UNIVERSIDADE DE SÃO PAULO
INSTITUTO DE GEOCIÊNCIAS

**The nitrogen biogeochemical cycle on Ediacaran rocks: A study on
carbonates from the Bambuí Group, São Francisco Basin**

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Dissertation presented to the Geosciences
Geochemistry and Geotectonics Graduate Program

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Deixe que o tempo passe e já veremos o que traz.
Gabriel Garcia Márquez

RESUMO

A transição Ediacarano-Cambriano é marcada pela diversificação dos metazoários. No entanto, isso não é observado nas rochas do Grupo Bambuí, no leste do Brasil, que, apesar da sua idade, possuem um pobre e escasso registro fóssilífero. As razões que levaram este ambiente a ser impróprio para o florescimento de vidas complexas nesta bacia progressivamente restrita ainda estão sendo investigadas. Assim, para compreender melhor as condições ambientais durante a deposição do Grupo Bambuí, este trabalho traz dados obtidos nas duas primeiras sequências de 2ª ordem. Isótopos estáveis de nitrogênio são a única ferramenta que permite reconstruir ciclos do N em tempos passados. Este elemento é uma parte essencial da vida e seus isótopos são úteis para investigar a estrutura redox de uma coluna de água, já que a estabilidade das espécies de N são condicionadas pela disponibilidade de oxigênio no ambiente. Neste trabalho, é descrita uma excursão $\delta^{15}\text{N}$ positiva no primeiro trato de sistema transgressivo da bacia. Neste ponto, o mar que deu origem às rochas do Grupo Bambuí ainda estava conectado ao oceano e essa excursão pode ser interpretada como um evento de aumento da oxigenação do mar, pois o aumento dos valores de $\delta^{15}\text{N}$ indica que a etapa dominante do ciclo do N foi da fixação direta do N_2 para assimilação do NO_3^- . Já no início do trato de mar alto, os dados de $\delta^{15}\text{N}$ mostram que o reservatório de nitrato que se estabeleceu durante a transgressão persistiu, entretanto, conforme a restrição da bacia progrediu, o nitrato tornou-se escasso e a fixação de N_2 passou a ser o mecanismo dominante de aquisição de N pelos microrganismos. Por fim, os dados de $\delta^{15}\text{N}$ da segunda sequência de 2ª ordem apontam novamente para a existência de um reservatório de nitrato durante este intervalo, porém não tão grande ou estável quanto o da primeira transgressão. Logo, os dados de $\delta^{15}\text{N}$ mostram que durante a deposição das unidades basais do Grupo Bambuí, a fixação de N_2 e a assimilação de NO_3^- alternaram-se como o mecanismo dominante do ciclo de N. É importante ressaltar que a instabilidade do ciclo do nitrogênio, das condições redox e a escassez de nitrato, especialmente durante a deposição do trato de mar alto tardio, podem ter afetado o desenvolvimento de formas de vida complexas.

Palavras-chave: isótopos de nitrogênio, ciclo biogeoquímico, Ediacarano-Cambriano, paleoambiente, quimioestratigrafia, Grupo Bambuí

ABSTRACT

The Ediacaran-Cambrian transition is marked by the diversification of metazoans. However, this is not true for the Bambuí Group, South-East Brazil, in which, despite its age, is almost fossil-barren. The reasons for such inhospitable conditions for the development of complex life forms in this progressively restricted foreland basin in the core of the West Gondwana continent are still being investigated. Thus, to enhance the comprehension of environmental conditions during the deposition of this basin, this work brings $\delta^{15}\text{N}_{\text{bulk}}$ data from rocks of its two lowermost 2nd-order sequences. Stable nitrogen isotopes are the only tool that allows the rebuilding of past N-cycles, and not only this is element is an essential part of life, they are a useful proxy to investigate the redox structure of the water column as the stability of N species are conditioned by the availability of oxygen in the environment. Here, a positive $\delta^{15}\text{N}$ excursion in the first transgressive system tract of the basin is reported, suggesting that the Bambuí basin was still connected to the global ocean. This excursion is interpreted as an event of increasing oxygenation of the Bambuí sea, as the increment of $\delta^{15}\text{N}$ values indicates that the dominant path of the N-cycle went from N_2 direct fixation to NO_3^- assimilation. At the Early Highstand System Tract $\delta^{15}\text{N}$ values show that the nitrate pool that was established during the transgression persisted, however, as the restriction of the basin progressed, nitrate became scarce and N_2 fixation became the main form of acquisition of N by microorganisms. Finally, $\delta^{15}\text{N}$ data from the second 2nd-order sequence points again to the existence of a nitrate pool during this interval, however, not as big or stable as the one from the first transgression. Hence, the data show that during the deposition of the basal Bambuí Group rocks, N_2 fixation and NO_3^- assimilation alternated as the dominant path of the N cycle. Importantly, the instability of the N-cycle and redox conditions plus the scarcity of nitrate, especially during the deposition of the late highstand system tract, might have affected the development of complex life forms.

Keywords: Nitrogen isotopes, biogeochemical cycle, Ediacaran-Cambrian, paleoenvironments, chemostratigraphy, Bambuí Group

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1 INTRODUCTION

1.1 Introduction

The Neoproterozoic (1000-541 Ma) is the last era before the Phanerozoic and it comprises a remarkable time for the Earth and its systems. In this era, Earth experienced a rise in its oxygen levels (Canfield et al., 2007; Och and Shields-Zhou, 2012; Ader et al., 2014), global glaciations (Marinoan and Sturtian) (Hoffman, 1998), biogeochemical turbulences (Halverson et al., 2010) and assemblage/break-up of supercontinents (Merdith et al., 2017). However, the most astonishing event of Neoproterozoic, the emergence of the metazoans (Ogg et al., 2016), happened in its last period, the Ediacaran, and perhaps it was a consequence of the previously mentioned events (Canfield et al., 2007; Scott et al., 2008).

The Ediacaran (635-541 Ma) starts after the Marinoan glaciation (~650-635 Ma) (Calver et al., 2013), which took place by the end of the Cryogenian (720-635 Ma) (Ogg et al., 2016). Although the Ediacaran does not register a global glaciation, it does register a regional one, named Gaskiers (~579 Ma) (Pu et al., 2016). Also, at this period, there is the largest negative carbon isotope excursion ever found, the Shuram-Wonoka excursion (Calver, 2000; Le Guerroué et al., 2006), which took place between 560-550 Ma and reached $\delta^{13}\text{C}_{\text{carb}}$ values as low as -12‰ (Minguez et al., 2015). Such an unique $\delta^{13}\text{C}_{\text{carb}}$ signature displays that something unusual happened and affected the global carbon cycle during that time. Furthermore, other geochemical proxies, such as strontium and sulfur isotopes show unique trends during the late Neoproterozoic (Halverson et al., 2010; Och and Shields-Zhou, 2012). Geochemical data are especially useful in the Precambrian. Since fossil record is rare, chemical fingerprints can be used to establish correlations, which is called chemostratigraphy. Moreover, stable isotopes are the most used tool for that purpose (Weissert et al., 2008). That said, this work aims to provide nitrogen isotopic data ($\delta^{15}\text{N}$) for the Western Gondwana Ediacaran-Cambrian carbonates of the Bambuí Group, Brazil.

Nitrogen is an important component of life and its biogeochemical cycle exerts a crucial role in primary productivity. In marine ecosystems, the availability of N species is controlled by the redox structure of the water, so are the reactions of the metabolic pathways performed by bacteria in order to assimilate nitrogen (Ader et al., 2016). Since these reactions impart different fractionation of N that is then preserved on the rock register, $\delta^{15}\text{N}$ values have been used to reconstruct the biogeochemical cycle of this element and also to infer water column redox structure conditions. However, there are few $\delta^{15}\text{N}$ data published in

sedimentary sequences of Western Gondwana (Beaumont and Robert, 1999; Ader et al. 2014; Godfrey and Falkowski, 2009) and Ediacaran-Cambrian in general, most of it is in South China (e.g., Wang et al., 2013; Chen et al., 2019; Xu et al., 2020). The $\delta^{15}\text{N}$ studies made in South China helped to understand how to apply N isotopic data to understand biological and environmental conditions. However, the relationship between nitrogen and the Cambrian explosion remains debated (e.g., Xu et al., 2020). Hence, this work brings $\delta^{15}\text{N}$ data applied to a geological setting that remained barren even during the Cambrian explosion, the Bambuí Group, in order to investigate if the N cycle played a role in the inhospitality of this environment.

The Bambuí Group is a Neoproterozoic unit situated in the São Francisco Craton (Dardenne, 1978; Reis et al., 2017) that was deposited in a foreland basin, which was generated in response to the uplift of the Brasília and Araçuaí belts. This group encompasses carbonates and siliciclastic rocks that were deposited on top of glaciogenic units (Martins-Neto and Hercos, 2002; Martins-Neto, 2009; Alkmim and Martins-Neto, 2012; Reis and Alkmim, 2015) and lately, it has been a matter of intense research regarding its paleogeographic evolution, its age and fossil record (e.g. Uhlein et al., 2016, 2017, 2019; Paula-Santos et al., 2017, 2018, 2020; Guacaneme et al., 2017; Paula-Santos and Babinski, 2018; Caxito et al., 2018; Okubo et al., 2018; Crockford et al., 2019; Hippertt et al., 2019; Caetano-Filho et al., 2019, 2021). It was recently proposed, based on geochronological data and C and Sr isotopic analyses that the Bambuí basin started as a sea connected to the global ocean that later evolved to a restricted environment (Paula-Santos et al., 2015, 2017), which conditioned its peculiar features, such as the absence of complex life forms (Hippertt et al., 2019; Paula-Santos, 2017), very high $\delta^{13}\text{C}_{\text{carb}}$ values (Iyer et al., 1995; Martins and Lemos, 2007; Kuchenbecker et al., 2016b; Guacaneme et al., 2017; Uhlein et al., 2019; Caetano-Filho et al., 2019, 2021) and anoxia (Paula-Santos et al., 2017; Uhlein et al., 2019; Hippertt et al., 2019). To contribute to this debate, here, $\delta^{15}\text{N}$ have been applied for the first time to three sections (Arcos, Well 1, Januária) that were already the object of study for other techniques, in order to establish relationships between nitrogen data, anoxia and life in a restricted environment in the core of West Gondwana.

1.2 Aims

- To generate the first nitrogen isotopic data in limestones of the Bambuí Group in order to understand how the biogeochemical cycle of this element operated in this geological setting and also to correlate the cycle with redox changes in the water column;

- To combine the obtained $\delta^{15}\text{N}$ data with chemical variations that occurred in the Neoproterozoic oceans, in order to evaluate the hypothesis that the Bambuí Group was deposited in a restricted sea environment;
- To investigate the nutrient distribution and temporal evolution in the Ediacaran-Cambrian São Francisco Basin and evaluate the way they have influenced life and possibly impeded the Cambrian explosion in this particular setting.

2 GEOLOGICAL SETTING

2.1 The São Francisco Craton

The São Francisco Craton (SFC) (Fig 2.1) (Almeida, 1977) is a tectonic entity located in the central-east of Brazil. The SFC is composed of Archean and Paleoproterozoic rocks, which are covered by units younger than 1.8 Ga, they are distributed in three tectonic domains: The São Francisco Basin, the Paramirim aulacogen and the Recôncavo-Tucano-Jatobá rift. Completing its tectonic frame, the craton is limited by Neoproterozoic belts (Sergipano, Riacho do Pontal, Brasília, Ribeira, Rio Preto and Araçuaí) (Fig. 2.1) that verge to the interior of the craton (Alkmim and Marshak, 1998; Alkmim, 2004; Alkmim et al., 2006; Heilbron et al., 2017). The São Francisco Basin, especially the Bambuí Group, which is the focus of this study, will be detailed below.

2.2 The São Francisco Basin

The São Francisco basin (SFB) occupies a large area on the São Francisco Craton. It has more than 350,000 km² and it displays an N-S trend (Fig. 2.1). SFB is a typical intracratonic basin and it encompasses many filling cycles that were developed for 1.4 Ga (from the Mesoproterozoic to the Phanerozoic) and mark tectonic and climate events that the basin recorded.

The tectonic compartmentation of the basin possesses large Proterozoic rifts and the most striking is the Pirapora Aulacogen, which is a NW-trend structure bounded by the Januária High to the North and the Sete Lagoas High to the South (Reis et al., 2017). It seems that rock strata older than 1.6 Ga is present in the aulacogen, which asserts that it was developed at an early stage of the SFB. However, seismic data also suggests that this structure remained positive during the Neoproterozoic. The basement highs previously mentioned are exposed in few areas and apparently were formed at an initial stage of the SFB as well, remaining as positive entities throughout the basin history (Reis and Alkmim, 2015; Reis and Suss, 2016; Reis et al., 2017). Other tectonic elements present in the basin are the Neoproterozoic marginal fold-thrust belts, which also limit it: the Brasília Belt to the west, the Araçuaí belt to the east and the Rio Preto belt to the North. The former and the second remarkably influenced the basin, incorporating and deforming its rocks at their external sections. Yet, the central portions of the São Francisco Basin remained undeformed. The other limits of the basin are an erosional unconformity to the south, which exposes Archean-Paleoproterozoic assemblages of the basement, and the Paramirim Corridor, a Neoproterozoic

deformation zone (Cruz and Alkmim, 2006, 2017), to the northeast (Alkmim and Martins-Neto, 2001; Reis et al., 2017). The basin also exhibits Cretaceous structures that were formed during the opening of the South Atlantic Ocean. These structures comprise Neoproterozoic thrusts-faults that were reactivated as grabens due to extensional tensions and folds and faults that were generated due to the emplacement of volcanic rocks (Reis and Alkmim, 2015).

Figure 2.1: The São Francisco Craton and the São Francisco Basin. Studied sections: A – Arcos; W- Well 1; J – Januária. Modified from Caetano-Filho et al. (2019).

2.2.1 Mesoproterozoic - The Espinhaço Supergroup

This unit represents a rift basin-fill succession and it is laterally associated with a passive margin that was developed at the western boundary of the SFC plate. The dominant lithologies are continental siliciclastic packages that laterally grades to marine deposits

(pelites, sandstones and carbonates). Considering this, the Espinhaço Supergroup is interpreted as a rift that evolved to a passive margin, although there is some discussion regarding this topic. Aeolian sandstones (Galho do Miguel Formation) cover the rift sediments, marking the beginning of thermal subsidence that eventually led to a marine incursion. During the marine stage of the basin, there were series of regressive-transgressive movements that are registered in the carbonate and siliciclastic rocks of the Conselheiro da Mata Group, which is divided into Santa Rita, Córrego do Borges, Córrego da Bandeira, Córrego Pereira and Rio Pardo Grande formations (Alkmim and Martins-Neto, 2001; Reis et al., 2017). Provenance studies for detrital zircons of the SE at the São Francisco basin indicate that the deposition of the sediments occurred between 1800 and 900 Ma (Chemale et al., 2012; Guadagnin et al., 2015; Kuchenbecker et al., 2015).

2.2.2 Early Neoproterozoic – Jequitaí Formation

The Jequitaí Formation is a glacial unit (Uhlein et al., 1999, 2016; Cukrov et al., 2005) that reaches more than 150 m of thickness at some portions and its most abundant lithology are diamictites. Also, subordinated intercalation of sandstone and pelites and alternation of siltstones and pebble-sized dropstones of quartzites occurs (Uhlein et al., 2016). The age of the Jequitaí Formation and its stratigraphic position are still debated. Some works argue that the unit is Cryogenian and that its diamictites are not the basal rocks of the overlying Bambuí Group (Vieira et al., 2007b; Kuchenbecker et al., 2011; Babinski et al., 2012; Reis and Suss, 2016), while others reason that Jequitaí rocks are late-Cryogenian to early Ediacaran and comprises the basal unit of Bambuí (Caxito et al., 2012, 2018; Uhlein et al., 2016; Perrella Júnior et al., 2017).

2.2.3 Late Neoproterozoic – Bambuí Group

The Bambuí Group (BG) outcrops in a large area of the São Francisco basin (Fig. 2.1). It encompasses carbonates, pelites and sandstones and minor occurrences of conglomerates are reported (Dardenne, 1978; Reis et al., 2017; Uhlein et al., 2017). The Bambuí Group age is still disputed, and this will be discussed further in this text. The BG represents a marine foreland basin that was generated in response to the uplift of the Brasília and Araçuaí belts, in the west and east of SFC, respectively, during the Brasiliano event (Alkmim and Martins-Neto, 2001; Reis et al., 2017). Seismic sections revealed the group has a wedge-shaped geometry, being thinner at the east of the basin and reaching about 3000 m of thickness to the

west (Martins-Neto, 2009; Reis and Suss, 2016; Reis et al., 2017). The basin can be divided into two major domains: a foredeep to the west and a forebulge to the east. The depocenters of these domains were largely controlled by the evolution of the Brasília belt (Martins-Neto, 2009; Reis and Suss, 2016; Uhlein et al., 2017). The sediment provenance of the the Bambuí Group is represented by the Brasília and Araçuaí thrust-belts and older Archean and Proterozoic units (Castro and Dardenne, 2000; Uhlein et al., 2017; Kuchenbecker et al., 2020).

2.2.3.1 Litho and Sequence Stratigraphy of the Bambuí Group

Dardenne (1978) updated the work done by Costa and Branco (1961) and divided the Bambuí Group into six units: a diamictite at its base which is covered by the Sete Lagoas, Serra de Santa Helena, Lagoa do Jacaré, Serra da Saudade and Três Marias formations. Dardenne (1978) considers that the basal unit of the Bambuí Group is the Jequitaiá Formation. However, in this work, the basal unit is considered to be the Carrancas Formation (following Vieira et al., 2007; Kuchenbecker et al., 2011, 2016b; Reis and Suss, 2016; Reis et al., 2017; Caetano-Filho et al., 2019), yet, the relationship between the Jequitaiá and Carrancas diamictites is still discussed, as well as their age. Other units of the group are the Samburá (Barbosa et al., 1970), Lagoa Formosa (Seer et al., 1989) and Gorutuba formations (Kuchenbecker et al., 2016a) (Fig. 2.2). Regarding the sequence stratigraphy of the Bambuí basin, following concepts defined by Catuneanu et al. (2005, 2011, 2012), the group is interpreted as a 1st-order sequence that was subdivided into four 2nd order shallowing upward sequences (Fig. 2.2) (Martins-Neto, 2009; Reis and Alkmim, 2015).

