses**

Mineralogical refinement is performed through scanning electron microscopical energy dispersive spectros (SEM/EDS) and cathodoluminescence (CL). CL was utilized to investigate diagenetic features further. CL analysis was performed using the LEICA DM 4500 P LED optical microscope coupled to the Optical cathodoluminescence CL 8200 MK5-2. s at the Cathodoluminescence Laboratory of the Federal University of Pará. The analysis conditions were as follows: electric current ranging from 14.9 to 15.1 kV, acceleration voltage ranging from 296 to 442 A, and exposure time of 10.8 seconds. In carbonate rocks, cathodoluminescence provides a basis for understanding the fundamental diagenetic relationships between grains, matrix, types of cement, porosity evolution, and common substitution reactions occurring in these rocks. CL also provided data on the spatial distribution of  $\text{Fe}^{+2}$  and  $\text{Mn}^{+2}$  in calcite, dolomite, and cement (Hiatt and Pufahl 2014). Additionally, analysis using scanning electron microscopical (SEM) and backscattered electron imaging (BSE), supported by energy-dispersive spectrum (EDS), was carried out at the Microanalysis Laboratory of the Federal University of Pará on thin sections previously coated with gold to characterize the mineral phases texturally and chemically. The operating conditions for the secondary and backscattered electrons imaging were as follows: electron beam current = 80  $\mu\text{A}$ , constant acceleration voltage = 20 kV, working distance = 8.5 mm. EDS analysis was performed using the Zeiss SIGMA-VP scanning electron microscope with the IXRF Sedona-SD EDS system attached. The operating conditions for EDS analysis were an electron beam current of 80  $\mu\text{A}$ , a constant acceleration voltage of 20 kV, a working distance of 10.1 mm, and an element analysis counting time of 30 seconds.

### 8.3.3 Electron probe microanalysis

Electron Probe Micro Analyzer (EPMA) analyses were performed using a JEOL 8230 with five WDS spectrometers at the Department of Geology, São Paulo State University, Brazil. The conditions for the quantitative point analyses are summarized in Supplementary Table 8.2. For the map analyses, the accelerating voltage was set to 15 kV and the probe current to 15 nA. Mg, Ca, Sr, and Mn were acquired in WDS mode, while Al, Si, P, and Fe were simultaneously acquired in EDS mode. Cathodoluminescence, secondary electrons, and backscattered electron images were also acquired. The step size and dwell time varied depending on the size of the mapping area. The detection limit of the microprobe analysis was approximately 280 ppm for each element.

### 8.3.4 $\mu$ -X-ray Fluorescence Analysis

Synchrotron Radiation nano-X-ray Fluorescence ( $\mu$ -XRF) mapping was conducted in micro-beam mode in 14 thin sections, employing polychromatic excitation and filtered by Ca and Fe foils. Beam dimensions ( $12 \times 25 \mu\text{m}$ ) were achieved using a KB focusing system at the XRF beamline at the Brazilian Synchrotron Light Laboratory (LNLS), Brazil. Mapping was performed with  $20 \mu\text{m}$  steps and an accumulation time of 0.2 s/point. The measurements were carried out using a monochromatic beam at an energy of 9 keV and 12 keV, with acquisition carried out in fly-scan mode. The data were processed using PyMca 4.6.0 software (developed by the European Synchrotron Radiation Facility ESRF, Solé *et al.* 2007) to generate elemental concentrations in semi-quantitative maps.

### 8.3.5 X-ray diffractometry analysis

Powder X-ray diffraction was used to characterize the present phases and determine the composition and degree of cation order for dolomite phases. Thirty samples were used for the total powder method, with 1g of each sample backloaded. A micro drill was used to individualize the cement matrix to individualize the analyzed phases. X-ray diffraction (XRD) analyses were performed using the Empyrean model X-ray Diffractometer (XRD) from PANalytical, with ceramic X-ray tubes, cobalt anode ( $K\alpha_1 = 1.789010 \text{ \AA}$ ), long fine focus, Fe  $K\beta$  filter, PIXCEL3D-Medpix3 1x1 detector, in scanning mode, with a voltage of 40 kV, current of 35mA. They were scanning range from  $2^\circ$  to  $80^\circ 2\theta$ , step size of  $0.026^\circ$  in  $2\theta$ , and a time/step of 31 s. Divergent slit:  $1/4^\circ$  and anti-scatter slit:  $1/2^\circ$ , mask: 10 mm. Data acquisition was performed using X'Pert Data Collector software, version 5.1, and data processing with X'Pert HighScore Plus software, version 5.0, also from

PANalytical. Mineral identification was carried out by comparing the obtained diffractogram with patterns (cards) from the ICDD-PDF (International Center for Diffraction Data – Powder Diffraction File) and COD (Crystallography Open Database) databases. The degree of cation order is reported as the ratio of the  $d_{015}$ :  $d_{110}$  superlattice reflection peaks following the methods of Goldsmith and Graf (1958).

Multivariate statistical analysis was performed using 50 representative samples. Hierarchical cluster analysis (HCA) and principal component analysis (PCA) are classical multivariate statistical methods traditionally used to evaluate chemical analytical results. These methods are frequently employed to identify patterns of correlation between variables. Recently, these tools have also been successfully applied to process X-ray diffractograms without requiring prior treatment or knowledge of mineral paragenesis. This approach allows for the classification of numerous samples in a short time, significantly reducing processing time and aiding data analysis (Macchiarola *et al.* 2007). The resulting clusters reveal variations in the multivariate database of mineralogical composition, thereby indicating different geological environments.

### 8.3.6 Micro-Raman spectroscopic analysis

Fifty thin sections were used for the micro-Raman spectra measurements with a Renishaw in Via Reflex equipment coupled to a Leica DM2500 M microscope, containing the lasers with excitation at 632.8 nm (He-Ne, Renishaw)-50 mW-, 785 nm (diode laser, Renishaw)-500 mW- and 532 nm (diode laser, Renishaw)-500 mW-. The equipment also contains two diffraction gratings, one with 1200 lines (used with the 632.8 or 785 nm lasers) and another with 2400 lines (used with the 532 nm laser), and a thermoelectrically cooled CCD detector (1040 x 256 pixels). The Wire 4.4 software was used to analyze the collected data. During this analysis, the 785 nm laser was chosen and was used at 1% of its power. The individual spectrum was collected using 30 accumulations of 2 s each, with the removal of cosmic rays. The Raman spectra were baselined, corrected, and normalized using Spectragryph software v.1.2.16.1.

## 8.4 RESULTS

### 8.4.1 Petrography

Complete descriptions of the petrographic appearance of the diagenetic phases and sequencing of the Puga Carbonate cap are reported by Santos *et al.* (2023) and summarized in Table 8.1. The main textural and mineralogical characteristics of the cap dolostone are as follows.

#### 8.4.1.1 Dolomicrite (DM)

Dolomicrite is characterized by pervasive replacive micritic dolomite with non-planar, irregular intercrystalline boundaries. It typically exhibits a grumose texture (Fig. 8.2 A-D), seen as diffuse peloids that cluster into non-individualized macroaggregates or isolated grumous structures. These peloids occasionally resemble shrubs (Fig. 8.2 E-F).

#### 8.4.1.2 Replacive Dolomite (RD)

Replacive dolomite is found across all facies, forming a fine to medium crystal mosaic with planar-e to planar-s textures, measuring 0.1-0.2 mm (Fig. 8.3 A, B). This phase retains the original tissue structure, with crystals featuring a cloudy core (DM) and a clear outer part (Fig. 8.3 E, F). Primary DM crystals are often embedded within RD mosaics (Fig. 8.3 B, D), indicating a transition between these phases. Additionally, RD affects gypsum (Gyp) composition while preserving its texture (Fig. 8.4).

#### 8.4.1.3 Fibrous Dolomite (FD)

Fibrous dolomite cement, appearing as gypsum pseudomorphs, fills fenestral porosities (Fig. 8.4 A, B), predominantly at the section's base. These 0.5-0.8 mm sized cements have a fibrous habit, with euhedral crystals growing in fascicular and radial/radial forms, indicative of swallowtail twinning (Fig. 8.4 C-F). This cement is a replacive dolomite (RD).

#### 8.4.1.4 Calcite Cement (CC)

Calcite cement consists of anhedral limpid crystals ranging from 0.4 to 2 mm (Fig. 8.2 C, D). It pervasively fills various pore types (Fig. 8.3 C, D), including fenestral, tubestone, interpeloidal, intercrystalline, and vuggy pores, and replaces dolomite rims (Fig. 8.4 A, B). In addition, pyrite pseudomorphs (Fe-oxyhydroxide) were identified in association with calcite (Fig. 8.4 E-F).



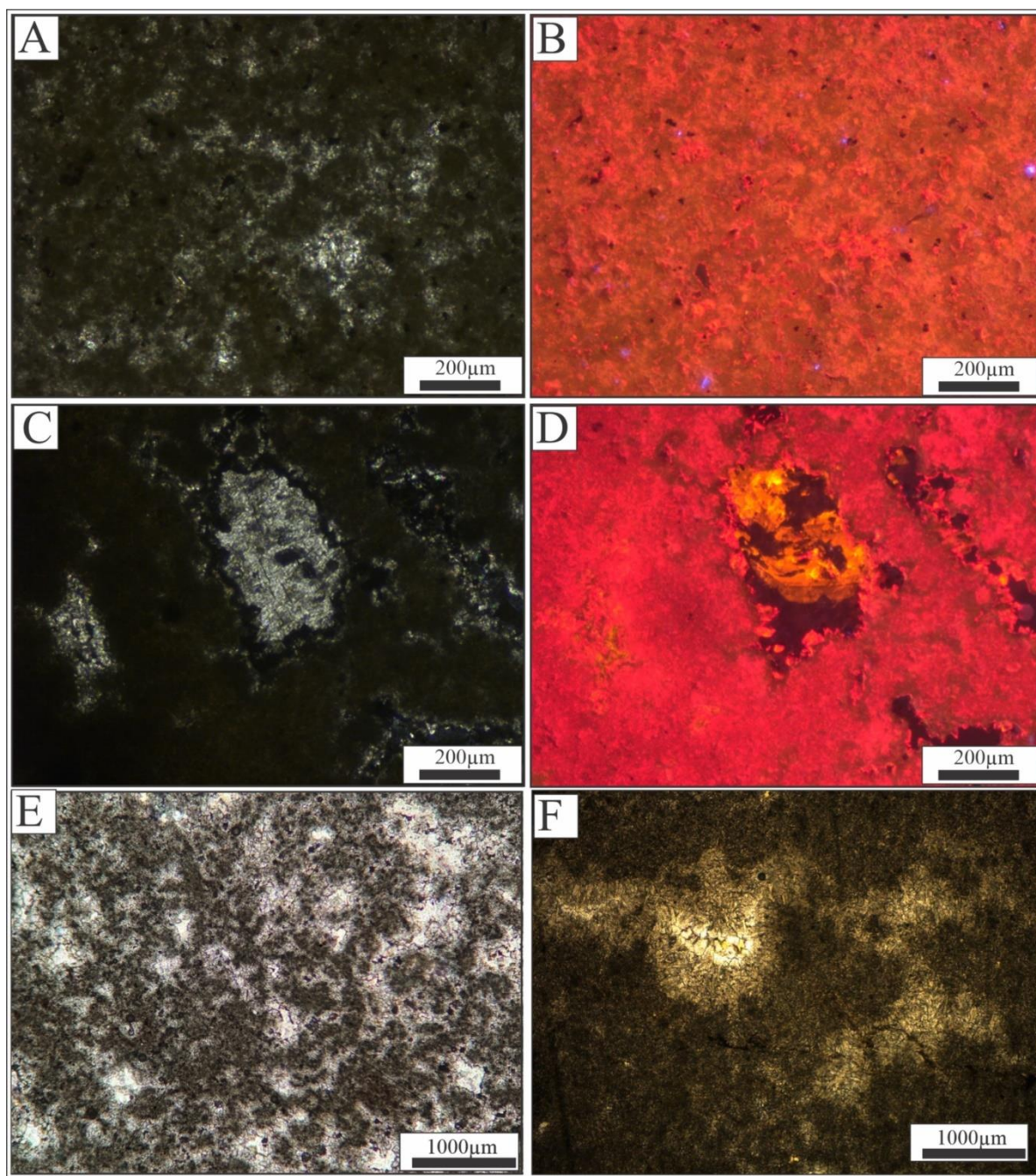


Figure 8.2- A)–F) Photomicrographs of dolomicrite constituents associated with microbialites from the cap carbonate succession. A) Dense dark laminae (opaque) alternating with irregular fenestral porosities, showing a predominance of coalescent grumose peloid textures and irregular intercrystalline boundaries (non-planar). B) and D) CL images illustrating the mottled luminescence of dolomicrite. It exhibits a predominant bright red to dull orange luminescence, with the brightest luminescence occurring in the most replacive (RD) portions and dull luminescence in the most micritic portions. In D), calcite cement is mainly non-luminescent, although there are zones with concentric zoning of bright orange luminescence. C) Detail of the microbialites phase, showing the predominance of coalescent grumose peloids texture with fenestrae filled with calcite. E) Coalescent grumose peloids with dendritic to dense patterns, similar to shrub facies. F) Coalescent grumose peloids with fenestral porosity filled by two generations of cement: (1) light brown fibrous dolomite and (2) light drusy dolomitic cement in the center of the porosity.



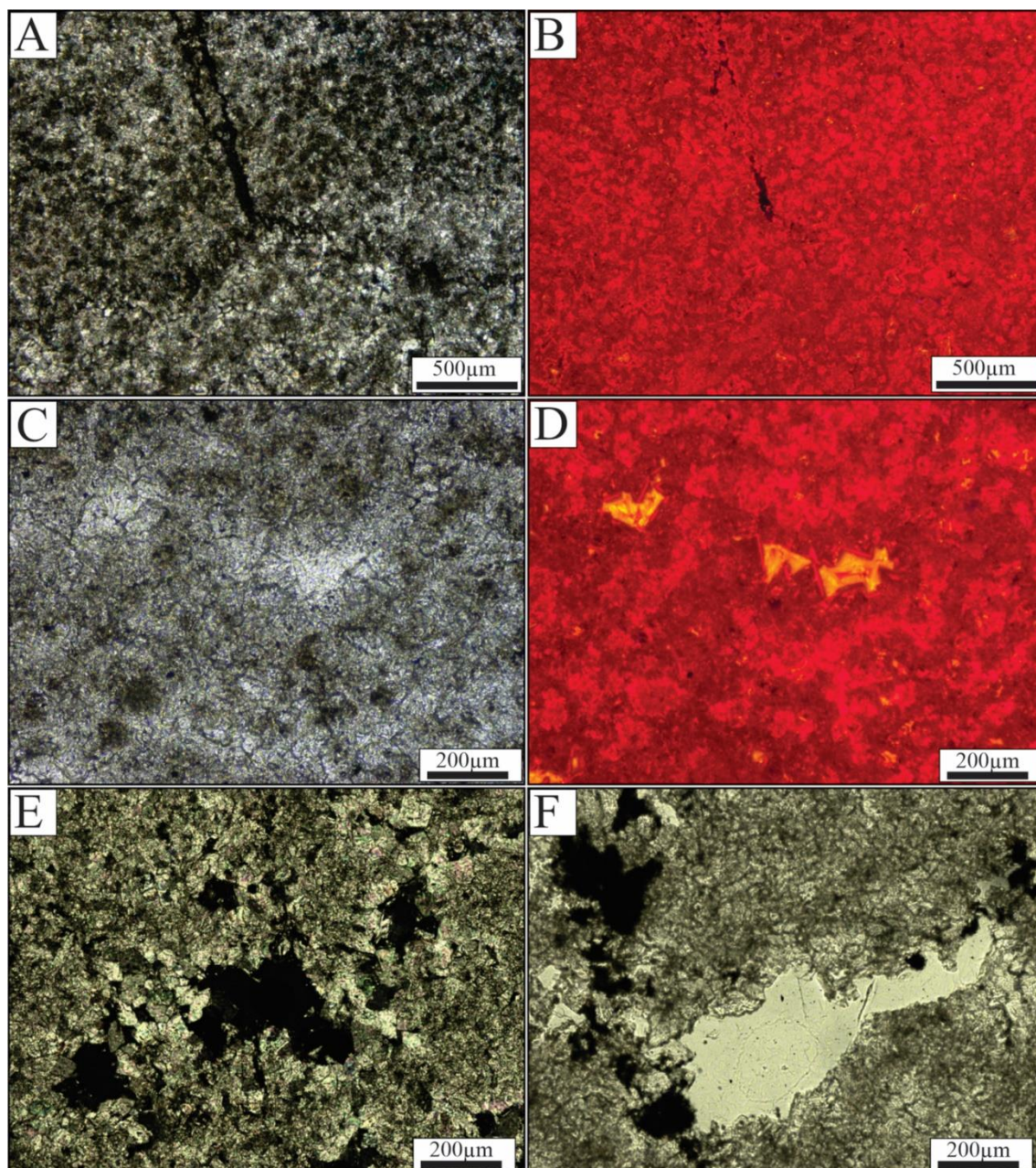


Figure 8.3- A) Coalesced grumose with advanced neomorphism forming replacive dolomite as a fine to medium planar-e to planar-s crystal mosaic. B) CL image displays blotchy zoning, with non-luminescent regions interspersed with zones of varying intensities ranging from bright red to dull red luminescence. C) Detail of dolomicrite with advanced neomorphism. D) CL image illustrating the blotchy zoning of RD. Note that the calcite cement is mainly non-luminescent, although there are zones with concentric zoning of bright orange luminescence. E) and F) Photomicrographs of RD depicting cloudy centers and light borders (with central remnants of DM in planar-s crystals), indicating a textural transition between the two phases.



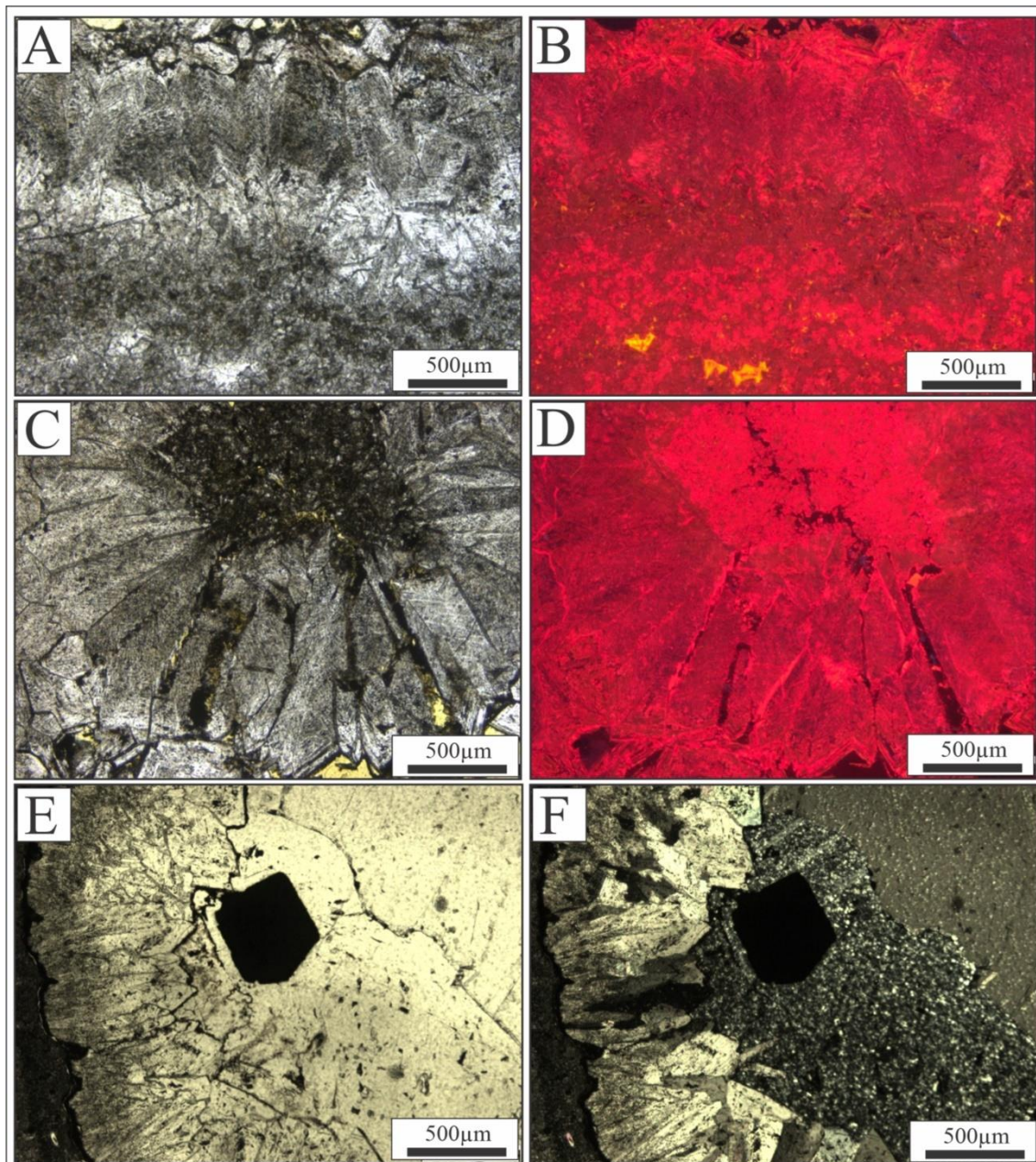


Figure 8.4- Photomicrographs of fibrous dolomite (FD - gypsum pseudomorphs). A) Filling inter-peloidal and fenestral porosity. B) CL image of A) where the DM exhibits bright red-orange luminescence, while the gypsum pseudomorph and the most substituted part of the matrix display blotchy zoning with dull red luminescence. C) Showing swallowtail twinned crystal fans, where the fascicular portion is turbid and the radial/radiaxial portion is limpid. D) CL image of C) showing the crystals with high iron content and/or inclusion-rich (dark) and different stages of diagenetic growth. E) Detail of fenestral pores filled with cement. F) Under plane-polarized light, showing the precipitation order of the paragenetic phases: dolomite, fibrous dolomite cement, pyrite, and calcite cement.

Table 8.1- Summary table of the microscopic features of the diagenetic phases in the cap dolostone based on transmitted light, and cathodoluminescence (CL)

| Diagenetic phase          | Size (µm) | Morphology                                           | Inclusions | Cathodoluminescence                                          | Distribution                                                                                                            |
|---------------------------|-----------|------------------------------------------------------|------------|--------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|
| Dolomicrite (DM)          | ~25       | Nonplanar                                            | Turbid     | Mottled bright red to orange (no zoning)                     | Dolostone matrix                                                                                                        |
| Fibrous dolomite (FD)     | 500-800   | Fascicular, radial/ radial with swallowtail twinning | Limpid     | Blotchy zoning: dull red to bright orange                    | Filling the majority of fenestral porosities                                                                            |
| Replacive dolomite (RD)   | 100-200   | Planar-s / planar-e                                  | Limpid     | Blotchy zoning: non-luminescent core a bright red/orange rim | Dolostone matrix                                                                                                        |
| Calcite Cement (CC)       | 400-2000  | Blocky                                               | Limpid     | Concentric zoning: non-luminescent core a bright orange rim  | Fills fenestral, tubestone, interpeloidal, intercrystalline, vuggy pores, dissolution seams and replacing dolomite rims |
| Pyrite (Py)               | 100-500   | Cubic                                                | —          | Nonluminescent                                               | Fills intercrystalline and intracrystalline pores                                                                       |
| Mn oxy-hydroxides (Mn-Ox) | 20-120    | Acicular/Colloidal                                   | —          | Nonluminescent                                               | Fills intercrystalline and intracrystalline pores                                                                       |
| Fe oxy-hydroxides (Fe-Ox) | 10-100    | Colloidal                                            | —          | Nonluminescent                                               | Fills intercrystalline and intracrystalline pores                                                                       |
| Fluorapatite (Ap)         | 15-30     | Tabular                                              | Limpid     | —                                                            | Intercrystalline porosity                                                                                               |

## 8.5 GEOCHEMICAL MICROANALYSIS

Microanalyses were conducted to determine the composition and map the distribution of elements in dolomite phases found in the cap dolostone: Dolomicrite (DM), Fibrous Dolomite (FD), and Replacive Dolomite (RD) (Table 8.1). Major and minor elements were measured at 181 points using a microprobe, the data is presented in Supplementary Table 8.1. Despite the distinct textural characteristics observed, these evaluations do not permit a chemical distinction between the grouped dolomites. In all analyses, the weight percentage (wt%) of CaO and MgO is similar, demonstrating homogeneity in the Mg/Ca ratio of 0.6, consistent with what had been previously reported in the bulk rock approach by Santos *et al.* (unpublished). The trace elements of interest were mainly below the detection limit of the microprobe (see Supplementary Table 8.1). The DM phase's Mg/Ca ratio, a key indicator of mineral composition, is 0.6 (Table 8.2), with average values of Fe = 1219.211 (Fig. 8.5 C), Mn = 374.8386 (Fig. 8.5 D),  $n = 28$ . This phase exhibits a low correlation for Mg/Ca vs. Mn  $R^2 = 0.3691$  (Fig. 8.5 A) and Mg/Ca vs. Fe  $R^2 = 0.1872$  (Fig. 8.5 B). Similarly, the Mg/Ca ratio of the RD phase is 0.6 (Table 8.2), with average values of Fe = 1423.255 (Fig. 8.5 D), Mn = 2224.249 (Fig. 8.5 C),  $n = 22$ . This phase shows a low correlation for Mg/Ca vs. Mn  $R^2 = 0.1621$  (Fig. 8.5 A) and Mg/Ca vs. Fe  $R^2 = 0.0795$  (Fig. 8.5 B). Lastly, the Mg/Ca ratio of the FD phase is 0.6 (Table 8.2), with average values of Fe = 1787.813 (Fig. 8.5 D), Mn = 353.1538 (Fig. 8.5 C),  $n = 80$ . This phase exhibits a very low correlation for Mg/Ca vs. Mn (Fig. 8.5 A),  $R^2 = 3 \times 10^{-6}$ , and Mg/Ca vs. Fe (Fig. 8.5 B),  $R^2 = 0.0024$ . The matrix Fe and Mn content variation (Table 8.2) is evident in cathodoluminescence images, showing luminescent and dull to non-luminescent zonings (Figs. 8.2 and 8.3). Besides dolomite, other minerals, such as calcite, iron oxide, and manganese oxide, were identified, filling the porosities. Compositional maps revealed a homogeneous distribution of the elements (Fig. 8.6).