The basal 2nd-order sequence comprises the Carrancas Formation and the base of the Sete Lagoas Formation. The Carrancas Formation comprises conglomerates with a sandy-calcareous matrix and clasts of gneiss, dolostone, limestone, granite and quartz. This formation used to be correlated to the glacial Jequitaiá Formation (Martins-Neto et al., 2001; Reis and Alkmim, 2015). However, since no unambiguous evidence of glaciation was ever found in its rocks, recently it was proposed that it consists of gravity flows deposits controlled by faulted basin margins (Vieira et al., 2007a; Uhlein et al., 2012, 2016) or a glacially-induced fluvial deposit in an incised valley on the basement (Delpomdor et al. 2020). The overlying Sete Lagoas Formation has carbonate rocks (dolostones, limestones, marlstones) as the predominant lithology (Dardenne, 1979; Iglesias and Uhlein, 2009), but organic-rich shales are also present (Reis and Suss, 2016). The carbonates from the base of the Sete Lagoas Formation, and within the first 2nd-order sequence, are interpreted as cap carbonates

and they register a Neoproterozoic glaciation whose age is still debated. For instance, Babinski et al. (2007) assigned them a Sturtian age; Caxito et al., (2012, 2018), Okubo et al. (2018) and Crockford et al. (2019) set a Marinoan age; Paula-Santos and Babinski (2018) and Kuchenbecker et al. (2015) attributed a late Ediacaran age.

Figure 2.2: Litho, sequence and chemostratigraphy of the São Francisco Basin. Yellow stars represent maximum depositional ages obtained in detrital zircons of the upper Sete Lagoas Formation (Paula-Santos et al., 2015) and Três Marias Formation (Rossi et al., 2020). The red star represents a Serra da Saudade concordia Age obtained by Moreira et al. (2020). Chemostratigraphic intervals (CI-1, CI-2 and CI-3) were defined by Paula-Santos et al. (2017). Cloudina occurrences are reported in Warren et al. (2014) and Perrella Júnior et al. (2017). Treptichnus pedum is reported in Sanchez et al. (2020) Modified after Caetano-Filho et al. (2019)

The two following transgressive-regressive 2nd-order sequences comprise the upper part of the Sete Lagoas, Serra de Santa Helena, Lagoa do Jacaré and lower Serra da Saudade

formations. The Serra de Santa Helena Formation represents the gradual inundation of the carbonate platform of the underlying unit. It is composed mainly of siltites, pelites, shales and marls intercalated with dark-grey limestones (Iglesias and Uhlein, 2009). The Lagoa do Jacaré Formation is characterized by the presence of dark pisolitic and oolitic limestones, marbles, intraclastic breccias and interspersed shales and siltites (Dardenne, 1978). These deposits characterize a regressive movement in opposition to the transgression that occurred in the Serra de Santa Helena Formation, which formed another carbonate platform. Since breccias and hummocky structures are present, this platform is interpreted as a high energy environment that was occasionally calm. Also, the presence of mudcracks suggest that the unit was not always submerged (Iglesias and Uhlein, 2009). The Serra da Saudade Formation is a succession of siltites and greenish shales that are thinly laminated. Uhlein et al. (2004) interpret these deposits as an event of rapid marine transgression, in which fine siliciclastic sedimentation overlapped the carbonate platform of the Lagoa do Jacaré Formation.

The fourth and uppermost 2nd-order sequence encompasses the upper Serra da Saudade and Três Marias Formation (Reis and Suss, 2016), which is described by Dardenne (1978) as arkoseans, fine-grained arenites and green siltstones that cover the rocks of the Serra da Saudade. Três Marias Formation records a shallow platform environment, in which waves and storms influenced the deposition (Iglesias and Uhlein, 2009; Uhlein *et al.*, 2004). Kuchenbecker et al. (2016a) proposed to split the eastern part of the Três Marias Formation into a different unit: The Gorutuba Formation. The authors argue that Gorutuba is different from Três Marias in many aspects such as lithology (mainly conglomerates and coarse arenites), sedimentary structures (related to fluvial and coastal environments), thickness (it is thinner than Três Marias) and sedimentary provenance (mainly Ediacaran, while Três Marias sources are mostly Paleo and Mesoproterozoic). Therefore, the Gorutuba Fm. is the only record of transitional and continental environments that developed at the eastern edge of the Bambuí Basin.

Outcropping only at the west portion of the basin, the Samburá (conglomerates and sandstones) and Lagoa Formosa (conglomerates, sandstones, arenites, siltites and limestones) formations are interpreted as the deposits of fan-deltas and submarine-fans, representing the gravitational flows that are associated with foreland basins (Uhlein et al., 2013; Reis et al., 2017).

2.2.3.2 Chemostratigraphy of the Bambuí Group

Many studies have been done to understand the chemostratigraphy of the Bambuí Group, especially applying C isotopes on carbonates ($\delta^{13}\text{C}_{\text{carb}}$) (e.g., Iyer et al., 1995; Santos et al., 2004; Vieira et al., 2007b; Martins and Lemos, 2007; Caxito et al., 2012; Kuchenbecker et al., 2016a; Paula-Santos et al., 2017; Guacaneme et al., 2017; Uhlein et al., 2019; Hippertt et al., 2019; Caetano-Filho et al., 2019). Considering that, and also $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, Paula-Santos et al. (2017) divided the basal Bambuí Group into three chemostratigraphic intervals and interpreted the shifts in the measurements in terms of connection and restriction of the basin (Fig. 2.2). The first interval (CI-1) is less than 10m-thick and it comprises the Sete Lagoas cap carbonates, in which $\delta^{13}\text{C}_{\text{carb}}$ values record a negative excursion (-3‰ to -5‰) followed by a positive excursion (-5‰ to 0‰). This positive excursion was interpreted as recovery from an Earth that presented high CO_2 partial pressures (post-glacial greenhouse) to a scenario in which the climatic conditions were stable, since the consumption of CO_2 was enhanced due to high rates of chemical weathering (Vieira et al., 2007b). However, Paula-Santos et al. (2017) disagree with this hypothesis, because it does not match with the $^{87}\text{Sr}/^{86}\text{Sr}$ data. At CI-1, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increase from 0.7074 to 0.7082, and, as the $\delta^{13}\text{C}_{\text{carb}}$ values, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios stabilize at the chemostratigraphic interval II (CI-2).

At CI-2, which corresponds to the middle of the Sete Lagoas Formation, $\delta^{13}\text{C}_{\text{carb}}$ is around 0‰ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are close to 0.7082. Hence, the similar evolution of $\delta^{13}\text{C}_{\text{carb}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic systems led Paula-Santos et al. (2017) to interpret them as an effect of marine transgression, in which a previously shallow environment, influenced by local conditions, evolved to a basin connected to the global pool. The very negative $\delta^{13}\text{C}_{\text{carb}}$ values were understood as the result of continental carbon input, and as the transgression evolved, the values became more positive culminating in the suppression of the continental inputs since the basin was homogenized with global seawater. Moreover, at CI-2 the marine late Ediacaran index fossil *Cloudina Sp.* (Grotzinger et al., 1995) was reported by Warren et al. (2014). This fact, added to the chemostratigraphic data, suggests that at this stage the São Francisco basin was connected to other Gondwana marine basins through a sea pathway, allowing the migration of metazoans and isotope homogenization.

Finally, the third interval (CI-3), encompasses the upper Sete Lagoas, Serra de Santa Helena and Lagoa do Jacaré Formations. At CI-3, $\delta^{13}\text{C}_{\text{carb}}$ reaches very high values (up to 16‰) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios decrease in relation to CI-2, being close to 0.7075. The reported $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are low for the late Ediacaran period or the early Cambrian, which can be

explained in a context where the basin was restricted, hence, it could not homogenize with external seawater, and its Sr signature was mostly controlled by weathering of ancient carbonate platforms (Paula-Santos et al., 2015, 2017). The boundary between connected and restricted Bambuí sea is still being debated. Paula-Santos et al. (2017) defined it was on the CI-2/ CI-3 transition, but other studies point that it was before the end of CI-2 (Caetano-Filho et al., 2019; Bedoya-Rueda, 2019; Paula-Santos et al., 2020;). Bedoya-Rueda (2019) divided the CI-2 of Paula Santos et al. (2017) into CI-2a and CI-2b, in which the former represent connection of the Bambuí with global waters and the latter represent the beginning of the restriction.

Despite the time it began, this restriction led the basin to inefficient circulation and collaborated to turn the waters from oxic to stratified and anoxic (Hippertt et al., 2019). As stated by Paula-Santos et al. (2017) such restriction was probably caused by the uplift of the marginal orogens of the São Francisco Craton and consequential isolation of the basin, which is supported by geochronological data, since basal Sete Lagoas Fm. presents sources that go from the Archean to the Tonian, while upper Sete Lagoas Fm. displays sources that are mainly Ediacaran, evidencing that the marginal belts were indeed uplifting by the end of the Ediacaran (Paula-Santos et al., 2015). Similarly to the very high $\delta^{13}\text{C}_{\text{carb}}$ values reported in CI-3, some studies have interpreted that this condition is the result of enhanced burial of organic matter and activity of methanogenic archaea under anoxic conditions (Iyer et al., 1995; Paula-Santos et al., 2017; Caetano-Filho et al., 2021; Cui et al., 2020). However, some studies affirm that it requires more than methanogenesis and organic burial in order to rise $\delta^{13}\text{C}_{\text{carb}}$ to this magnitude. Hence, the authors argue that a complex interplay of causes (such as poor ventilation, change in total carbon input and carbonate recycling) led to the ^{13}C enrichment and these causes are related to a restricted environment (Uhlein et al., 2019; Cui et al., 2020). The chemostratigraphic division made by Paula-Santos et al. (2017) was later corroborated by Paula-Santos et al. (2018) since the Rare Earth Elements + yttrium (REY) patterns reported by the authors present secular trends that matches the intervals CI-1, CI-2 and CI-3.

Besides Sr and C, other less conventional chemostratigraphic studies were conducted in the Bambuí Basin. Crockford et al. (2019) measured the isotopic composition of Ba in barites from cap carbonates successions around the world, including the Bambuí Group. The authors came to the conclusion that Ba accumulated in the oceans during glaciations and in deglaciations it was carried by the water masses to the surface, reaching SO_4 derived from weathering and consequently precipitating barite layers in the cap carbonates successions.

Crockford et al. (2018) reported very low $\Delta^{17}\text{O}$ values (-1.05‰) in the Sete Lagoas cap carbonate and the authors associated this feature with changes in the ozone layers driven by anomalously high $p\text{CO}_2$. These signals, known as Marinoan Oxygen-17 Depletion, up to this date, were only found in the Marinoan deposits. Paula-Santos (2017) applied Li and Mg isotopes to the chemostratigraphic intervals CI-1, CI-2 and CI-3 and interpreted them in terms of silicate weathering in the orogens surrounding the Bambuí Basin. Caxito et al. (2018) developed a model for the deposition of the cap carbonates using geochemical proxies such as C, O, Sr, Nd, Pb and Cr isotopes, besides trace elements. At the early postglacial succession $\epsilon\text{Nd}(t)$ values go from -6 to -8, and coupled with Al and Mn contents, they suggest that by this time the input of particles from the continent was high. Also, Silva-Tamayo et al. (2010) reported $\delta^{40}\text{Ca}$ values around 0‰ at the base of the Sete Lagoas carbonates, which also can be interpreted in terms of high continental input. At the late postglacial succession, REY patterns and low Al and Mn concentrations argue for the dominance of marine waters over glacial meltwaters. Moreover, $\delta^{53}\text{Cr}$ data from this interval suggest that the surface waters were oxygenated (Caxito et al., 2018). Uhlein et al. (2020) also used $\delta^{53}\text{Cr}$ data in microbial mats from the Jaíba Member, upper Serra da Saudade Formation. However, the authors concluded that the obtained signals reflect metabolic reactions and not seawater signals. In order to further examine the redox conditions of the Bambuí Basin, Hippertt et al. (2019) using iron speciation, Ce and redox-sensitive elements data proposed a model for the evolution of the basin, in which by the time of the deposition of the early Sete Lagoas carbonates, the water was oxygenated. Then, in the middle of Sete Lagoas Formation, it became stratified (anoxic/ferruginous at the bottom and oxygenated at the top) and finally, due to the restriction, the water column became fully anoxic, which is recorded at the Serra de Santa Helena and Lagoa do Jacaré formations. The authors also argue that the lack of connection to a global ocean led to a shortage of nutrients, sulfate and finally oxygen, which precluded the rise of Cambrian metazoans. Another study performed on the basin using REY mass fractions detected that the progressive restriction of the basin led it to become very alkaline. Also, the increase in alkalinity happened at the same interval that *Cloudina* fossils are reported. Hence, the authors suggest that there might be a link between biomineralization and these environmental changes (Paula-Santos et al., 2020).

2.2.3.3 Age of the Bambuí Group

The age of the Bambuí Group is still controversial and it has been a matter of debate. Babinski et al. (2007) determined a Pb-Pb isochron age of 740 ± 22 Ma on cap carbonates at

the base of the Sete Lagoas Formation. That age suggest that these carbonates are related to the mid-Cryogenian Sturtian glaciation (Hoffman, 1998). However, Caxito et al. (2012) based on the presence of a pink cap dolostone on the cap carbonate section concluded that the carbonates record a post-Marinoan event (Hoffman and Schrag, 2002), since pink dolostones are broadly recognized as typical of the late-Cryogenian glaciation (see Shields, 2005 for review). The authors reinforced their hypothesis by reporting that the rocks have characteristics that allegedly are exclusive for post-Marinoan carbonates, such as aragonite pseudomorphs and $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$ signatures similar to others of the same proposed age. Recently, Okubo et al. (2018) described barite crystal fans and diagenetic barite present at the base of the Sete Lagoas Formation, which is also a feature of Marinoan cap carbonates. Furthermore, these barites presented anomalous $\Delta^{17}\text{O}$ values that are similar to other cap carbonates of the same proposed age reported in other basins throughout the world (Crockford et al., 2018, 2019). In addition to all data corroborating a Marinoan age, Caxito et al. (2018) obtained a Pb-Pb whole-rock isochron age of 608 ± 19 Ma for cap carbonates at the northern part of the basin. In spite of the arguments presented for a late-Cryogenian age for the basal Sete Lagoas Formation, that age is still disputed.

Paula-Santos et al. (2015) determined U-Pb ages in detrital zircons extracted from pelites intercalated with carbonates from the upper part of the Sete Lagoas Formation and concluded that most of the deposition of this formation took place after 560 Ma, at the end of the Ediacaran. Also, the discovery of fossils of *Cloudina* sp. and *Corumbella Werner* (550-542 Ma) (Grotzinger et al., 1995) in the middle Sete Lagoas Formation (Warren et al., 2014; Perrella Júnior et al., 2017) corroborate the ages that were found by Paula-Santos et al. (2015). If the cap carbonate is indeed Marinoan (Caxito et al., 2012, 2018), considering the Sturtian age reported by Babinski et al. (2007) at the basal Sete Lagoas and the Ediacaran age reported by Warren et al. (2014) and Paula-Santos et al., (2015) for the middle and upper Sete Lagoas respectively, this would imply that: i) the deposition of the first 100 m of the Sete Lagoas Formation took 85 or 200 Ma to complete or; ii) there is an unconformity between CI-1 and CI-2 (Paula-Santos and Babinski, 2018). The first alternative is unlikely since the required time span is too long for a second-order sequence (Perrella Júnior et al., 2017). Furthermore, the lack of secular variations on the CI-2 Sr isotope ratios argues against this hypothesis (Paula-Santos et al., 2017). The second one is plausible. Uhlein et al. (2017) proposed a model, based on distinct zircon patterns, in which the putative unconformity was generated in response to flexure of the foreland basin, but by now, no unconformity was found, neither in the field (Caxito et al., 2012; Perrella Júnior et al., 2017; Uhlein et al., 2019;

Caetano-Filho et al., 2019), nor in drillcores (Kuchenbecker et al., 2016b; Reis and Suss, 2016).

Therefore, the absence of an unconformity leads some researchers to argue that the Sete Lagoas cap carbonate is the record of an Ediacaran glaciation (Paula-Santos et al., 2015; Paula-Santos and Babinski, 2018). Crockford et al. (2019) state that the presence of anomalous $\Delta^{17}\text{O}$ barites related to non-Marinoan glaciations cannot be ruled out, but, if they exist, they are yet to be found. Regarding the 740 ± 22 Ma Sturtian age reported by Babinski et al. (2007), Paula-Santos and Babinski (2018) proposed that this carbonate could be related to an earlier glacial event, but the idea requires further investigation. Recently, Moreira et al. (2020) reported that ten prismatic zircon grains extracted from a k-bentonite volcanoclastic bed intercalated to green siltstones in the upper Serra da Saudade Formation defined an U-Pb Concordia age of $520 \text{ Ma} \pm 5 \text{ Ma}$, confirming that the deposition of Bambuí, or at least a great part of it, took place close to the Ediacaran-Cambrian boundary. In another study, U-Pb data of detrital zircons established that the maximum deposition age of the Três Marias Formation is 555 Ma (Rossi et al., 2020). And finally, the fossil *Treptichnus pedum* was reported in the upper Três Marias Formation, which places the deposition age of this unit in the early Paleozoic (Sanchez et al., 2020).

2.2.4 Phanerozoic units

There are four Phanerozoic units at the São Francisco basin: Santa Fé, Areado, Mata da Corda and Urucuia Groups. The Santa Fé Group is a Permo-Carboniferous unit that comprises 180 m of diamictites, dropstones-bearing shale, sandstones, varvites and tillites. This unit does not outcrop in a large area, occurring mostly at the central and northwest portions of the basin and it is regularly associated with striated pavement, which argues in favor of its glacial origin (Reis et al., 2017). The Areado Group (Barremian to Aptian) is a 300 m-thick unit that encompasses fluvial sandstones and conglomerates that grades into aeolian and lacustrine deposits. However, in spite of its continental register, this group presents in its upper formation (Três Barras) typical marine fossils, which is a feature that is yet to be understood (Alkmim and Martins-Neto, 2001). The Cretaceous Mata da Corda Group outcrops at the west of Minas Gerais state and it is composed of alkaline volcanic and volcanoclastics, besides of alkaline-carbonatitic rocks. The also Cretaceous Urucuia comprises aeolian sandstones and fluvial deposits, but its precise age and stratigraphic correlations are not well defined (Reis et al., 2017). Areado, Mata da Corda and Urucuia are interpreted as a result of the opening of the South Atlantic Ocean (Mohriak and Leroy, 2013).

3 THEORETICAL FRAMEWORK

3.1 Nitrogen Isotopes – An introduction

Chemostratigraphy is the branch of stratigraphy in which chemical fingerprints of sedimentary sequences are used to investigate paleoenvironmental conditions by the time that the rock was deposited (Weissert et al., 2008). It can also be used to correlate succession in a basinal to a global scale and it is especially useful in Precambrian sequences, due to their scarce fossil record (Halverson et al., 2010). Although radiogenic isotopes such as Sr and Nd are used in chemical stratigraphy studies, the highlight of the technique is the use of stable isotopes, a group that encompasses nitrogen isotopic studies.

Nitrogen is the fifth most common element in the solar system and it is widely distributed within Earth's reservoirs. Johnson and Goldblatt (2015) calculated the nitrogen budget of Bulk Silicate Earth based on two approaches, one using compiled data of chondrites and another using terrestrial rocks and minerals and both approaches yielded similar results, pointing that most of the N of Earth is contained within the Bulk Silicate Earth. Therefore, although N₂ is the most abundant gas in the atmosphere, accounting for 78% of its volume, a huge part of the N budget of Earth is kept in its rocks. Nitrogen has two stable isotopes, ¹⁴N and ¹⁵N, and they occur in a proportion of 99.633% and 0.337%, respectively (Meija et al., 2016). Since relative differences in isotopic ratios are more precisely determined than absolute isotopic ratios, nitrogen isotopic compositions are expressed in delta notation ($\delta^{15}\text{N}$), which is reported in part per thousand (‰) (Sharp, 2007). In this notation, the ¹⁵N/¹⁴N isotopic ratio is defined by equation 3.1, which compares the composition of a sample with a standard and in the case of N is atmospheric air (AIR), whose internationally accepted absolute ¹⁵N/¹⁴N ratio is 0.00367 ± 0.00004 (Junk and Svec, 1958) and $\delta^{15}\text{N}$ value is 0‰ by definition (Mariotti, 1984). Therefore, a positive $\delta^{15}\text{N}$ means that the sample is enriched in ¹⁵N as compared to the standard and a negative $\delta^{15}\text{N}$ means the opposite.

$$\delta^{15}\text{N} = \left[\frac{\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{sample}}}{\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{AIR}}} - 1 \right] \times 1000 \quad (\text{equation 3.1})$$

Due to its abundance, ability to build chemical bonds with carbon and to join redox reactions when it is dissolved in liquid water, nitrogen is an important component in Earth's life system (Stüeken et al., 2016). In seawater, N is found mostly as N₂ (di-nitrogen), NO₂⁻

(nitrite), NO_3^- (nitrate), NH_4^+ (ammonium) and N_{org} (dissolved or particulate organic nitrogen) (Thomazo et al., 2011). Also, the abundances of these species are associated with the redox structure of the water column, which also controls the reactions of the biogeochemical cycle of the nitrogen (e.g. NH_4^+ is abundant at reducing conditions, but is readily oxidized at oxygenic environments). In addition, when dealing with N isotopes, it is assumed that the measured $\delta^{15}\text{N}$ of a rock/sediment reflects the isotopic signature of primary producers and also that the $\delta^{15}\text{N}$ of such producers is associated with the $\delta^{15}\text{N}$ of the N sources. Therefore, due to the relation of N and $\delta^{15}\text{N}$ with life and redox conditions, this proxy enables to understand changes and to obtain valuable information about modifications in both redox structure of ancient water bodies (Godfrey and Falkowski, 2009; Quan et al., 2013; Wang et al., 2013; Ader et al., 2014; Wang et al., 2015; Azmy et al., 2015; Wang et al., 2018a; Chen et al., 2019) and past N-biogeochemical cycle paths (Cremonese et al., 2013; Sun et al., 2019; Cox et al., 2019; Xu et al., 2020). Although the use of N isotope composition as a paleoenvironmental tracer is more common in recent sediment (Quan et al., 2013), this approach is increasingly being applied to interpret Precambrian environments (see reviews in Thomazo et al., 2009; Thomazo and Papineau, 2013; Ader et al., 2016; Stüeken et al., 2016).

3.2 The modern biogeochemical cycle of N

In order to understand the biogeochemical cycle of nitrogen in the past, it is important to understand how it operates now, since, even if not accurate, the modern N cycle is used as the basis of comparison to understand ancient systems. When they are not completed, the reactions of this cycle imparts isotopic fractionation (i.e., the relative partitioning of the heavier and lighter isotopes between two coexisting phases in a natural system; Tiwari et al., 2015) that are mostly of the kinetic type (unidirectional).

In order to evaluate the magnitude of the fractionation, the kinetic isotope effect, ϵ , expressed in part per thousand (‰) is applied and it is defined by equation 3.2, in which ^{14}k and ^{15}k are the rate coefficients of the reaction for N stable isotopes. When ϵ is much smaller than 1000‰, ϵ can be defined by equation 3.3, that is, ϵ is approximately the difference between $\delta^{15}\text{N}$ of the reactant and $\delta^{15}\text{N}$ of the product (Sigman et al., 2009; Sigman and Fripiat, 2019). Also, primary producers record the N isotopic composition of their sources (mainly N_2 , NO_3^- , NH_4^+ and N_{org}), and as they sink, this composition is transmitted to the sediment and later to the rock. Therefore, the measured $\delta^{15}\text{N}$, which is the result of such fractionations, allows investigating oceanic processes related to N.

$$\varepsilon = \left(\frac{{}^{14}k}{{}^{15}k} - 1 \right) \times 1000 \quad (\text{equation 3.2})$$

$$\text{If } \varepsilon \ll 1000\text{‰}, \quad \varepsilon = \delta^{15}N_{\text{product}} - \delta^{15}N_{\text{reactant}} \quad (\text{equation 3.3})$$

The modern biogeochemical cycle of N in the oceans operates as follows (Fig. 3.1):

- i) Nitrogen enters the ocean when N_2 is fixed by bacteria and archaea, the diazotrophs ($\varepsilon = -7$ to $+1\text{‰}$, Zhang et al., 2014; Sigman and Fripiat, 2019). Subsequently, N_2 is converted to a biologically available form of N, the NH_3 gas, which is quickly converted to the soluble NH_4^+ (Glass et al., 2009). The fractionation on this step depends strongly on which cofactor is used by the nitrogenase enzyme. Mo-based nitrogenase imparts a small fractionation (-2 to 1‰), while Fe or V-based ones lead to a much larger isotopic differentiation, reaching values as low as -7‰ (Zhang et al., 2014);
- ii) During organic matter mineralization, N_{org} is converted into NH_4^+ ($\varepsilon = 0$ to -2.3‰ , Möbius, 2013). This NH_4^+ can be fixed into clays ($\varepsilon = 0$, Ader et al., 2016), since its ionic radius is similar to the potassium one (Müller, 1977; Greenfield, 1992) or it can be assimilated by organisms ($\varepsilon = 0$ to -27‰ , Hoch et al., 1992; Pennock et al., 1996; Liu et al., 2013). NH_4^+ can also be nitrified, i.e. NH_4^+ is oxidized to NO_2^- ($\varepsilon = -14$ to -38‰ , Casciotti, 2009) and NO_2^- is rapidly oxidized to NO_3^- ($\varepsilon = +12.8$, Casciotti, 2009). Finally, NH_4^+ can contribute to the loss of fixed N in the ocean in a process called anammox, in which NO_2^- is used to oxidize NH_4^+ , generating N_2 ($\varepsilon = -23.5$ to -29.1‰ for $\varepsilon_{NH_4^+ - N_2}$ and $\varepsilon = -16.5\text{‰}$ for $\varepsilon_{NO_2^- - N_2}$, Brunner et al., 2013);
- iii) Denitrification ($\varepsilon = -25$ to -30‰ in the water column and 0 to -3‰ in sediments, Granger et al., 2008; Casciotti, 2009; Kessler et al., 2014), the conversion of NO_3^- to N_2/N_2O , is the major sink of fixed N in modern oceans. It occurs in the sediments and in the water column where oxygen levels are low. The remarkable difference in the fractionation of N in the two environments where the process happens is explained by the fact that in sediment pore waters nitrate is almost fully consumed, leading to a small fractionation (Sigman and Fripiat, 2019). NO_3^- is an important nutrient, accounting for most of the fixed N in marine ecosystems. When it is assimilated by microorganisms ($\varepsilon = 0$ to -10‰ , Casciotti, 2009; Granger et al., 2010) its fractionation depends on the abundance of the species, the more scarce is

the nutrient, the closer to 0‰ the kinetic isotopic effect is (Fogel and Cifuentes, 1993). Another important pathway of the N-Cycle is the direct conversion of NO_3^- to NH_4^+ , known as dissimilatory nitrate reduction to ammonium (DNRA). Although the isotopic effect of this process is not very well known, it can account for fractionations larger than -30‰ (McCready et al., 1983).

Figure 3.1: The modern marine biogeochemical cycle of Nitrogen. ϵ is expressed in parts per thousand.

In modern seafloor sediments, the combination of these biogeochemical reactions results in a $\delta^{15}\text{N}_{\text{sed}}$ mode value of 6.7‰ (Tesdal et al., 2013), which is discussed in the conceptual scenario presented by Ader et al. (2016) (Fig. 3.2). Since that ocean is oxygenated at its bottom, nitrate is stable, and denitrification only happens at oxygen minimal zones (not quantitative reaction) and water-sediment interfaces (quantitative reaction, hence $\epsilon = 0$ ‰). Because denitrification favors the loss of ^{14}N and nitrate is the most abundant N nutrient in modern oceans, the enriched residual NO_3^- is exported and consumed at surface waters, causing an enrichment that is later transferred to the sediments.

Figure 3.2: The modern N cycle and its register on sediments. Denitrification at oxygen minimal zones leads to a ^{15}N enriched nitrate pool, hence, sediments record $\delta^{15}\text{N}$ positive values. Extracted from Ader et al. (2016).

3.3 $\delta^{15}\text{N}$ as a paleoenvironmental tool applied to the Precambrian rocks

$\delta^{15}\text{N}$ data allow to rebuilt past biogeochemical cycles, and it is a useful proxy for paleoenvironmental interpretations. Although the understanding of N isotopic signals in deep time is evolving, it is still discussed what kind of sample better preserve the primary nitrogen isotopic signature, kerogen extracts ($\delta^{15}\text{N}_{\text{ker}}$) or bulk rock ($\delta^{15}\text{N}_{\text{bulk}}$). As NH_4^+ and K have a similar ionic radius, during mineralization/diagenesis of the organic matter, N can be lost in the form of NH_4^+ , subsequently substituting K in potassic minerals, such as phyllosilicates and feldspars. It is intuitive to think that kerogen is a better approach to primary signal since it is the residue of biomass and it does not involve displacement of N from one phase to another, as in N associated with clay-minerals. However, this is not always a valid premise, since diagenesis and metamorphism can significantly alter $\delta^{15}\text{N}_{\text{ker}}$. Also, Kerogen extracts suitable for stable isotopic analysis demand toilful HF extractions and depending on the chosen method to isolate the insoluble organic matter, contamination can occur. For instance, Ader et al. (2006) reported that NH_4 -bearing fluorides precipitated during the kerogen extraction of semi-graphites.

On Precambrian rocks, the ratio of formed NH_4 -bearing fluorides/total organic carbon can be high. Since the NH_4^+ comes from the dissolved silicates phases or the atmosphere, such

fluorides can substantially alter the isotopic signal of the kerogen. But even if the chosen extraction method dissolves formed fluorides, for example using a BF_3 step to dissolve them (e.g. Robl and Davis, 1993), it still should be investigated if it is better to use $\delta^{15}\text{N}_{\text{ker}}$ or $\delta^{15}\text{N}_{\text{bulk}}$ as the best approach for obtaining the original isotopic composition.

Regarding the impact of metamorphism on $\delta^{15}\text{N}_{\text{ker}}$, a previous study showed that on an increasingly metamorphosed series of coal, $\delta^{15}\text{N}_{\text{ker}}$ did not change from anchimetamorphism to low greenschist facies (Ader et al., 2006). However, this seems not to be valid for sedimentary Precambrian rocks, in which carbon TOC is usually low and metamorphism is intense. Stüeken et al. (2017) addressed this issue by measuring both $\delta^{15}\text{N}_{\text{ker}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ of multiple Precambrian samples of different metamorphic grades. The conclusion was that for samples up to greenschist facies and in which more than 40% of the nitrogen is silicate-bound, bulk rock measurements are probably closer to the original values and for higher metamorphic grades or rocks in which N is more than 60% kerogen-bound, kerogen isolates are a better approach for paleoenvironmental interpretation.

When sediment settles, all the N is organic-bound, hence, at this stage, all the N is kerogen-bound. However, during diagenesis, internal isotopic fractionation occurs and N is partitioned, favoring migration of N to clays, especially ^{15}N . Therefore, as diagenesis is processed, kerogen becomes isotopic lighter than original biomass and clay-bound NH_4^+ becomes heavier. Considering this, and knowing that metamorphism drives to the preferential loss of ^{14}N proportionally to the metamorphic degree, when the N of a sample is more than 60% bounded to kerogen and suffered metamorphism above greenschist facies, kerogen is a better approach to primary signals. This is because (i) it is hard to disturb a large reservoir; (ii) the loss of ^{15}N during diagenesis is suppressed by the loss of ^{14}N during metamorphism. Similarly, when the N reservoir is mainly clay-bound (>40%) and it is under greenschist facies, bulk rock is a better indicator of original biomass signature. Even if clays are enriched in ^{15}N during diagenesis and metamorphism, due to fact that the reservoir is larger than the kerogen one, it is harder to isotopically disturb it, making it a better approach than $\delta^{15}\text{N}_{\text{ker}}$.

Many studies (e.g. Godfrey and Falkowski, 2009; Stüeken et al., 2015a; Kipp et al., 2018; Koehler et al., 2019; Yang et al., 2019; Mettam et al., 2019) measured both $\delta^{15}\text{N}_{\text{ker}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ in order to evaluate the degree of post-depositional alteration that a rock has been submitted. Since it is unlikely they would progress in the same way during diagenesis/metamorphism, the offset between the measurements helps to evaluate the degree of the alteration.

When one is analyzing $\delta^{15}\text{N}$ values on sedimentary rocks, it is important to investigate

the conditions of the sedimentation environment, such as diagenesis under oxic or anoxic conditions. The former can modify the primary signal, increasing $\delta^{15}\text{N}_{\text{bulk}}$ for up to 4‰, while the latter does not change the values significantly, increasing it less than 1‰. High-grade metamorphism can also considerably modify the primary $\delta^{15}\text{N}$ signal too. Hence, it is not recommended to interpret $\delta^{15}\text{N}_{\text{bulk}}$ data in terms of paleoenvironmental changes when the data were obtained on high metamorphic facies rocks. Below greenschist facies the enrichment of $\delta^{15}\text{N}_{\text{bulk}}$ is less than 1‰, within greenschist, it is around 1-2‰. Amphibolite facies enriches $\delta^{15}\text{N}_{\text{bulk}}$ by 3-4‰ and above it, the enrichment is around 6 to 10‰ (reviewed by Thomazo and Papineau, 2013; Ader et al., 2016; Stüeken et al., 2016).

In the Precambrian, most of the $\delta^{15}\text{N}$ data are between -2 and +10‰ as reviewed by Ader et al. (2016) (Fig. 3.3), and lower values are usually reported on kerogen samples. There are measurements of $\delta^{15}\text{N}$ in rocks as old as 3.8 Ga (Beaumont and Robert, 1999; Pinti et al., 2009, 2009; Zhang et al., 2014), but the meaning and interpretation of such data are still disputed since most of these rocks were affected by greenschist facies metamorphism or higher. In any case, these data suggest that the biogeochemical cycle of nitrogen was already operating at the very early beginning of the Earth.

Figure 3.3: $\delta^{15}\text{N}$ data through the geological time. Extracted from (Ader et al., 2016).

However, at the Meso and Neoarchean (3.2-2.5 Ga) $\delta^{15}\text{N}$ record is less ambiguous since rocks are less metamorphosed and datasets are more clustered. On the Mesoarchean, values of $\delta^{15}\text{N}$ are usually low, around +1‰ (see Stüeken et al., 2015; Koehler et al., 2019; Ossa Ossa et al., 2019) suggesting an anaerobic N cycle, in which nitrogen fixation was the main path. Importantly, values are not low enough to support the hypothesis that alternative nitrogenases, which uses V or Fe as cofactors and fractionates N up to -8‰ were relevant at that time. The available data support that Mo-based nitrogenase was the most significant process, and even if it is generally accepted that Mesoarchean ocean water was low in Mo (Zerkle, 2005; Anbar, 2008) it has been shown that very low Mo concentrations can maintain diazotrophic activity in modern environments (Glass et al., 2010).

The Neoarchean is marked by an increase in the $\delta^{15}\text{N}$ values (mean of +4.2‰, $n = 160$ - reviewed by Stüeken et al. (2016) with data collected from Yamaguchi, 2002; Garvin et al., 2009; Godfrey and Falkowski, 2009; Busigny et al., 2013 and Stüeken et al., 2015) which is generally understood as a register of marine oxygen oases, where aerobic pathways of the N biogeochemical cycle, such as nitrate assimilation, could occur. As oceans were not fully oxygenated yet, basins of this era present a great variation on $\delta^{15}\text{N}$ values. For instance, in 30 meters of section, the $\delta^{15}\text{N}$ record of the Mount McRae Shale of the Hamersley Group in Australia goes from +1‰, reaches a maximum of +7.5‰ and returns to 2.5‰ (Garvin et al., 2009), demonstrating the instability of the redox structure of the oceans in the Neoarchean.