Table 8.2- Estimated mean values of microprobe analytical results for each element in the dolomite phases. For more details, see Supplementary Table 8.1 for the individual dolomites' measured data points.

| Dolomite phase | Mg       | Ca       | Mg/Ca | Fe       | Mn       |
|----------------|----------|----------|-------|----------|----------|
| Means          |          |          |       |          |          |
| Dm, n= 28      | 127957,3 | 218082,1 | 0,6   | 1219,211 | 374,8386 |
| RD, n =22      | 126408,6 | 217950,6 | 0,6   | 1423,255 | 2224,249 |
| FD, n = 80     | 127454,3 | 217541,8 | 0,6   | 1787,813 | 353,1538 |

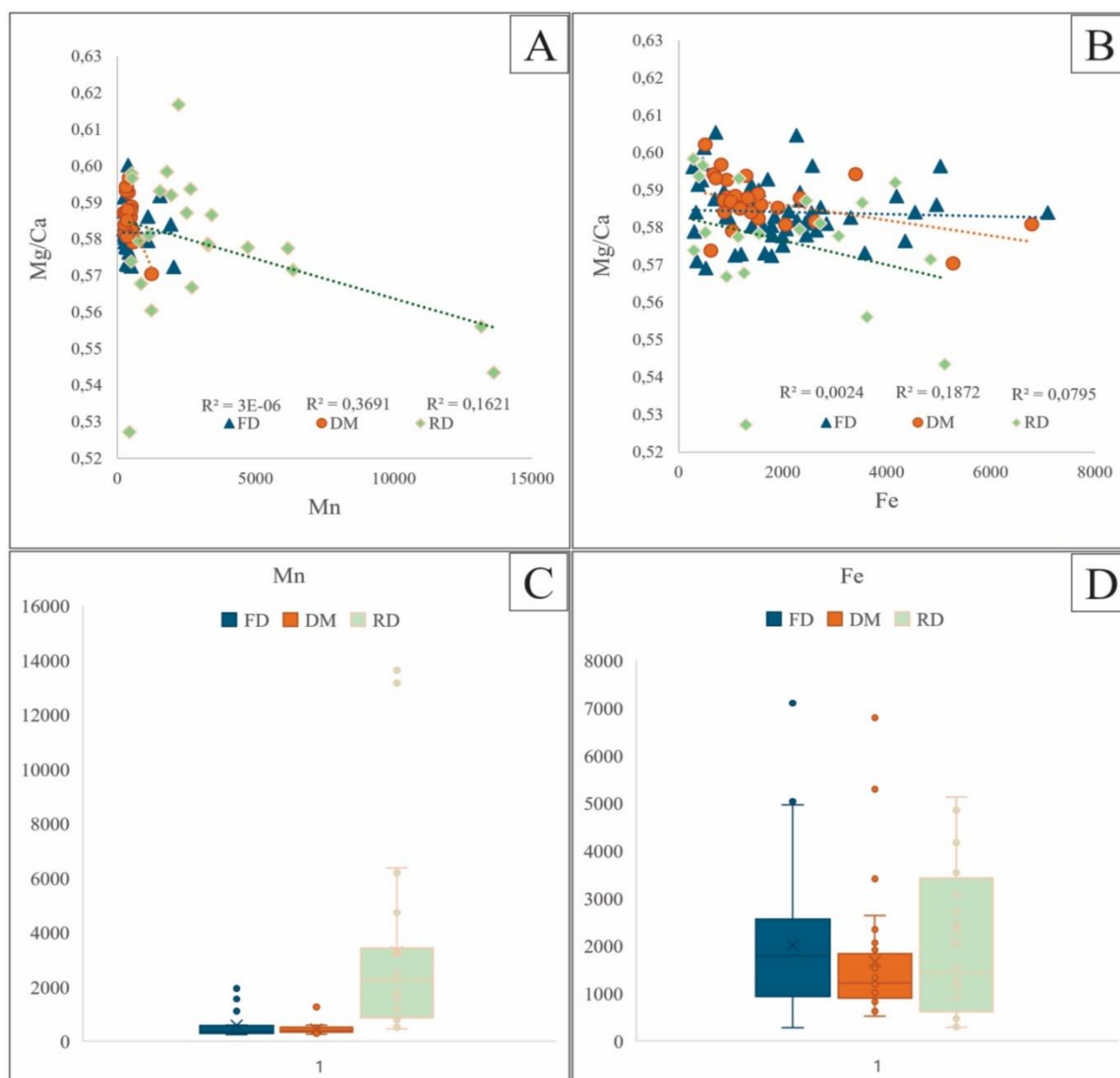


Figure 8.5- Scatterplots showing the relationships (A) Mg/Ca ratio vs. Mn and (B) Mg/Ca ratio vs. Fe, including Dolomitic (DM), Replacive dolomite (RD), and Fibrous dolomite (FD). The DM phase exhibits a low correlation for Mg/Ca vs. Mn ( $R^2 = 0.3691$ ) and Mg/Ca vs. Fe ( $R^2 = 0.1872$ ). Similarly, the Mg/Ca ratio of the RD phase shows a low correlation for Mg/Ca vs. Mn ( $R^2 = 0.1621$ ) and Mg/Ca vs. Fe ( $R^2 = 0.0795$ ). Lastly, the Mg/Ca ratio of the FD phase exhibits a very low correlation for Mg/Ca vs. Mn ( $R^2 = 3 \times 10^{-6}$ ) and Mg/Ca vs. Fe ( $R^2 = 0.0024$ ). D) Box-plot distribution of Mn in the dolomitic phases. Note the higher enrichment of Mn in the replacive dolomite. For more details see supplementary table 8. 1

The  $\mu$ -XRF analyses demonstrated higher Ca intensities than other trace elements. As previously indicated in microporosities, the more significant accumulation of trace elements is associated with microprobe and SEM analyses (Fig. 8.7). However,  $\mu$ -XRF maps revealed Zn, Cu, Ni, Fe, Mn, V, and As concentration, which may be associated with arsenopyrite, iron and manganese oxides, and sphalerite (Fig. 8.7). Similarly, microprobe elemental maps did not show clear compositional distinction between dolomitic phases (Fig. 8.6).



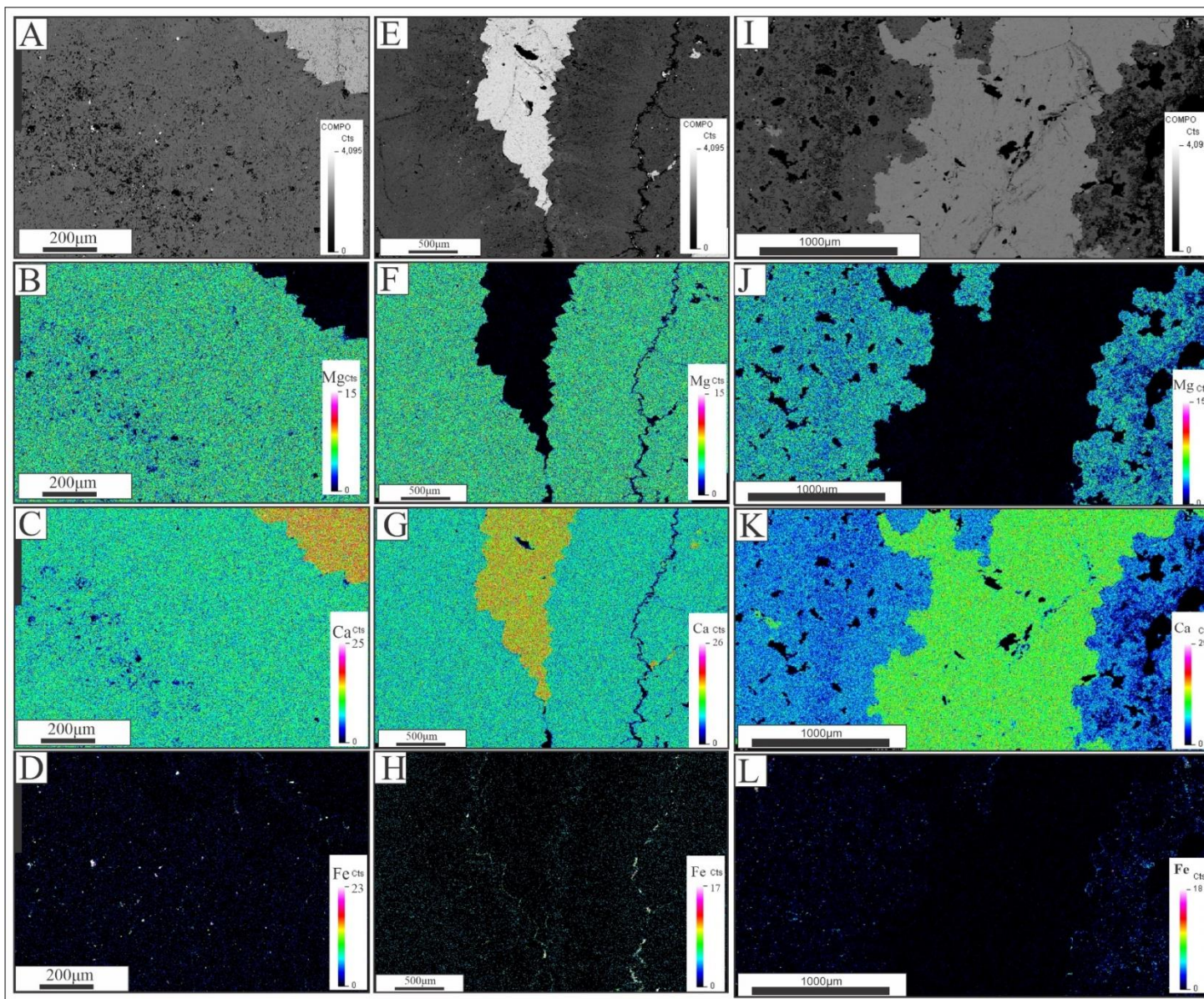


Figure 8.6- Backscattered electron image and b) cathodoluminescence showing electronic microprobe distribution maps obtained for Mg, Ca, and Fe in Dolomicrite (DM) and Fibrous dolomite (FD). Warmer colors represent higher concentrations. MgO, Fe, and CaO are distributed in higher concentrations. Note the high Mg/Ca ratio and predominant concentration in all mapped dolomitic phases. A) to D) represent the contact between the dolomitic matrix and the fibrous dolomite cement (preferentially filling fenestrae and interparticle porosities), E) to H) detail the fibrous dolomite, with remarkably well-preserved swallowtail twinning in contact with calcite cementation. Note the enrichment of Ca in G) between the crystals. I) to L) detail the dolomicrite with a grumose texture. The enrichment of Ca in K) is related to the calcite cementation phase. For more details see supplementary table 8. 1



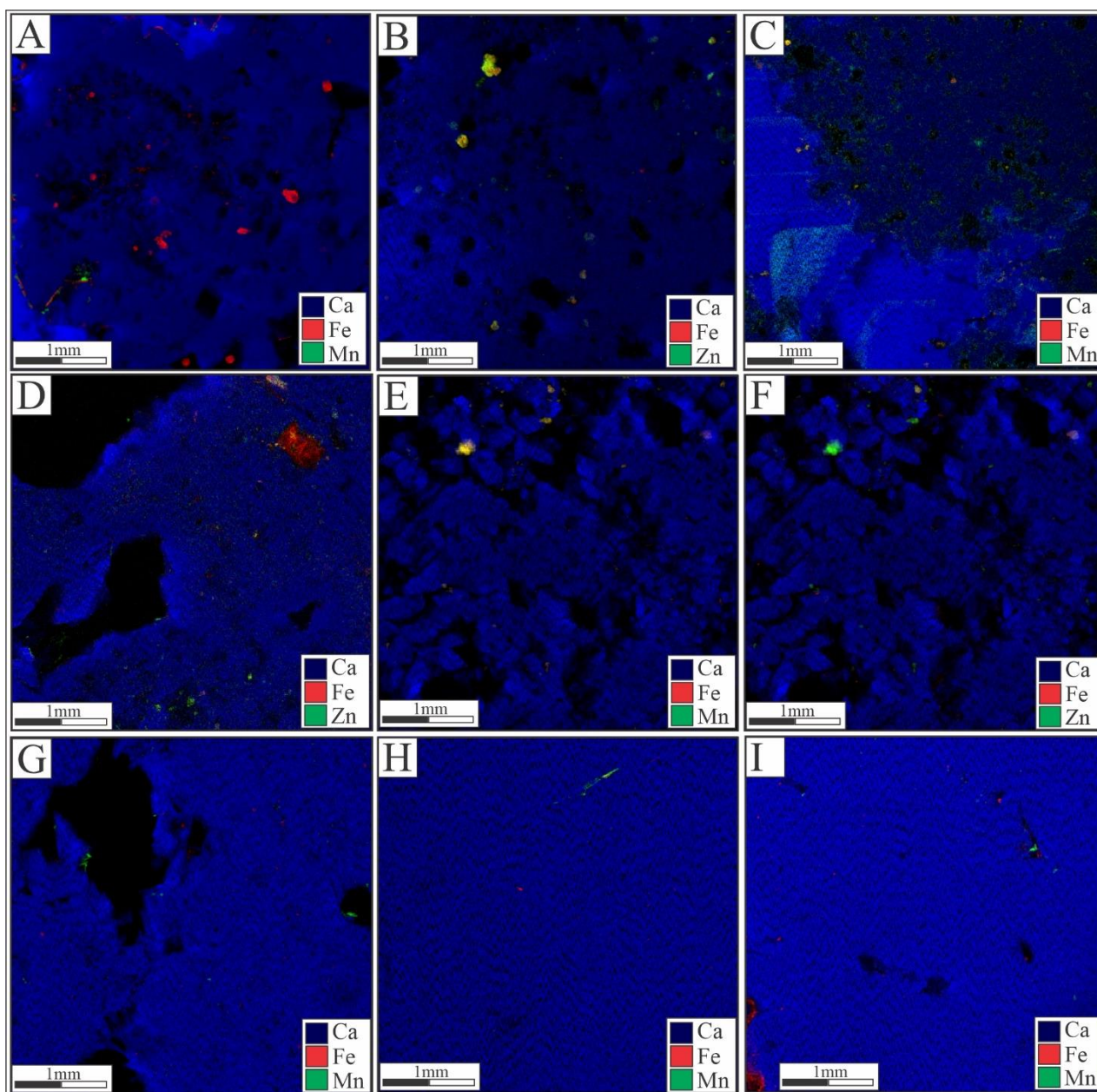


Figure 8.7-  $\mu$ -X-Ray fluorescence elemental maps of the dolomite phases in the sample, including Dolomicrite (DM), Replacive dolomite (RD), and Fibrous dolomite (FD). Elemental maps with 8  $\mu$ m step size (XRF beamline, LNLS) of an area covering the DM, RD, and FD phases. Scale bar = 1 mm. A) DM (2) of the microbialites phases shows the composition of Ca (blue), Mn (green), and Fe (red). B) DM (2) of the microbialites phases shows the composition of Ca (blue), Zn (green), and Fe (red). C) DM (3) of the wave-rippled dolostone facies shows the composition of Ca (blue), Zn (green), and Fe (red). D) DM (2) shows the composition of Ca (blue), Zn (green), and Fe (red). E) DM (2) shows the composition of Ca (blue), Mn (green), and Fe (red). F) DM (2) shows the composition of Ca (blue), Zn (green), and Fe (red). G) RD shows the composition of Ca (blue), Mn (green), and Fe (red). H) and I) FD phase shows the composition of Ca (blue), Mn (green), and Fe (red).

The micro-Raman spectroscopy analyses were performed on the main dolomitic phases from cap dolostone, including dolomicrite (DM), replacive dolomite (RD), and fibrous dolomite (FD) (Table 8. 1). The main mode of rhombohedral carbonates is the asymmetric stretching vibration ( $\nu_1$ ), which arises between 1024 and 1100  $\text{cm}^{-1}$  (Rividi *et al.* 2010). For dolomite and calcite in Puga cap dolostone, this micro-Raman peak occurs at  $\sim 1095 \text{ cm}^{-1}$  and  $\sim 1085$



$\text{cm}^{-1}$ , respectively. All these dolomite phases showed a major peak at  $1098 \text{ cm}^{-1}$ , and typical Micro-Raman shifts around  $1097 \text{ cm}^{-1}$  and  $1100 \text{ cm}^{-1}$  are associated with dolomite (Fig. 8.8). The calcite and dolomite spectra exhibit three subordinate bands in the regions of  $153\text{--}173 \text{ cm}^{-1}$ ,  $279\text{--}296 \text{ cm}^{-1}$ , and  $710\text{--}725 \text{ cm}^{-1}$ , corresponding to the rhombohedral carbonate lattice vibrational modes (T, L) and internal modes ( $\nu_4$ ) (Rividi *et al.* 2010). Other mineral phases were identified, such as indeterminate sulfate ( $1113 \text{ cm}^{-1}$ ) and some peaks related to calcite ( $1089 \text{ cm}^{-1}$ ). Additionally, the full width at half maximum (FWHM) analyses provided indications of crystallinity in situ. DM (1) showed mean values =  $7.13 \pm 0.36$ ,  $n=143$ , DM (2) =  $5.65 \pm 0.63$ ,  $n=180$ , DM (3) =  $7.12 \pm 1.2$ ,  $n=94$ , RD =  $5.7 \pm 0.83$ ,  $n=101$ , while FD =  $7.19 \pm 0.44$ ,  $n=74$  (Fig. 8.9). Additionally, for comparison, DM (4) represents measurements of cap dolostone from the Terconi Section and presented mean values of  $5.6 \pm 0.22$ ,  $n=116$  (Fig. 8.9 A). For more details, see supplementary material 8.3. The shift of the characteristic bands of dolomite between  $1097 \text{ cm}^{-1}$  and  $1100 \text{ cm}^{-1}$  in dolomiticite potentially indicates more than one phase of dolomites (Fig. 8.8 A, C, and D), while the more crystalline dolomite (replacive dolomite) shows better ordering (Fig. 8.8 B and 8.8 F).

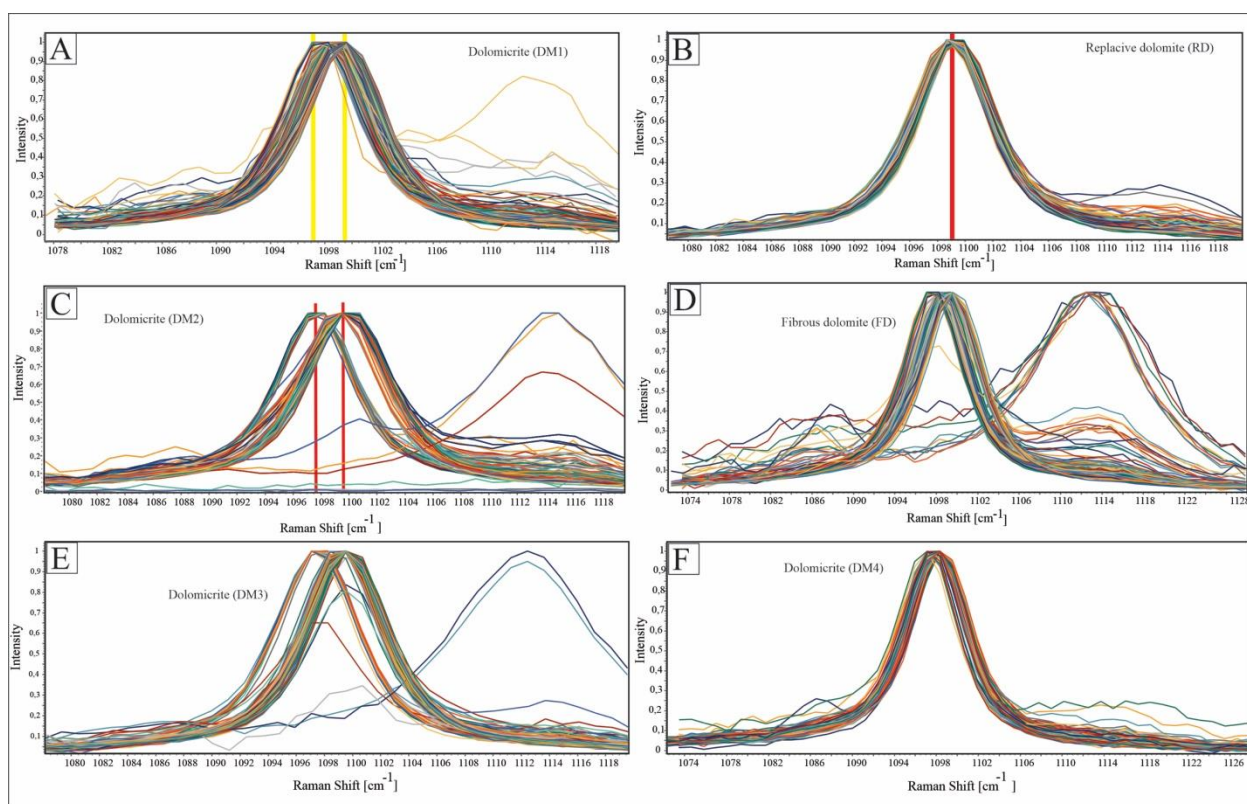


Figure 8.8- Raman spectra and peak width analyses. Measurement of the width of the  $1098 \text{ cm}^{-1}$  and  $1099 \text{ cm}^{-1}$  peaks, including Dolomiticite (DM), Replacive dolomite (RD), and Fibrous dolomite (FD). The lines indicate the measured peak widths (FWHM [ $1/\text{cm}$ ]). Note that the constituents occur with varying crystallinities, and notably, the false dolomiticite exhibits intense shifts in the characteristic dolomite peak.

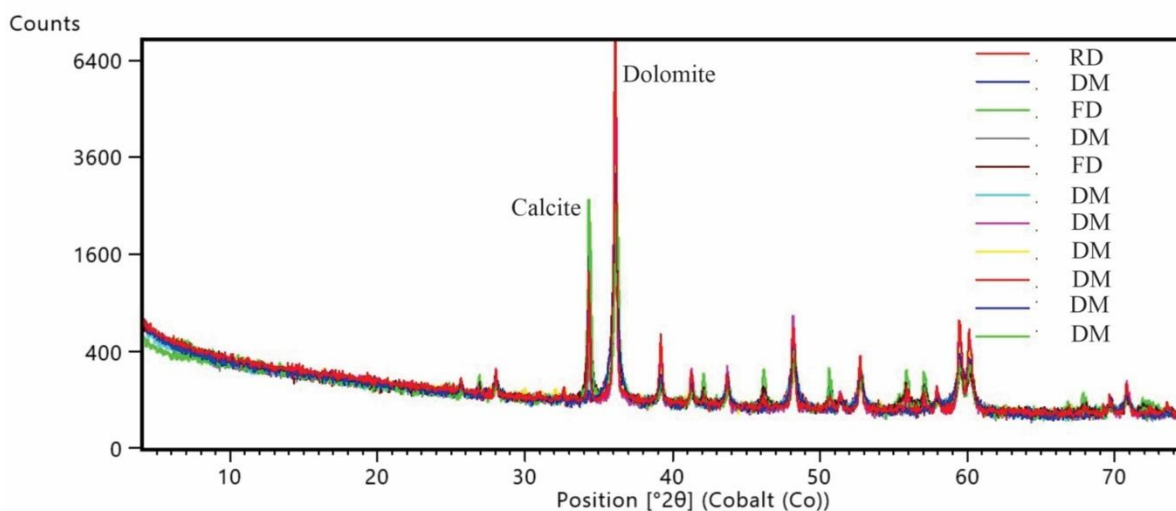


Figure 8.9- The XRD patterns for micro-drilled powders of cap dolostones samples (dolomicrite (DM), replacive dolomite (RD), and fibrous dolomites (FD) dolomite and calcite in varying proportions

Mineral abundances of micro-drilled dolomite samples (dolomicrite (DM), replacive dolomite (RD), and fibrous dolomites (FD) were determined by XRD (Fig. 8.9). The carbonate samples (dolomite and calcite in varying proportions) are rich in Ca and Mg and exhibit high loss on ignition (CO<sub>2</sub>). While the dolomitic phase is predominant, calcite is commonly found in the analyses as a cementation phase. Other low concentrations and variable proportions phases include quartz, albite, and K-feldspar (Fig. 8.9). The dolomite samples' X-ray diffraction (XRD) patterns reveal significant crystallinity and mineral composition variations (Fig. 8.9 and Fig. 8.10 B). These samples correspond to the dolomicrite phase (DM) related to the microbialites, with only sample JOR 183 corresponding to the wave-rippled dolostone facies of the cap dolostone succession. The replacive dolomite is described throughout the succession; however, in some portions, the neomorphism process was more intense, as exemplified by sample JOR 7 (Fig. 8.10 B). Sample "JOR 171" exhibits an FWHM of 0.168, indicating a highly crystalline dolomite composition of 96.2% dolomite and 3.8% calcite. "JOR 183", with a FWHM of 0.340, displays the lowest crystallinity among the dolomite samples, consisting of 98.6% dolomite and 1.4% potassium feldspar (Kfs). Sample "JOR 79" shows a FWHM of 0.312, containing 97.8% dolomite and 2.2% calcite. "JOR 38" presents an FWHM of 0.219, with 99.4% dolomite and 0.6% calcite, indicating high purity. The "TP" sample has an FWHM of 0.148, showing a diverse composition of 59.4% dolomite and 40.6% calcite. Finally, "JOR 7" has the smallest FWHM of 0.126, indicating the highest crystallinity among the samples, with 90.6% dolomite and 9.4% calcite.