Nevertheless, the role of oxygen on the N cycle of the late Archean is still disputed and an alternative scenario is proposed by Mettam et al. (2019). It relies on the fact that shallow-water deposits of the Griqualand West Basin in South Africa do not show any evidence of aerobic N cycle, although Godfrey and Falkowski (2009) had argued, based on small positive shifts of $\delta^{15}\text{N}$ on deep facies of the same basin, that the cycle had nitrification/denitrification phases, which are oxygen-dependent. Since it is unlikely that the shallowest portions of a basin are anoxic while the deeper ones are oxygenated, Mettam et al. (2019) argue that such positive shifts might be the result of transportation and assimilation of a heavy ammonium pool on deep environments. NH_4^+ is a stable nutrient in anoxic environments, but microbiota prefers to assimilate ^{14}N . This results in the generation of an NH_4^+ pool enriched in ^{15}N , which could be transported to deeper environments and increase $\delta^{15}\text{N}$ values. Besides the Griqualand West Basin, the Manjeri Formation in the Belingwe Greenstone Belt, Zimbabwe, also shows evidence that ammonium assimilation was a main path on the Late Archean (Yang et al., 2019).

In figure 3.3, very positive values of $\delta^{15}\text{N}$ (up to +50‰), measured in both kerogen and bulk rock, around 2.7 Ga call attention. Most of them are reported on the Tumbiana Formation, Pilbara Craton, Australia, and their meaning are still discussed. A study points out that these values are related to partial nitrification of NH_4^+ to NO_2^- , which would be rapidly converted to N_2O and lost to the atmosphere. This process favors the loss of ^{14}N and enriches the NH_4^+ residual pool in ^{15}N . Since concentration of oxygen on the water was low, NH_4^+ was the main N nutrient available and its assimilation from the ^{15}N rich pool drove the $\delta^{15}\text{N}$ to very high values (Thomazo et al., 2011). Another interpretation for these data set is that NH_4^+ dissociated to H^+ and volatile NH_3 , a reaction that is favored under alkaline conditions and enriches the residual NH_4^+ pool in ^{15}N . Then, the enriched NH_4^+ was assimilated by microorganisms and enhanced $\delta^{15}\text{N}$ values (Stüeken et al., 2015b).

At the beginning of the Paleoproterozoic (2.5-1.6 Ga), around 2.32 Ga, the “Great Oxidation Event” (GOE) marks the rise of the atmospheric levels of oxygen to more than 10^{-5} times that of the present atmospheric concentration (Bekker et al., 2004), which caused a huge impact on the N cycle. The increasing amount of oxygen in the oceans made it possible to accumulate nitrate, as this species is stable under oxic conditions. However, since the bottom of the oceans were still anoxic, a strong chemocline caused denitrification rates to be very high, which turned the residual NO_3^- pool heavy (Stüeken et al., 2016), resulting in high $\delta^{15}\text{N}$ signatures (e.g. Kump et al., 2011; Ishida et al., 2017; Kipp et al., 2018; Cheng et al., 2019).

At 1.9 Ga, phosphoritic shales of the Aravalli Group, India, present a wide range of $\delta^{15}\text{N}$ values, from -5 to +27‰ (Fig. 3.3). The negative values were interpreted as a result of nitrogen fixation. Productivity was probably high due to the phosphorous abundance; hence, nitrate became a limiting source of N, which boosted other paths of acquiring nitrogen. The very positive values were interpreted as ammonium assimilation of NH_4^+ that was already isotopically heavy, since it came from the decomposition of enriched biomass (Papineau et al., 2009, 2013).

Mesoproterozoic (1.6-1.0 Ga) $\delta^{15}\text{N}$ data reflect trends that are facies dependent. Onshore deposits present more positive values, which indicate that nitrate was available as a source of N, meanwhile, offshore deposits are around 0‰, reflecting that N_2 -fixation was the main N cycle path on deep waters (Stüeken, 2013; Koehler et al., 2017). These basal gradients are not observed in any other geological era and this implies that during the Mesoproterozoic oceans faced a nitrate minimum, in which NO_3^- concentration was at its lowest in anoxic deep waters (Koehler et al., 2017). This view corroborates the hypothesis that anoxia and euxinia in the oceans had their peak during the mid-Proterozoic, surpassing

any other time after the GOE (Shen et al., 2003; Planavsky et al., 2011).

The Neoproterozoic (1.0-0.541 Ga) $\delta^{15}\text{N}$ record mode is around +4‰ (Ader et al., 2014), which suggests that the cycle was operating in a similar way that it does nowadays, whose mode of bulk seafloor sediment is approximately +6.7‰ (Tesdal et al., 2013). The slightly positive mode of this era indicates that waters were pervasively oxygenated, allowing NO_3^- to accumulate and serve as a major N pool. As in the modern ocean, denitrification in oxygen minimum zones was responsible for the enrichment of the residual nitrate reservoir, driving $\delta^{15}\text{N}$ towards positive values. Still, the positive tail of $\delta^{15}\text{N}$ data from 1.0 to 0.541 Ga is less significant than the one of present times, while its negative tail is more preeminent, indicating less oxygen dissolved in the water. Notably, as it can be seen in figure 3.3, $\delta^{15}\text{N}$ was quite stable during the Neoproterozoic, suggesting that the Neoproterozoic Oxygen Event (NOE; 0.8-0.5 Ga, Och and Shields-Zhou, 2012) did not influence the redox structure of the oceans, implying that the oceans were oxygenated before 0.75 Ga (Ader et al., 2014). However, more studies regarding N isotopes must be done on Neoproterozoic rocks, as the data is scarce.

Most of the N isotopic data from the Ediacaran to early Cambrian (635 - 521 Ma) were obtained in the Yangtze Block, South China. However, there are also data from Norway, Canada and Central-West Brazil (Ader et al., 2014; Spangenberg et al., 2014; Oliveira et al., 2019). Data from South China generally show a decrease in $\delta^{15}\text{N}$ values from the early Ediacaran to the early Cambrian, in which the high Ediacaran values were interpreted as heavy NO_3^- reservoir due to denitrification and deep water oxygenation (Cremonese et al., 2013; Kikumoto et al., 2014; Ader et al., 2014; Xiang et al., 2018; Wang et al., 2018a; Chen et al., 2019), while the lower Cambrian values are interpreted as the result of N_2 fixation using Mo as metalloenzyme and ammonium assimilation (Wang et al., 2015; Chen et al., 2019; Xu et al., 2020). The existing Ediacaran N isotopic data in Brazil are from carbonates of the Paraguay belt. They are mostly positive values, indicating that waters were oxygenated and nitrate was available as an N source (Ader et al., 2014; Spangenberg et al., 2014; Oliveira et al., 2019). However, some negative $\delta^{15}\text{N}_{\text{ker}}$ values ranging from -3.3‰ to -2.0‰ are also reported in some samples, which was interpreted as the result of the contribution of sulfur bacteria metabolism, a hypothesis that is corroborated by anoxic/euxinic episodes pointed by other proxies such as trace elements (Spangenberg et al., 2014).

4 GEOLOGY OF STUDIED SECTIONS

Three sections were studied in this work: (i) Januária, in the central-east portion of the Basin and associated with the Januária High domain; (ii) Arcos; and (iii) Well 1, at the South of the Basin, associated to the Sete Lagoas High domain (Fig. 2.1). They correspond to the two first 2nd-order sequences of the Bambuí Basin.

Using geochemical data and two major stratigraphic surfaces, the maximum flooding surface (MFS) and the first sequence boundary (SB1), which are recognizable throughout the basin, Caetano-Filho et al. (2019) proposed a sequence stratigraphy model of the Bambuí Group, establishing correlations between these three sections, and classifying its basal units in terms of system tracts identified both at the Sete Lagoas and at the Januária highs. In their study, the authors defined two system tracts for the Bambuí basal units: transgressive system tract (TST) and the highstand system tract (HST), which is divided into early highstand system tract (EHST) and late highstand system tract (LHST). The evolution of the mixed carbonate-siliciclastic successions of the Bambuí foreland basin was also tracked.

The basal tract, TST, corresponds to a retrogradational pattern that marks a transgression over the forebulge of the Bambuí basin, and it comprises deposits of diamictites from Carrancas Formation and carbonates from the basal Sete Lagoas Formation. Regarding its chemostratigraphy, the cap carbonates present a negative $\delta^{13}\text{C}_{\text{carb}}$ excursion followed by a positive one, after which values stabilize close to 0‰. Such a trend is observable at all the studied sections, except Well 1, in which there were no carbonate facies available for analysis. TST is also Sr-poor and hence has a low average Sr/Ca ratio (0.001). The authors argue that it might be due to neomorphism or high terrigenous content. This sequence ends at the maximum flood surface.

Above the TST, a progradational pattern signals that a regression occurred, marking the EHST. At this segment, which is part of the Sete Lagoas Formation, carbonates are the main lithology. Sr concentration increases, however, the Sr/Ca ratio is still of 0.001, representing the stabilization of the marine carbonate ramp. The $\delta^{13}\text{C}_{\text{carb}}$ values are around 0‰ in most of the sequences, but such values are preceded by a positive excursion registered right above the MFS. The boundary between EHST and LHST is defined by a sharp increase in the Sr/Ca ratio since the latter present an average value of 0.004. This growth might represent environmental changes such as high alkalinity and high carbonate precipitation rates or aragonitic conditions.

LHST comprises very pure carbonates that become coarser towards the top of the

sequence and despite the increase on the Sr/Ca ratios, $\delta^{13}\text{C}_{\text{carb}}$ is still around 0‰, except for Well 1, in which it is about 3‰. This last tract ends with the surface identified as SB1, marking the beginning of the second 2nd-order sequence, which is characterized by anomalous features such as very high $\delta^{13}\text{C}_{\text{carb}}$ values and the persistence of high Sr content and Sr/Ca ratios. We present here a brief description of the geology of each of these sections.

4.1 Januária Section

The Januária composite section (Fig 4.1) is composed of three minor sections, Cônego Marinho (CM), Barreiro (BAR) and Januária-Lontra (JL), all located at the North of Minas Gerais State, within the area of Januária city (Fig 2.2). Corresponding to the first 2nd-order sequence of the Bambuí Basin, the CM section encompasses the lower Sete Lagoas Formation that overlies the gneissic basement, presenting a thickness of ~58 m. Above CM, the BA section (~50 m) comprises the upper Sete Lagoas Formation. Finally, the uppermost section, Januária-Lontra, (~20 m) corresponds to the Lagoa do Jacaré Formation and, therefore, to the second 2nd-order sequence of the Bambuí Basin. The assemblage of the composite Januária section was made through correlation between these three minor sections, based on the presence of lithological similarities, sedimentological features and $\delta^{13}\text{C}_{\text{carb}}$ data.

This section represents a shallow domain of the forebulge setting and its facies and depositional environment (outer, mid or inner ramp) are detailed described in Caetano-Filho et al. (2019). Here, a brief synthesis is presented. Above the unconformity that separates the Bambuí Group from the basement (Fig 4.2A), grey calcilutites (0 to 4 m) presenting aragonite pseudomorphs (cap carbonates) are overlapped by pink carbonates (Fig 4.2B) (4 to 19 m) that transition to light grey fine-grained carbonates (19 – 25 m) interleaved with pelitic siliciclastic layers. The presence of such layers was interpreted as evidence for a deep environment, therefore, at this interval, Caetano-Filho et al. (2019) set the maximum flood surface for the section. Overlying the light grey limestones, there are dark grey calcisiltites (25 to 58 m) (Fig 4.2C) intercalated with thin beds of clay. SEM analysis on this interval suggests that it corresponds to the predominance of microbial carbonates deposition (Caetano-Filho et al., 2019). From 58 to 98 m, carbonates become gradually coarser (Fig 4.2D) and flat pebble breccias, which was associated with seismic activity on the Bambuí basin (Okubo et al., 2020), are a common feature. Microbial structures are still presented but on a minor scale. At the top of the Sete Lagoas Formation, there are dolostones (98 to 100 m) with intraclasts and vugular porosity, which are interpreted as the result of a shallow to subaerial conditions

(Caetano-Filho et al., 2019). Above them, an unconformity marks the end of the first 2nd-order sequence. Following a gap of unknown thickness, the Serra de Santa Helena Fm. outcrops in a 20 m-thick succession of laminated to massive siltstones and mudstones and it is overlapped by the 20 m-thick package of limestones of the Lagoa do Jacaré Formation, which shows features such as oolites, intraclastic breccias and planar-parallel lamination.

Figure 4.1: The Januária section: depositional environments, lithology, structures, facies, chemostratigraphic data and its sequence stratigraphy framework. System tracts: TST – Transgressive System Tract; MFS – Maximum Flooding Surface; EHST – Early Highstand System Tract; LHST – Late Highstand System Tract; SB1 – Sequence Boundary. Granulometry scale: C – clay; S – sand; G – gravel. Extracted from Caetano-Filho et al. (2019).

Figure 4.2: Januária section facies. A) Basal contact (red line) between Sete Lagoas Formation cap carbonate and gneiss from the basement (extracted from Caetano-Filho et al. (2019)). B) Pinkish carbonates that overlie the cap carbonate. C) Calcisiltites presenting horizontal planar lamination. D) Coarse carbonate from the Sete Lagoas Formation

4.2 Well 1 Section

The Well 1 section (Fig. 4.3) is a continuous drill core that was drilled in the southern São Francisco basin (Fig. 2.2) during hydrocarbon exploration campaigns. The detailed stratigraphy and depositional environment of Well 1 is present by Reis and Suss (2016), in a work in which the authors defined 12 carbonate and 8 siliciclastic facies for this section. Well 1 is interpreted as the record of mixed-carbonate siliciclastic deposits in a forebulge graben (Reis and Suss, 2016). Hence, it is the only section in this work associated with deep environments.

Its base, which will be investigated in this work, is approximately 430 m-thick, consisting of the thickest studied section presented here. It represents the first and the beginning of the second 2nd-order sequences of the Bambuí basin. An erosional unconformity marks the appearance of the Carrancas diamictite (muddy matrix sustaining clasts of metasedimentary rocks, granitoids and quartz veins) above the basement. The conglomerate grades upward to recrystallized dolomites (Fig. 4.4A) (~80 m-thick) cemented by sparry dolomite and chert; wave ripples and hummocky stratification are present as well. From 1100 to 1075 m-depth dark shales intercalate with limestones, and from 1075 to 1045 m-depth a thick layer of shale containing pyrite closes this portion of the drill core (Fig. 4.4B and 4.4C). In the middle of this interval, the maximum flood surface was set, as it represents deeper facies.

This section does not feature aragonite pseudomorphs which was explained by Caetano-Filho et al. (2019) as a consequence of a highly-energetic environment and abundance of terrigenous content. Above the shaly interval, until approximately 880 m-depth, greenish siltstones intercalate with calcilutites, calcarenites and calcirudites. Structures such as wavy, lisen and flaser beddings, wave ripples and hummocky stratification are reported. From 880 to 720 m-depth the section comprises dark-limestones of varied granulometry (Fig. 4.4D), in which wavy ripples, gutter casts, hummocky and horizontal planar lamination are described at the base of this segment and ooids, trough cross-bedding, planar cross-stratification and microbial lamination at the top. Also, associated with these microbial laminations, there is the boundary of the first 2nd-order sequence, an erosional surface at the base of peritidal channels limestones. This is the only studied section in which there are no dolostones associated with the end of the first 2nd-order sequence. The uppermost 30 m of Well 1 comprises shales with minor intercalations of calcirudites and calcarenites, pyrite is a common feature.

Figure 4.3: Well 1 drillcore section: depositional environments, lithology, structures, facies, chemostratigraphic data and its sequence stratigraphy framework. System tracts: TST – Transgressive System Tract; MFS – Maximum Flooding Surface; EHST – Early Highstand System Tract; LHST – Late Highstand System Tract; SB1 – Sequence Boundary. Granulometry scale: C – clay; S – sand; G – gravel. Extracted from Caetano-Filho et al. (2019).

Figure 4.4: Well 1 drillcore samples and features. A) Contact (red line) between the Carrancas Diamictite and Sete Lagoas Carbonate. B and C) In B, Shale from Well 1 and in C, a polished slab of this lithology containing pyrite. D) Coarse-grained limestone. A, B and D were extracted from Reis and Suss (2016) and C from Caetano-Filho et al. (2019). Well cores diameters: 8.9 cm.

4.3 Arcos Section

The Arcos section (Fig. 4.5) consists of two drillcores of about 200 m that were obtained by mining companies within the area of the city of Arcos, Minas Gerais, Brazil (Figure 2.2). It represents a shallow domain of the forebulge setting and a complete description of its stratigraphy can be found in Kuchenbecker et al. (2011) and will be summarized here. The basement comprises slightly deformed dark-green to grey granodiorites, above it, in an irregular contact, a 0.5 m-thick layer of the Carrancas diamictite occurs, containing clasts from the basement, besides clasts of limestones, siltite and quartz. Kuchenbecker et al. (2013) interpreted this unit as a lodgment tilite. The next 9 meters of the section encompasses light-grey impure (up to 40% of detrital fragments) limestone intercalated with calcilutites. Microbial lamination is present (Fig. 4.6A) so is fenestral

porosity, commonly filled with sparry calcite and more rarely with cryptocrystalline silica.

From 600 to 608 m, the terrigenous content diminishes and calcilutites are the dominant lithology and, occasionally, there is the occurrence of impure calcarenite. Stylolites and other dissolution structures are present, and at the top of this segment, there are aragonite pseudomorphs. Pyrite crystals, euhedric or framboidal, are a common feature (Fig 4.6B).

Between 608 and 627 m the detrital content increases remarkably and the interval is marked by mudstones and siltstones, and, more rarely, by calcilutites. Such enhance in the detrital content was used as a guide to determine the maximum flood surface of the Arcos section (Caetano-Filho et al., 2019). Again, from 627 to 668 m, the terrigenous content is very low and limestones featuring microbial laminations predominate. However, from time to time, intraclastic calcarenites are also found and stylolites are common (Fig. 4.6C).

At the segment that goes from 668 to 705 m, calcilutite exhibiting microbial structures intercalates with black shaly rocks presenting a crinkled lamination. Then, until 718 m, calcilutites are the major lithology. At 718 to 738 m there are oolitic and intraclastic calcarenites. The interval between 738 and 761 m is heavily dolomitized, featuring oolitic and intraclastic doloarenites, sometimes laminated. The dolomitization is evidence of regression; therefore, at this interval, there is an unconformity that marks the end of the first 2nd-order sequence and the beginning of the second sequence. Following the dolomitic rocks, the Arcos section comprises, again, calcilutites with microbial structures, until the end of the section.

Figure 4.5: Arcos section: depositional environments, lithology, structures, facies, chemostratigraphic data and its sequence stratigraphy framework. System tracts: TST – Transgressive System Tract; MFS – Maximum Flooding Surface; EHST – Early Highstand System Tract; LHST – Late Highstand System Tract; SB1 – Sequence Boundary. Granulometry scale: C – clay; S – sand; G – gravel. Extracted from Caetano-Filho et al. (2019).

Figure 4.6: Arcos structures. A) Microbial lamination at the base of the Arcos Section. B) A layer of limestone with abundant pyrite. C) Stylolites, a common feature at this part of the section.

5 MATERIALS AND METHODS

5.1 Studied Sections

Three sections, Arcos, Well 1, and Januária, encompassing the first and second 2nd-order sequences of the Bambuí basin were investigated in this work (Fig. 2.1). Arcos and Well 1 are associated with the Sete Lagoas High Domain, on the south of the São Francisco basin. The former is representative of shallow parts of a forebulge setting, while the latter consists of deposits of deeper environments, a forebulge graben. Januária is within the area of the Januária High domain and it represents shallow environments of the forebulge setting at the Central-East of the basin. These sections were extensively studied by other geochemical proxies such as $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}$, Sr/Ca, $^{87}\text{Sr}/^{86}\text{Sr}$ (Kuchenbecker et al., 2016b; Caetano-Filho et al., 2019), $\delta^{13}\text{C}_{\text{org}}$ (Caetano-Filho et al., 2019) and Rare Earth Elements plus Yttrium (REY) (Paula-Santos et al., 2020).

5.2 Petrography

Thin sections of Arcos and Januária were observed under a Carl-Zeiss Axioplan 2 polarized light microscope aiming to observe possible diagenetic/metamorphic features that could have altered the primary nitrogen isotopic signature. No thin sections from Well 1 were observed because there was not enough material available to prepare them.

5.3 Sample Preparation for N Analysis

86 rock samples from Well 1, 46 from Januária and 45 from Arcos, totalizing 177 samples were analyzed in a stratigraphic resolution of 1 m for the cap carbonate interval, except Well 1, in which the resolution was 3 meters. Also, for the second sequence of the Januária section, the resolution of sampling was 1 meter. For the rest of the sections, the interval was of five meters, encompassing all the systems tract intervals defined by Caetano-Filho et al. (2019). Rocks were crushed into small sizes using mortar and pestle and subsequently were pulverized using a tungsten carbide mill. To concentrate the nitrogen on the samples, the carbonate fraction was removed. For this, 25mL of HCl 5N was added to 3 to 5 g of samples for 12 h at 25° C. Then, the samples were heated at 80° C for 2h. The residue of this procedure was rinsed with distilled water until its pH was neutral and was then dried in an oven at 50 °C. The residue was submitted to the N isotope analysis.

5.4 $\delta^{15}\text{N}$ and Total N – Elemental Analyzer

To obtain the $\delta^{15}\text{N}_{\text{bulk}}$ data, 5 to 10 mg of the insoluble residue were analyzed on an elemental analyzer Thermo Scientific EA Flash 2000 coupled to a Thermo Scientific 185 Delta V+, at Pôle de Spectrométrie Océan, University of Western Brittany, France. The procedure was the same used by Pasquier et al. (2018), as it follows. An autosampler dropped the samples into an oxidation furnace at 1020 °C. An 8 second injection time of dioxygen at a flux of 240 mL/min was used to accomplish the flash combustion. To avoid incomplete oxidation of the flash combustion products, chromium(III) oxide and silver-plated cobalt oxide were added to the oxidation reactor. The produced gas was transported by continuous helium flow (100 mL/min) to a reducing column containing activated copper (heated at 650 °C), which enabled the removal of oxygen in excess and the conversion of NO_x to N_2 . Water vapor was removed from the gas using anhydrous magnesium perchlorate. The rest of the gases were separated using gas chromatography and were introduced into the mass spectrometer via a Thermo Scientific ConFlo IV universal interface. Total nitrogen (TN) was measured by the Thermal Conductivity Detector of the Flash EA 2000 and in this work, we report $\text{TN}_{\text{decarb}}$ as the measured N concentration in the insoluble residue obtained after HCl leaching. $\delta^{15}\text{N}_{\text{bulk}}$ data are reported in per mil (‰) deviation from the atmospheric N isotopic composition ($\delta^{15}\text{N}_{\text{air}} = 0\text{‰}$). The average uncertainty was calculated according to measurements of internal and reference standards and it was better than 0.15‰ (2σ) for $\delta^{15}\text{N}_{\text{bulk}}$ and better than 0.03% (2σ) for N total concentration. The used standards were: (i) LIPG, yeast from the Institut de Physique du Globe de Paris, Paris, France; and (ii) SED-IVA (IVA reference number: 33802151). This work also reports total nitrogen in samples (TN_{bulk}), which was calculated gravimetrically based on the amount of mass of sample remaining after the HCl decarbonation.

5.5 $\delta^{15}\text{N}$ and total N – Sealed tube combustion + dual inlet mass spectrometer

Some samples from Arcos, Well 1 and Januária did not yield results using the EA method, and in these cases, samples were measured using the classical sealed tube method (Ader et al., 1998, 2016). Here, the N_2 is extracted and purified using a vacuum line (Fig. 5.1) (Ader et al., 1998, 2016). In this method, quartz tubes of 6 mm in diameter and 32.5 cm in length were filled with previously purified at 950 °C CuO (~3.5 g) and Cu (~1 g) wires. This size of tubes prevents them from exploding due to CO_2 overpressure during the combustion step. Then, the tubes were loaded with sample powder, which is separated from the cupric

reactants using quartz wool (also purified at 950 °C). At this point, it is important to weight a quantity of sample that is enough to provide a good measurement at the spectrometer, but also a quantity that will not make the combustion step inefficient. For the Bambuí samples, the weighted amount contained approximately 2 μmol of N₂. However, due to the low N content of some samples, this amount of N₂ was not reachable for all of them and, in this case, measurements were performed using 1.5 μmol of N₂, which at the end resulted in masses ranging from 200 to 400 mg of powder. After the tubes were loaded with Cu, CuO and samples, they were attached in the vacuum line and were degassed under 150 °C until the vacuum was better than 10⁻⁶ mbar, which usually takes about 12 hours (Fig. 5.1A). Subsequently, the tubes were flame sealed and proceeded to the combustion step (Fig. 5.2). At this stage, the tubes were heated in a furnace under 950 °C for 6 hours to allow the CuO to decompose into Cu and O, as the liberated O causes the combustion of the sample, which generates water, dinitrogen, carbon dioxide and oxides of nitrogen as products (equation 5.1 – not balanced). Then, the tubes are cooled until 600 °C for two hours, to allow the oxides of nitrogen to react with Cu, which generates N₂ and CuO (equation 5.2 – not balanced). The final products of the combustion step are N₂, Cu, CuO, H₂O and CO₂.

After the combustion step, a glass cutter was used to make a scission in the quartz tubes, which are placed inside a tube cracker device. The device was placed in the vacuum line and when the vacuum was good enough (~10⁻⁶ mbar), the tube was cracked and the gases generated during the combustion step were released into the line (Fig. 5.1B). The purification of the gas was done by two furnaces containing CuO (450 °C) and Cu (600° C), respectively, in which the gas cycled before its collection (Fig. 5.1C). Also, the CO₂ and H₂O of the gas were separated from N₂ using a liquid nitrogen trap, whose temperature was always held lower than -175 °C (Fig. 5.1D). After the purification step, the resulting N₂ was concentrated and pushed into a sample vessel using a Toepler pump, which also allows the quantification of the extracted N₂ (Fig. 5.1E). To access that there was no contamination coming from the vacuum line, blanks of the line (i.e doing the entire extraction process but with no sample) were commonly done, yielding less than 0.02 μmol of gas within the vacuum line system, which is neglectable considering the amount of N₂ in the Bambuí samples. After each sample extraction, the cryogenically trapped gases were released and the pressure exercised by them

was measured, to check if the N₂ was properly purified. Then, all the valves are open and the remaining gases are pumped out of the line. The next extraction is only done when the vacuum is good enough again ($\sim 10^{-6}$ mbar).

Figure 5.1: Sketch of the extraction vacuum line, arrows indicate the path of gases inside the line. Tubes are filled with Cu, CuO, quartz wool and sample and are degassed overnight under 150 °C (A). The tubes are flame sealed and heated for 2 hours at 950 °C and then for 6 hours at 600°C using a furnace. The “cooked” tubes are placed at the line and cracked using a tube cracker device (B). The liberated gas is purified using more CuO/CuO (C) ovens and a liquid nitrogen trap (D). The resulting N₂ is quantified and pushed to a sample vessel using a Toppler pump (E). Subsequently, the gas nitrogen isotopic composition is measured in a Dual Inlet IRMS. After the gas is purified all the valves of the line are open and the remaining gases are pumped out of it. The next extraction is only done when the vacuum is good enough.

sample and the results yielded by the equipment are the average of these ten measurements, except when there is an outlier. In this case, the outlier is not used to calculate the mean $\delta^{15}\text{N}_{\text{bulk}}$ of the results. To access the reliability of the data the reference gas was measured against itself after and before each sample measurement. The precision of $\delta^{15}\text{N}_{\text{bulk}}$ values were better than 0.5‰ (1σ), estimated from the reproducibility of the measurements of certified materials, IAEA-N1 and IAEA-N2 and IPGP internal standard MS#5. Triplicates from a batch of samples were also done.

5.6 K and Al content

K and Al contents were measured using a portable XRF device Thermo Scientific Niton XL3t provided by the Geological Survey of Brazil (CPRM). Samples were polished and veins or terrigenous laminations were avoided. A blank (SiO_2) and a certified reference material (QC 180-673, Thermo) were run after every batch of 30 samples. The K blanks were less than 0.01 ppm and the reproducibility of the standard was better than 0.2% (1σ). Blanks of Al were lower than the detection limits and the reproducibility of standards was better than 0.5% (1σ). K and Al content are reported in percentage (%).

6 RESULTS

6.1 $\delta^{15}\text{N}$ data and total N

From the initial batch of 177 carbonate samples, 153 results were obtained: 39 from Januária (Fig. 6.1), 34 from Arcos (Fig. 6.2) and 80 from Well 1 (Fig. 6.3). The results of the isotopic compositions of bulk nitrogen ($\delta^{15}\text{N}_{\text{bulk}}$), total nitrogen in residues ($\text{TN}_{\text{decarb}}$) and total nitrogen in bulk rock (TN_{bulk}) are shown in Table 6.1. The results were paired with total organic carbon in the insoluble residue ($\text{TOC}_{\text{decarb}}$), total carbon in bulk rock (TOC_{bulk}) and $\delta^{13}\text{C}_{\text{org}}$ data published by Caetano-Filho et al. (2021) except for 11 samples from the 2nd sequence of Januária and one from Arcos, whose $\text{TOC}_{\text{decarb}}$ and TOC_{bulk} were obtained in this work. $\text{C}_{\text{org}}/\text{N}$ ratios were calculated from measured $\text{TOC}_{\text{decarb}}$ and $\text{TN}_{\text{decarb}}$ on an atomic basis and are also reported in Table 6.1 and figures 6.1, 6.2 and 6.3.

The $\delta^{15}\text{N}_{\text{bulk}}$ values are fairly constant on the three sections ranging from a minimum of -1.4‰ in Well 1 to a maximum of +5.0‰ in Arcos. Importantly, the -1.4‰ value is an outlier and will not be considered for further interpretations. The average value of $\delta^{15}\text{N}_{\text{bulk}}$ is +2.9‰ (n = 152). Arcos section has the heaviest N mean isotopic composition, 3.4‰ (n = 34) with $\delta^{15}\text{N}_{\text{bulk}}$ ranging from +1.6‰ to +5.0‰. Januária samples average $\delta^{15}\text{N}_{\text{bulk}}$ is 3.1‰ (n = 39), ranging from +1.3‰ to +4.3‰, while Well 1 has the lowest $\delta^{15}\text{N}_{\text{bulk}}$ mean, 2.5‰ (n = 79), with N signatures ranging from 1.4‰ to 4.0‰.

$\delta^{15}\text{N}_{\text{bulk}}$ values seems not to be related to lithology, but some excursions are present along the profiles. The cap carbonates from Well 1 present a little positive $\delta^{15}\text{N}_{\text{bulk}}$ shift going from +1.5‰ to +2.8‰. The same trend is observed in Januária, in which a pronounced positive excursion from +1.2‰ to +3.8‰ also occurs on the post-glacial carbonates. In Arcos, this trend is also present, and $\delta^{15}\text{N}_{\text{bulk}}$ values range from +3.2 to +5.0‰.

In the EHST and LHST $\delta^{15}\text{N}_{\text{bulk}}$ values of the Well 1 section are around a plateau of +2.5‰. In the EHST, Januária values form plateaus around +3.0‰ and in the LHST, Januária's $\delta^{15}\text{N}_{\text{bulk}}$ data oscillate between ~2‰ and ~4‰. Arcos, however, does not show a plateau behavior. In this latter section, the EHST $\delta^{15}\text{N}_{\text{bulk}}$ values start at +3.4‰ reaching a minimum of +1.6‰ near the transition to the LHST and then return to +3.4‰.

During the second 2nd-order sequence, the sections associated with the Sete Lagoas High are slightly more positive than Januária. The mean $\delta^{15}\text{N}_{\text{bulk}}$ value of Arcos section during such interval is 3.8‰ (n = 3) and in Well 1 it is 3.2‰ (n = 6), meanwhile in Januária, the average $\delta^{15}\text{N}_{\text{bulk}}$ value is 3.0 ‰ (n = 13).

TN_{bulk} (ppm) values are low in all sections, with an average value of 119.3 ppm (n =

152). However, the sections from the shallow domains of the São Francisco Basin are poorer in N than the one extracted from the forebulge graben. Arcos and Januária average TN_{bulk} is 37.1 ppm ($n = 34$) and 29.6 ppm ($n = 39$) respectively, while in Well 1 the mean concentration is 198.0 ppm ($n = 79$). Also, it can be seen in Table 6.1, TN_{bulk} concentrations increase as the amount of carbonate minerals diminish. This feature generated a remarkable zigzag pattern on the EHST of Well 1 section, in which limestones more or less rich in insoluble residue intercalates (Fig. 6.3).

C_{org}/N ratios range from 0.63, in Januária, to a maximum of 107.4, in Arcos, while the average value for the three sections is 20.3 ($n = 152$), which is above the Redfield Ratio (6.6) for C/N. Even if our average C_{org}/N ratio is low for Precambrian rocks, similar C_{org}/N ratios have been reported on the Ediacaran/Cambrian transition in China (Kikumoto et al., 2014). In all sections, nearby the transition from the EHST to the LHST there are samples remarkably enriched in N compared to the Redfield value. In Januária, the enrichment is present in 13 samples with an average C_{org}/N of 2.7, extending from CM-01-c to CM-12, which corresponds to the cap carbonates and the upper limit of the EHST. In Well 1 the same pattern is present from samples CLS-1a to CLS-53 ($n = 46$), except for values > 6.6 that occur near the Maximum Flood surface (Fig. 2.3) and rise the mean value of this interval to 7.3. In Arcos, the N enrichment ends earlier than in the other sections, in the middle of the EHST, between samples M4 to K28a ($n = 17$). Sample M15 is an exception in this segment, with a C_{org}/N ratio of 67.0, which drives the mean value of this interval to 12.5. Without M15 sample, the average value for Arcos low C_{org}/N interval would be 8.3. During the LHST and after the sequence boundary C_{org}/N ratios are higher than 6.6, except in Well 1, in which occasionally samples with low C_{org}/N are reported.

6.2 K and Al content

The average K content of samples is 0.4%, 0.6% and 2.9%, whereas the average Al content is 1.0%, 1.3% and 2.1% in Januária, Arcos and Well 1, respectively. Higher K and Al contents are reported for samples deposited during transgressions, while the samples from regressions show lower values (Table 6.2).