Multivariate statistical analysis was performed to correlate the mineralogical composition patterns in the multivariate database with the dolomite phases (Fig. 8.10 B). The

predominance of carbonate lithology throughout the succession prompted the application of statistical analysis to define the dolomite type better. Hierarchical cluster analysis (HCA), principal component analysis (PCA), and FWHM analyses can identify patterns in the multivariate elements and graphically produce groups with similar mineralogical compositions. With the combinations of this parameter, it was possible to group the dolomite phases into Dolomicrite (DM), Replacive dolomite (RD), and Fibrous dolomite (FD). Since the samples are very homogeneous compositionally, crystallinity was the main factor for grouping. The dolomite in the "RD phase" appears to be more well-ordered, as indicated by the sharper and more intense peaks, compared to the "DM phase," which shows evidence of both ordered and disordered dolomite (Fig. 8.10 B; See supplementary Material 8.4 for more details). The Micro-Raman and petrographic data and geochemical information (microprobe (Fig. 8.6) and nano-XRF (Fig. 8.7), enhance the description of these mineral clusters (Fig. 8.10). The HCA dendrogram (Fig. 8.10 B) also presents the representative composition of each cluster for bulk rock and shows a similar trend in the micro-Raman in situ analysis (Fig. 8.10 A).

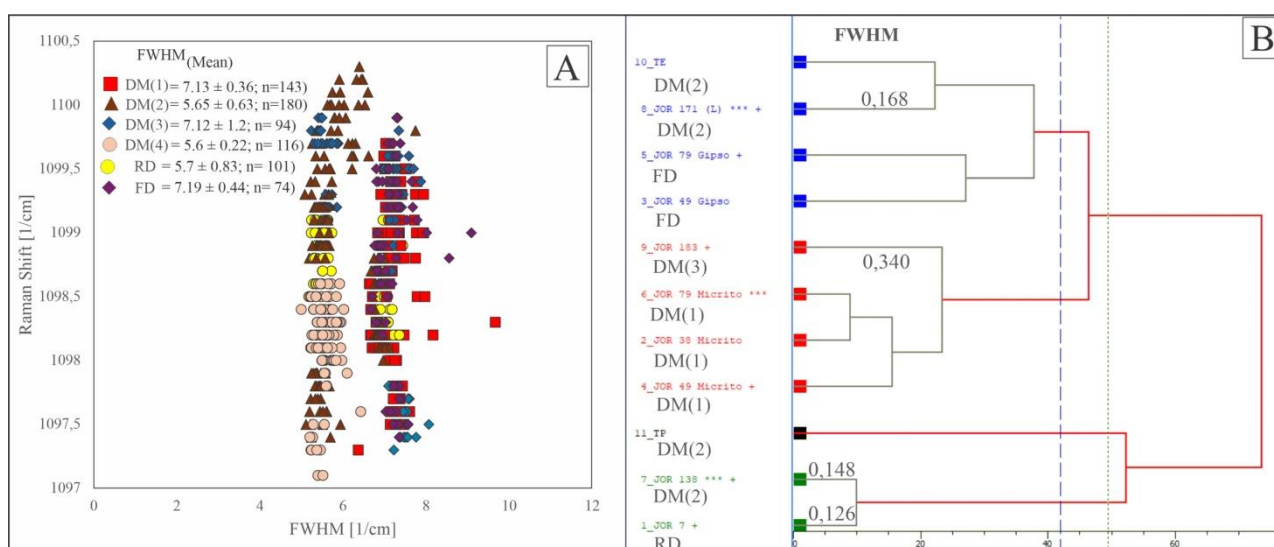


Figure 8.10- A) Cross-plot of FWHM [1/cm] versus Raman Shift [1/cm]: Dolomicrite (DM), Replacive dolomite (RD) and Fibrous dolomite (FD). Note the presence of distinct dolomite phases, suggesting the presence of multiple dolomitic phases in the samples. B) Mineral composition and multivariate statistical analysis. The hierarchical cluster analysis (right) dendrogram shows three clusters corresponding to the dolomite phases. The boxes (on the right) show the average composition of the respective clusters. Note that the dolomites were grouped based on compositional and crystallinity criteria. The composition is homogeneous; however, crystallinity varies among the analyzed phases. Note that both the Raman data in A) and the XRD data in B) show the same crystallinity relationship, in situ and bulk rock, respectively.

## 8.6 DISCUSSION

### 8.6.1 Comparison of dolomite phases:

In general, the cap dolostones from the Terconi and Tangará sections exhibit the following similarities:

- Samples of carbonates (calcite and dolomite in varying proportions) rich in Ca and

Mg, with a high loss on ignition (CO<sub>2</sub>).

- All dolomites occur with Mg/Ca ratios = 0.6.
  - Dolomitization is predominantly pervasive and homogeneous across all sections.
  - There is no compositional difference in the dolomites, only in texture and crystallinity.
  - Dolomicrite predominate, with a predominantly granular pattern, although occasionally peloids partly resemble shrubs, especially in the Tangará section.
  - Subhedral dolomite crystals, up to 300 µm long in the matrix, forming a fine to medium planar-e to planar-s crystal mosaic with sizes ranging from 0.1-0.2 mm, dominate all samples from the four sections (being predominant at the base of the Tangará section and predominating in the Terconi section).
  - Fibrous dolomite, well-developed with sizes ranging from 0.5-0.8 mm, fills the majority of fenestral porosities within the cap dolostone (better characterized in the Tangará section, although it also occurs at the base of the Terconi section).
  - Fractures and porosity (e.g., vug) through the dolostones in all sections are filled with calcite cement and minor amounts of iron and manganese oxides.
  - Stylolites filled with (phyllo-)silicate minerals (e.g., quartz, clay).
- Micro-raman spectra and XRD diffractograms corroborate the presence of a disordered dolomite phase.
- Dolomicrites vary in preservation and crystallinity (FWHM) in both sections.
  - The most preserved phases of dolomicrites contain up to 9% disordered dolomites.
  - The most preserved phases of dolomicrites exhibit displacement and lower crystallinities.
  - The least preserved phases exhibit characteristic peaks and FWHM compatible with high crystallinities in both sections.

### 8.6.2 Syndepositional evidence

Previous studies have underscored the cap dolostone robust textural and compositional preservation (Soares *et al.* 2020, Santos *et al.* 2023). Notably, whole-rock analyses have revealed a lack of correlation between elements such as Mn, Sr, and Mg/Ca with isotopes of  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$ . This finding, which is further supported by the minimal impact of post-depositional fluids on this succession (Sansjofre *et al.* 2014, Santos *et al.* unpublished), bolsters the argument for syndepositional dolomitization. Moreover, the available isotopic data of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  provide compelling evidence that the dolomite is primary or at least syndepositional. The absence of a positive correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  suggests a dominance of

syndepositional processes (Nogueira *et al.* 2003, Font *et al.* 2006, Sansjofre *et al.* 2014, Santos *et al.* 2023, Santos *et al.* unpublished). In situ analyses, initially with the microprobe, revealed low concentrations of these elements, most below the detection limit. However, the portions that yielded counts showed a low correlation with Mg/Ca, further reinforcing the interpretation of syndepositional dolomitization. The use of nano-XRF analyses, with their higher resolution and efficiency in detecting elements even in trace amounts, confirmed the low influence of these elements across all dolomitic phases. The combination of nano-XRF and microprobe compositional maps demonstrated a minimal impact of post-depositional fluids, such as Fe and Mn, on the dolomitic phases. Despite the Mn distribution differs between the replacive dolomite (RD) and dolomicrite (DM). The replacive dolomite showed a higher enrichment of Mn compared to other phases, which could be related to neomorphism events discussed by Santos *et al.* (2023), potentially explaining the differences in luminescence under cathodoluminescence. Mn and Fe are not randomly distributed in the dolomicrite matrix, rather, they preferentially fill microporosity, described as Mn-Fe oxy-hydroxide by Santos *et al.* (2023), associated with late diagenesis. The compositional maps reproduce the detailed shape of the analyzed dolomite phases and thus allow a direct comparison of the crystalline organization and Mn and Fe distribution.

The crystallinity and ordering index varied among the studied dolomitic phases in whole-rock (XRD) and in situ analyses by micro-Raman. A corresponding pattern with textural characteristics was observed. For example, well-preserved grumous-textured dolomicrite exhibited a pattern of low crystallinity and a higher percentage of disordered dolomites, as seen in XRD, with more shifted bands in micro-Raman. In contrast, dolomicrosparite showed higher crystallinity and more excellent ordering with more advanced neomorphism and more pronounced calcite cementation associated with the late diageneses process (Santos *et al.* 2023).

XRD data on dolomitic phases indicated peaks that could be interpreted as Fe and Mg entering the structure, replacing Mg, and resulting in Fe-dolomite or related to disordered, low-crystallinity dolomite, texturally associated with finer, micritic dolomite. The interpretation of disordered dolomite is strongly supported by micro-Raman data, which indicated more significant blue shifts in micritic dolomites with preserved microbial textures, corroborated by in situ compositional data revealing low iron content and low correlation. The magnesium content directly influences the Raman band positions in the carbonate minerals. In the spectra of Mg-calcite, all peaks exhibit a consistent and linear increase in Raman shifts as the magnesium content rises. This trend is due to the reduced inter-atomic distances that result from substituting the larger  $\text{Ca}^{2+}$  ions with the smaller  $\text{Mg}^{2+}$  ions (Borromeo *et al.* 2017).

Despite textural and crystallinity differences, the composition has no significant impact. Ideally, ordered dolomite has a formula of  $\text{CaMg}(\text{CO}_3)_2$  and consists of alternating layers of  $\text{Ca}^{2+}\text{-CO}_3^{2-}$ -  $\text{Mg}^{2+}\text{-CO}_3^{2-}$ -  $\text{Ca}^{2+}$ , etc., perpendicular to the crystallographic c-axis. Most natural dolomite has up to a few percent Ca-surplus (and a corresponding Mg-deficit) and less than ideal-ordering (Machel, 2004). The well-ordered nature of the dolomite crystal lattice results in a series of superstructure reflections in X-ray diffraction (XRD). The height of the d015 ordering peak relative to the d110 peak measures the degree of ordering (Goldsmith and Graf, 1958). Most modern dolomites exhibit a low degree of order, which was observed in this study when comparing cap dolomites with modern dolomites from Lagoa Salgada, which showed lower ordering and crystallinity. A similar relationship was observed when evaluating Cenomanian-aged dolomites related to the Alcantara Formation.

Our detailed sedimentological and petrographic observations reveal that dolomite occurrences and contents are homogeneous throughout the studied succession. Furthermore, compared to another cap dolostone section, they exhibit the same characteristics (Nogueira *et al.* 2003, Font *et al.* 2006, Sansjofre *et al.* 2014, Romero *et al.* 2022). These deposits are associated with microbialites origin, which occurs with predominant microcrystalline dolomite with preserved peloidal textures. The peloidal texture of these stromatolites, appearing as micritized forms of photosynthetic cyanobacteria (Romero *et al.* 2020, Santos *et al.* 2021), corresponds with the presence of biomarkers of photosynthetic cyanobacteria described by Elie *et al.* (2007), Souza *et al.* (2016), and van Maldegem *et al.* (2018). These dolomites' microbial origin has also been due to organomineralization processes primarily associated with sulfate-reducing bacteria (Nogueira *et al.* 2003, Font *et al.* 2010, Sansjofre *et al.* 2014). The possibility of a replacement or secondary origin for the dolomitic matrix of the cap dolostone is strongly dismissed, primarily due to its intimate association with microbialites in shallow post-Marinoan environments on the Amazon craton. The change in fabric coincides with the platform's deepening, stromatolites' decline, and oversaturation of  $\text{CaCO}_3$  associated with long-term transgression (xx). Spatic calcite is the predominant cementation phase throughout the cap dolostone deposits, filling interpeloidal porosities and vugs. This evidence suggests that dolomite formed before calcite and that widespread post-depositional dolomitization did not occur.

Fibrous dolomite (gypsum pseudomorphs) fills fenestral and interpeloidal porosities of basal dolomitic deposits of the Puga cap carbonate succession. Gypsum is interpreted as a product of upwelling related to water mixing processes (seawater and meltwater), leading to gypsum precipitation from pore water supersaturation (Santos *et al.* 2021, 2023). The supersaturation of sulfate ions derived from hypersaline water results in gypsum precipitation within the fenestral

pores, driven by concentrations exceeding solubility at the water-sediment interface. The alkaline nature reduces the solubility of sulfate ions, promoting gypsum precipitation in fenestral and interpeloidal porosity (Santos *et al.*2023). The well-preserved fibrous dolomite provides clear evidence of syndepositional dolomitization (Santos *et al.*2021, 2023).

### 8.6.3 Dolomitization Models

Pervasively dolomitized Neoproterozoic carbonates that directly overlie Marinoan glacial deposits throughout the world have commonly been referred to as "cap dolostones" (Fairchild 1993, Hoffman *et al.*1998,2017, Yu *et al.*2020). However, the precipitation mechanism of cap dolostones has not been fully elucidated, two main hypotheses have been proposed: 1) the first hypothesis suggests that dolostones formed directly, retaining their primary characteristics and reflecting the chemistry of the original depositional environment (Kennedy 1996, Shields 2005, Nogueira *et al.*2003, Nedeléc *et al.*2007, Font *et al.*2006, Santos *et al.*2021, 2023), 2) the second hypothesis proposes that the dolostones underwent secondary dolomitization, wherein an aragonite or calcite precursor was transformed into dolomite (Gammon 2012, Gammon *et al.*2012, Fabre *et al.*2013, Higgins *et al.*2018, Ahm *et al.*2019). The alkalinity source for cap carbonate precipitation continues to be debated. Triggers to consider include alkalinity increases associated with extensive hydrothermal activity along basin-bounding faults (Gernon *et al.*2016), gas hydrate destabilization, and massive methane release (Jiang *et al.*2003, Jiang *et al.*2006, Kennedy *et al.*2008, Wang *et al.*2008), alkalinity increases related to microbial activity (e.g., sulfate reduction) (Nogueira *et al.*2003, 2007, 2022, Font *et al.*2006), and ocean warming as a significant factor driving carbonate oversaturation in a post-Snowball ocean (Fabre *et al.*2013).

Marine chemistry changes are commonly associated with secular modifications such as the Mg/Ca ratio, pH, redox state of the ocean, climate (icehouse-greenhouse conditions), pCO<sub>2</sub>, and extent of continental weathering (Sandberg 1983, Hardie 1996, 2003, Stanley and Hardie 1998, Hood and Wallace 2018). The cap dolostone-cap limestone transition in Puga cap carbonate increased the concentration of Sr covariance with Zr and Th. The abrupt transition in Sr concentrations followed a decrease in the Mg/Ca ratio (Santos *et al.* unpublished). The cap dolostones displayed a low Sr content, ranging from 30 to 70 ppm, in contrast to the cap limestones, which have Sr concentrations between 300 and 1400 ppm (Santos *et al.* unpublished). The interpretations of primary dolomite precipitation by Nogueira *et al.* (2003, 2019), Font *et al.* (2006), Romero *et al.* (2020), Soares *et al.* (2020), and Santos *et al.* (2021, 2023) are consistent with our data because ancient dolomite commonly has significantly lower Sr

concentrations (20–70 ppm) (Baker and Burns 1985, Vahrenkamp and Swart 1990).

According to Ahm *et al.* (2019), dolomitization related to an aragonitic primary fabric is consistent with fluid flow and seawater upwelling during global deglaciation. The paleoceanographic model by Santos *et al.* (unpublished) supports the occurrence of upwelling and a syn-deglacial dolomitization event, as previously discussed: 1) restricted paleoenvironment with ideal conditions for microbial communities' flourishing, 2) mixing of meltwater and deep seawater (brine fluids), 3) shallow seawater interacts with deep water (high Eu/Eu anomalies, suggesting the upwelling of syndepositional T-high hydrothermal fluids), 4) a low correlation between Mg/Ca and  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , suggesting that dolomitization occurred at least during the early diagenesis, 5) the excellent preservation of gypsum pseudomorphs indicates early dolomitization (see Santos *et al.* 2021, 2023).

The concentration of Mg remained constant during the restriction of paleoenvironmental conditions on dolomitic platforms. Rapid sea-level rise facilitated the dispersion of Mg ions, leading to the definitive interruption of dolomite precipitation, which was abruptly replaced by  $\text{CaCO}_3$ -supersaturated seas with massive aragonite precipitation influenced by long-term transgression, which still occurred during the early Ediacaran (Nogueira *et al.* 2019, Santos *et al.* (unpublished). The high radiogenic values of  $^{87}\text{Sr}/^{86}\text{Sr}$  associated with Nd values and the concentration of rare earth elements in the units indicate mixing processes of meltwater and seawater associated with intense continental weathering. This mixing process could generate dolomitization related to a freshwater-seawater mixing zone (Santos *et al.* (unpublished). Thus, this evidence from the cap dolostone points out a primary or at least syndepositional origin of the dolomite.

The proposal by Kim *et al.* (2023) suggests that the mechanism underlying the formation of modern dolomite is its predominant occurrence in natural environments with pH or salinity fluctuations. More broadly, it indicates that deliberate periods of mild dissolution can facilitate defect-free crystal growth and maturation of the dolomite crystals. Cap dolostone precipitation occurs during the mixwater process of hypersaline seawater and meltwater, primarily linked to upwelling processes (Shields, 2005, Hoffman *et al.* 2017, Rame and Marotzke 2022, Yu *et al.* 2022, Santos *et al.* unpublished). According to Ahm *et al.* (2019), dolomite is not a primary precipitate but a product of secondary early dolomitization of calcium carbonate. This finding, which aligns the dolomitization of platform sediments with fluid flow and seawater recirculation during global deglaciation, is well-established. Similarly, the proposal by Kim *et al.* (2023) suggests that salinity fluctuations could explain the massive dolomite precipitation. The paleoceanographic model of the Puga cap carbonate supports these models but also



demonstrates a strong influence on microbial communities. These communities may have been favored by the increased alkalinity conditions associated with post-Snowball Earth continental weathering.

#### 8.6.4 Microbial/organogenic dolomitization model

The intriguing preferential occurrence of dolomite associated with microbialites in the Puga cap carbonate succession (Nogueira *et al.* 2003, 2022, Font *et al.* 2006, 2010, Sansjofre *et al.* 2014, Romero *et al.* 2020, Santos *et al.* 2021, 2023) suggests an organogenic origin for the dolomite. These dolomites, consisting of numerous similarly sized spherical to ellipsoidal crystals with grumous and shrub textures, indicate a potential microbial origin. Micro-Raman spectroscopy and XRD revealed crystallographic patterns for these dolomites and indicated a higher proportion of disordered dolomites associated with the most well-preserved microbial textures. Microbial mats, functioning as 'geochemical bioreactors', have two primary components. The microbial community, through its metabolic activities, acts as an 'alkalinity engine', altering the geochemical environment by modulating the concentrations of ions  $\{Ca^{2+}\}$  and  $\{CO_3^{2-}\}$ . The EPS (extracellular polymeric substances) matrix, on the other hand, influences mineral formation by binding and releasing cations, thereby providing mineral nucleation sites. The formation of microbialites is ultimately driven by the delicate balance of microbial and physico-chemical processes, which vary according to the specific environmental conditions (Dupraz *et al.* 2009).

It is also possible that the cap dolostone initially precipitated from seawater as non-stoichiometric and disordered proto-dolomite or very high-Mg calcites through microbial mediation (and associated organic matter), and that they were subsequently transformed into ordered dolomite during early burial (i.e., the organogenic dolomite model) (Nordeng and Sibley 1994, Bahniuk *et al.* 2015). Organogenic proto-dolomite produced in laboratory experiments typically forms globular, cauliflower-, and dumbbell-shaped aggregates and is commonly associated with extracellular polymeric substances (EPS) (Warthmann *et al.* 2000, Liu *et al.* 2019). In modern sediments, similar protodolomite has also been observed within microbial mats (Bontognali *et al.* 2010). In most Holocene successions, organogenic proto-dolomite typically appears as Ca-rich, imperfectly ordered rhombohedral carbonate phases (Gregg *et al.* 2015), interpreted as primary or early diagenetic in origin (Diloreto *et al.* 2019). Protodolomite has also been reported to occur as sub-micrometer spherulitic crystals that easily transform into more stoichiometric euhedral rhombohedra with increasing burial depth. At the same time, associated EPS structures disappear due to the degradation and natural dehydration of the organic matrix

during burial (Gregg and Frank 2009).

The dolomite may form syndepositionally or early post-depositionally at depths ranging from a few centimeters to a few hundred meters, influenced or promoted by bacterial sulfate reduction and methanogenesis (Vasconcelos and McKenzie 1997, Burns *et al.* 2000, Mazzulo 2000). In this context, the crucial role of microbial community activities becomes apparent, as they could overcome the kinetic barriers to dolomite precipitation and nucleation even at low temperatures (e.g., Vasconcelos *et al.* 1995, Roberts *et al.* 2004, Sánchez-Román *et al.* 2008, McKenzie and Vasconcelos 2009, Deng *et al.* 2010, Bontognali *et al.* 2014, Petrash *et al.* 2017, Liu *et al.* 2019, 2020, Han *et al.* 2022, 2024). In natural conditions, the dehydration of magnesium ions is a critical and often limiting step in dolomite nucleation, however, organomineralization processes can lead to a reduction in Mg- and Ca-hydration, an increase in alkalinity, or a pH change (Kenward *et al.* 2013).

Microbially-induced dolomites produced experimentally are generally disordered in Mg and Ca content (Gregg *et al.* 2015). Thus, the product of organomineralization is termed disordered dolomite or proto dolomite *stricto sensu* (Zhang *et al.* 2012, Gregg *et al.* 2015, Kaczmarek *et al.* 2017). Protodolomite has about 55-60% Ca, is poorly ordered, i.e., the alternating cation layer structure is poorly developed. It is common as a metastable precursor of well-ordered, nearly stoichiometric dolomite in both laboratory experiments and in nature (Graf and Goldsmith 1956, Gaines 1977). Disordered dolomite (with 36-55 mol% Mg<sup>2+</sup>) shares the same space group as calcite but contains a higher Mg content compared to Mg-calcite (<36 mol% Mg<sup>2+</sup>) (Zhang *et al.* 2012). In shallow-marine to supratidal environments, penecontemporaneous dolomites typically form in quantities of <5 vol%, primarily as Ca-rich and poorly ordered microcrystalline to fine-crystalline cement or directly from aqueous solution. The dolomite-forming fluid is normal and evaporated seawater, sometimes mixed with evaporated groundwater. Microbial/organogenic dolomites may act as nuclei for subsequent, more pervasive dolomitization during burial. Despite the metastable nature of disordered dolomite, it can progressively transform into ordered dolomite under burial conditions (Zheng *et al.* 2021).

#### 8.6.5 Dolostone Model

The origin of the ubiquitous occurrence of Precambrian dolomite deposits remains enigmatic. However, our multiproxies study in cap dolostone findings dismiss specific models and reinforce the organomineralization model of dolomitization, demonstrating a strong correlation by microbialites origin. The well-preserved microbial textures, disordered signatures, and lower crystallinity observed in XRD, and micro-Raman spectroscopy provide robust support

for this primary precipitation model. Disordered dolomite, a crucial crystalline precursor of ordered sedimentary dolomite (e.g., Gregg *et al.*2015), likely formed through the mediation of cyanobacteria and sulfate-reducing bacteria, as indicated by studies of organic fossils (Elie *et al.*2007, Souza *et al.*2016, van Maldegem *et al.*2018). According to Dupraz *et al.* (2009), The alkalinity engine has two components: an intrinsic (microbial metabolism) and an extrinsic (the environment) component. **Intrinsic:** Microbial communities increase the alkalinity and concentrate  $Mg^{2+}$  in local environments, producing EPS to overcome the  $Mg^{2+}$  hydration effect and providing nucleation templates in a shallow environment (e.g., Roberts *et al.*2004, Sánchez-Román *et al.*2008, McKenzie and Vasconcelos, 2009, Deng *et al.*2010, Han *et al.*2022, 2024). **Extrinsic:** This post-Snowball Earth environment is marked by increased alkalization associated with intense continental weathering (Hoffman *et al.*2017). A super greenhouse climate was moderate and possibly short-lived after the global glaciation. Marinoan cap dolostones could have formed just a few thousand years after the start of deglaciation, concurrent with rapid warming and recovery of biological activity, further promoting rapid precipitation of cap carbonates (Ramme *et al.*2024). In the Amazon Craton, microbial communities thrive in clear and shallow waters, characterized by low siliciclastic content but influenced significantly by meltwater, with minimal wave action (Santos *et al.* unpublished).