Table 6.1: $\delta^{15}\text{N}_{\text{bulk}}$ and TN data for the Bambuí basin:

Section	Sample	m	System Tract	$\delta^{15}\text{N}_{\text{bulk}}$ (‰)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	TN _{bulk} (ppm)	TN _{decarb} (ppm)	TOC _{bulk} (%)	TOC _{decarb} (%)	K (%)	Al (%)	C _{org} /N	IR (%)	Combustion Method
Januária	CM-01c	13.8	TST	2.4	-26.13	31.9	505.1	0.01	0.13	0.6	1.42	2.99	6.3	Flash 2000
Januária	CM-02	14.2	TST	1.3	-25.44	33.9	422.5	0.01	0.12	0.4	1.13	3.39	8.0	Flash 2000
Januária	CM-02b	14.6	TST	2.7	-21.36	34.3	460.6	0.01	0.12	0.4	0.91	2.93	7.4	Flash 2000
Januária	CM-03	15.2	TST	3.1	-22.17	30.1	378.8	0.01	0.09	0.4	1.03	2.88	8.0	Flash 2000
Januária	CM-03c	15.8	TST	2.5	-24.90	118.8	2433.1	0.04	0.92	0.6	1.84	4.41	4.9	Flash 2000
Januária	CM-03f	16.5	TST	3.1	-26.25	22.1	443.2	0.01	0.14	0.1	1.01	3.60	5.0	Flash 2000
Januária	CM-03h	16.9	TST	3.4	--	20.8	282.5	0.01	0.09	0.4	0.82	3.64	7.4	Sealed tube
Januária	CM-04a	17.3	TST	3.8	-25.71	21.6	372.9	0.00	0.05	0.4	0.76	1.64	5.8	Flash 2000
Januária	CM-04c	17.7	TST	3.5	-28.68	32.2	348.3	0.01	0.06	0.5	0.63	1.85	9.2	Flash 2000
Januária	CM-05	18.3	TST	3.5	-28.53	27.8	363.9	0.00	0.05	0.6	0.88	1.45	7.6	Flash 2000
Januária	CM-06	19.3	TST	3.5	-26.92	35.5	323.4	0.00	0.02	0.7	1.07	0.63	11.0	Flash 2000
Januária	CM-07	29.5	TST	3.3	-27.91	27.3	322.6	0.00	0.05	0.5	0.70	1.67	8.5	Flash 2000
Januária	CM-12	34.5	EHST	3.2	-28.19	26.8	202.9	0.01	0.06	0.8	1.02	3.62	13.2	Flash 2000
Januária	CM-22	44.9	EHST	2.6	-30.84	14.5	687.7	0.04	2.03	0.1	<LD	34.40	2.1	Flash 2000
Januária	CM-27	51.1	LHST	3.4	-29.13	7.6	537.2	0.04	2.82	<LD	0.54	61.35	1.4	Flash 2000
Januária	CM-32	56.1	LHST	3.1	-30.29	12.6	843.2	0.04	2.94	0.1	<LD	40.69	1.5	Flash 2000
Januária	CM-37	61.8	LHST	2.8	-29.54	8.0	1216.8	0.03	4.63	<LD	<LD	44.40	0.7	Flash 2000
Januária	CM-42	67.5	LHST	3.0	-29.92	11.8	1308.4	0.03	3.79	<LD	0.48	33.78	0.9	Flash 2000
Januária	CM-45	70.5	LHST	4.0	-29.64	9.6	772.5	0.02	1.32	<LD	<LD	19.95	1.2	Flash 2000
Januária	BAR-10	72.5	LHST	2.9	-30.10	10.3	995.4	0.05	4.38	<LD	0.34	51.29	1.0	Flash 2000
Januária	BAR-15	77.3	LHST	4.1	--	12.1	794.5	0.02	1.54	0.1	<LD	22.60	1.5	Flash 2000
Januária	BAR-20	82.5	LHST	2.8	-29.38	10.2	552.7	0.03	1.85	<LD	0.57	39.02	1.8	Flash 2000
Januária	BAR-25	87.5	LHST	3.2	-30.65	10.8	587.1	0.02	1.04	<LD	0.74	20.64	1.8	Flash 2000
Januária	BAR-30	93.3	LHST	2.3	-30.14	10.1	875.5	0.02	1.96	<LD	0.47	26.17	1.2	Flash 2000
Januária	BAR-35	98.7	LHST	4.3	-29.19	11.1	1044.6	0.02	1.73	<LD	<LD	19.37	1.1	Flash 2000
Januária	BAR-40	105.5	LHST	2.7	-30.02	7.0	1365.4	0.02	3.98	<LD	0.51	34.03	0.5	Flash 2000
Januária	JL-01	140.0	2nd-seq.	2.9	-21.19	71.2	405.0	0.07	0.42	0.5	1.23	12.15	17.6	Sealed tube
Januária	JL-02	141.0	2nd-seq.	2.5	--	45.6	463.0	0.03	0.31	1.2	2.90	7.81	9.8	Sealed tube
Januária	JL-04	143.0	2nd-seq.	3.0	--	17.9	438.0	0.05	1.23	0.4	1.60	32.76	4.1	Sealed tube
Januária	JL-06	145.0	2nd-seq.	2.9	--	6.4	781.0	0.02	2.08	0.2	1.09	31.07	0.8	Sealed tube
Januária	JL-07	146.0	2nd-seq.	3.7	--	14.7	460.0	0.02	0.66	0.09	0.65	16.74	3.08	Sealed tube
Januária	JL-08	147.0	2nd-seq.	2.9	--	14.9	412.0	0.04	1.14	--	0.42	32.28	3.6	Sealed tube
Januária	JL-09	148.0	2nd-seq.	2.9	-20.27	10.8	231.0	0.04	0.85	--	--	42.75	4.7	Sealed tube
Januária	JL-10	149.0	2nd-seq.	3.0	--	9.4	431.0	0.02	0.89	0.1	0.75	24.09	2.2	Sealed tube

Section	Sample	m	System Tract	$\delta^{15}\text{N}_{\text{bulk}}$ (‰)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	TN_{bulk} (ppm)	$\text{TN}_{\text{decarb}}$ (ppm)	TOC_{bulk} (%)	$\text{TOC}_{\text{decarb}}$ (%)	K (%)	Al (%)	$\text{C}_{\text{org}}/\text{N}$	IR (%)	Combustion Method
Januária	JL-11	150.0	2nd-seq.	3.8	--	4.1	431.0	0.01	0.55	0.1	0.51	14.89	0.9	Sealed tube
Januária	JL-12	151.0	2nd-seq.	3.4	--	8.9	414.0	0.03	1.61	--	0.34	45.37	2.2	Sealed tube
Januária	JL-14	156.0	2nd-seq.	3.0	-19.27	25.0	383.0	0.06	0.94	0.2	0.83	28.66	6.5	Sealed tube
Januária	JL-15	157.5	2nd-seq.	2.7	--	296.1	380.0	0.04	0.16	0.7	1.94	4.91	22.1	Sealed tube
Januária	JL-16	158.5	2nd-seq.	2.9	--	71.2	461.0	0.18	1.19	0.7	1.86	30.12	15.5	Sealed tube
Arcos	M4	592.0	TST	3.2	--	18.5	74.0	--	--	0.4	1.1	--	25.0	Sealed tube
Arcos	M5	593.0	TST	3.9	-26.92	8.4	80.0	0.01	0.12	0.1	0.8	17.66	10.4	Sealed tube
Arcos	M6	594.0	TST	4.4	-27.03	17.2	140.0	0.01	0.08	0.3	0.9	6.57	12.3	Sealed tube
Arcos	M7	595.0	TST	4.0	-26.14	36.6	260.2	0.01	0.08	0.7	1.1	3.54	14.1	Flash 2000
Arcos	M8	596.0	TST	3.9	-27.14	30.6	85.0	0.02	0.05	0.3	2.4	7.41	35.9	Sealed tube
Arcos	M9	596.6	TST	5.0	-27.08	43.1	129.0	0.01	0.04	0.7	2.8	3.99	33.4	Sealed tube
Arcos	M12	599.3	TST	3.7	-27.83	29.1	266.8	0.03	0.28	0.7	1.2	12.05	10.9	Flash 2000
Arcos	M13	600.2	TST	4.0	-30.72	58.2	344.0	0.11	0.64	0.9	1.5	21.68	16.9	Sealed tube
Arcos	M15	601.7	TST	2.9	-30.28	52.8	282.1	0.30	1.62	0.7	1.5	66.97	18.7	Flash 2000
Arcos	M17	602.6	TST	3.3	-27.33	64.2	338.9	0.02	0.08	1.1	1.9	2.84	18.9	Flash 2000
Arcos	M18	604.8	TST	4.0	-26.42	26.1	294.0	0.01	0.07	0.7	1.2	2.67	8.9	Flash 2000
Arcos	M19	605.9	TST	3.9	--	16.5	410.0	--	--	0.4	1.0	--	4.0	Sealed tube
Arcos	M20	606.5	TST	3.3	-26.36	32.4	366.0	0.03	0.35	0.4	0.8	11.30	8.9	Flash 2000
Arcos	M21	606.9	TST	3.4	-29.24	102.3	337.9	0.10	0.32	1.0	3.0	10.95	30.3	Flash 2000
Arcos	M24	612.0	TST	3.7	-26.61	282.8	338.0	0.02	0.03	2.7	7.7	0.97	83.7	Flash 2000
Arcos	M27	626.4	EHST	3.4	-26.58	127.2	298.1	--	--	1.5	2.9	--	42.7	Flash 2000
Arcos	K28a	632.2	EHST	3.3	-26.47	21.9	465.4	0.01	0.24	0.0	0.4	5.95	4.7	Flash 2000
Arcos	K29a	637.0	EHST	3.4	-26.31	11.3	470.3	0.01	0.39	--	0.2	9.70	2.4	Flash 2000
Arcos	K30a	642.0	EHST	4.2	-26.20	8.3	567.0	0.01	0.58	--	0.3	11.88	1.5	Sealed tube
Arcos	K31c	649.0	EHST	3.4	--	10.2	759.0	--	--	0.2	0.4	--	1.3	Sealed tube
Arcos	K32d	655.0	EHST	3.6	-25.79	3.9	743.0	0.01	1.81	--	--	28.41	0.5	Flash 2000
Arcos	K34c	664.2	EHST	3.0	-25.81	9.7	626.0	0.04	2.44	--	0.5	45.44	1.5	Flash 2000
Arcos	K35d	669.4	EHST	3.1	-25.80	26.3	657.9	0.09	2.23	--	--	39.48	4.0	Flash 2000
Arcos	K37c	679.4	EHST	2.5	-25.51	30.2	1102.2	0.09	3.38	0.1	0.6	35.82	2.7	Flash 2000
Arcos	K38c	684.4	LHST	1.7	-24.16	10.7	1241.9	0.10	11.43	--	0.3	107.40	0.9	Flash 2000
Arcos	M40	690.9	LHST	1.6	-25.17	19.3	2319.1	0.10	12.38	--	0.3	62.28	0.8	Flash 2000
Arcos	M42	701.7	LHST	2.5	-25.60	9.7	1330.9	0.04	4.85	--	0.3	42.54	0.7	Flash 2000
Arcos	K42d	705.4	LHST	2.0	-25.79	15.7	2029.8	0.07	9.42	--	--	54.12	0.8	Flash 2000
Arcos	M44	711.4	LHST	2.6	-24.96	12.6	2585.9	0.07	14.89	--	--	67.16	0.5	Flash 2000
Arcos	M45	716.4	LHST	3.4	-24.35	9.1	703.0	0.05	4.05	--	--	67.25	1.3	Sealed tube
Arcos	M50	741.9	LHST	4.5	-22.74	17.6	477.6	0.09	2.31	0.2	0.4	56.35	3.7	Flash 2000
Arcos	K52a	753.2	2nd-seq.	4.1	-22.54	16.8	1027.8	0.08	4.61	0.1	0.4	52.33	1.6	Flash 2000

Section	Sample	m	System Tract	$\delta^{15}\text{N}_{\text{bulk}}$ (‰)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	TN _{bulk} (ppm)	TN _{decarb} (ppm)	TOC _{bulk} (%)	TOC _{decarb} (%)	K (%)	Al (%)	C _{org} /N	IR (%)	Combustion Method
Arcos	M53	757.2	2nd-seq.	4.3	-22.17	11.6	521.1	0.04	2.01	0.1	0.3	44.99	2.2	Flash 2000
Arcos	M55	767.2	2nd-seq.	2.9	-22.22	71.1	459.0	0.13	0.84	0.8	--	21.32	15.5	Flash 2000
Well 1	CLS-01b	1118	TST	1.5	-27.58	69.2	259.1	0.04	0.17	--	1.4	7.57	26.7	Flash 2000
Well 1	CLS-02a	1116	TST	1.7	-27.06	54.5	254.2	0.03	0.15	0.6	1.7	6.68	21.4	Flash 2000
Well 1	CLS-02b	1112	TST	1.7	-26.64	40.0	812.0	0.02	0.41	0.4	0.7	5.92	4.9	Flash 2000
Well 1	CLS-03a	1110	TST	2.0	-27.75	97.7	527.9	0.03	0.17	1.2	2.6	3.75	18.5	Flash 2000
Well 1	CLS-03b	1109	TST	1.9	-27.41	67.9	944.4	0.04	0.62	0.7	1.4	7.66	7.2	Flash 2000
Well 1	CLS-04	1107	TST	2.4	-27.43	63.1	718.1	0.03	0.39	1.0	3.0	6.33	8.8	Flash 2000
Well 1	CLS-05	1099	TST	1.4	-28.89	132.6	383.2	0.09	0.27	--	--	8.08	34.6	Flash 2000
Well 1	CLS-07	1092	TST	2.8	-29.63	561.3	762.1	0.62	0.84	2.5	6.2	12.90	73.7	Flash 2000
Well 1	CLS-09	1080	TST	2.0	-28.63	188.1	366.5	0.20	0.39	--	--	12.36	51.3	Flash 2000
Well 1	CLS-11	1072	TST	2.3	-30.30	689.0	763.4	1.79	1.99	3.0	8.2	30.37	90.2	Flash 2000
Well 1	CLS-12	1067	TST	3.6	-28.36	122.5	218.0	0.21	0.47	--	--	25.20	43.8	Sealed tube
Well 1	CLS-15	1057	EHST	2.6	-29.07	654.3	743.5	2.64	3.00	--	--	47.11	88.0	Flash 2000
Well 1	CLS-18	1043	EHST	1.9	-28.22	442.7	613.7	0.97	1.35	1.3	3.5	25.59	72.1	Flash 2000
Well 1	CLS-20	1034	EHST	2.8	-26.82	217.3	524.8	0.13	0.31	0.4	1.0	6.97	41.4	Flash 2000
Well 1	CLS-21	1030	EHST	3.0	-26.23	253.5	464.5	0.12	0.22	0.4	1.0	5.46	54.6	Flash 2000
Well 1	CLS-22	1025	EHST	3.2	-26.67	432.6	562.3	0.13	0.17	0.5	2.8	3.58	76.9	Flash 2000
Well 1	CLS-23	1020	EHST	2.6	-25.90	35.9	411.6	0.04	0.47	0.3	1.4	13.20	8.7	Flash 2000
Well 1	CLS-24	1016	EHST	3.2	-26.91	117.9	520.7	0.02	0.08	1.3	4.4	1.71	22.6	Flash 2000
Well 1	CLS-25	1010	EHST	2.7	-25.23	204.0	442.4	0.06	0.13	2.5	9.4	3.50	46.1	Flash 2000
Well 1	CLS-26	1007	EHST	2.6	-25.45	151.3	495.8	0.07	0.22	0.5	1.6	5.19	30.5	Flash 2000
Well 1	CLS-27	1002	EHST	2.5	-26.87	202.0	464.7	0.05	0.11	1.1	4.4	2.83	43.5	Flash 2000
Well 1	CLS-28	996.8	EHST	2.8	-26.95	60.8	313.0	0.03	0.18	0.4	2.3	6.65	19.4	Flash 2000
Well 1	CLS-29	992.0	EHST	2.2	-26.18	121.4	407.7	0.04	0.13	0.3	0.9	3.67	29.8	Flash 2000
Well 1	CLS-30	987.0	EHST	2.3	-27.12	68.2	411.1	0.06	0.36	0.8	2.8	10.14	16.6	Flash 2000
Well 1	CLS-31	982.4	EHST	2.4	-27.87	47.1	346.8	0.04	0.31	0.5	1.7	10.32	13.6	Flash 2000
Well 1	CLS-32	977.8	EHST	2.0	-27.71	93.3	369.2	0.04	0.14	0.3	1.4	4.45	25.3	Flash 2000
Well 1	CLS-33	973.3	EHST	2.6	-27.71	182.0	390.8	0.04	0.09	0.6	2.3	2.66	46.6	Flash 2000
Well 1	CLS-34	968.7	EHST	1.8	-27.15	220.7	415.4	0.02	0.04	0.7	3.8	1.21	53.1	Flash 2000
Well 1	CLS-35	964.3	EHST	2.4	-27.28	255.7	405.5	0.03	0.05	0.6	3.2	1.53	63.0	Flash 2000
Well 1	CLS-36	959.5	EHST	2.6	-27.52	138.0	353.6	0.03	0.09	0.3	1.5	2.86	39.0	Flash 2000
Well 1	CLS-38	950.1	EHST	2.6	-26.78	164.2	318.7	0.02	0.04	2.1	8.6	1.61	51.5	Flash 2000
Well 1	CLS-39	945.6	EHST	2.8	-25.46	70.7	265.7	0.02	0.07	0.5	2.0	3.05	26.6	Flash 2000
Well 1	CLS-40	940.8	EHST	2.7	-25.78	108.4	291.2	0.03	0.08	0.5	2.4	3.08	37.2	Flash 2000
Well 1	CLS-41	936.3	EHST	2.2	-26.94	69.7	192.5	0.03	0.09	0.3	0.8	5.36	36.2	Flash 2000
Well 1	CLS-42	932.2	EHST	2.5	-26.42	135.1	281.0	0.06	0.12	0.8	3.4	5.04	48.1	Flash 2000

Section	Sample	m	System Tract	$\delta^{15}\text{N}_{\text{bulk}}$ (‰)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	TN_{bulk} (ppm)	$\text{TN}_{\text{decarb}}$ (ppm)	TOC_{bulk} (%)	$\text{TOC}_{\text{decarb}}$ (%)	K(%)	Al (%)	$\text{C}_{\text{org}}/\text{N}$	IR (%)	Combustion Method
Well 1	CLS-43	927.6	EHST	2.5	-26.70	231.3	307.7	0.03	0.04	0.3	1.1	1.70	75.2	Flash 2000
Well 1	CLS-44	922.9	EHST	3.0	-26.50	155.5	341.1	0.04	0.09	0.2	0.5	2.99	45.6	Flash 2000
Well 1	CLS-45	918.5	EHST	2.4	-27.42	173.1	295.9	0.04	0.06	0.6	2.6	2.49	58.5	Flash 2000
Well 1	CLS-46	913.5	EHST	3.3	-28.10	65.5	162.0	0.05	0.12	0.5	0.9	8.56	40.4	Flash 2000
Well 1	CLS-47	909.2	EHST	2.6	-28.14	112.2	234.2	0.02	0.05	0.4	1.9	2.34	47.9	Flash 2000
Well 1	CLS-48	904.3	EHST	2.6	-28.60	235.8	324.3	0.05	0.07	0.6	2.4	2.55	72.7	Flash 2000
Well 1	CLS-49	899.7	EHST	2.5	-28.60	137.2	270.2	0.03	0.06	0.5	1.8	2.69	50.8	Flash 2000
Well 1	CLS-50	895.1	EHST	2.6	-28.00	42.7	120.7	0.01	0.03	0.6	1.9	2.97	35.4	Flash 2000
Well 1	CLS-51	890.3	EHST	1.6	-27.97	135.3	206.0	0.01	0.04	0.8	2.6	2.29	34.3	Sealed tube
Well 1	CLS-52	886.0	EHST	1.6	-28.34	114.1	199.7	0.03	0.05	0.6	3.3	2.68	57.2	Flash 2000
Well 1	CLS-53	881.2	EHST	2.4	-28.15	145.2	237.3	0.04	0.06	0.3	1.4	2.99	61.2	Flash 2000
Well 1	CLS-54	876.7	EHST	2.7	-21.17	55.8	427.1	0.13	0.97	0.2	0.8	26.47	13.1	Flash 2000
Well 1	CLS-55	872.2	LHST	2.4	-20.12	43.5	462.4	0.11	1.21	0.2	0.9	30.55	9.4	Flash 2000
Well 1	CLS-56	867.7	LHST	2.6	-19.68	482.1	819.3	0.53	0.91	--	0.4	12.95	58.8	Flash 2000
Well 1	CLS-58	859.1	LHST	2.0	-20.21	502.7	957.8	0.45	0.85	2.4	6.6	10.34	52.5	Flash 2000
Well 1	CLS-59	854.6	LHST	2.5	-20.14	41.6	915.0	0.06	1.27	0.1	0.6	16.23	4.5	Flash 2000
Well 1	CLS-60	850.1	LHST	2.8	-19.71	174.2	1156.9	0.26	1.71	--	0.3	17.20	15.1	Flash 2000
Well 1	CLS-61	845.2	LHST	2.2	-20.08	26.7	914.7	0.09	3.01	--	0.6	38.34	2.9	Flash 2000
Well 1	CLS-62	840.7	LHST	2.6	-19.41	3.3	1673.4	0.01	4.23	0.1	0.4	29.46	0.2	Flash 2000
Well 1	CLS-63	836.1	LHST	2.9	-20.30	89.5	816.2	0.24	2.20	0.4	1.0	31.48	11.0	Flash 2000
Well 1	CLS-64	832.0	LHST	2.4	-20.56	17.2	1168.1	0.06	3.77	0.1	0.6	37.68	1.5	Flash 2000
Well 1	CLS-65	827.1	LHST	2.1	-20.09	33.3	1288.7	0.11	4.20	0.1	0.3	38.06	2.6	Flash 2000
Well 1	CLS-66	822.8	LHST	2.1	-20.34	17.4	1046.1	0.09	5.18	0.0	0.4	57.81	1.7	Flash 2000
Well 1	CLS-67	818.1	LHST	2.7	-22.15	437.5	735.2	0.32	0.54	0.3	1.4	8.56	59.5	Flash 2000
Well 1	CLS-68	813.7	LHST	2.3	-22.37	92.2	829.6	0.20	1.76	--	0.6	24.68	11.1	Flash 2000
Well 1	CLS-69	809.0	LHST	2.4	-22.02	121.9	709.6	0.30	1.78	0.2	1.5	29.19	17.2	Flash 2000
Well 1	CLS-70	804.4	LHST	2.5	-22.21	400.2	685.4	0.26	0.45	0.3	1.6	7.66	58.4	Flash 2000
Well 1	CLS-71	799.4	LHST	2.5	-20.28	24.7	545.0	0.09	2.04	0.1	1.2	43.62	4.5	Flash 2000
Well 1	CLS-72	794.5	LHST	2.9	-22.37	598.2	725.4	0.71	0.86	0.4	1.8	13.80	82.5	Flash 2000
Well 1	CLS-73	789.9	LHST	2.5	-20.66	35.0	615.6	0.11	2.00	--	0.7	37.94	5.7	Flash 2000
Well 1	CLS-74	784.9	LHST	2.3	-20.86	16.2	684.4	0.07	2.78	0.1	0.5	47.40	2.4	Flash 2000
Well 1	CLS-75	780.2	LHST	1.9	-21.36	12.1	240.0	0.05	1.01	0.1	0.8	49.31	5.0	Sealed tube
Well 1	CLS-76	775.4	LHST	3.2	-21.40	12.1	236.0	0.06	1.19	0.1	0.8	58.86	5.1	Sealed tube
Well 1	CLS-77	770.0	LHST	2.9	-22.33	484.0	554.6	0.21	0.24	--	--	4.97	87.3	Flash 2000
Well 1	CLS-79	761.6	LHST	2.8	-20.08	207.9	633.7	0.30	0.91	--	--	16.71	32.8	Flash 2000
Well 1	CLS-83	743.3	LHST	4.0	-14.33	121.1	1580.8	0.45	5.87	--	0.3	43.35	7.7	Flash 2000
Well 1	CLS-84	738.6	LHST	3.1	-15.93	57.1	1414.9	0.41	10.28	--	0.2	84.75	4.0	Flash 2000

Section	Sample	m	System Tract	$\delta^{15}\text{N}_{\text{bulk}}$ (‰)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	TN_{bulk} (ppm)	$\text{TN}_{\text{decarb}}$ (ppm)	TOC_{bulk} (%)	$\text{TOC}_{\text{decarb}}$ (%)	K (%)	Al (%)	$\text{C}_{\text{org}}/\text{N}$	IR (%)	Combustion Method
Well 1	CLS-85	733.9	LHST	3.1	-17.98	327.3	920.7	0.70	1.97	6.5	2.0	24.90	35.5	Flash 2000
Well 1	CLS-86	729.1	2nd-seq.	3.2	-17.31	408.7	926.4	0.91	2.07	13.5	1.3	26.02	44.1	Flash 2000
Well 1	CLS-87	724.5	2nd-seq.	3.3	-17.07	92.7	829.2	0.16	1.40	7.2	1.8	19.69	11.2	Flash 2000
Well 1	CLS-88	719.2	2nd-seq.	3.3	-17.21	678.2	887.9	0.95	1.25	2.3	2.5	16.38	76.4	Flash 2000
Well 1	CLS-89	715.0	2nd-seq.	2.8	-17.79	606.3	860.8	0.81	1.14	6.1	2.3	15.50	70.4	Flash 2000
Well 1	CLS-90	710.2	2nd-seq.	3.4	-18.13	716.9	1003.3	0.63	0.88	19.9	3.3	10.25	71.5	Flash 2000
Well 1	CLS-93	695.7	2nd-seq.	3.1	-21.46	617.6	783.6	0.20	0.25	1.5	2.9	3.70	78.8	Flash 2000

IR = Insoluble Residue, calculated from the residual fraction after HCl leaching on carbonates. 2nd-sequence = Second 2nd-order sequence. System tracts were based on Caetano-Filho et al. (2019). TOC and $\delta^{13}\text{C}_{\text{org}}$ were extracted from Caetano-Filho et al. (2021). Errors on the ratios and concentrations were presented in the text. TST = Transgressive system tract. EHST = Early Highstand system tract. LHST= Late Highstand system tract

Table 6.2: Al and K content average values during the transgressions and regressions periods

Section	Average K content – TST and 2 nd -sequence	Average K content - HST	Average Al content – TST and 2 nd -sequence	Average Al content - HST
Januária	0.4%	0.3%	1.1%	0.6%
Arcos	0.7%	0.4%	1.7%	0.6%
Well 1	4.6%	0.7%	2.9%	1.9%

Figure 6.1: The Januária section: lithologies, structures and sequence stratigraphy framework. $\delta^{15}\text{N}$ data were obtained in this study and the axis on the $\delta^{15}\text{N}$ (+2) indicates the boundary between N_2 fixation and NO_3^- assimilation. $\delta^{13}\text{C}_{\text{org}}$ was published by Caetano-Filho et al. (2021). The axis on the $\text{C}_{\text{org}}/\text{N}$ is fixed on the Redfield ratio (6.6) System tracts: TST – Transgressive System Tract; MFS – Maximum Flooding Surface; EHST – Early Highstand System Tract; LHST – Late Highstand System Tract; SB1 – Sequence Boundary. Granulometry scale: C – clay; S – sand; G – gravel. Adapted after Caetano-Filho et al. (2019).

Figure 6.2: Arcos section: lithologies, structures and sequence stratigraphy framework. $\delta^{15}\text{N}$ data were obtained in this study and the axis on the $\delta^{15}\text{N}$ (+2) indicates the boundary between N_2 fixation and NO_3^- assimilation. $\delta^{13}\text{C}_{\text{org}}$ was published by Caetano-Filho et al. (2021). The axis on the $\text{C}_{\text{org}}/\text{N}$ is fixed on the Redfield ratio (6.6) System tracts: TST – Transgressive System Tract; MFS – Maximum Flooding Surface; EHST – Early Highstand System Tract; LHST – Late Highstand System Tract; SB1 – Sequence Boundary. Granulometry scale: C – clay; S – sand; G – gravel. Adapted after Caetano-Filho et al. (2019).

Figure 6.3: Well 1 section: lithologies, structures and sequence stratigraphy framework. $\delta^{15}\text{N}$ data were obtained in this study and the axis on the $\delta^{15}\text{N}$ (+2) indicates the boundary between N_2 fixation and NO_3^- assimilation. $\delta^{13}\text{C}_{\text{org}}$ was published by Caetano-Filho et al. (2021). The axis on the $\text{C}_{\text{org}}/\text{N}$ is fixed on the Redfield ratio (6.6) System tracts: TST – Transgressive System Tract; MFS – Maximum Flooding Surface; EHST – Early Highstand System Tract; LHST – Late Highstand System Tract; SB1 – Sequence Boundary. Granulometry scale: C – clay; S – sand; G – gravel. Adapted after Caetano-Filho et al. (2019).

7 DISCUSSION

7.1 Preservation of $\delta^{15}\text{N}$ primary signals

In order to identify the $\delta^{15}\text{N}$ values that represent primary signals, effects of diagenesis and metamorphism have to be evaluated on samples. In sedimentary rocks N occurs in two phases: within the organic fraction or present as clay-bound NH_4^+ substituting K^+ in crystal lattices (Müller, 1977; Greenfield, 1992). Together they compose the N_{bulk} reservoir (NH_4^+ can be adsorbed by clay minerals too, but it is less common than K^+ replacement; Stevenson and Dhariwal, 1959).

The clay-bound NH_4^+ is formed mainly from the degradation of organic matter, although it can come from external sources, for example, a fluid (e.g. Schimmelmann et al., 2009). During the early diagenesis, as organic matter is degraded and N_{org} is liberated as NH_4^+ (this process presents minimum isotopic fractionation and therefore it records the original biomass isotopic signature; Möbius, 2013) a pool of ammonium within the pore waters is generated. Then, NH_4^+ , depending on the mineralogy, permeability and porosity of sediments (Stüeken et al., 2017), can either be fixed into clay minerals substituting K (Müller, 1977; Greenfield, 1992) without fractionation (Ader et al., 2016) or/and it can be oxidized into less reduced species (NO_2^- , NO_3^- and N_2), which depends on the O_2 concentration in the environment. Since partial oxidation of NH_4^+ leads to isotopic fractionation, diagenetic effects on $\delta^{15}\text{N}_{\text{bulk}}$ are enhanced under oxic conditions, as it favors the instability of ammonium. Under anoxic environments diagenetic effects increase primary $\delta^{15}\text{N}$ signal of bulk sediments less than 1‰, while in oxic environments the increment can be up to 4‰ (Altabet et al., 1999; Lehmann et al., 2002) (see section 3.3).

Studies using Rare Earth Elements indicate that the bottom waters of the Bambuí sea were anoxic (Paula-Santos et al., 2018) and even though carbonate diagenesis features such as recrystallization (Fig. 7.1 A), pressure solution seams (Fig. 7.1 B), dolomitization (Fig. 7.1 C) and filled fractures (Fig. 7.1 D) were observed in some parts of the sections (see Caetano-Filho et al., 2019, 2021 for details), anoxic conditions of bottom Bambuí waters (Hippertt et al., 2019) diminished the effects of diagenesis on the N isotopic signatures of the samples.

Figure 7.1: Carbonate diagenesis features. A) Recrystallization on the EHST of Arcos. B) pressure solution seams on the LHST of Arcos section. C) Dolomitization on TST of Arcos section. D) Filled fractures on the LHST of Januária section.

Well 1 and Arcos section samples show a moderate and strong correlation $R^2 = 0.58$ and 0.89 , respectively, between TN_{decarb} and TOC_{decarb} (Fig. 7.2 A and B), indicating that N came mainly from the primary organic matter (Calvert, 2004). In Januária the correlation is weaker, $R^2 = 0.32$ (Fig. 7.2 C), however its coefficient of determination is influenced by sample CM-03-3, an outlier heavily enriched in N. When the outlier is excluded, R^2 rises to 0.75 . None of the trendlines of TN_{decarb} and TOC_{decarb} plots pass through the origin, suggesting that a fraction of N in the samples are clay-bound. The presence of NH_4^+ linked to clay minerals is also notable when Al_{bulk} values are plotted against N_{bulk} concentrations. In Well 1 (Fig. 7.2 D) a clear positive correlation between these variables is not seen during the HST, which drives its R^2 to 0.19 . However, the correlation is clear during the TST and 2nd-sequence of this section. In Arcos (Fig. 7.2 E) and Januária (Fig. 7.2 F), the correlation is also clear, with a R^2 of 0.90 and 0.32 , respectively. The low R^2 of Januária is caused by one N_{bulk} -rich sample present in its 2nd-sequence, when this outlier is removed, R^2 rises to 0.44 .

One remarkable feature in all sections is the low C_{org}/N ratio intervals at the bottom of all of them (for the extent of these intervals see chapter 6). Since the C_{org}/N ratio in the

Proterozoic organic matter was likely similar to the one of modern phytoplankton (6.6; Redfield ratio), such low ratios indicate that these samples are enriched in nitrogen when compared to the organic matter from which they were generated. This N enrichment, when coupled to the fact that there is a certain degree of N linked to clays and not organic matter, must be further investigated since the excess in N can be explained by two alternatives: (i) post-depositional addition of non-primary N (terrestrial input or metasomatism) or (ii) preferential preservation of N at the expense of C. If the first one is true, the samples cannot be used for paleoenvironmental reconstruction.

Terrestrial organic input, despite the fact that it is an important source of N in modern oceans (Sigman et al., 2009), seems unlikely in the Neoproterozoic considering that life on land got complex during the Ordovician (Servais et al., 2019). Metasomatic alteration and late NH_4^+ addition could have happened in the sections, especially along intervals in which lithologies intercalate frequently and facilitates fluid percolation, like in the EHST of Well 1. However, such external ammonium would have been preserved in clay minerals and the lack of correlation between K_{bulk} and $\delta^{15}\text{N}$ in all three sections (Fig. 7.2 G, H and I) argues against external N contamination or, if present, it did not change N signatures.

Therefore, the low C_{org}/N observed at the base of the sections was likely caused by exceptional preservation of N, which occurred due to the degradation of organic matter in-situ and release of NH_4^+ that was later trapped by clay-rich sediments while C was lost. Another evidence for this is that the $\text{Al}_{\text{bulk}}/\text{TOC}_{\text{bulk}}$ ratios are higher in the low C_{org}/N intervals (Table 7.1). This ratio shows that clays were abundant in relation to organic matter, which creates a proper condition for exceptional preservation of N bounded to clays.

Table 7.1: $\text{Al}_{\text{bulk}}/\text{TOC}$ in low and high C_{org}/N ratios interval

Section	$\text{Al}_{\text{bulk}}/\text{TOC}_{\text{bulk}}$ in low C_{org}/N segments	$\text{Al}_{\text{bulk}}/\text{TOC}_{\text{bulk}}$ in high C_{org}/N segments
Januária	~112	~17
Arcos	~46	~4
Well 1	~112	-17

Figure 7.2: Analyses of total nitrogen (TN), total organic carbon (TOC), Al, K and $\delta^{15}N$ in Well 1, Arcos and Januária sections.

As discussed earlier, the conversion of N_{org} to mineralized NH_4^+ that is subsequently trapped into clays does not imply in significant changes on the original primary $\delta^{15}N_{bulk}$ signal, especially under anoxic conditions. This hypothesis also is corroborated by the strong correlation observed between TOC_{decarb} and C_{org}/N ratios of the sections (Fig. 7.3 A, B and C) (Calvert, 2004), suggesting that carbon is the major responsible for C_{org}/N variations. This scenario requires a process that oxidizes C and preserves N, which can be achieved Microbial Sulfate Reduction, a plausible scenario considering that is more pyrite in the base of all sections than in its upperparts. As sulfate cannot oxidize NH_4^+ under most of the environmental conditions, NH_4^+ tends to accumulate in anoxic pore waters (Stüeken et al.,

2016) and then it is trapped in clay minerals.

Metamorphism effects on $\delta^{15}\text{N}$ signatures increases with metamorphic grade, as ^{14}N is preferentially volatilized (Thomazo and Papineau, 2013; Ader et al., 2016). Fortunately, samples from the Bambuí are metamorphosed under greenschist facies and their signature was unlikely altered by more than 1‰ (Ader et al., 2016). Negative correlation between $\delta^{15}\text{N}$ and $\text{TN}_{\text{decarb}}$ is also an indicator of metamorphic effects on $\delta^{15}\text{N}$ values due to metamorphism, as during thermal alteration mainly ^{14}N is lost from the system, lowering N content and enhancing $\delta^{15}\text{N}$ primary signatures. Except for Arcos, which presents a moderate negative correlation ($R^2 = 0.48$) (Fig. 7.3 E) between $\delta^{15}\text{N}$ and $\text{TN}_{\text{decarb}}$, the other sections do not present such a negative trend (Fig 7.3 D and F). However, Arcos average $\delta^{15}\text{N}_{\text{bulk}}$ values (3.4, $n = 34$) are similar to ones of Well 1 (2.5, $n = 79$) and Januária (3.1, $n = 39$), which discredits the hypothesis of heavy alteration of primary $\delta^{15}\text{N}$. Furthermore, the sections do not show relevant correlations between $\delta^{15}\text{N}_{\text{bulk}}$ and $\text{C}_{\text{org}}/\text{N}$ (Fig. 7.3 G, H and I), which would be expected if metamorphic alteration of N signals was relevant. In fact, Arcos shows a weak negative trend ($R^2 = 0.35$), but metamorphism leads to increment of $\text{C}_{\text{org}}/\text{N}$ ratios jointly with the increase of $\delta^{15}\text{N}_{\text{bulk}}$ values, as N is preferentially lost in relation to C in higher temperature (Ader et al., 2006), which would generate positive correlation.