Our evidence, derived from a high-resolution mapping and crystal architecture study, suggests that dolomite initially precipitates as disordered protodolomite, progressively becoming more ordered and crystalline with burial. Despite these post-depositional processes, our study revealed minimal impact of diagenetic fluids on the composition of the analyzed dolomites, reflecting excellent preservation of isotopic data in cap dolostone. This interpretation aligns with recent studies demonstrating that disordered dolomites formed by organomineralization are precursors to stoichiometric dolomite (Chang *et al.*2020, Xiao *et al.*2024). The robustness of our methodology and the consistency of our findings across various studies strongly support our proposed model.

Our research, which suggests that microbially dominated environments may have played a significant role in the widespread occurrence of dolostones in the Paleozoic and Precambrian, not only enhances our understanding of dolostone formation but also opens exciting possibilities for the study of other planetary surfaces, such as Mars.

## 8.6.6 ASTROBIOLOGICAL IMPLICATIONS

The primary motivation for research on Mars is the search for past habitable environments (Amador *et al.* 2018, Rampe *et al.* 2020). Mineralogy and sedimentology

characterizations have provided essential insights into habitability criteria. The Martian crust is not as bimodal as Earth's. Still, both planets contain a wide variety of sedimentary rocks, including clastic (sandstone and siltstone, shale and mudstone, and conglomerate) and chemical rocks (mostly evaporitic sulfate and some carbonate) (McSween 2015). These rocks can preserve ancient biosignatures similar to Earth's Precambrian ones (Burnie *et al.* 2023).

We know three major biosignatures as essential: 1) Primary Microbial Sedimentary Textures, 2) Diagenetic, and 3) Organomineral Assemblages. As discussed in our study, the Puga cap carbonate succession dolomites are best correlated with the dolomitization model by organomineralization. Their association with stromatolites and their excellent compositional and isotopic preservation make the cap dolostone of the southern Amazon craton an excellent analog for extreme environments, given their association with the aftermath of the Snowball Earth event (Marinoan ~635 Ma).

Recently, orbiter data identified carbonate deposits, specifically magnesium carbonate, at Jezero Crater, making this location a priority target (Ehlmann *et al.* 2008, Grant *et al.* 2018, Hoggan *et al.* 2020, Scheller *et al.* 2021). Jezero Crater, with a diameter of 45 kilometers, is a paleo lacustrine system believed to have been active until the Early Hesperian Era, ~ 3.5 Ga, where water interactions with the atmosphere led to the formation of these minerals (Goudge *et al.* 2018). The role of the Perseverance rover in this detection underscores the practical application of our research and its potential to contribute to our understanding of Mars's past habitability. Studying magnesium carbonate on Mars is critical because these minerals can provide insights into the planet's past climate and water activity. On Earth, carbonates typically form in aqueous environments, suggesting that water once played a significant role in their formation on Mars as well (Ehlmann *et al.* 2008, Edwards and Ehlmann 2015, McSween *et al.* 2015).

The rover contains a suite of instruments, including Raman spectroscopy and X-ray diffraction (XRD), that can detect carbonate phases such as magnesium carbonate. Raman spectroscopy also identified organic compounds. Eventually, the results of Perseverance Labs may identify potential biosignatures on the surface of ancient Mars or even at the time the samples return to Earth (Farley *et al.* 2020, 2022, Scheller *et al.* 2021).

Spectroscopic techniques are refined through extensive terrestrial studies, such as ours, of high-resolution mapping and crystal architecture in microbial dolomitic deposits. They are essential for proposing new and more effective ways of identifying and characterizing minerals and potential biosignatures in Martian samples. Their application enhances the interpretation of Martian geology and astrobiology, guiding sample collection strategies and providing invaluable data for the search for past life on Mars and other rocky worlds.

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8.7 SUPPLEMENTARY MATERIAL: HIGH-RESOLUTION MAPPING AND CRYSTAL ARCHITECTURE OF MARINOAN CAP DOLOSTONE (~635 MA): INSIGHTS INTO THE DOLOMITE PROBLEM AND ITS POTENTIAL AS AN ASTROBIOLOGICAL ANALOG

**Supplementary Table 8.1-** Microprobe chemical analyses in the cap dolostone.

**Supplementary Table 8.2-** Conditions for Quantitative Spot Analyses of Microprobe Chemical Analyses in the Cap Dolostone

**Supplementary Table 8.3-** Raman spectra and peak width analyses. Measurement of the width of the  $1098\text{ cm}^{-1}$  and  $1099\text{ cm}^{-1}$  peaks and their respective FWHM values ( $1/\text{cm}$ )

**Supplementary Material 8.4-** The XRD patterns for micro-drilled powders of cap dolostones samples (dolomicrite (DM), replacive dolomite (RD), and fibrous dolomites (FD)).

Supplementary Table 8. 1 Microprobe chemical analyses in the cap dolostone.

|       |                 | Mg                            | Ca       | Fe       | Mn       | Sr  | Si  | Ti  | Ba       | P   | Mg/Ca |
|-------|-----------------|-------------------------------|----------|----------|----------|-----|-----|-----|----------|-----|-------|
|       | detection limit | 253                           | 312      | 275      | 250      | 350 | 223 | 159 | 564      | 410 |       |
| Point | Comment         | ppm above the detection limit |          |          |          |     |     |     |          |     |       |
| 1     | JOR49-1         | 3446,717                      | 400693,7 | bd       | bd       | bd  | bd  | bd  | bd       | bd  | 0,01  |
| 2     | JOR49-2         | 2236,295                      | 402560,5 | bd       | bd       | bd  | bd  | bd  | bd       | bd  | 0,01  |
| 3     | JOR49-3         | 2542,067                      | 398120,1 | 421,302  | bd       | bd  | bd  | bd  | bd       | bd  | 0,01  |
| 4     | JOR49-4         | 130683,9                      | 216811,4 | bd       | bd       | bd  | bd  | bd  | bd       | bd  | 0,60  |
| 5     | JOR49-5         | 128378,9                      | 224816   | 350,5668 | bd       | bd  | bd  | bd  | bd       | bd  | 0,57  |
| 6     | JOR49-6         | 130211,7                      | 219707,4 | 443,844  | bd       | bd  | bd  | bd  | 675,9817 | bd  | 0,59  |
| 7     | JOR49-7         | 129855,9                      | 220524,3 | bd       | bd       | bd  | bd  | bd  | bd       | bd  | 0,59  |
| 8     | JOR49-8         | 128097,8                      | 223313,7 | bd       | bd       | bd  | bd  | bd  | bd       | bd  | 0,57  |
| 9     | JOR49-9         | 130389,6                      | 223229,4 | 331,9114 | 271,061  | bd  | bd  | bd  | bd       | bd  | 0,58  |
| 10    | JOR49-10        | 126502                        | 215825,8 | 4962,347 | 1111,35  | bd  | bd  | bd  | bd       | bd  | 0,59  |
| 11    | JOR49-11        | 128368                        | 219676,6 | 2115,838 | 572,3259 | bd  | bd  | bd  | bd       | bd  | 0,58  |
| 12    | JOR171-1        | 127557,5                      | 218388,7 | 886,9107 | bd       | bd  | bd  | bd  | bd       | bd  | 0,58  |

|    |           |          |          |          |          |    |          |    |    |          |      |
|----|-----------|----------|----------|----------|----------|----|----------|----|----|----------|------|
| 13 | JOR171-2  | 128903,6 | 219184,9 | 938,2132 | 499,5267 | bd | bd       | bd | bd | bd       | 0,59 |
| 14 | JOR171-3  | 126723,4 | 217882,7 | 2633,526 | 281,129  | bd | bd       | bd | bd | bd       | 0,58 |
| 15 | JOR171-4  | 126579,2 | 216015,2 | 1591,931 | 489,4587 | bd | bd       | bd | bd | bd       | 0,59 |
| 16 | JOR171-5  | 2788,131 | 396667,1 | 303,9282 | bd       | bd | bd       | bd | bd | bd       | 0,01 |
| 17 | JOR171-6  | 2796,575 | 393962,7 | bd       | 3310,042 | bd | bd       | bd | bd | bd       | 0,01 |
| 18 | JOR171-7  | 128727,5 | 216794,2 | 1301,994 | bd       | bd | bd       | bd | bd | bd       | 0,59 |
| 19 | JOR171-8  | 122263,4 | 211126,7 | 1036,154 | 575,4238 | bd | 12955,57 | bd | bd | bd       | 0,58 |
| 20 | JOR171-9  | 130588,6 | 220336,3 | 928,8855 | 406,5915 | bd | bd       | bd | bd | bd       | 0,59 |
| 21 | JOR171-10 | 123223,6 | 210063,2 | 1021,385 | 307,4606 | bd | 4663,649 | bd | bd | bd       | 0,59 |
| 22 | JOR171-11 | 129238,9 | 220094   | 881,4695 | 260,993  | bd | bd       | bd | bd | bd       | 0,59 |
| 23 | JOR171-12 | 1479,404 | 405679,4 | 321,8063 | 2206,437 | bd | bd       | bd | bd | bd       | 0,00 |
| 24 | JOR171-13 | 1602,437 | 409387,3 | bd       | 820,1531 | bd | bd       | bd | bd | bd       | 0,00 |
| 25 | JOR171-14 | 2014,354 | 406334,8 | bd       | bd       | bd | bd       | bd | bd | bd       | 0,00 |
| 26 | JOR171-15 | 127712,5 | 219310,7 | 1543,738 | 542,122  | bd | bd       | bd | bd | bd       | 0,58 |
| 27 | JOR171-16 | 127626,2 | 217401   | 1249,914 | 326,8221 | bd | bd       | bd | bd | bd       | 0,59 |
| 28 | JOR171-17 | 130206,3 | 219109,2 | 680,9236 | 340,7624 | bd | bd       | bd | bd | bd       | 0,59 |
| 33 | JOR7-5    | 60398,66 | 315278,5 | 1054,032 | 1356,854 | bd | bd       | bd | bd | 469,5879 | 0,19 |



|    |         |          |          |          |          |          |    |    |          |          |      |
|----|---------|----------|----------|----------|----------|----------|----|----|----------|----------|------|
| 34 | JOR7-6  | 125284,4 | 216865,7 | 3078,148 | 4724,98  | bd       | bd | bd | bd       | bd       | 0,58 |
| 35 | JOR7-7  | 3482,299 | 404079,2 | 1072,688 | bd       | bd       | bd | bd | bd       | 819,5968 | 0,01 |
| 36 | JOR7-8  | 120287,7 | 228125,8 | 1295,776 | 449,1868 | bd       | bd | bd | bd       | bd       | 0,53 |
| 37 | JOR7-9  | 124931,6 | 222878,5 | bd       | 1232,166 | bd       | bd | bd | bd       | bd       | 0,56 |
| 38 | JOR7-10 | 125853,1 | 217933,5 | 1141,091 | 6180,191 | bd       | bd | bd | bd       | bd       | 0,58 |
| 39 | JOR7-11 | 2411,194 | 393934,1 | 839,4948 | bd       | bd       | bd | bd | bd       | 568,6553 | 0,01 |
| 40 | JOR7-12 | 126066   | 222008   | 1262,351 | 858,1017 | bd       | bd | bd | bd       | bd       | 0,57 |
| 41 | JOR7-13 | 124762,1 | 220101,2 | 921,8897 | 2695,895 | bd       | bd | bd | bd       | bd       | 0,57 |
| 42 | JOR7-14 | 129547,7 | 223543,2 | 2328,821 | 782,2046 | bd       | bd | bd | 818,3408 | bd       | 0,58 |
| 43 | JOR7-15 | 84667,4  | 280098,8 | 1215,713 | 2798,898 | bd       | bd | bd | bd       | bd       | 0,30 |
| 44 | JOR7-16 | 7681,082 | 384056,9 | 1846,889 | bd       | bd       | bd | bd | bd       | 1231,141 | 0,02 |
| 45 | JOR7-17 | 126862,1 | 219382,2 | 1550,733 | 3285,259 | 433,7877 | bd | bd | bd       | bd       | 0,58 |
| 46 | JOR7-18 | 126658,8 | 217950,6 | 2724,472 | 1147,75  | bd       | bd | bd | bd       | bd       | 0,58 |
| 47 | JOR2-1  | 117454,9 | 216113,8 | 5120,141 | 13623,53 | bd       | bd | bd | bd       | bd       | 0,54 |
| 48 | JOR2-2  | 131116,4 | 221056,7 | 1164,41  | 1554,341 | bd       | bd | bd | bd       | bd       | 0,59 |
| 49 | JOR2-3  | 128522,4 | 216471,2 | 390,9869 | 2656,398 | bd       | bd | bd | bd       | bd       | 0,59 |
| 50 | JOR2-4  | 119562,2 | 214988,2 | 3624,597 | 13165,05 | bd       | bd | bd | bd       | bd       | 0,56 |

|    |                  |          |          |          |          |    |    |    |    |    |      |
|----|------------------|----------|----------|----------|----------|----|----|----|----|----|------|
| 51 | JOR2-5           | 132146,4 | 214228,5 | bd       | 2224,249 | bd | bd | bd | bd | bd | 0,62 |
| 52 | JOR2-6           | 126408,6 | 218428   | 512,2473 | 3269,77  | bd | bd | bd | bd | bd | 0,58 |
| 53 | JOR2-7           | 117927,8 | 200852,9 | 2458,632 | 2513,123 | bd | bd | bd | bd | bd | 0,59 |
| 54 | JOR2-8           | 126627,5 | 220652,9 | 293,8232 | 508,0458 | bd | bd | bd | bd | bd | 0,57 |
| 55 | JOR2-9           | 124511,2 | 212251,6 | 3532,874 | 3409,947 | bd | bd | bd | bd | bd | 0,59 |
| 56 | JOR2-10          | 122394,9 | 214157   | 4847,305 | 6364,512 | bd | bd | bd | bd | bd | 0,57 |
| 57 | JOR2-11          | 130433,6 | 218110,7 | bd       | 511,9181 | bd | bd | bd | bd | bd | 0,60 |
| 58 | JOR2-12          | 130697,8 | 218398,7 | 283,7182 | 1790,552 | bd | bd | bd | bd | bd | 0,60 |
| 59 | JOR2-13          | 129482   | 217015,1 | 465,6087 | 541,3475 | bd | bd | bd | bd | bd | 0,60 |
| 60 | JOR2-14          | 127696,2 | 215708,6 | 4167,159 | 1959,384 | bd | bd | bd | bd | bd | 0,59 |
| 61 | JOR49-<br>Map1-1 | 125462,3 | 218884   | 3578,735 | 333,0178 | bd | bd | bd | bd | bd | 0,57 |
| 62 | JOR49-<br>Map1-2 | 126058,2 | 215828,7 | 4546,486 | bd       | bd | bd | bd | bd | bd | 0,58 |
| 63 | JOR49-<br>Map1-3 | 125320   | 217428,9 | 4356,045 | 418,9829 | bd | bd | bd | bd | bd | 0,58 |
| 64 | JOR49-<br>Map1-4 | 126029,2 | 216281,8 | 3306,677 | 274,1588 | bd | bd | bd | bd | bd | 0,58 |



|    |               |          |          |    |          |    |    |    |    |    |      |
|----|---------------|----------|----------|----|----------|----|----|----|----|----|------|
| 75 | JOR49-Map1-15 | 1592,787 | 406482,1 | bd | 370,9663 | bd | bd | bd | bd | bd | 0,00 |
| 76 | JOR49-Map1-16 | 2537,845 | 408584   | bd | bd       | bd | bd | bd | bd | bd | 0,01 |
| 77 | JOR49-Map1-17 | 958,3259 | 408947,1 | bd | bd       | bd | bd | bd | bd | bd | 0,00 |
| 78 | JOR49-Map1-18 | 623,0023 | 406916,6 | bd | 520,4371 | bd | bd | bd | bd | bd | 0,00 |
| 79 | JOR49-Map1-19 | 1606,658 | 406957,3 | bd | 490,2332 | bd | bd | bd | bd | bd | 0,00 |
| 80 | JOR49-Map1-20 | 579,5791 | 394460,8 | bd | 321,4009 | bd | bd | bd | bd | bd | 0,00 |
| 81 | JOR49-Map1-21 | 809,9633 | 407464   | bd | bd       | bd | bd | bd | bd | bd | 0,00 |
| 82 | JOR49-Map1-22 | 129884,2 | 212716,9 | bd | bd       | bd | bd | bd | bd | bd | 0,61 |
| 83 | JOR49-Map1-23 | 129279,3 | 215374,1 | bd | 389,5534 | bd | bd | bd | bd | bd | 0,60 |
| 84 | JOR49-Map1-24 | 130701,4 | 217974,2 | bd | bd       | bd | bd | bd | bd | bd | 0,60 |

|    |                   |          |          |          |          |          |    |    |          |    |      |
|----|-------------------|----------|----------|----------|----------|----------|----|----|----------|----|------|
| 85 | JOR49-<br>Map1-25 | 131001,2 | 217053,7 | bd       | bd       | bd       | bd | bd | bd       | bd | 0,60 |
| 90 | JOR49-<br>Map1-30 | 128256,5 | 216837,1 | 376,9954 | 257,1207 | bd       | bd | bd | 637,4821 | bd | 0,59 |
| 91 | JOR49-<br>Map1-31 | 126904,3 | 215976,6 | 698,8017 | 257,1207 | 361,0669 | bd | bd | bd       | bd | 0,59 |
| 92 | JOR49-<br>Map1-32 | 125879,6 | 219708,1 | 1200,944 | 379,4854 | bd       | bd | bd | bd       | bd | 0,57 |
| 93 | JOR49-<br>Map1-33 | 127454,3 | 217009,4 | 2341,258 | bd       | bd       | bd | bd | bd       | bd | 0,59 |
| 94 | JOR51-<br>Map1-1  | 809,3602 | 399576,6 | bd       | bd       | bd       | bd | bd | bd       | bd | 0,00 |
| 95 | JOR51-<br>Map1-2  | 2209,155 | 401199   | bd       | bd       | bd       | bd | bd | bd       | bd | 0,01 |
| 96 | JOR51-<br>Map1-3  | 1779,145 | 399530,2 | bd       | bd       | bd       | bd | bd | bd       | bd | 0,00 |
| 97 | JOR51-<br>Map1-4  | 129291,4 | 221795,7 | 912,5619 | 587,0407 | bd       | bd | bd | bd       | bd | 0,58 |
| 98 | JOR51-<br>Map1-5  | 126389,3 | 215895,1 | 2727,581 | bd       | bd       | bd | bd | bd       | bd | 0,59 |

|     |                   |          |          |          |          |    |    |    |    |    |      |
|-----|-------------------|----------|----------|----------|----------|----|----|----|----|----|------|
| 99  | JOR51-<br>Map1-6  | 126140,2 | 220077,6 | 1652,561 | 353,1538 | bd | bd | bd | bd | bd | 0,57 |
| 100 | JOR51-<br>Map1-7  | 127108,1 | 221990,1 | 1089,789 | 497,9778 | bd | bd | bd | bd | bd | 0,57 |
| 101 | JOR51-<br>Map1-8  | 127062,3 | 212987   | 2569,01  | bd       | bd | bd | bd | bd | bd | 0,60 |
| 102 | JOR51-<br>Map1-9  | 126452   | 217826,3 | 1787,813 | bd       | bd | bd | bd | bd | bd | 0,58 |
| 103 | JOR51-<br>Map1-10 | 126075,6 | 215891,6 | 7099,172 | bd       | bd | bd | bd | bd | bd | 0,58 |
| 104 | JOR51-<br>Map1-11 | 128020,6 | 215913,7 | 1713,191 | bd       | bd | bd | bd | bd | bd | 0,59 |
| 105 | JOR51-<br>Map1-12 | 128164,8 | 218273   | bd       | bd       | bd | bd | bd | bd | bd | 0,59 |
| 106 | JOR51-<br>Map1-13 | 126057,5 | 218211,5 | bd       | bd       | bd | bd | bd | bd | bd | 0,58 |
| 107 | JOR51-<br>Map1-14 | 126716,7 | 218751,1 | bd       | bd       | bd | bd | bd | bd | bd | 0,58 |
| 108 | JOR51-<br>Map1-15 | 125300,7 | 215595,7 | 2434,535 | 273,3844 | bd | bd | bd | bd | bd | 0,58 |

|     |                   |          |          |          |          |         |    |    |    |          |      |
|-----|-------------------|----------|----------|----------|----------|---------|----|----|----|----------|------|
| 109 | JOR51-<br>Map1-16 | 126228,2 | 218413   | 1801,805 | 313,6563 | bd      | bd | bd | bd | bd       | 0,58 |
| 110 | JOR51-<br>Map1-17 | 127054,5 | 219247,8 | 1601,259 | 353,1538 | bd      | bd | bd | bd | bd       | 0,58 |
| 111 | JOR51-<br>Map1-18 | 126197,5 | 216876,4 | 2271,3   | 283,4524 | 404,192 | bd | bd | bd | bd       | 0,58 |
| 112 | JOR51-<br>Map1-19 | 125429,7 | 215264,1 | 958,4232 | 236,9848 | bd      | bd | bd | bd | 420,7089 | 0,58 |
| 113 | JOR51-<br>Map1-20 | 126006,9 | 217113,7 | 1406,154 | 286,5502 | bd      | bd | bd | bd | bd       | 0,58 |
| 114 | JOR51-<br>Map1-21 | 125086   | 215947,3 | 2648,295 | 290,4225 | bd      | bd | bd | bd | bd       | 0,58 |
| 115 | JOR51-<br>Map1-22 | 124798,9 | 218000,7 | 1786,258 | 2049,221 | bd      | bd | bd | bd | bd       | 0,57 |
| 116 | JOR51-<br>Map1-23 | 127668,4 | 217171,6 | bd       | bd       | bd      | bd | bd | bd | bd       | 0,59 |
| 117 | JOR51-<br>Map1-24 | 127354,2 | 220605,7 | bd       | bd       | bd      | bd | bd | bd | bd       | 0,58 |
| 118 | Tubo-Map1-<br>1   | 130978,8 | 217529,7 | 518,4658 | bd       | bd      | bd | bd | bd | bd       | 0,60 |

|     |                  |          |          |          |          |          |    |    |    |    |      |
|-----|------------------|----------|----------|----------|----------|----------|----|----|----|----|------|
| 119 | Tubo-Map1-<br>2  | 128289,6 | 217840,6 | 1530,523 | 520,4371 | 410,9567 | bd | bd | bd | bd | 0,59 |
| 120 | Tubo-Map1-<br>3  | 127915,7 | 218592,4 | 1913,737 | bd       | bd       | bd | bd | bd | bd | 0,59 |
| 121 | Tubo-Map1-<br>4  | 126070,2 | 217075,1 | 6791,357 | 590,1385 | bd       | bd | bd | bd | bd | 0,58 |
| 122 | Tubo-Map1-<br>5  | 129343,8 | 218082,1 | 719,0118 | 337,6646 | bd       | bd | bd | bd | bd | 0,59 |
| 123 | Tubo-Map1-<br>6  | 128520,6 | 218633,2 | 2338,148 | 505,7224 | bd       | bd | bd | bd | bd | 0,59 |
| 134 | Tubo-Map1-<br>7  | 128082,8 | 217673,3 | 1091,343 | bd       | bd       | bd | bd | bd | bd | 0,59 |
| 125 | Tubo-Map1-<br>8  | 127957,3 | 218951,2 | bd       | 322,1754 | bd       | bd | bd | bd | bd | 0,58 |
| 126 | Tubo-Map1-<br>9  | 127664,8 | 218616,7 | 1399,158 | 292,7459 | bd       | bd | bd | bd | bd | 0,58 |
| 127 | Tubo-Map1-<br>10 | 127240,8 | 221758,5 | 620,2934 | bd       | bd       | bd | bd | bd | bd | 0,57 |
| 128 | Tubo-Map1-<br>11 | 1902,781 | 394828,2 | bd       | 502,6245 | bd       | bd | bd | bd | bd | 0,00 |



|     |                  |          |          |          |          |          |    |    |    |    |      |
|-----|------------------|----------|----------|----------|----------|----------|----|----|----|----|------|
| 129 | Tubo-Map1-<br>12 | 324,4678 | 400745,9 | bd       | bd       | bd       | bd | bd | bd | bd | 0,00 |
| 130 | Tubo-Map1-<br>13 | 1885,291 | 402893,5 | bd       | 573,1004 | 444,7803 | bd | bd | bd | bd | 0,00 |
| 131 | Tubo-Map1-<br>14 | 449,9126 | 402427,6 | bd       | bd       | bd       | bd | bd | bd | bd | 0,00 |
| 132 | Tubo-Map1-<br>15 | 674,8689 | 405612,3 | bd       | 832,5445 | bd       | bd | bd | bd | bd | 0,00 |
| 133 | Tubo-Map1-<br>16 | 830,4687 | 401880,8 | bd       | 567,6792 | bd       | bd | bd | bd | bd | 0,00 |
| 134 | Tubo-Map1-<br>17 | 1864,785 | 398755,4 | bd       | 550,6411 | 360,2213 | bd | bd | bd | bd | 0,00 |
| 135 | Tubo-Map1-<br>18 | 128155,7 | 215659,3 | 3404,618 | 330,6944 | bd       | bd | bd | bd | bd | 0,59 |
| 136 | Tubo-Map1-<br>19 | 130266,6 | 221958,7 | 1007,394 | bd       | 362,7581 | bd | bd | bd | bd | 0,59 |
| 137 | Tubo-Map1-<br>20 | 130253,3 | 218255,8 | 821,6167 | 434,4721 | bd       | bd | bd | bd | bd | 0,60 |
| 138 | Tubo-Map1-<br>21 | 119214,2 | 208990,4 | 5285,708 | 1251,527 | bd       | bd | bd | bd | bd | 0,57 |

|     |               |          |          |          |          |    |          |    |         |          |      |
|-----|---------------|----------|----------|----------|----------|----|----------|----|---------|----------|------|
| 139 | Tubo-Map1-22  | 124706,6 | 214762,3 | 2059,872 | 360,1239 | bd | bd       | bd | bd      | bd       | 0,58 |
| 140 | Tubo-Map1-23  | 129228,6 | 219821   | 1332,309 | 389,5534 | bd | bd       | bd | 624,052 | bd       | 0,59 |
| 141 | Tubo-Map1-24  | 126760,2 | 216680,6 | 1188,507 | 360,1239 | bd | bd       | bd | bd      | bd       | 0,59 |
| 142 | JOR58-Map1-1  | 127813,2 | 220496,4 | 2066,09  | bd       | bd | bd       | bd | bd      | bd       | 0,58 |
| 143 | JOR58-Map1-2  | 126567,8 | 219072,7 | 1993,023 | 350,8304 | bd | bd       | bd | bd      | bd       | 0,58 |
| 144 | JOR58-Map1-3  | 2072,252 | 385004,6 | 799,0747 | bd       | bd | 1184,493 | bd | bd      | 618,8436 | 0,01 |
| 145 | JOR58-Map1-4  | 125195,1 | 217639   | 2005,46  | bd       | bd | bd       | bd | bd      | bd       | 0,58 |
| 146 | JOR58-Map1-9  | 125988,2 | 220394,2 | bd       | bd       | bd | bd       | bd | bd      | bd       | 0,57 |
| 147 | JOR58-Map1-10 | 128675   | 219563,7 | bd       | bd       | bd | bd       | bd | bd      | bd       | 0,59 |
| 148 | JOR58-Map1-11 | 130486,1 | 215810,8 | 2264,304 | bd       | bd | bd       | bd | bd      | bd       | 0,60 |

|     |               |          |          |          |          |          |    |    |    |          |      |
|-----|---------------|----------|----------|----------|----------|----------|----|----|----|----------|------|
| 149 | JOR58-Map1-12 | 130031,4 | 217810,5 | 464,0541 | bd       | bd       | bd | bd | bd | bd       | 0,60 |
| 150 | JOR58-Map1-13 | 128544,1 | 217195,9 | bd       | 1548,146 | bd       | bd | bd | bd | bd       | 0,59 |
| 151 | JOR58-Map1-14 | 129413,8 | 217075,1 | 278,277  | bd       | bd       | bd | bd | bd | bd       | 0,60 |
| 152 | JOR58-Map1-15 | 128109,9 | 218305,8 | bd       | bd       | bd       | bd | bd | bd | bd       | 0,59 |
| 153 | JOR58-Map1-16 | 130112,2 | 216364,7 | 487,3734 | bd       | bd       | bd | bd | bd | bd       | 0,60 |
| 154 | JOR58-Map1-17 | 129524,8 | 216985,8 | bd       | bd       | 445,6259 | bd | bd | bd | bd       | 0,60 |
| 155 | JOR58-Map1-18 | 130615,2 | 214731,6 | bd       | bd       | bd       | bd | bd | bd | 456,4953 | 0,61 |
| 156 | JOR58-Map1-19 | 589,2287 | 403123   | bd       | bd       | bd       | bd | bd | bd | bd       | 0,00 |
| 157 | JOR58-Map1-20 | 1010,796 | 404558,8 | bd       | bd       | 350,9199 | bd | bd | bd | bd       | 0,00 |
| 158 | JOR58-Map1-21 | 434,232  | 408132,3 | bd       | bd       | bd       | bd | bd | bd | bd       | 0,00 |

|     |                   |          |          |          |    |    |         |    |          |    |      |
|-----|-------------------|----------|----------|----------|----|----|---------|----|----------|----|------|
| 159 | JOR58-<br>Map1-22 | 489,7172 | 408196,6 | bd       | bd | bd | bd      | bd | bd       | bd | 0,00 |
| 160 | JOR58-<br>Map1-23 | 774,9835 | 406242,6 | bd       | bd | bd | bd      | bd | bd       | bd | 0,00 |
| 161 | JOR58-<br>Map1-24 | 942,6453 | 401196,1 | bd       | bd | bd | bd      | bd | bd       | bd | 0,00 |
| 162 | JOR58-<br>Map1-25 | 131649,5 | 215820,1 | bd       | bd | bd | bd      | bd | bd       | bd | 0,61 |
| 163 | JOR58-<br>Map1-26 | 130860   | 216255,4 | bd       | bd | bd | bd      | bd | bd       | bd | 0,61 |
| 164 | JOR58-<br>Map1-27 | 128100,2 | 216404   | bd       | bd | bd | bd      | bd | 634,7961 | bd | 0,59 |
| 165 | JOR58-<br>Map1-28 | 127630,4 | 215829,4 | 1399,158 | bd | bd | bd      | bd | bd       | bd | 0,59 |
| 166 | JOR58-<br>Map1-29 | 126242,7 | 216688,5 | bd       | bd | bd | bd      | bd | bd       | bd | 0,58 |
| 167 | JOR58-<br>Map1-30 | 126787,9 | 216411,2 | bd       | bd | bd | 7658,07 | bd | bd       | bd | 0,59 |
| 168 | JOR58-<br>Map1-31 | 127875,9 | 218533,8 | 1445,019 | bd | bd | bd      | bd | bd       | bd | 0,59 |

|     |                   |          |          |          |          |    |    |    |    |    |      |
|-----|-------------------|----------|----------|----------|----------|----|----|----|----|----|------|
| 169 | JOR58-<br>Map1-32 | 125548,5 | 214975,3 | 2553,463 | 1932,278 | bd | bd | bd | bd | bd | 0,58 |
| 170 | JOR58-<br>Map1-33 | 128654,5 | 213169,3 | bd       | bd       | bd | bd | bd | bd | bd | 0,60 |
| 171 | JOR58-<br>Map1-34 | 131712,8 | 217541,8 | 712,7933 | bd       | bd | bd | bd | bd | bd | 0,61 |
| 172 | JOR58-<br>Map1-35 | 127264,4 | 213395,8 | 5032,305 | bd       | bd | bd | bd | bd | bd | 0,60 |
| 173 | JOR58-<br>Map1-36 | 127009,2 | 221048,1 | bd       | bd       | bd | bd | bd | bd | bd | 0,57 |
| 174 | JOR58-<br>Map1-37 | 127294,5 | 215960,9 | 2331,93  | bd       | bd | bd | bd | bd | bd | 0,59 |
| 175 | JOR58-<br>Map1-38 | 129165,3 | 218927,6 | 1539,851 | bd       | bd | bd | bd | bd | bd | 0,59 |
| 176 | JOR58-<br>Map1-39 | 127421,8 | 218430,2 | 2571,341 | bd       | bd | bd | bd | bd | bd | 0,58 |
| 177 | JOR58-<br>Map1-40 | 126890,4 | 218616   | 1415,482 | bd       | bd | bd | bd | bd | bd | 0,58 |
| 178 | JOR58-<br>Map1-41 | 125516   | 217183,8 | 2460,186 | bd       | bd | bd | bd | bd | bd | 0,58 |

|     |                   |          |          |          |          |    |    |    |    |    |      |
|-----|-------------------|----------|----------|----------|----------|----|----|----|----|----|------|
| 179 | JOR58-<br>Map1-42 | 127164,2 | 218166,5 | 1845,334 | bd       | bd | bd | bd | bd | bd | 0,58 |
| 180 | JOR58-<br>Map1-43 | 129020,6 | 218791,1 | 873,6964 | 363,9962 | bd | bd | bd | bd | bd | 0,59 |
| 181 | JOR58-<br>Map1-44 | 124816,4 | 219282,1 | 527,0162 | bd       | bd | bd | bd | bd | bd | 0,57 |

Supplementary Table 8. 2- Conditions for Quantitative Spot Analyses of Microprobe Chemical Analyses in the Cap Dolostone

Measurement conditions (wds) for the quantitative point analyses of carbonate. The beam size was set to 10  $\mu\text{m}$ . P&H: P and H Developments Ltd, PMCS: Mcswiggen & Associates, SMS: Smithsonian Museum

|  |   | Ele-<br>ment | X-<br>ray | Crystal | Acc.v<br>(kV) | Current<br>(nA) | Peak<br>(s) | Back<br>(s) | Standard               |
|--|---|--------------|-----------|---------|---------------|-----------------|-------------|-------------|------------------------|
|  | 1 | Mg           | Ka        | TAP     | 15            | 15              | 10          | 5           | Olivine San Carlos SMS |
|  | 2 | Si           | Ka        | TAP     | 15            | 15              | 20          | 10          | Wollastonite P&H       |
|  | 3 | Ca           | Ka        | PETJ    | 15            | 15              | 10          | 5           | Wollastonite P&H       |
|  | 4 | Ba           | La        | PETJ    | 15            | 15              | 20          | 10          | Baryte_PnH             |
|  | 5 | P            | Ka        | PETJ    | 15            | 15              | 10          | 5           | Apatita P&H            |
|  | 6 | Sr           | La        | PETL    | 15            | 15              | 20          | 10          | Celestine P&H          |
|  | 7 | Ti           | Ka        | PETL    | 15            | 15              | 20          | 10          | Ilmenite PMCS          |
|  | 8 | Fe           | Ka        | LIFH    | 15            | 15              | 20          | 10          | Ilmenite PMCS          |
|  | 9 | Mn           | Ka        | LIFH    | 15            | 15              | 20          | 10          | Rhodonite P&H          |

Electron Probe Micro Analyzer (EPMA) analyses were carried out using a JEOL 8230 equipped with five WDS spectrometer. The conditions for the quantitative point analyses are summarized in Table XX. For the map analyses, the accelerating voltage was set to 15 kV and the probe current to 15 nA. Mg, Ca, Sr and Mn were acquired in WDS mode, while Al, Si, P and Fe were simultaneously acquired in EDS mode. Cathodoluminescence, secondary electrons and backscattered electron images were also acquired. The step size and dwell time varied depending on the size of the mapping area.

Supplementary Table 8.3- Supplementary Table 8.3 Raman spectra and peak width analyses. Measurement of the width of the 1098  $\text{cm}^{-1}$  and 1099  $\text{cm}^{-1}$  peaks and their respective FWHM values ( $1/\text{cm}$ )

| Samples/points                                                                     | Raman Shift [ $1/\text{cm}$ ] | FWHM [ $1/\text{cm}$ ] |
|------------------------------------------------------------------------------------|-------------------------------|------------------------|
| JOR36A_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__                            | 1097,3                        | 6,3593                 |
| JOR36A_grumo_peloidal_785nm_centro800_pt_1_2s_30ac_50x__                           | 1098,6                        | 6,6268                 |
| JOR36B_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__                            | 1098,1                        | 6,9474                 |
| JOR36B_grumo_peloidal_785nm_centro800_pt_1_2s_30ac_50x__                           | 1098,6                        | 6,6742                 |
| JOR36C_grumo_peloidal_785nm_centro800_pt_0_1_5s_30ac_5x__                          | 1098,2                        | 7,4688                 |
| JOR36C_grumo_peloidal_785nm_centro800_pt_1_2s_30ac_50x__                           | 1098,5                        | 7,024                  |
| JOR36C_grumo_peloidal_785nm_centro800_pt_1_5s_30ac_5x__                            | 1098                          | 7,1203                 |
| JOR36C1_grumo_peloidal_785nm_centro800_pt_1_2s_30ac_50x__                          | 1098,5                        | 7,7816                 |
| JOR36D_grumo_peloidal_785nm_centro800_pt_1_2s_30ac_50x_escuro__                    | 1098,5                        | 7,9664                 |
| JOR36D_grumo_peloidal_785nm_centro800_pt_1_5s_30ac_5x__                            | 1098                          | 7,2391                 |
| JOR36D2_grumo_peloidal_785nm_centro800_pt_1_5s_30ac_50x_talvez_gipsita_aragonita__ | 1098,7                        | 6,8938                 |
| JOR36E_grumo_peloidal_785nm_centro800_pt_1_5s_30ac_5x__                            | 1098,2                        | 6,9389                 |
| JOR36F_grumo_peloidal_785nm_centro800_pt_1_5s_30ac_5x__                            | 1098,3                        | 7,0018                 |



|                                                                                        |        |        |
|----------------------------------------------------------------------------------------|--------|--------|
| JOR36G_grupo_peloidal_785nm_cen-<br>tro800_pt_1_5s_30ac_5x__                           | 1098,2 | 6,767  |
| JOR36H_grupo_peloidal_785nm_cen-<br>tro800_pt_1_5s_30ac_5x__                           | 1098,2 | 6,8933 |
| JOR41_A1_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,1 | 7,1516 |
| JOR41_B1_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099   | 7,0001 |
| JOR41_C1_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1098,9 | 7,1607 |
| JOR41_D1_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1098,8 | 6,9705 |
| JOR41_E1_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1098,8 | 7,7426 |
| JOR41_F1_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099   | 7,1606 |
| JOR41_G1_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,1 | 7,291  |
| JOR41_H1_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,2 | 7,256  |
| JOR41_L1_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,3 | 7,0838 |
| JOR41_M1_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,2 | 7,0183 |

|                                                                             |        |        |
|-----------------------------------------------------------------------------|--------|--------|
| JOR50A_dolomita_suspeita_gypsum_secundaria_785nm_centro800_pt_1_5s_30ac_50x | 1098,3 | 6,8175 |
| JOR50A_dolomita_suspeita_primaria_785nm_centro800_pt_1_5s_30ac_50x__        | 1098,1 | 6,9443 |
| JOR50B_dolomita_suspeita_gypsum_secundaria_785nm_centro800_pt_1_5s_30ac_50x | 1098,2 | 6,9442 |
| JOR50B_dolomita_suspeita_primaria_785nm_centro800_pt_1_5s_30ac_50x__        | 1098,2 | 7,2161 |
| JOR50C_dolomita_suspeita_gypsum_secundaria_785nm_centro800_pt_1_5s_30ac_50x | 1098,4 | 6,6645 |
| JOR50C_dolomita_suspeita_primaria_785nm_centro800_pt_1_5s_30ac_50x__        | 1098,2 | 8,1616 |
| JOR50D_dolomita_suspeita_gypsum_secundaria_785nm_centro800_pt_1_5s_30ac_50x | 1098,3 | 7,0231 |
| JOR50D_dolomita_suspeita_primaria_785nm_centro800_pt_1_5s_30ac_50x__        | 1098,1 | 7,0425 |
| JOR50E_dolomita_suspeita_gypsum_secundaria_785nm_centro800_pt_1_5s_30ac_50x | 1098,3 | 6,7895 |
| JOR50E_dolomita_suspeita_primaria_785nm_centro800_pt_1_5s_30ac_50x__        | 1098,1 | 7,2164 |
| JOR50E_dolomita_suspeita_primaria_785nm_centro800_pt_1_5s_30ac_50x__        | 1098,1 | 7,2164 |
| JOR50F_dolomita_suspeita_gypsum_secundaria_785nm_centro800_pt_1_5s_30ac_50x | 1098,5 | 6,7011 |
| JOR50F_dolomita_suspeita_primaria_785nm_centro800_pt_1_5s_30ac_50x          | 1098   | 7,2891 |
| JOR50G_dolomita_suspeita_primaria_785nm_centro800_pt_1_5s_30ac_50X          | 1098,3 | 9,6617 |
| JOR50H_dolomita_suspeita_primaria_785nm_centro800_pt_1_5s_30ac_50x__        | 1098,1 | 7,0418 |
| JOR50I_dolomita_suspeita_primaria_785nm_centro800_pt_1_5s_30ac_50x          | 1098,1 | 7,0744 |

|                                                                                |        |        |
|--------------------------------------------------------------------------------|--------|--------|
| JOR50J_dolomita_suspeita_primaria_785nm_centro800_pt_1_5s_30ac_50x             | 1098   | 7,2439 |
| JOR58_A1_dolomita_suspeita_nE-OMO_primaria_785nm_centro800_pt_1_5s_30ac_50x__  | 1097,8 | 7,2094 |
| JOR58_A10_dolomita_suspeita_nE-OMO_primaria_785nm_centro800_pt_1_5s_30ac_50x__ | 1097,6 | 7,4225 |
| JOR58_A11_dolomita_suspeita_nE-OMO_primaria_785nm_centro800_pt_1_5s_30ac_50x__ | 1097,7 | 7,3683 |
| JOR58_A12_dolomita_suspeita_nE-OMO_primaria_785nm_centro800_pt_1_5s_30ac_50x__ | 1097,5 | 7,1329 |
| JOR58_A13_dolomita_suspeita_nE-OMO_primaria_785nm_centro800_pt_1_5s_30ac_50x__ | 1097,5 | 7,3143 |
| JOR58_A14_dolomita_suspeita_nE-OMO_primaria_785nm_centro800_pt_1_5s_30ac_50x__ | 1097,7 | 7,3717 |
| JOR58_A15_dolomita_suspeita_nE-OMO_primaria_785nm_centro800_pt_1_5s_30ac_50x__ | 1097,6 | 7,5991 |
| JOR58_A16_dolomita_suspeita_nE-OMO_primaria_785nm_centro800_pt_1_5s_30ac_50x__ | 1097,5 | 7,4617 |
| JOR58_A2_dolomita_suspeita_nE-OMO_primaria_785nm_centro800_pt_1_5s_30ac_50x__  | 1097,6 | 7,3228 |
| JOR58_A3_dolomita_suspeita_nE-OMO_primaria_785nm_centro800_pt_1_5s_30ac_50x__  | 1097,6 | 7,1937 |
| JOR58_A4_dolomita_suspeita_nE-OMO_primaria_785nm_centro800_pt_1_5s_30ac_50x__  | 1097,6 | 7,1474 |

|                                                                                        |        |        |
|----------------------------------------------------------------------------------------|--------|--------|
| JOR58_A5_dolomita_suspeita_nE-<br>OMO_primaria_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1097,7 | 7,2357 |
| JOR58_A6_dolomita_suspeita_nE-<br>OMO_primaria_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1097,7 | 7,2837 |
| JOR58_A7_dolomita_suspeita_nE-<br>OMO_primaria_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1097,7 | 7,2045 |
| JOR58_A8_dolomita_suspeita_nE-<br>OMO_primaria_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1097,6 | 7,3274 |
| JOR58_A9_dolomita_suspeita_nE-<br>OMO_primaria_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1097,8 | 7,4275 |
| JOR67A_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x   | 1099,3 | 7,0326 |
| JOR67AA2_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,7 | 7,1146 |
| JOR67B_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x   | 1099,3 | 7,0626 |
| JOR67C_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x   | 1099,3 | 6,9016 |
| JOR67D_dolomita_suspeita_prima-<br>ria_GRUMOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x   | 1099,1 | 7,3657 |
| JOR67E_dolomita_suspeita_primaria_GRU-<br>MOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x   | 1099,3 | 7,4153 |
| JOR67F_dolomita_suspeita_primaria_GRU-<br>MOSE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x   | 1099,4 | 7,1681 |

|                                                                            |        |        |
|----------------------------------------------------------------------------|--------|--------|
| JOR67G_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,4 | 7,1389 |
| JOR67H_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,5 | 6,9954 |
| JOR67I_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,6 | 7,2173 |
| JOR67J_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,3 | 7,3018 |
| JOR67K_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,4 | 7,2899 |
| JOR67M_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,5 | 7,4737 |
| JOR67O_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,6 | 6,9756 |
| JOR67P_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,4 | 7,3868 |
| JOR67Q_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,3 | 7,7385 |
| JOR67R_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,5 | 7,5293 |
| JOR67S_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,6 | 7,2527 |
| JOR67T_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,6 | 7,1642 |

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| JOR67U_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,6 | 6,9845 |
| JOR67V_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,7 | 7,0272 |
| JOR67X_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,3 | 7,9326 |
| JOR67Z_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1099,4 | 7,7834 |
| JOR3A                                                                      | 1098,4 | 6,8    |
| JOR3B                                                                      | 1098,3 | 6,8038 |
| JOR3C                                                                      | 1098,2 | 7,2071 |
| JOR3D                                                                      | 1098,3 | 7,0821 |
| JOR3F                                                                      | 1098,3 | 6,9528 |
| JOR3G                                                                      | 1098,6 | 7,0699 |
| JOR3H                                                                      | 1098,5 | 7,0747 |
| JOR3I                                                                      | 1098,2 | 7,3523 |
| JOR3J                                                                      | 1098,4 | 7,1258 |
| JOR3M                                                                      | 1098,5 | 6,8914 |
| JOR3N                                                                      | 1098,5 | 7,0575 |
| JOR3O                                                                      | 1098,5 | 6,9872 |
| JOR4_A1                                                                    | 1099   | 7,0902 |
| JOR4_A10                                                                   | 1099,2 | 7,3352 |
| JOR4_A11                                                                   | 1098,9 | 7,4191 |
| JOR4_A12                                                                   | 1099   | 7,185  |
| JOR4_A13                                                                   | 1098,9 | 7,2219 |
| JOR4_A14                                                                   | 1098,9 | 7,218  |

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| JOR4_A15 | 1099   | 7,3269 |
| JOR4_A16 | 1098,8 | 7,403  |
| JOR4_A17 | 1099   | 7,2707 |
| JOR4_A18 | 1099   | 7,0935 |
| JOR4_A19 | 1099   | 6,9184 |
| JOR4_A2  | 1099,1 | 7,1656 |
| JOR4_A3  | 1099,1 | 7,0563 |
| JOR4_A4  | 1099,1 | 6,9602 |
| JOR4_A5  | 1099   | 7,0915 |
| JOR4_A6  | 1099,1 | 7,0859 |
| JOR4_A7  | 1099,1 | 7,1418 |
| JOR4_A8  | 1098,9 | 7,4335 |
| JOR4_A9  | 1099,1 | 7,1638 |
| JOR7A    | 1098,6 | 6,9116 |
| JOR7B    | 1098,4 | 7,1786 |
| JOR7C    | 1098,7 | 7,1707 |
| JOR7D    | 1098,8 | 7,0235 |
| JOR7E    | 1098,8 | 7,0748 |
| JOR7F    | 1098,8 | 7,03   |
| JOR7G    | 1098,6 | 6,9924 |
| JOR7H    | 1098,6 | 6,9172 |
| JOR7I    | 1098,8 | 6,9794 |
| JOR7J    | 1098,7 | 6,9865 |
| JOR7L    | 1098,4 | 6,9005 |
| JOR7M    | 1098,6 | 6,9934 |
| JOR7N    | 1098,6 | 6,9022 |
| JOR7O    | 1098,7 | 6,9521 |

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| JOR 161_A1_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,9 | 5,3611 |
| JOR 161_A10_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1098,9 | 5,4137 |
| JOR 161_A11_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099,2 | 5,353  |
| JOR 161_A12_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1098,9 | 5,4885 |
| JOR 161_A13_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099,2 | 5,3693 |
| JOR 161_A15_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099,2 | 5,41   |
| JOR 161_A16_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099,2 | 5,3072 |
| JOR 161_A17_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099,2 | 5,4145 |
| JOR 161_A18_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1098,8 | 5,4105 |
| JOR 161_A19_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,4033 |
| JOR 161_A2_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1099,1 | 5,3992 |
| JOR 161_A20_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099   | 5,4588 |



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| JOR 161_A3_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__       | 1099,3 | 5,2384 |
| JOR 161_A4_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__       | 1098,8 | 5,2566 |
| JOR 161_A5_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__       | 1099,2 | 5,3479 |
| JOR 161_A6_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__       | 1098,8 | 5,1852 |
| JOR 161_A7_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__       | 1098,9 | 5,313  |
| JOR 161_A8_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__       | 1099,3 | 5,0802 |
| JOR 161_A9_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__       | 1099,1 | 5,5326 |
| JOR110_A1_grupo_peloidal_785nm_cen-tro800_pt_0_1_5s_30ac_5x__                   | 1099,2 | 5,4756 |
| JOR110_A11_grupo_peloidal_785nm_cen-tro800_pt_0_1_5s_30ac_5x__                  | 1099,5 | 5,6799 |
| JOR110_A12_grupo_peloidal_785nm_cen-tro800_pt_0_1_5s_30ac_5x__                  | 1099,5 | 5,5635 |
| JOR110_A15_grupo_peloidal_duvida_du-vida_785nm_cen-tro800_pt_0_1_5s_30ac_5x____ | 1099,6 | 5,3363 |
| JOR110_A16_grupo_peloidal_duvida_du-vida_785nm_cen-tro800_pt_0_1_5s_30ac_5x____ | 1099,5 | 6,2144 |

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| JOR110_A17_grumo_peloidal_duvida_duvida_785nm_centro800_pt_0_1_5s_30ac_5x____  | 1099,6 | 5,5397 |
| JOR110_A2_grumo_peloidal_785nm_centro800_pt_0_1_5s_30ac_5x__                   | 1099,4 | 5,217  |
| JOR110_A3_grumo_peloidal_785nm_centro800_pt_0_1_5s_30ac_5x__                   | 1099,3 | 5,5494 |
| JOR110_A4_grumo_peloidal_785nm_centro800_pt_0_1_5s_30ac_5x__                   | 1099,3 | 5,6536 |
| JOR110_A5_grumo_peloidal_785nm_centro800_pt_0_1_5s_30ac_5x__                   | 1099,5 | 5,3814 |
| JOR110_A6_grumo_peloidal_785nm_centro800_pt_0_1_5s_30ac_5x__                   | 1099,4 | 5,3252 |
| JOR110_A7_grumo_peloidal_785nm_centro800_pt_0_1_5s_30ac_5x__                   | 1099,4 | 5,7249 |
| JOR110_A8_grumo_peloidal_785nm_centro800_pt_0_1_5s_30ac_5x__                   | 1099,5 | 5,6917 |
| JOR110_A9_grumo_peloidal_785nm_centro800_pt_0_1_5s_30ac_5x__                   | 1099,5 | 5,6605 |
| JOR131_A1_dolomita_suspeita primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x  | 1097,6 | 5,4451 |
| JOR131_A10_dolomita_suspeita primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1097,5 | 5,213  |
| JOR131_A11_dolomita_suspeita primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1097,6 | 5,4363 |
| JOR131_A12_dolomita_suspeita primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1097,7 | 5,4619 |
| JOR131_A13_dolomita_suspeita primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1097,6 | 5,6073 |

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| JOR131_A14_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1097,5 | 5,5088 |
| JOR131_A15_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1097,8 | 5,4089 |
| JOR131_A16_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1097,9 | 5,3663 |
| JOR131_A17_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1097,6 | 5,5934 |
| JOR131_A2_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x  | 1097,4 | 5,6957 |
| JOR131_A3_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x  | 1097,7 | 5,3947 |
| JOR131_A4_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x  | 1097,7 | 5,2157 |
| JOR131_A5_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x  | 1097,7 | 5,334  |
| JOR131_A6_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x  | 1097,6 | 5,5099 |
| JOR131_A7_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x  | 1097,5 | 5,9321 |
| JOR131_A8_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x  | 1097,8 | 5,6117 |
| JOR131_A9_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x  | 1097,8 | 5,3615 |

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| JOR131_B1_dolomita_suspeita_primaria_GRUMOSE(MATRIZ)_785nm_centro800_pt_1_5s_30ac_50x | 1097,9 | 5,4664 |
| JOR131_B2_dolomita_suspeita_primaria_GRUMOSE(MATRIZ)_785nm_centro800_pt_1_5s_30ac_50x | 1097,9 | 5,3648 |
| JOR131_B3_dolomita_suspeita_primaria_GRUMOSE(MATRIZ)_785nm_centro800_pt_1_5s_30ac_50x | 1097,8 | 5,3234 |
| JOR131_B4_dolomita_suspeita_primaria_GRUMOSE(MATRIZ)_785nm_centro800_pt_1_5s_30ac_50x | 1097,6 | 5,1906 |
| JOR131_B5_dolomita_suspeita_primaria_GRUMOSE(MATRIZ)_785nm_centro800_pt_1_5s_30ac_50x | 1097,4 | 5,2328 |
| JOR131_B6_dolomita_suspeita_primaria_GRUMOSE(MATRIZ)_785nm_centro800_pt_1_5s_30ac_50x | 1097,5 | 5,104  |
| JOR131_B7_dolomita_suspeita_primaria_GRUMOSE(MATRIZ)_785nm_centro800_pt_1_5s_30ac_50x | 1097,9 | 5,285  |
| JOR131_C1_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x         | 1097,8 | 5,6668 |
| JOR131_C2_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x         | 1097,9 | 5,5747 |
| JOR131_C3_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x         | 1097,8 | 5,4397 |
| JOR131_C4_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x         | 1097,9 | 5,3806 |
| JOR131_C5_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x         | 1097,9 | 5,3287 |

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| JOR131_C6_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1097,8 | 5,4647 |
| JOR131_C7_dolomita_suspeita_primaria_GRUMOSE_785nm_centro800_pt_1_5s_30ac_50x | 1097,9 | 5,2412 |
| JOR160_A1_grumo_peloidal_duvida_duvida_785nm_centro800_pt_0_1_5s_30ac_5x____  | 1099,7 | 5,2556 |
| JOR160_A10_grumo_peloidal_duvida_duvida_785nm_centro800_pt_0_1_5s_30ac_5x____ | 1099,8 | 5,871  |
| JOR160_A11_grumo_peloidal_duvida_duvida_785nm_centro800_pt_0_1_5s_30ac_5x____ | 1099,8 | 5,3673 |
| JOR160_A12_grumo_peloidal_duvida_duvida_785nm_centro800_pt_0_1_5s_30ac_5x____ | 1099,7 | 6,2929 |
| JOR160_A13_grumo_peloidal_duvida_duvida_785nm_centro800_pt_0_1_5s_30ac_5x____ | 1099,6 | 6,249  |
| JOR160_A14_grumo_peloidal_duvida_duvida_785nm_centro800_pt_0_1_5s_30ac_5x____ | 1099,6 | 6,6098 |
| JOR160_A15_grumo_peloidal_duvida_duvida_785nm_centro800_pt_0_1_5s_30ac_5x____ | 1100,1 | 5,9305 |
| JOR160_A16_grumo_peloidal_duvida_duvida_785nm_centro800_pt_0_1_5s_30ac_5x____ | 1100   | 5,72   |
| JOR160_A17_grumo_peloidal_duvida_duvida_785nm_centro800_pt_0_1_5s_30ac_5x____ | 1099,9 | 5,79   |
| JOR160_A18_grumo_peloidal_duvida_duvida_785nm_centro800_pt_0_1_5s_30ac_5x____ | 1099,8 | 5,7064 |

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| JOR160_A19_grumo_peloidal_duvida_du-<br>vida_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____    | 1099,7 | 6,2214 |
| JOR160_A2_grumo_peloidal_duvida_du-<br>vida_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____     | 1099,7 | 5,4605 |
| JOR160_A20_grumo_peloidal_duvida_du-<br>vida_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____    | 1099,8 | 7,7423 |
| JOR160_A3_grumo_peloidal_duvida_du-<br>vida_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____     | 1099,7 | 6,1221 |
| JOR160_A4_grumo_peloidal_duvida_du-<br>vida_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____     | 1099,6 | 6,1986 |
| JOR160_A5_grumo_peloidal_duvida_du-<br>vida_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____     | 1099,9 | 6,0585 |
| JOR160_A6_grumo_peloidal_duvida_du-<br>vida_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____     | 1099,9 | 6,0585 |
| JOR160_A7_grumo_peloidal_duvida_du-<br>vida_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____     | 1099,9 | 5,8028 |
| JOR160_A8_grumo_peloidal_duvida_du-<br>vida_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____     | 1100   | 5,6795 |
| JOR160_A9_grumo_peloidal_duvida_du-<br>vida_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____     | 1100   | 5,7112 |
| JOR171_A1_grumo_peloidal_MUDANÇA-<br>TEXTXURAL_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____  | 1099,9 | 5,9081 |
| JOR171_A10_grumo_peloidal_MUDAN-<br>ÇATEXTXURAL_785nm_cen-<br>tro800_pt_0_1_5s_30ac_5x____ | 1100,2 | 6,4702 |

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| JOR171_A11_grumo_peloidal_MUDANÇATEXTXURAL_785nm_centro800_pt_0_1_5s_30ac_5x____    | 1100,1 | 5,7432 |
| JOR171_A12_grumo_peloidal_MUDANÇATEXTXURAL_785nm_centro800_pt_0_1_5s_30ac_5x____    | 1100   | 6,0244 |
| JOR171_A14_grumo_peloidal_MUDANÇATEXTXURAL_785nm_centro800_pt_0_1_5s_30ac_5x____    | 1100,3 | 6,3865 |
| JOR171_A15_grumo_peloidal_MUDANÇATEXTXURAL_785nm_centro800_pt_0_1_5s_30ac_5x____    | 1100,2 | 6,4336 |
| JOR171_A2_grumo_peloidal_MUDANÇATEXTXURAL_785nm_centro800_pt_0_1_5s_30ac_5x____     | 1100   | 6,5232 |
| JOR171_A3_grumo_peloidal_MUDANÇATEXTXURAL_785nm_centro800_pt_0_1_5s_30ac_5x____     | 1100   | 5,6214 |
| JOR171_A4_grumo_peloidal_MUDANÇATEXTXURAL_785nm_centro800_pt_0_1_5s_30ac_5x____     | 1100   | 5,9003 |
| JOR171_A6_grumo_peloidal_MUDANÇATEXTXURAL_785nm_centro800_pt_0_1_5s_30ac_5x____     | 1100   | 6,3712 |
| JOR171_A7_grumo_peloidal_MUDANÇATEXTXURAL_785nm_centro800_pt_0_1_5s_30ac_5x____     | 1100,2 | 5,9064 |
| JOR171_A8_grumo_peloidal_MUDANÇATEXTXURAL_785nm_centro800_pt_0_1_5s_30ac_5x____     | 1100,2 | 6,322  |
| JOR171_A9_grumo_peloidal_MUDANÇATEXTXURAL_785nm_centro800_pt_0_1_5s_30ac_5x____     | 1100,1 | 6,599  |
| JBN2_A1_dolomita_suspeita_primaria_NE-OMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1098,6 | 5,2873 |

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| JBN2_A10_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099   | 5,4468 |
| JBN2_A11_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1098,7 | 5,5007 |
| JBN2_A12_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099   | 5,4714 |
| JBN2_A14_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099   | 5,2321 |
| JBN2_A15_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099   | 5,4674 |
| JBN2_A16_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,2952 |
| JBN2_A17_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,2663 |
| JBN2_A18_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,2362 |
| JBN2_A19_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,3295 |
| JBN2_A2_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1098,5 | 5,1688 |
| JBN2_A20_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099   | 5,5872 |
| JBN2_A3_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1098,6 | 5,3401 |



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| JBN2_A4_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,6 | 5,3531 |
| JBN2_A5_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,8 | 5,2891 |
| JBN2_A6_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,9 | 5,3587 |
| JBN2_A7_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,8 | 5,3259 |
| JBN2_A8_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1099   | 5,4843 |
| JBN2_A9_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,8 | 5,5247 |
| JBN5_B1_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,9 | 5,5837 |
| JBN5_B10_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__     | 1099   | 5,4036 |
| JBN5_B11_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__     | 1099   | 5,6137 |
| JBN5_B12_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__     | 1098,9 | 5,6025 |
| JBN5_B13_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__     | 1099   | 5,526  |
| JBN5_B14_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__     | 1099   | 5,6208 |

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| JBN5_B15_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1098,6 | 5,6897 |
| JBN5_B16_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1098,7 | 5,7105 |
| JBN5_B2_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1099   | 5,4627 |
| JBN5_B3_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1099   | 5,5618 |
| JBN5_B4_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1098,7 | 5,5033 |
| JBN5_B5_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1099   | 5,3239 |
| JBN5_B6_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1098,9 | 5,4529 |
| JBN5_B7_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1098,8 | 5,6405 |
| JBN5_B8_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1099   | 5,5753 |
| JBN5_B9_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1099,1 | 5,5667 |
| JBN6_A1_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1099,1 | 5,5434 |
| JBN6_A10_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,6146 |

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| JBN6_A11_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,6027 |
| JBN6_A12_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099   | 5,6156 |
| JBN6_A13_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099,2 | 5,5393 |
| JBN6_A14_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099   | 5,6333 |
| JBN6_A15_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099   | 5,6988 |
| JBN6_A16_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,5436 |
| JBN6_A17_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,5147 |
| JBN6_A18_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,5983 |
| JBN6_A19_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099   | 5,5858 |
| JBN6_A2_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1099,2 | 5,5803 |
| JBN6_A20_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__ | 1099   | 5,729  |
| JBN6_A3_dolomita_suspeita_primaria_NEOMORFIZADA_785nm_centro800_pt_1_5s_30ac_50x__  | 1099,2 | 5,4655 |

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| JBN6_A4_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,6319 |
| JBN6_A6_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1099   | 5,6057 |
| JBN6_A7_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1099   | 5,5452 |
| JBN6_A8_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1099,1 | 5,6113 |
| JBN6_A9_dolomita_suspeita_primaria_NE-<br>OMORFIZADA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1099,2 | 5,4638 |
| JBN38A_GRUMOSE_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__              | 1099   | 7,759  |
| JBN38B_GRUMOSE_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__              | 1098,7 | 7,1799 |
| JBN38C_GRUMOSE_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__              | 1099   | 7,26   |
| JBN38D_GRUMOSE_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__              | 1099   | 7,936  |
| JBN38E_GRUMOSE_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__              | 1099,1 | 7,123  |
| JBN38F_GRUMOSE_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__              | 1099   | 7,3501 |
| JBN38G_GRUMOSE_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__              | 1098,9 | 7,3837 |

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| JBN38H_GRUMOSE_DOLOMITE_PRI-MARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x__    | 1098,8 | 7,3061 |
| JBN38I_GRUMOSE_DOLOMITE_PRI-MARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x__    | 1099   | 7,3094 |
| JBN38J_GRUMOSE_DOLOMITE_PRI-MARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x__    | 1099   | 7,336  |
| JBN38L_GRUMOSE_DOLOMITE_PRI-MARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x__    | 1099   | 7,2741 |
| JBN38M_GRUMOSE_DOLOMITE_PRI-MARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x__    | 1098,8 | 7,2828 |
| JBN38N_GRUMOSE_DOLOMITE_PRI-MARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x__    | 1099   | 7,2814 |
| JBN38O_GRUMOSE_DOLOMITE_PRI-MARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x__    | 1099   | 7,2588 |
| JBN38P_GRUMOSE_DOLOMITE_PRI-MARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x__    | 1099,1 | 7,7138 |
| JBN38Q_GRUMOSE_DOLOMITE_PRI-MARÁRIA_Fe_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099,1 | 7,2595 |
| JBN38R_GRUMOSE_DOLOMITE_PRI-MARÁRIA_Fe_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099   | 7,2514 |
| JBN38S_GRUMOSE_DOLOMITE_PRI-MARÁRIA_Fe_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099   | 7,1923 |
| JBN38T_GRUMOSE_DOLOMITE_PRI-MARÁRIA_Fe_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099   | 7,3134 |

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| JBN38U_GRUMOSE_DOLOMITE_PRI-MARÁRIA_ESTRANHO_785nm_cen-tro800_pt_1_5s_30ac_50x__    | 1098,8 | 7,409  |
| JBN38U_GRUMOSE_DOLOMITE_PRI-MARÁRIA_Fe_785nm_cen-tro800_pt_1_5s_30ac_50x__          | 1098,8 | 7,279  |
| JBN38V_GRUMOSE_DOLOMITE_PRI-MARÁRIA_Fe_ESTRANHO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099   | 7,9163 |
| JBN38X_GRUMOSE_DOLOMITE_PRI-MARÁRIA_Fe_ESTRANHO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1098,8 | 7,4701 |
| JBN48_A1_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__             | 1099   | 7,0327 |
| JBN48_A10_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__            | 1098,9 | 7,0051 |
| JBN48_A11_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__            | 1098,8 | 7,0946 |
| JBN48_A12_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__            | 1098,7 | 7,1808 |
| JBN48_A13_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__            | 1098,6 | 7,1204 |
| JBN48_A14_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__            | 1098,5 | 7,04   |
| JBN48_A15_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__            | 1098,7 | 7,1264 |
| JBN48_A16_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__            | 1099   | 6,8336 |

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| JBN48_A17_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099   | 6,887  |
| JBN48_A18_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1098,9 | 6,929  |
| JBN48_A19_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1098,9 | 7,0154 |
| JBN48_A2_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1099   | 7,0682 |
| JBN48_A20_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1099   | 6,9526 |
| JBN48_A3_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1099   | 6,9669 |
| JBN48_A4_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1099   | 7,0916 |
| JBN48_A5_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1099   | 6,9207 |
| JBN48_A6_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,9 | 7,0248 |
| JBN48_A7_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,7 | 7,1282 |
| JBN48_A8_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,9 | 7,0461 |
| JBN48_A9_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1099   | 6,8302 |

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| JBN62_A1_gruome_DOLOMITE_PRIMA-<br>RÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____  | 1098,2 | 6,8302 |
| JBN62_A10_gruome_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1098,2 | 6,7314 |
| JBN62_A11_gruome_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1098,1 | 6,885  |
| JBN62_A12_gruome_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1098,2 | 6,7888 |
| JBN62_A13_gruome_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1098,1 | 6,979  |
| JBN62_A14_gruome_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1098,1 | 6,6976 |
| JBN62_A15_gruome_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1098,1 | 6,8797 |
| JBN62_A16_gruome_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1098,2 | 6,8527 |
| JBN62_A17_gruome_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1098,1 | 6,7631 |
| JBN62_A18_gruome_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1098,2 | 6,7715 |
| JBN62_A19_gruome_DOLOMITE_PRI-<br>MARÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1098,2 | 6,6543 |
| JBN62_A2_gruome_DOLOMITE_PRIMA-<br>RÁRIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____  | 1098,2 | 6,996  |



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| JBN62_A20_gruome_DOLOMITE_PRI-MARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x____ | 1098,2 | 6,6831 |
| JBN62_A3_gruome_DOLOMITE_PRIMARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x____   | 1098,1 | 6,8631 |
| JBN62_A4_gruome_DOLOMITE_PRIMARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x____   | 1098,1 | 6,8307 |
| JBN62_A5_gruome_DOLOMITE_PRIMARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x____   | 1098,2 | 6,8955 |
| JBN62_A7_gruome_DOLOMITE_PRIMARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x____   | 1098,1 | 6,8752 |
| JBN62_A8_gruome_DOLOMITE_PRIMARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x____   | 1098,2 | 6,8429 |
| JBN62_A9_gruome_DOLOMITE_PRIMARÁRIA_785nm_cen-tro800_pt_1_5s_30ac_50x____   | 1098,1 | 6,9914 |
| JBN80_A1_grumo_peloidal_785nm_cen-tro800_pt_1_2s_30ac_50x____               | 1098,2 | 6,9658 |
| JBN80_A10_grumo_ (estranho)_785nm_cen-tro800_pt_1_2s_30ac_50x____           | 1098,1 | 7,0537 |
| JBN80_A11_grumo_ (estranho)_785nm_cen-tro800_pt_1_2s_30ac_50x____           | 1098,2 | 6,742  |
| JBN80_A12_grumo_ (estranho)_785nm_cen-tro800_pt_1_2s_30ac_50x____           | 1098,1 | 7,0904 |
| JBN80_A13_grumo_ (estranho)_785nm_cen-tro800_pt_1_2s_30ac_50x____           | 1098,3 | 6,9194 |

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| JBN80_A14_grupo_ (estra-<br>nho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__ | 1098,2 | 6,8065 |
| JBN80_A15_grupo_ (estra-<br>nho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__ | 1098,1 | 7,096  |
| JBN80_A16_grupo_ (estra-<br>nho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__ | 1098   | 6,9619 |
| JBN80_A17_grupo_ (estra-<br>nho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__ | 1098,2 | 6,9192 |
| JBN80_A18_grupo_ (estra-<br>nho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__ | 1098,2 | 6,8427 |
| JBN80_A19_grupo_ (estra-<br>nho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__ | 1098,2 | 6,9375 |
| JBN80_A2_grupo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__          | 1098,2 | 6,8269 |
| JBN80_A20_grupo_ (estra-<br>nho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__ | 1098,1 | 6,8584 |
| JBN80_A21_grupo_ (estra-<br>nho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__ | 1098,4 | 6,762  |
| JBN80_A3_grupo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__          | 1098,2 | 6,9363 |
| JBN80_A4_grupo_ (estranho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__       | 1098,2 | 6,9742 |
| JBN80_A5_grupo_ (estranho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__       | 1098,2 | 6,8433 |
| JBN80_A6_grupo_ (estranho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__       | 1098,3 | 6,9468 |

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| JBN80_A7_grumo_ (estranho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__ | 1098,1 | 6,9191 |
| JBN80_A8_grumo_ (estranho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__ | 1098,2 | 6,9144 |
| JBN80_A9_grumo_ (estranho)_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__ | 1098,1 | 7,0055 |
| JBN92_A1_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__    | 1098,6 | 6,767  |
| JBN92_A10_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__   | 1098,7 | 6,8852 |
| JBN92_A11_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__   | 1098,7 | 6,8904 |
| JBN92_A12_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__   | 1098,6 | 6,7514 |
| JBN92_A15_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__   | 1098,8 | 6,8662 |
| JBN92_A16_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__   | 1098,8 | 6,8386 |
| JBN92_A17_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__   | 1098,8 | 6,8913 |
| JBN92_A18_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__   | 1098,7 | 6,9928 |
| JBN92_A19_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__   | 1098,7 | 6,7366 |
| JBN92_A2_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__    | 1098,7 | 6,6768 |
| JBN92_A20_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__   | 1098,7 | 6,6989 |
| JBN92_A21_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__   | 1098,7 | 6,758  |
| JBN92_A22_grumo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__   | 1098,8 | 6,9906 |

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| JBN92_A24_grupo_ (MO)peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x____           | 1098,7 | 6,8181 |
| JBN92_A25_grupo_ (MO)peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x____           | 1098,8 | 6,7468 |
| JBN92_A26_grupo_ (MO)peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x____           | 1098,7 | 6,8158 |
| JBN92_A3_grupo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__                   | 1098,6 | 6,9414 |
| JBN92_A4_grupo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__                   | 1098,6 | 6,8464 |
| JBN92_A5_grupo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__                   | 1098,7 | 6,8398 |
| JBN92_A6_grupo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__                   | 1098,7 | 6,6721 |
| JBN92_A7_grupo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__                   | 1098,7 | 6,8849 |
| JBN92_A8_grupo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__                   | 1098,7 | 6,8952 |
| JBN92_A9_grupo_peloidal_785nm_cen-<br>tro800_pt_1_2s_30ac_50x__                   | 1098,7 | 6,9925 |
| JOR183_A1_dolomita_primaria_MI-<br>CRITO_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__  | 1097,4 | 7,5326 |
| JOR183_A10_dolomita_primaria_MI-<br>CRITO_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1097,6 | 7,4778 |
| JOR183_A11_dolomita_primaria_MI-<br>CRITO_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1097,8 | 7,0912 |
| JOR183_A12_dolomita_primaria_MI-<br>CRITO_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1097,6 | 7,5379 |

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|---------------------------------------------------------------------------|--------|--------|
| JOR183_A13_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,6 | 7,448  |
| JOR183_A14_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,6 | 7,448  |
| JOR183_A15_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,7 | 7,5928 |
| JOR183_A18_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,4 | 7,7551 |
| JOR183_A19_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,4 | 7,4887 |
| JOR183_A2_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,5 | 7,3263 |
| JOR183_A20_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,5 | 8,065  |
| JOR183_A3_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,3 | 7,2156 |
| JOR183_A4_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,5 | 7,5086 |
| JOR183_A5_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,4 | 7,4597 |
| JOR183_A6_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,4 | 7,3887 |
| JOR183_A7_dolomita_primaria_MI-CRITO_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,4 | 7,5559 |

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| JOR183_A8_dolomita_primaria_MI-<br>CRITO_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__             | 1097,5 | 7,5427 |
| JOR183_A9_dolomita_primaria_MI-<br>CRITO_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__             | 1097,7 | 7,5593 |
| JOR188_A1_dolomita_suspeita_prima-<br>ria_MACROPELOIDE_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1098,7 | 7,1686 |
| JOR188_A10                                                                                   | 1099,4 | 7,1148 |
| JOR188_A11                                                                                   | 1099,5 | 7,0964 |
| JOR188_A12                                                                                   | 1099,4 | 7,111  |
| JOR188_A13                                                                                   | 1099,5 | 7,5644 |
| JOR188_A2                                                                                    | 1098,9 | 7,1974 |
| JOR188_A3                                                                                    | 1099,1 | 7,2381 |
| JOR188_A4                                                                                    | 1099,1 | 7,1097 |
| JOR188_A5                                                                                    | 1099,3 | 7,4495 |
| JOR188_A7                                                                                    | 1099,2 | 7,3818 |
| JOR188_A8                                                                                    | 1099,3 | 7,1406 |
| JOR188_A9                                                                                    | 1099,3 | 7,1217 |
| JOR188_B1                                                                                    | 1099,5 | 7,5644 |
| JOR188_B10                                                                                   | 1099,5 | 7,0472 |
| JOR188_B11                                                                                   | 1099,6 | 7,1674 |
| JOR188_B12                                                                                   | 1099,5 | 7,1972 |
| JOR188_B4                                                                                    | 1099,5 | 7,0375 |
| JOR188_B5                                                                                    | 1099,5 | 7,0832 |
| JOR188_B6                                                                                    | 1099,5 | 7,0035 |
| JOR188_B7                                                                                    | 1099,5 | 7,0749 |
| JOR188_B8                                                                                    | 1099,5 | 6,9492 |

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|-----------------------------------------------------------|--------|--------|
| JOR188_B9                                                 | 1099,5 | 7,0633 |
| JOR191_A1                                                 | 1099,5 | 6,9772 |
| JOR191_A10                                                | 1099,5 | 7,0796 |
| JOR191_A11                                                | 1099,6 | 7,1024 |
| JOR191_A12                                                | 1099,6 | 7,1707 |
| JOR191_A13                                                | 1099,5 | 7,1983 |
| JOR191_A14                                                | 1099,5 | 7,2254 |
| JOR191_A15                                                | 1099,5 | 7,3149 |
| JOR191_A16                                                | 1099,8 | 7,3422 |
| JOR191_A17                                                | 1099,5 | 7,2767 |
| JOR191_A18                                                | 1099,5 | 7,6941 |
| JOR191_A19                                                | 1099,4 | 7,8659 |
| JOR191_A2                                                 | 1099,6 | 7,1244 |
| JOR191_A20                                                | 1099,6 | 7,5813 |
| JOR191_A21                                                | 1099,6 | 7,2097 |
| JOR191_A22                                                | 1099,6 | 7,3262 |
| JOR191_A3                                                 | 1099,6 | 7,2319 |
| JOR191_A4                                                 | 1099,6 | 7,23   |
| JOR191_A5                                                 | 1099,6 | 7,2608 |
| JOR191_A6                                                 | 1099,6 | 7,1413 |
| JOR191_A7                                                 | 1099,6 | 7,0722 |
| JOR191_A8                                                 | 1099,5 | 7,1958 |
| JOR191_A9                                                 | 1099,5 | 7,1332 |
| G4_A1_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x  | 1099,7 | 5,6039 |
| G4_A11_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,8 | 5,4589 |

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| G4_A12_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,7 | 5,4985 |
| G4_A15_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,8 | 5,2321 |
| G4_A16_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,7 | 5,8798 |
| G4_A17_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,7 | 5,7137 |
| G4_A18_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,7 | 5,6749 |
| G4_A19_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,7 | 5,8499 |
| G4_A2_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x  | 1099,9 | 5,4709 |
| G4_A20_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,7 | 5,8405 |
| G4_A21_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,7 | 5,6727 |
| G4_A22_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1099,7 | 5,7417 |
| G4_A3_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x  | 1099,8 | 5,3932 |
| G4_A4_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x  | 1099,8 | 5,4269 |
| G4_A5_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x  | 1099,7 | 5,3119 |
| G4_A6_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x  | 1099,9 | 5,4069 |
| G4_A7_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x  | 1099,7 | 5,3934 |
| G4_A8_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x  | 1099,8 | 5,4627 |



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| G4_A9_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                     | 1099,9 | 5,4895 |
| G5 A9_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                     | 1099,3 | 5,7235 |
| G5 A1_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                     | 1099,2 | 5,8495 |
| G5 A2_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                     | 1099,2 | 5,5738 |
| G5 A3_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                     | 1099,3 | 5,588  |
| G5 A4_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                     | 1099,1 | 5,5838 |
| G5 A5_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                     | 1099,1 | 5,545  |
| G5 A6_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                     | 1099,1 | 5,6225 |
| G5 A7_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                     | 1099,2 | 5,5208 |
| G5 A8_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                     | 1099,2 | 5,6411 |
| G5 A9_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                     | 1099,2 | 5,6788 |
| G5 A10_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                    | 1099,2 | 5,5579 |
| G5 A11_macropeloide_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                    |        |        |
| G2B_B1_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1098,9 | 5,4079 |
| G2B_B10_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1098,9 | 5,5276 |

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| G2B_B11_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1099,2 | 5,4422 |
| G2B_B12_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1098,9 | 5,6659 |
| G2B_B13_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1098,8 | 5,5641 |
| G2B_B14_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1098,8 | 5,3487 |
| G2B_B15_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1098,9 | 5,6003 |
| G2B_B2_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1098,9 | 5,6165 |
| G2B_B3_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1098,9 | 5,4437 |
| G2B_B4_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1098,9 | 5,3494 |
| G2B_B5_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1099,2 | 5,4231 |
| G2B_B6_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1099,2 | 5,3528 |
| G2B_B7_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1098,9 | 5,3718 |
| G2B_B8_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1098,9 | 5,4207 |

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| G2B_B9_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1099,2 | 5,497  |
| G2B_C1_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1099,1 | 5,5554 |
| G2B_C10_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1099,1 | 5,4672 |
| G2B_C11_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1099,1 | 5,3058 |
| G2B_C12_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1098,9 | 5,4379 |
| G2B_C13_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1099,1 | 5,3011 |
| G2B_C14_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1098,9 | 5,2604 |
| G2B_C15_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____ | 1099   | 5,4348 |
| G2B_C2_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1099,1 | 5,5554 |
| G2B_C3_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1099,1 | 5,6062 |
| G2B_C4_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1099,2 | 5,45   |
| G2B_C5_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x_____  | 1099   | 5,6526 |

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| G2B_C6_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x____     | 1099,2 | 5,5371 |
| G2B_C7_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x____     | 1098,9 | 5,4819 |
| G2B_C8_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x____     | 1098,9 | 5,5762 |
| G2B_C9_PELOIDE_GRUMO_MA-<br>TRIZ_785nm_cen-<br>tro800_pt_1_2s_30ac_50x____     | 1099,1 | 5,6344 |
| TubA_gruome_DOLOMITE_PRIMARÁ-<br>RIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1099,2 | 5,7273 |
| TubB_gruome_DOLOMITE_PRIMARÁ-<br>RIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1099,3 | 5,6584 |
| TubC_gruome_DOLOMITE_PRIMARÁ-<br>RIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1099,2 | 5,506  |
| TubD_gruome_DOLOMITE_PRIMARÁ-<br>RIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1099,2 | 5,716  |
| TubE_gruome_DOLOMITE_PRIMARÁ-<br>RIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1099,3 | 5,6475 |
| TubF_gruome_DOLOMITE_PRIMARÁ-<br>RIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1099,3 | 5,6063 |
| TubH_gruome_DOLOMITE_PRIMARÁ-<br>RIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1099,2 | 5,6928 |
| TubJ_gruome_DOLOMITE_PRIMARÁ-<br>RIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x____ | 1099,3 | 5,753  |

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| TuGF_gruome_DOLOMITE_PRIMARÁ-<br>RIA_785nm_cen-<br>tro800_pt_1_5s_30ac_50x___ | 1099,3 | 5,664  |
| AM8_A10_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                | 1098,4 | 5,6631 |
| AM8_A11_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                | 1098,4 | 6,0145 |
| AM8_A12_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                | 1098,4 | 5,7103 |
| AM8_A13_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                | 1098,6 | 5,4079 |
| AM8_A14_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                | 1098,4 | 5,5605 |
| AM8_A15_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                | 1098,5 | 5,6077 |
| AM8_A2_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                 | 1098,4 | 5,7489 |
| AM8_A3_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                 | 1098,2 | 5,8027 |
| AM8_A4_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                 | 1098,3 | 5,8185 |
| AM8_A5_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                 | 1098,5 | 5,6627 |
| AM8_A6_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                 | 1098,3 | 5,6738 |
| AM8_A7_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                 | 1098,3 | 5,9495 |
| AM8_A8_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                 | 1098,3 | 5,8878 |
| AM8_A9_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x___                 | 1098,3 | 5,9063 |
| MA_A1_Macropeloide_grumo_peloi-<br>dal_532nm_centro800_pt_1_5s_30ac_5x___     | 1098,3 | 5,4151 |

|                                                                        |        |        |
|------------------------------------------------------------------------|--------|--------|
| MA_A10_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__   | 1098,3 | 5,7917 |
| MA_A11_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__   | 1098,2 | 5,8147 |
| MA_A12_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__   | 1098,2 | 5,5619 |
| MA_A2_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__    | 1098,2 | 5,8605 |
| MA_A3_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__    | 1098,3 | 5,6685 |
| MA_A4_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__    | 1098,3 | 5,5665 |
| MA_A5_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__    | 1098,3 | 5,7116 |
| MA_A6_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__    | 1098,3 | 5,7273 |
| MA_A7_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__    | 1098,3 | 5,5182 |
| MA_A8_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__    | 1098,3 | 5,6666 |
| MA_A9_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__    | 1098,3 | 5,6582 |
| MA_B1_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__    | 1098,2 | 5,7754 |
| MA_B10_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x____ | 1098,2 | 5,5967 |
| MA_B11_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x____ | 1098,2 | 5,6539 |
| MA_B12_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x____ | 1098,1 | 5,2181 |

|                                                                            |        |        |
|----------------------------------------------------------------------------|--------|--------|
| MA_B2_Macropeloide_grumo_peloidal_532nm_centro800_pt_1_5s_30ac_5x__        | 1098,2 | 5,6034 |
| MA_B4_Macropeloide_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x____ | 1098,3 | 5,8541 |
| MA_B5_Macropeloide_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x____ | 1098,3 | 5,7505 |
| MA_B6_Macropeloide_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x____ | 1098,3 | 5,601  |
| MA_B7_Macropeloide_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x____ | 1098,1 | 5,496  |
| MA_B8_Macropeloide_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x____ | 1098,1 | 5,5182 |
| MA_B9_Macropeloide_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x____ | 1098,2 | 5,6607 |
| MO_10_A1_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__             | 1097,9 | 5,5749 |
| MO_10_A10_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__            | 1098,2 | 5,2444 |
| MO_10_A12_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__            | 1098,1 | 5,4367 |
| MO_10_A13_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__            | 1098,2 | 5,5305 |
| MO_10_A14_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__            | 1098,2 | 5,6295 |
| MO_10_A15_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__            | 1098,3 | 5,3705 |
| MO_10_A2_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__             | 1098   | 5,5618 |

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|-----------------------------------------------------------------|--------|--------|
| MO_10_A3_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098   | 5,4877 |
| MO_10_A4_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,1 | 5,3117 |
| MO_10_A5_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,1 | 5,4123 |
| MO_10_A6_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,1 | 5,237  |
| MO_10_A7_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098   | 5,5206 |
| MO_10_A8_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,1 | 5,5592 |
| MO_10_A9_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,1 | 5,4459 |
| MO_10_B1_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098   | 5,4904 |
| MO_10_B10_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__ | 1098,1 | 5,3509 |
| MO_10_B2_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,1 | 5,9387 |
| MO_10_B3_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,3 | 5,6131 |
| MO_10_B4_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,3 | 5,739  |
| MO_10_B5_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,3 | 5,722  |
| MO_10_B6_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,4 | 5,4711 |
| MO_10_B7_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,3 | 5,3763 |
| MO_10_B8_grumo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__  | 1098,3 | 5,5039 |



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|----------------------------------------------------------------|--------|--------|
| MO_10_B9_grupo_peloidal_532nm_cen-<br>tro800_pt_1_5s_30ac_5x__ | 1098,2 | 5,371  |
| MO_2_A1                                                        | 1098,4 | 5,2844 |
| MO_2_A10                                                       | 1098,6 | 5,4888 |
| MO_2_A2                                                        | 1097,8 | 5,6049 |
| MO_2_A3                                                        | 1098,4 | 5,2915 |
| MO_2_A4                                                        | 1098,5 | 5,2075 |
| MO_2_A5                                                        | 1098,4 | 4,9922 |
| MO_2_A6                                                        | 1098,5 | 5,264  |
| MO_2_A7                                                        | 1097,6 | 6,4194 |
| MO_2_A8                                                        | 1098,4 | 5,4617 |
| MO_2_A9                                                        | 1098,5 | 5,6712 |
| MR_A1                                                          | 1098,2 | 5,3461 |
| MR_A10                                                         | 1098,2 | 5,4357 |
| MR_A12                                                         | 1098,1 | 5,7221 |
| MR_A13                                                         | 1098,2 | 5,6585 |
| MR_A2                                                          | 1098,3 | 5,4874 |
| MR_A3                                                          | 1098,2 | 5,4257 |
| MR_A4                                                          | 1098,2 | 5,29   |
| MR_A5                                                          | 1098,1 | 5,3979 |
| MR_A6                                                          | 1098,2 | 5,5008 |
| MR_A7                                                          | 1098,1 | 5,6344 |
| MR_A8                                                          | 1098,2 | 5,6061 |
| San_B1                                                         | 1098,4 | 5,4556 |
| San_B10                                                        | 1098,6 | 5,4953 |
| San_B11                                                        | 1098,6 | 5,7118 |
| San_B12                                                        | 1098,6 | 5,6418 |

|               |        |        |
|---------------|--------|--------|
| San_B13       | 1098,6 | 5,4533 |
| San_B2        | 1098,5 | 5,4747 |
| San_B3        | 1098,5 | 5,2334 |
| San_B4        | 1098,5 | 5,8334 |
| San_B5        | 1098,6 | 5,9161 |
| San_B6        | 1098,3 | 5,8355 |
| San_B7        | 1098,5 | 5,357  |
| San_B8        | 1098,5 | 5,5938 |
| San_B9        | 1098,5 | 5,3467 |
| TRF-03_A1     | 1097,1 | 5,3945 |
| TRF-03_A10    | 1097,5 | 5,5476 |
| TRF-03_A11    | 1097,3 | 5,2243 |
| TRF-03_A2     | 1097,3 | 5,2403 |
| TRF-03_A3     | 1097,4 | 5,2257 |
| TRF-03_A4     | 1097,4 | 5,2664 |
| TRF-03_A5     | 1097,3 | 5,4505 |
| TRF-03_A6     | 1097,3 | 5,3679 |
| TRF-03_A7     | 1097,5 | 5,2797 |
| TRF-03_A8     | 1097,1 | 5,5118 |
| TRF-03_A9     | 1097,4 | 5,2003 |
| Tubestone_A1  | 1098   | 5,7141 |
| Tubestone_A10 | 1098   | 5,9684 |
| Tubestone_A11 | 1098   | 5,7486 |
| Tubestone_A12 | 1098,1 | 5,7326 |
| Tubestone_A2  | 1098,1 | 5,6173 |
| Tubestone_A3  | 1098   | 5,7834 |
| Tubestone_A5  | 1098,2 | 5,5028 |

|                                                                           |                    |             |
|---------------------------------------------------------------------------|--------------------|-------------|
| Tubestone_A6                                                              | 1098               | 5,8291      |
| Tubestone_A7                                                              | 1097,8             | 5,5926      |
| Tubestone_A8                                                              | 1097,9             | 5,5456      |
| Tubestone_A9                                                              | 1097,9             | 6,0965      |
| Gypum pseudormorph                                                        | Raman Shift [1/cm] | FWHM [1/cm] |
| JBN38A_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                     | 1099,2             | 7,4089      |
| JBN38B_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                     | 1099,4             | 7,1898      |
| JBN38C_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                     | 1099,4             | 7,2431      |
| JBN38D_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                     | 1099,3             | 7,3383      |
| JBN38E_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                     | 1099,4             | 7,175       |
| JBN38F_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                     | 1099,4             | 7,299       |
| JBN38G_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                     | 1099               | 7,3139      |
| JBN38H_GYPSUM_CALCITA CON-<br>TATO785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1099,3             | 7,3555      |
| JBN38I_GYPSUM_CALCITA CON-<br>TATO785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1099,3             | 7,2947      |
| JBN38L_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                     | 1099,1             | 7,7781      |
| JBN38M_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                     | 1099               | 8,0104      |
| JBN38N_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                     | 1098,8             | 8,5534      |

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|----------------------------------------------------------------------|--------|--------|
| JBN38O_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                | 1099   | 9,0862 |
| JBN38S_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                | 1099,1 | 7,5358 |
| JBN38T_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                | 1099,2 | 7,3571 |
| JBN38U_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                | 1098,6 | 7,0762 |
| JBN48_A1_PSEUIDOGYP-<br>SUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__  | 1098,5 | 6,7043 |
| JBN48_A10_PSEUIDOGYP-<br>SUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,7 | 6,8242 |
| JBN48_A11_PSEUIDOGYP-<br>SUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,9 | 6,7961 |
| JBN48_A12_PSEUIDOGYP-<br>SUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,9 | 6,8528 |
| JBN48_A13_PSEUIDOGYP-<br>SUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1099   | 6,8221 |
| JBN48_A14_PSEUIDOGYP-<br>SUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,7 | 6,8747 |
| JBN48_A15_PSEUIDOGYP-<br>SUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,9 | 6,9261 |
| JBN48_A16_PSEUIDOGYP-<br>SUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,8 | 7,2693 |
| JBN48_A17_PSEUIDOGYP-<br>SUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__ | 1098,6 | 7,1776 |

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|--------------------------------------------------------------|--------|--------|
| JBN48_A18_PSEUIDOGYP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1098,9 | 6,9882 |
| JBN48_A2_PSEUIDOGYP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,8 | 6,8888 |
| JBN48_A3_PSEUIDOGYP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,7 | 6,8133 |
| JBN48_A4_PSEUIDOGYP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,6 | 6,859  |
| JBN48_A5_PSEUIDOGYP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,9 | 6,7596 |
| JBN48_A6_PSEUIDOGYP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,5 | 7,0605 |
| JBN48_A7_PSEUIDOGYP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,7 | 7,0145 |
| JBN48_A8_PSEUIDOGYP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,6 | 6,9124 |
| JBN48_A9_PSEUIDOGYP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1098,9 | 6,8918 |
| JOR41_A2_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x            | 1099,2 | 7,0475 |
| JOR41_B2_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x            | 1099,2 | 7,1595 |
| JOR41_C2_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x            | 1099,2 | 7,2972 |
| JOR41_D2_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x            | 1099,2 | 7,3133 |

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|---------------------------------------------------------------------------------------|--------|--------|
| JOR41_F2_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                                 | 1099,3 | 7,0981 |
| JOR41_G2_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                                 | 1099,4 | 6,8505 |
| JOR41_H2_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                                 | 1099,5 | 6,7993 |
| JOR41_I2_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                                 | 1099,4 | 6,8031 |
| JOR41_J2_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                                 | 1099,4 | 7,6459 |
| JOR41_L2_GYPSUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x                                 | 1087,5 | 5,2281 |
| JOR50A_dolomita_suspeita_gypsum_se-<br>cundaria_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1098,3 | 6,8175 |
| JOR50B_dolomita_suspeita_gypsum_secun-<br>daria_785nm_centro800_pt_1_5s_30ac_50x      | 1098,2 | 6,9448 |
| JOR50C_dolomita_suspeita_gypsum_secun-<br>daria_785nm_centro800_pt_1_5s_30ac_50x      | 1098,4 | 6,6644 |
| JOR50D_dolomita_suspeita_gypsum_se-<br>cundaria_785nm_cen-<br>tro800_pt_1_5s_30ac_50x | 1098,3 | 7,023  |
| JOR50E_dolomita_suspeita_gypsum_secun-<br>daria_785nm_centro800_pt_1_5s_30ac_50x      | 1098,3 | 6,793  |
| JOR50F_dolomita_suspeita_gypsum_secun-<br>daria_785nm_centro800_pt_1_5s_30ac_50x      | 1098,5 | 6,7008 |
| JOR58_A1_PSEUIDOGYP-<br>SUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                   | 1097,4 | 7,3436 |
| JOR58_A10_PSEUIDOGYP-<br>SUM_785nm_cen-<br>tro800_pt_1_5s_30ac_50x__                  | 1097,6 | 7,0224 |

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|--------------------------------------------------------------|--------|--------|
| JOR58_A11_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,7 | 7,4011 |
| JOR58_A12_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,6 | 7,2757 |
| JOR58_A13_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,8 | 7,2105 |
| JOR58_A14_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,8 | 7,2492 |
| JOR58_A15_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,8 | 7,3619 |
| JOR58_A16_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,8 | 7,2181 |
| JOR58_A2_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,5 | 7,3468 |
| JOR58_A3_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,5 | 7,252  |
| JOR58_A4_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,5 | 7,3446 |
| JOR58_A5_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,5 | 7,5682 |
| JOR58_A6_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,5 | 7,3326 |
| JOR58_A7_PSEUIDOGRP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__  | 1097,5 | 7,198  |

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|-------------------------------------------------------------|--------|--------|
| JOR58_A8_PSEUIDOGYP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,7 | 7,3439 |
| JOR58_A9_PSEUIDOGYP-SUM_785nm_cen-tro800_pt_1_5s_30ac_50x__ | 1097,6 | 7,1431 |
| JOR67_BB1_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x          | 1099,4 | 6,9447 |
| JOR67_BB10_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x         | 1099,7 | 7,0799 |
| JOR67_BB2_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x          | 1099,5 | 7,0908 |
| JOR67_BB3_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x          | 1099,6 | 7,2686 |
| JOR67_BB4_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x          | 1099,2 | 7,6771 |
| JOR67_BB5_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x          | 1099,7 | 7,3707 |
| JOR67_BB6_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x          | 1099,7 | 7,2145 |
| JOR67_BB7_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x          | 1099,9 | 7,3123 |
| JOR67_BB8_GYPSUM_785nm_cen-tro800_pt_1_5s_30ac_50x          | 1099,9 | 7,2829 |



## Supplementary Material 4- The XRD patterns for micro-drilled powders of cap dolostones samples

### Dolomicrite phase (DM)

Samples from the "JOR 49 Micrito" (example of the dolomicrite phase, DM), show this phase corresponds to stratiform doloboundstones with gypsum pseudomorph facies. This phase shows characteristic dolomite reflection peaks 104 ( $2\theta = 31.0^\circ$ ), 015 ( $2\theta = 41.0^\circ$ ), 021 ( $2\theta = 51.0^\circ$ ), and additional peaks around  $61.0^\circ$  (Fig. 8.1). The (104) reflection position of identified dolomite is around  $2\theta 31.0^\circ$ , suggesting that the dolomite has an average  $\text{MgCO}_3$  content consistent with typical dolomite structures. The intensity ratio of the weak d015 and d021 peaks indicates that the dolomite is well-ordered. The dolomite content estimated by the area of peak d104 is approximately 87.7 wt%. The XRD patterns also show peaks characteristic of disordered dolomite at 9.8%. These disordered dolomite peaks overlap with the ordered ones but show slightly different intensities, indicating some disorder in the crystal structure. Additionally, calcite is present in the sample, with the most intense peak observed at  $2\theta = 29.0^\circ$ , alongside other peaks at approximately  $39.0^\circ$ ,  $47.0^\circ$ , and  $48.0^\circ$  (Fig. 8.1). These calcite peaks suggest calcite contents up to 2.5%, confirming the presence of calcite in the sample. The relative intensities of these peaks indicate that the calcite is less prevalent than ordered and disordered dolomite in the sample.

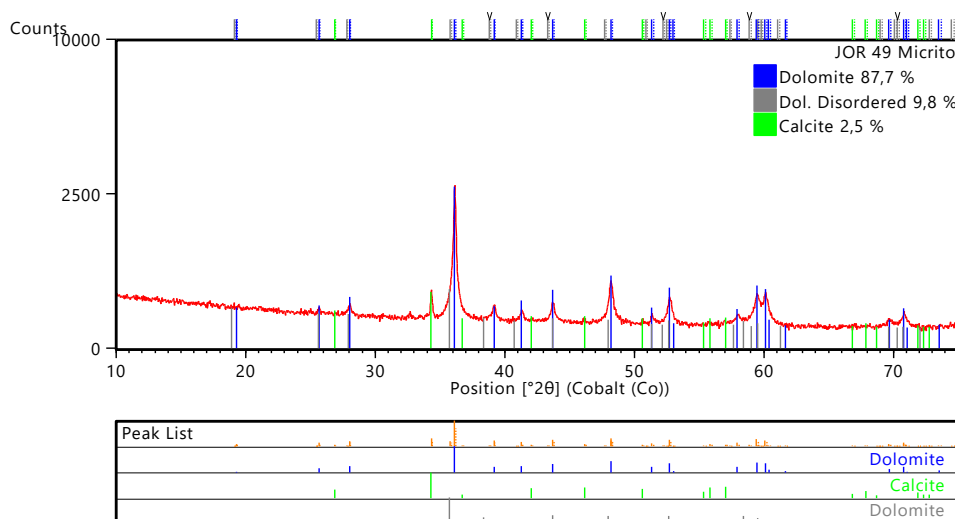


Figure 8.1- The XRD patterns for micro-drilled powders of dolomicrite (DM), dolomite, and calcite in varying proportions. Note that the dolomite content estimated by the area of peak d104 is approximately 87.7 wt%. The XRD patterns also show peaks characteristic of disordered dolomite at 9.8%. The lower part of the figure shows reflection positions for both dolomite and calcite, with dolomite peaks marked in blue, calcite peaks in green, and disordered dolomite marked in gray.

### Replacive Dolomite phase (RD)

Samples from the "JOR 7" (example of the replacive dolomite phase) This phase corresponds to stratiform doloboundstones with gypsum pseudomorphs facies. However, these samples correspond to the basal portion in contact with the diamictite. This portion exhibits textures that are more obliterated by neomorphism. This phase shows characteristic dolomite reflection peaks 104 ( $2\theta = 31.0^\circ$ ), 015 ( $2\theta = 41.0^\circ$ ), 021 ( $2\theta = 51.0^\circ$ ), and additional peaks around  $61.0^\circ$  (Fig. 2). The (104) reflection position of identified dolomite is around  $2\theta = 31.0^\circ$ , suggesting that the dolomite has an average  $\text{MgCO}_3$  content consistent with typical dolomite structures. The intensity ratio of the weak d015 and d021 peaks indicates that the dolomite is well-ordered. The dolomite content estimated by the area of peak d104 is approximately 90.9 wt%. XRD patterns also show peaks characteristic of calcite, with the most intense peak observed at  $2\theta = 29.0^\circ$ , alongside other peaks at approximately  $39.0^\circ$ ,  $47.0^\circ$ , and  $48.0^\circ$  (Fig. 2). These calcite peaks suggest calcite contents up to 9.1%, confirming the presence of calcite in the sample. The relative intensities of these peaks indicate that the calcite is less prevalent than dolomite in the sample.

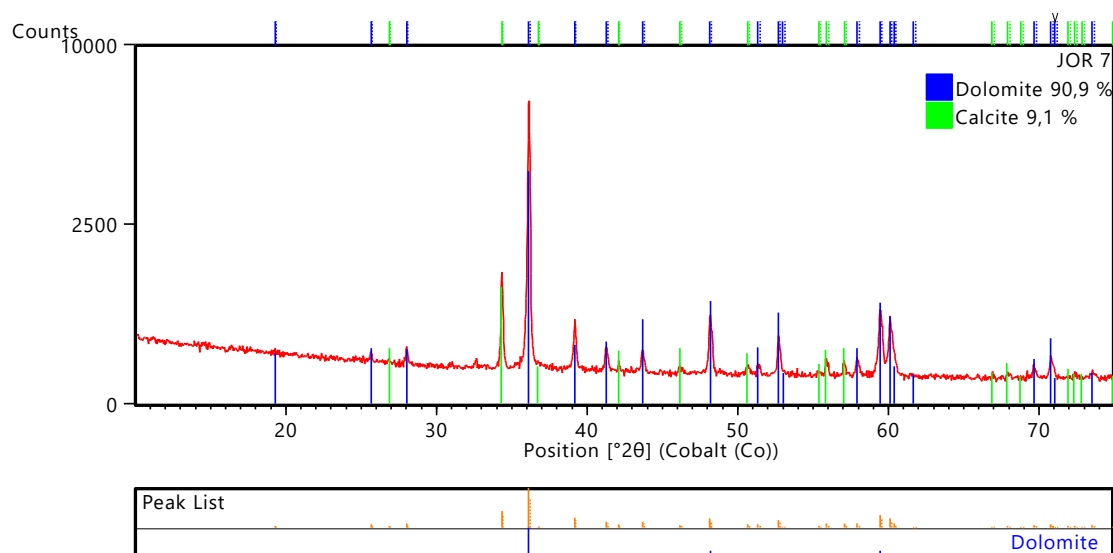


Figure 8.2- The XRD patterns for micro-drilled powders of dolomicrite (DM), dolomite, and calcite in varying proportions. Note that the content estimated by the area of peak d104 is approximately 90.9 wt%. Calcite peaks suggest that calcite contents are up to 9.1%. The lower part of the figure shows reflection positions for both dolomite and calcite, with dolomite peaks marked in blue, and calcite peaks in green.

### Dolomicrite phase (DM)

Samples from the "JOR 183" (example of the dolomicrite phase, DM). This phase corresponds to wave-rippled dolostone facies. This phase shows characteristic dolomite reflection peaks 104 ( $2\theta = 31.0^\circ$ ), 015 ( $2\theta = 41.0^\circ$ ), 021 ( $2\theta = 51.0^\circ$ ), and additional peaks around  $61.0^\circ$  (Fig. 8.3). The (104) reflection position of identified dolomite is around  $2\theta 31.0^\circ$ , suggesting that the dolomite has an average  $\text{MgCO}_3$  content consistent with typical dolomite structures. The intensity ratio of the weak 015 and 021 peaks indicates that the dolomite is well-ordered. The dolomite content estimated by the area of peak 104 is approximately 98.6 wt%. XRD patterns also show peaks characteristic of microcline, with peaks observed at approximately  $2\theta = 25.0^\circ$ ,  $30.0^\circ$ ,  $45.0^\circ$ , and  $60.0^\circ$  (Fig. 8.3). These microcline peaks suggest microcline contents up to 1.4% in the sample. The relative intensities of these peaks indicate that microcline is much less prevalent than dolomite in the sample.

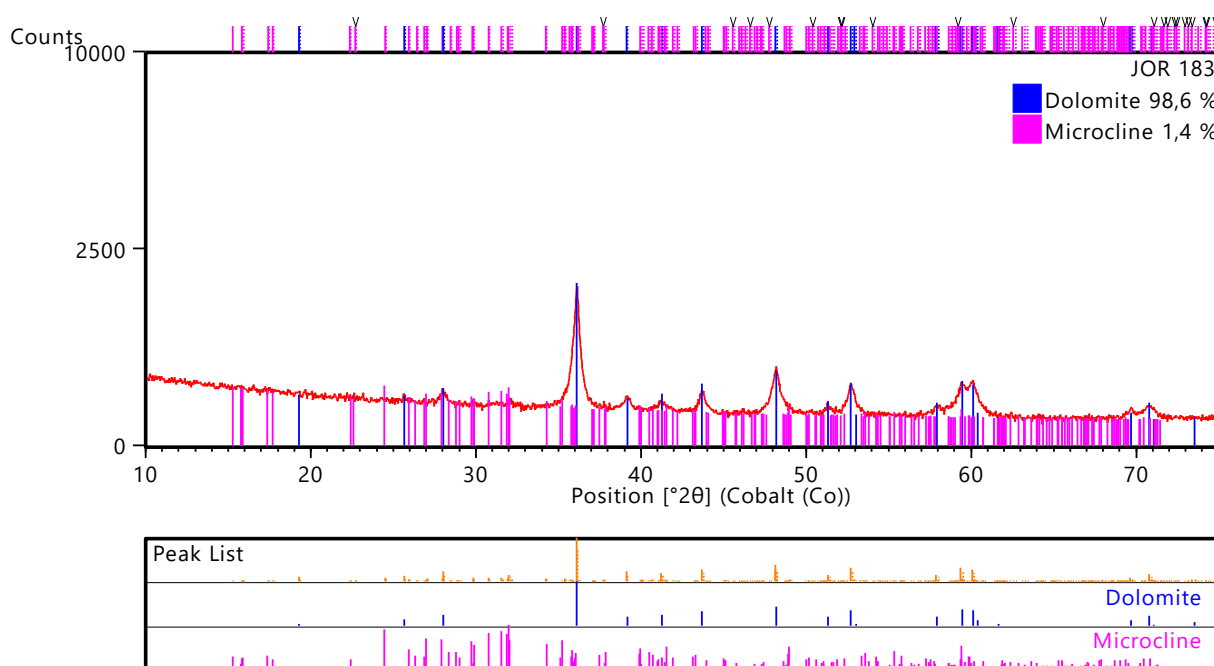


Figure 8.3- The XRD patterns for micro-drilled powders of dolomicrite (DM), dolomite, and calcite in varying proportions. Note that the content estimated by the area of peak d104 is approximately 98.6 wt%. Microcline peaks suggest that siliciclastic contents are up to 1.4 wt%. The lower part of the figure shows reflection positions for both dolomite and microcline, with dolomite peaks marked in blue, and microcline in pink

### Dolomicrite phase (DM)

Samples from the "TP" (example of Dolomicrite phase (DM)). This phase corresponds to dolomicrite doloboundstones with tubestone facies. This analysis pertains to the filling of tubestones and shows characteristic dolomite reflections. peaks 104 ( $2\theta = 31.0^\circ$ ), 015 ( $2\theta = 41.0^\circ$ ), 021 ( $2\theta = 51.0^\circ$ ), and additional peaks around  $61.0^\circ$  (Fig. 8.4). The (104) reflection position of identified dolomite is around  $2\theta 31.0^\circ$ , suggesting that the dolomite has an average  $\text{MgCO}_3$  content consistent with typical dolomite structures. The intensity ratio of the weak 015 and 021 peaks indicates that the dolomite is well-ordered. The dolomite content estimated by the area of peak 104 is approximately 59.4 wt%. XRD patterns also show peaks characteristic of calcite, with the most intense peak observed at  $2\theta = 29.0^\circ$ , alongside other peaks at approximately  $39.0^\circ$ ,  $47.0^\circ$ , and  $48.0^\circ$  (Fig. 8.4). These calcite peaks suggest calcite contents up to 40.6%, confirming the presence of calcite in the sample. The relative intensities of these peaks indicate that calcite is significantly prevalent in the sample. Additionally, minor phases such as smectite (Sme), gypsum (Gv), goethite (Gt), quartz (Qtz), potassium feldspar (Kfs), and hematite (Hem) are identified with their respective peaks, confirming the presence of these minerals in smaller quantities.

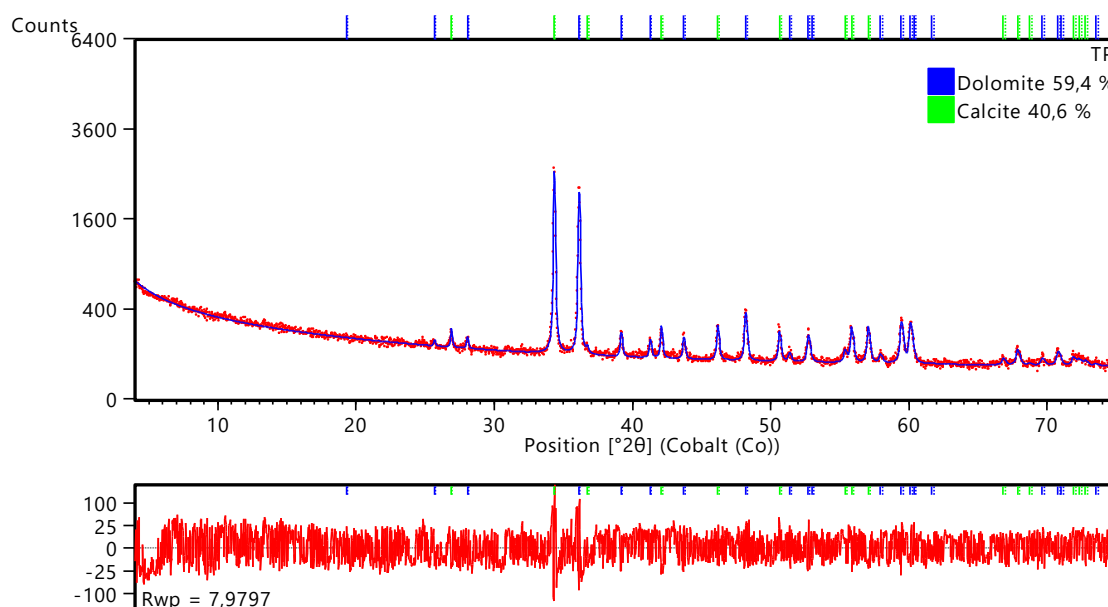


Figure 8.4- The XRD patterns for micro drilled powders of dolomicrite (DM) filling tubestone, dolomite, and calcite in varying proportions. Note that the content estimated by the area of peak d104 is approximately 59.4 wt%. Calcite peaks suggest that siliciclastic contents are up to 40.6 wt%. The lower part of the figure shows reflection positions for both dolomite and microcline, with dolomite peaks marked in blue, and calcite in green.

### Fibrous dolomite (FD)

Samples from the "JOR 79" (example of the fibrous dolomite) correspond to stratiform doloboundstones facies with gypsum pseudomorphs. This cement is described as a fibrous dolomite or gypsum pseudomorph. The XRD pattern for the "JOR 79" sample reveals prominent peaks indicating the presence of dolomite and calcite (Fig. 8.5). The characteristic dolomite reflection peaks include the 104 peaks at approximately  $2\theta = 31.0^\circ$ , the 015 peak at approximately  $2\theta = 41.0^\circ$ , the 021 peak at approximately  $2\theta = 51.0^\circ$ , and additional peaks around  $2\theta = 61.0^\circ$  (Fig. 8.5). These peaks suggest a well-ordered dolomite structure. The (104) reflection position at around  $2\theta = 31.0^\circ$  implies an average  $\text{MgCO}_3$  content typical of dolomite structures. The estimated dolomite content, based on the area of the peak d104, is about 74.2 wt%. Additionally, the XRD pattern displays peaks characteristic of calcite, with the most intense peak at approximately  $2\theta = 29.0^\circ$  and other peaks at approximately  $2\theta = 39.0^\circ$ ,  $47.0^\circ$ , and  $48.0^\circ$ . These peaks suggest calcite contents up to 25.8%.

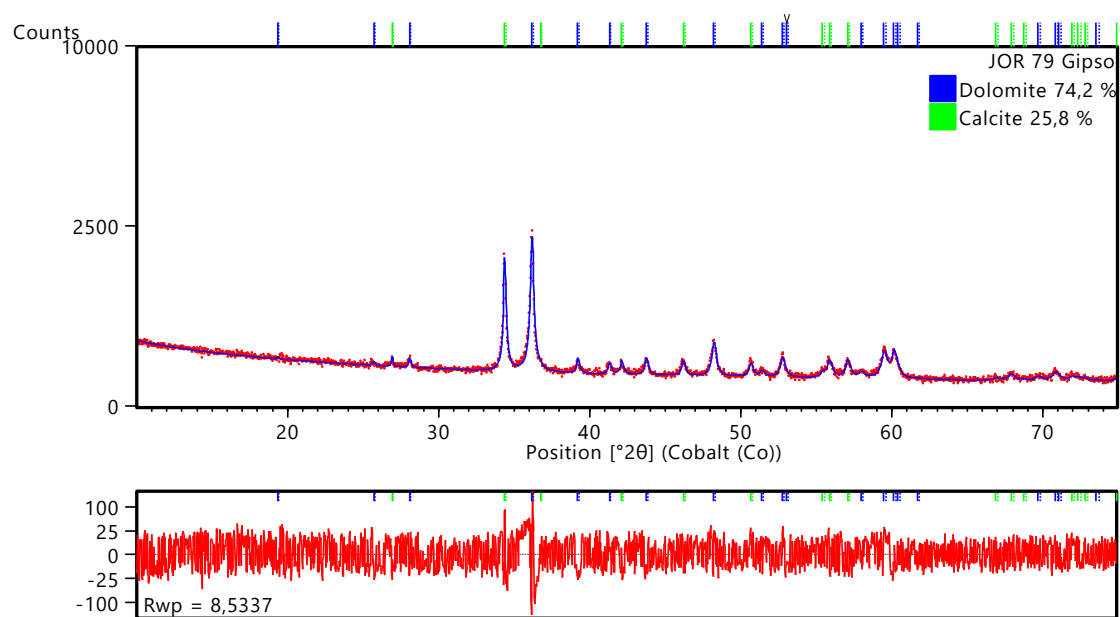


Figure 8.5- The XRD patterns for micro-drilled powders of fibrous dolomite (FD), dolomite, and calcite in varying proportions. Note that the content estimated by the area of peak d104 is approximately 74.2 wt%. Calcite peaks suggest that siliciclastic contents are up to 25.8 wt%. The lower part of the figure shows reflection positions for both dolomite and microcline, with dolomite peaks marked in blue, and calcite in green.

The dolomite samples' X-ray diffraction (XRD) patterns reveal significant crystallinity and mineral composition variations. These samples correspond to the dolomicrite phase (DM) related to the microbialites, with the only sample "JOR 183" corresponding to the reworking facies of the unit. The replacive dolomite is described throughout the succession; however, in some portions, the neomorphism process was more intense, as exemplified by sample "JOR 7".

- Sample "JOR 183"(DM) exhibits an FWHM of 0.340, displaying the lowest crystallinity among the dolomite samples, consisting of 98.6% dolomite and 1.4% potassium feldspar (Kfs).
- Sample "JOR 79" (DM) shows an FWHM of 0.312, containing 74.2% dolomite and 25.8% calcite.
- The "TP" (DM) sample has an FWHM of 0.148, showing a diverse composition of 59.4% dolomite and 40.6% calcite.
- Finally, "JOR 7" (RD) has the smallest FWHM of 0.126, indicating the highest crystallinity among the samples, with 90.6% dolomite and 9.4% calcite.

This comparative analysis highlights the variability in crystallinity and composition among the different samples, with "JOR 183" having the highest purity of dolomite and the lowest crystallinity. At the same time "TP" shows a significant presence of calcite and a high degree of crystallinity.

## 9 CAPÍTULO 9- CONCLUSÕES

A sucessão de capa carbonática Puga possui um papel-chave no entendimento das mudanças paleoclimáticas e paleoceanográficas durante a transição Criogeniano-Ediacarano na margem sul do Cráton Amazônico. Esta tese examinou detalhadamente as condições marinhas pós-glaciais e as dinâmicas ambientais durante essa transição, através de uma análise de alta resolução dos principais constituintes primários e secundários da capa carbonática Puga, bem como seus padrões de elementos de terras raras (REE+Y), metais traços autigenicos e isótopos radiogênico da capa carbonática Marinoana (~635 Ma). Os padrões de REE+Y observados na capa carbonática Puga oferecem importantes indicativos das condições marinhas após o evento *Snowball Earth*. Os baixos índices de Y/Ho capa dolomitica sugerem uma diluição da composição da água do mar devido ao influxo de água de degelo dos continentes. Em contraste, altas razões de Y/Ho e anomalias positivas de Eu/Eu\* nas dolomititas basais indicam a ressurgência de águas hipersalinas influenciadas por fluidos hidrotermais. Esses dados sugerem que a desestratificação oceânica está associada à circulação oceânica e ao ajuste isostático glacial (GIA), com uma redução no influxo de siliciclásticos apoiando um modelo de escassez siliciclástica.

Os dados isotópicos de Nd radiogênico, combinados com os isótopos de  $^{87}\text{Sr}/^{86}\text{Sr}$  e  $\delta^{13}\text{C}$ , revelam mudanças nas fontes no ambiente marinho raso durante a precipitação da capa dolomítica, possibilitando discernir padrões nas contribuições do intemperismo continental, circulação oceânica e paleoprodutividade. Observou-se um aumento consistente nos valores de  $\epsilon\text{Nd}(t)$  de aproximadamente -14 para -6 e  $^{87}\text{Sr}/^{86}\text{Sr}$  menos radiogênico nas porções superiores do depósito, indicativo de uma influência terrestre decrescente e um fortalecimento da exportação de água marinha através de processos de ressurgência. Estas variações nas fontes de intemperismo e na troca de massas de água com o oceano aberto são fatores chave que influenciam as flutuações temporais nos valores de  $\epsilon\text{Nd}(t)$  e nas razões de  $^{87}\text{Sr}/^{86}\text{Sr}$  observadas nas águas da plataforma continental e nas misturas de massas de água associadas ao processo de ressurgência marinha. As condições marinhas rasas durante o início da transgressão são atribuídas ao recuo local das camadas de gelo (*ice gravite*), levando à elevação contínua da zona costeira, declínio relativo do nível do mar, e à criação de uma plataforma isolada protegida pela dinâmica oceânica. Fácies indicativas de ilha barreira não foram observadas na sucessão de plataforma estudada, indicando que morfologias irregulares de diamicton podem ter criado áreas protegidas contra a ação de ondas. O contato deformado diamictito-capas dolomíticas indica rápida acumulação de dolomicrita depositada sobre um diamicton ainda plástico ligado a um evento de escala regional compatível com ajustes isostáticos glaciais/gravidade do gelo na zona costeira. O substrato diamicton foi colonizado por comunidades microbianas em águas

estratificadas e rasas, com águas límpidas, evidenciadas pelos baixos constituintes siliciclásticos e ação mínima das ondas, estas condições associadas aos nutrientes associados a água de degelo, favoreceram a alta produtividade orgânica culminando nos estromatólitos gigantes nas áreas costeiras do sul do Cráton Amazônico.

Os proxies Mo, U, V, Cr, Ni e Co indicam que os microbialitos na capa dolomítica se formaram sob condições predominantemente oxigenadas. Existia uma ligação direta entre as comunidades microbianas e a produção inicial de oxigênio logo após a glaciação Marinoana. E o fim destas condições ideais para proliferação das comunidades estaria relacionada a persistência do estresse ecológico associados principalmente à ação hidrodinâmica associado a ação de onda, e à rápida subida do nível do mar. O aumento contínuo do nível do mar levou ao afogamento das regiões costeiras e causou uma rápida modificação do ciclo biogeoquímico sob condições disóxicas. A concentração de Mg permaneceu constante durante a restrição das condições paleoambientais nas plataformas dolomíticas rasas. Durante esta fase, as comunidades microbianas tiveram papel crucial no aumento da alcalinidade da água produzindo EPS para superar o efeito de hidratação do  $Mg^{2+}$  e fornecendo condições cinéticas para a nucleação de uma protodolomita desordenada, tornando-se progressivamente mais ordenada e cristalina com o soterramento. A rápida elevação do nível do mar (*long term-transgression*) facilitou a dispersão de íons Mg, e o declínio das comunidades microbianas é associado ao aumento da turbidez pelo influxo de siliciclásticos, registrado principalmente na deposição de margas dolomíticas sobre os estromatólitos gigantes, levando à interrupção definitiva da precipitação de dolomita. A turbidez inibiu parcialmente a entrada de luz para o ciclo biogeoquímicos dos microorganismos bentônicos causando a supressão da vida microbiana. Estas condições precederam a mudança da fábrica carbonática, um prelúdio para o declínio total da estratificação marinha e da expansão térmica dos oceanos, abruptamente substituída por mares supersaturados de  $CaCO_3$  com precipitação maciça de aragonita.

A pesquisa desenvolvida nesse programa de doutorado forneceu informações e dados valiosos sobre a complexa interação dos processos paleoambientais durante a mistura de água de degelo e água do mar, impactando os ciclos biogeoquímicos relacionados a rápida recuperação da bioprodutividade primária. Esse modelo paleoceanográfico aprimorou a compreensão das flutuações climáticas pré-cambrianas da dinâmica paleoambientais do início do Ediacarano. A análise desses cenários geológicos anômalos do Pré-Cambriano, pelos quais a Terra passou, com registros de climas extremos e o desenvolvimento de vida extremófila em ambientes estressantes, fornece um arcabouço geológico-biológico robusto que pode ser usado pela humanidade para o entendimento de outras superfícies planetárias.



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UNIVERSIDADE FEDERAL DO PARÁ  
INSTITUTO DE GEOCIÊNCIAS  
PROGRAMA DE PÓS-GRADUAÇÃO EM GEOLOGIA E GEOQUÍMICA

## PARECER

### Sobre a Defesa Pública da Tese de Doutorado de RENAN FERNANDES DOS SANTOS

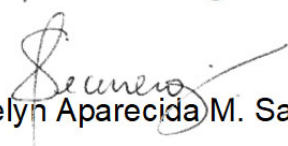
A banca examinadora da Tese de Doutorado de **RENAN FERNANDES DOS SANTOS** orientando do Prof. Dr. Afonso Cesar Rodrigues Nogueira (UFPA), com coorientação do Prof. Dr. Pierre Sansjofre (MNHN, IPMC, Sorbonne, Univ. Paris, Fr), e composta pelos professores doutores Evelyn Aparecida M. Sanchez (UFVJM), Marly Babinski (USP), Ricardo Ivan F. Trindade (USP), Jean Michel Lafon (UFPA) após apresentação da sua tese intitulada “**A CAPA CARBONÁTICA DO SUL DO CRÁTON AMAZÔNICO: MULTIPROXIES APLICADOS NA RECONSTITUIÇÃO PALEOCEANOGRÁFICA E GEOBIOLÓGICA DO INÍCIO DO EDIACARANO**”, emite o seguinte parecer:

O candidato realizou sua apresentação de forma clara, bem organizada e segura no tempo estipulado. Na arguição mostrou domínio da temática abordada e respondeu às perguntas formuladas pela banca de forma circunstanciada e segura. O trabalho escrito foi apresentado na forma de cinco artigos, sendo um já publicado e dois submetidos a periódicos de impacto internacional, estando os dois outros ainda em elaboração. Dessa forma, o documento atende plenamente às exigências de uma tese de doutorado.

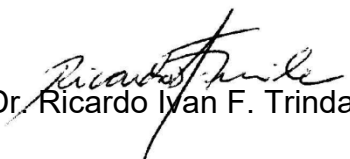
Finalmente, a banca examinadora decidiu por unanimidade aprovar a tese de doutorado. Considerando a qualidade científica do trabalho, a banca examinadora confere a **Aprovação com Distinção**.

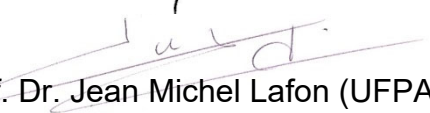
Belém, 30 de agosto de 2024

  
Prof. Dr. Afonso Cesar Rodrigues Nogueira (Orientador-UFPA)

  
Prof.ª Dr.ª Evelyn Aparecida M. Sanchez (UFVJM)

  
Prof.ª Dr.ª Marly Babinski (USP)

  
Prof. Dr. Ricardo Ivan F. Trindade (USP)

  
Prof. Dr. Jean Michel Lafon (UFPA)