Lastly, $\text{C}_{\text{org}}/\text{N}$ ratios are mainly under 100, which is consistent with Proterozoic data with little $\delta^{15}\text{N}_{\text{bulk}}$ alteration (e.g. Beaumont and Robert, 1999; Chen et al., 2019). Hence, considering this evidence it is possible to affirm that $\delta^{15}\text{N}_{\text{bulk}}$ data of Bambuí rocks reflect mainly the primary signals of the organic matter and the data can be used for paleoenvironmental reconstructions.

Figure 7.3: Analyses of total nitrogen (TN), total organic carbon (TOC), C_{org}/N and $\delta^{15}N$ in Well 1, Arcos and Januária sections.

7.2 The nitrogen biogeochemical cycle in the Bambuí sea

$\delta^{15}N_{bulk}$ values can be used to interpret how the Nitrogen biogeochemical cycle operated in the past, as it reflects the main N paths that occurred in the water column. Additionally, they can be used to investigate the redox structure of the environment and biological implications associated with N. Here, the geological meaning of $\delta^{15}N_{bulk}$ data from the Bambuí rocks will be investigated according to the sequence stratigraphy framework of the basin defined by Caetano-Filho et al. (2019).

7.2.1 Increasing oxygenation during the deposition of TST

All the studied sections (Fig. 6.1, 6.2 and 6.3) present a positive excursion in $\delta^{15}\text{N}_{\text{bulk}}$ values during the first transgression registered in the Bambuí Group. In Well 1, $\delta^{15}\text{N}_{\text{bulk}}$ values rise from 1.5‰ to 2.4‰. In Arcos, the positive shift ranges from 3.2‰ to 5.0‰, while in Januária the excursion is from 1.2‰ to 3.8‰, returning to 3.3‰ near the MFS. Considering this information, it is possible to evaluate the changes on the N-cycle paths that took place in the Bambuí basin.

Two scenarios can generate $\delta^{15}\text{N}_{\text{bulk}}$ values between -2‰ and +1‰ (Zhang et al., 2014):

- (i) biological N_2 fixation using Mo-based nitrogenase as a dominant path of the N cycle;
- (ii) assimilation of NO_3^- from an ocean where denitrification occurs only on in sediments. This would require a fully oxygenated water column to prevent the conversion of NO_3^- to N_2 while the former is transported/sunk (Casciotti, 2009; Sigman and Fripiat, 2019).

In Bambuí Group carbonates, the reported low values on TST (~1‰) cannot be explained by a fully oxygenated ocean without denitrification on the water column. This scenario is unrealistic for the Precambrian (Canfield et al., 2010; Ader et al., 2016; Stüeken et al., 2016) and does not fit the published geochemical data available for the Bambuí rocks (e.g. Paula-Santos et al., 2018; Caxito et al., 2018; Hippertt et al., 2019). Hence, the reported low $\delta^{15}\text{N}_{\text{bulk}}$ signature of Well 1 and Januária sections was caused by N_2 fixation using Mo-based nitrogenase. The covalent bonds present in the N_2 molecule makes the conversion of N_2 to NH_3 energetically costly. Consequently, N_2 fixation requires more energy than $\text{NO}_3^-/\text{NH}_4^+$ direct assimilation to be processed (Alexander, 1984) and can only happen when no other form of N nutrient (NH_4^+ or NO_3^-) is available. As N_2 fixers are sensitive to O_2 (Gallon, 1981) anoxic conditions favours diazotroph and the presence of nutrient phosphorous (Tyrrell, 1999) and Mo (Seefeldt et al., 2009) are also important for the success of Mo-based N_2 fixation.

Hence, $\delta^{15}\text{N}_{\text{bulk}}$ points that at the beginning of the TST of Well 1 and Januária sections, the water column was mainly anoxic and the anoxia reached the euphotic zone, which made N_2 fixation the main path of the N-cycle. The NH_4^+ and NO_3^- concentrations were low and these species would be rapid and fully consumed by anammox/denitrification,

respectively. Phosphorus would also be in abundant supply as melting water from glaciers would deliver it to the Bamuí sea. Besides that, as anoxic conditions enhance P residence time in the water column, environmental conditions prevented it from binding with Fe oxyhydroxides and being sequestered into sediments (Van Cappellen and Ingall, 1994). Finally, previous studies on the Bamuí basin show that Mo availability was high enough to support N₂ fixation (Hippertt et al., 2019). In fact, despite microbiological culture studies showing that low Mo-conditions might harm nitrogenase enzyme operation (Zerkle, 2005), there is no evidence that Mo-scarcity played a role in diazotrophy activity in geological time (Stüeken et al., 2016).

Values of $\delta^{15}\text{N}_{\text{bulk}} > +2\text{‰}$ in an anoxic photic zone (i.e. NH_4^+ is the main dissolved N species) can be interpreted as:

- (i) assimilation of NH_4^+ from a reservoir in which NH_3 dissociated from NH_4^+ and was volatilized (e.g. Stüeken et al., 2015b);
- (ii) non-quantitative assimilation of NH_4^+ (conceptual scenario, no real examples);
- (iii) assimilation from an NH_4^+ pool that faced non-quantitative nitrification while the resultant nitrite and nitrate were completely reduced (Thomazo et al., 2011).

However, it is unlikely that samples from the TST whose $\delta^{15}\text{N}_{\text{bulk}}$ values are higher than +2‰ reflect any path involving ammonium as a main nutrient. Firstly, NH_4^+ can be dissociated to H^+ and volatile NH_3 and, as this reaction proceeds, ^{14}N -rich NH_3 is lost to the atmosphere and the remaining ammonium pool becomes strongly enriched in ^{15}N (Li et al., 2012). Thus, when this enriched NH_4^+ is assimilated, the sediments will yield very high $\delta^{15}\text{N}$ values. However, this process is observed only in high alkaline environments ($\text{pH} > 9.25$) which is not the case of TST (Li et al., 2012; Stüeken et al., 2015b). The second alternative, non-quantitative assimilation of NH_4^+ is also unlikely. Microorganisms prefer to assimilate ^{14}N , which would generate negative $\delta^{15}\text{N}_{\text{bulk}}$ values. However, non-quantitative assimilation of NH_4^+ drives the residual NH_4^+ pool to be enriched in ^{15}N . This creates a heavy residual NH_4^+ reservoir that will be assimilated and recorded in the geological register. Nonetheless, no negative values are reported in any section, which would prove the existence of the light reservoir. Finally, nitrification occurs even when oxygen concentrations are in nanomolar levels (Füssel et al., 2012) and it is usually a complete reaction. Very few records of incomplete nitrification are reported on the geological history (Thomazo et al., 2011; Morales et al., 2014) and none of them took place during Ediacaran/Cambrian, which discredit the

third alternative. Importantly, all these paths involving NH_4^+ as the main nutrient leads to intense and scattered fractionation ranges, which does not match the mild and consistent fractionation data reported from the Bambuí rocks.

On the other hand, values of $\delta^{15}\text{N}_{\text{bulk}} > +2\text{‰}$ in an oxidized photic zone (i.e. nitrate is stable) is usually interpreted as:

- (i) non-quantitative assimilation of NO_3^- (e.g. Sigman et al., 1999).
- (ii) assimilation from a nitrate reservoir that experienced some degree of denitrification (e.g. Godfrey and Falkowski, 2009; Tesdal et al., 2013);
- (iii) assimilation from a nitrate reservoir that experienced dissimilatory nitrate reduction (DNRA) (e.g. An and Gardner, 2002; Dong et al., 2011; Jensen et al., 2011);

In the Bambuí, non-quantitative assimilation of upwelled NO_3^- is improbable. This alternative would require a large reservoir of nitrate to have built on deep waters, hence, it would require deep waters oxygenation, which is not supported by previous geochemical studies (Paula-Santos et al., 2018; Hippertt et al., 2019). Therefore, it is likely that $\delta^{15}\text{N}_{\text{bulk}} > 2\text{‰}$ reported on the discussed interval is linked to the assimilation of a NO_3^- reservoir that faced dissimilatory nitrate reduction or denitrification. However, if DNRA was a main path, one would expect to find in another samples a complementary light reservoir opposing the enriched $\delta^{15}\text{N}_{\text{bulk}}$ reported, since on DNRA, differently from denitrification, N does not escape from the water column, but it is converted to light bioavailable NH_4^+ . As the light reservoir was not found in any section, the importance of DNRA was likely minimal. Hence, discarded all others possibilities, the positive $\delta^{15}\text{N}_{\text{bulk}}$ excursion reported at the basal Januária and Well 1 section probably represents a shallow sea that was initially dominated by Mo-based N_2 fixation and later was enough oxygenated to support nitrate accumulation and assimilation from a pool that suffered denitrification, as it happens in modern ocean, where part of the nitrate reservoir is denitrified in oxygen minimum zones (Sigman and Fripiat, 2019) (Fig. 7.4A).

The built-up of a nitrate reservoir during the transgressive tract on the euphotic zone matches geochemical data that suggests progressive oxygenation of Bambuí sea associated with the input of oxygenated freshwater. For instance, positively fractionated $\delta^{53}\text{Cr}$ values (Caxito et al., 2018), punctual negative Ce anomalies (Caxito et al., 2018; Hippertt et al., 2019; Paula-Santos et al., 2020) and iron speciation/redox-sensitive elements data (Hippertt et al., 2019) were reported in this interval.

Importantly, in Januária and Well 1 samples, $\delta^{15}\text{N}_{\text{bulk}}$ values associated with nitrate assimilation are low (maximum value of 3.8‰ in Januária) when compared to the mean value of modern nitrate (~5‰, Tesdal et al. 2013). This implies that N_2 fixation was still playing an important role on bioproduction and also that nitrate reservoir was small and denitrification occurred in high rates due to a shallow redoxcline and contact with anoxic upwelled deep waters. Although high denitrification rates on the water column elevates $\delta^{15}\text{N}$ of the residual nitrate reservoir, it also causes low NO_3^- availability and consequently, it lowers the impact of complete nitrate assimilation by biomass recorded by $\delta^{15}\text{N}_{\text{bulk}}$, as the effect is diluted. In Arcos, the lowermost sample (M4), presents a $\delta^{15}\text{N}_{\text{bulk}}$ value of 3.2‰, which means that at the beginning of the transgression there was already a nitrate reservoir in this part of the basin. However, Arcos' values rise to 5.0‰, implying that the pool became larger, as this value is similar to the one of the modern ocean (Tesdal et al., 2013). This also shows that surface waters were more oxygenated in the paleohighs, while oxygenation was less pervasive in the forebulge grabens area (Well 1). Oxygenation in Arcos TST was also observed by Paula-Santos et al. (2020) using Ce anomalies.

Interestingly, the positive $\delta^{15}\text{N}_{\text{bulk}}$ excursions are coupled with negative $\delta^{13}\text{C}_{\text{org}}$ excursions. In the Tumbiana Formation, such negative correlation was associated with aerobic methanotrophy (drive $\delta^{13}\text{C}_{\text{org}}$ values to be very low) and incomplete ammonium oxidation (drives $\delta^{15}\text{N}$ values to be very high) (Thomazo et al., 2011). However, the $\delta^{13}\text{C}_{\text{org}}$ data from the TST samples of the Bambuí Group is too high to be explained by the production of methanotrophic biomass, likewise, $\delta^{15}\text{N}$ values do not support assimilation from an ammonium pool that went through partial nitrification. Alternatively, the negative correlation here can be explained by an effect of increasing oxygenation causing the oxidation of ^{13}C -poor carbon phases coupled to the progressively more important assimilation of NO_3^- pool that went through partial denitrification.

Figure 7.4: Possible scenario of the N-cycle in the Bambuí Basin during the deposition of its basal sequences. A) During the TST, a stable nitrate pool was established and the most dominant form of N available was nitrate that went through partial denitrification on zones of low oxygenation. B) During the LHST, the high input of nutrients coming from the continent and P recovery under anoxic bottom waters conditions, caused the limitation of NO_3^- in superficial waters, making N_2 fixation the main form of N acquisition by phytoplankton.

7.2.2 The highstand system tract

During the highstand system tract samples present similar $\delta^{15}N_{bulk}$ values, but different trends. Regarding the sections located at the Sete Lagoas High domain, Arcos shows a negative excursion whose onset is at the boundary that separates the LHST and EHST, while in Well 1 values are distributed in a plateau of about 2.5‰ in both LHST and EHST. Meanwhile, Januária $\delta^{15}N_{bulk}$ signatures vary largely and present a zigzag pattern in the LHST. These differences in the behavior of the three sections show that local controls played an important role in the redox structure of the seawater and its N cycle.

Caetano-Filho et al. (2019) based on Sr and $\delta^{13}C$ data argued that the EHST marks the stabilization of the marine carbonate platform after the transgression recorded in the TST. The $\delta^{15}N_{bulk}$ data for this interval also points to stable conditions, as no significant shift in N isotopic signature is observed in any of the sections. The $\delta^{15}N_{bulk}$ average values for the

EHST are 2.9‰, 3.3‰ and 2.5‰ in Januária, Arcos and Well 1, respectively, suggesting the maintenance of the nitrate reservoir established in surface waters during the TST. Also, REY data shows that freshwater input was still happening during the EHST (Paula-Santos et al., 2020), which might have contributed to the maintenance of a nitrate on surface waters. However, oxygenation was not pervasive, as $\delta^{15}\text{N}_{\text{bulk}}$ values are still low when compared to the modern nitrate reservoir, suggesting that the redoxcline was shallow (i.e. the Bambuí sea was stratified) and intense nitrate loss was compensated by N_2 Mo-based fixation. The $\delta^{15}\text{N}_{\text{bulk}}$ values from Arcos sections are slightly higher than in Well 1, hence, seawater shallow domains had a more oxygenated water column than waters overlying forebulge grabens.

Light REY data from LHST present a shale normalized depleted distribution, which is similar to the one of seawater and is markedly different from the one of the EHST, which suggest a mix of fresh and seawater (Paula-Santos et al., 2020). However, as LREY depletion also occurs in the restricted CI-3 interval of Paula-Santos et al. (2017), this feature does not necessarily imply that the Bambuí basin was fully connected to the ocean at this stage. Actually, coupled to the anomalous high Sr content in the carbonate rocks from the LHST, this interval was interpreted as the one that marks the onset of environmental changes that took place on the Bambuí basin due to its progressive restriction in response to the advance of orogenic fronts (Caetano-Filho et al., 2019; Paula-Santos et al., 2020).

Such environmental changes are also tracked by N data. The LHST is understood as a period of intense bioproductivity, due to high ionic influx proceeding from the weathering of the surroundings orogenic fronts (Paula-Santos et al., 2020). This hypothesis is corroborated by higher TOC when compared to other systems tracts (Caetano-Filho et al., 2021) (Figs. 6.1, 6.2, 6.3).

A negative excursion is present at the lower Arcos LHST and sometimes its $\delta^{15}\text{N}_{\text{bulk}}$ values fell within the N_2 fixation range ($< 2\text{‰}$). As in the TST, there is no evidence that ammonium incomplete assimilation was a main path in the LHST. NH_4^+ assimilation fractionation factor goes from -4‰ to -27‰ (Hoch et al., 1992). Thus, following a Rayleigh distillation path and assuming that the initial $\delta^{15}\text{N}$ value of the NH_4^+ pool was 0, 10 to 45% of the initial ammonium must be assimilated and buried into sediments before the remaining NH_4^+ pool being able to generate signatures of N_{org} around $+2\text{‰}$ ($\delta^{15}\text{N}_{\text{NH}_4} = \varepsilon \times \ln(f)$ $\delta^{15}\text{N}_{\text{NH}_4}$: isotopic composition of the pool; ε : fractionation factor; f : fraction of ammonium remaining). In addition, this distillation mechanism implies that $\delta^{15}\text{N}_{\text{bulk}}$ values between -

26‰ and -3‰ must be recorded somewhere else in the basin, as they correspond to the light counterpart of the NH_4^+ pool that was already assimilated. However, such as low values like these are not reported and although NH_4^+ assimilation cannot be entirely discarded, it is unlikely. Hence, the negative shift in Arcos transition from EHST to LHST could be caused either by (i) excess of nitrate and its incomplete assimilation or (ii) exhaustion of the nitrate reservoir forcing microorganisms to fix N.

The first alternative is unlikely since excess of nitrate is only achieved when its supply is higher than the phosphorus one. In modern environments, this is only achieved in zones named high-nutrient, low chlorophyll (HNLC) zones, where despite the abundance of macronutrients, the phytoplankton biomass is low, due to a shortage of iron (Edwards et al., 2004). However, not only other geochemical proxies points to enhanced delivery of nutrients (no shortage of phosphorus) during the deposition of the LHST (Paula-Santos et al., 2020), higher TOC during this interval also attests that biomass was not low as in modern HNLC zones. Also, at this stage, not only the input of phosphorus via weathering was high, but progressively anoxic conditions also favored the recycling of this nutrient (Van Cappellen and Ingall, 1994; Ingall and Jahnke, 1997), making it abundant when compared to nitrate. Finally, in modern environments, HNLC conditions are usually met in open oceans, a different scenario from the restricted Bamuí sea during the LHST.

Then, the drop in the $\delta^{15}\text{N}_{\text{bulk}}$ values during Arcos EHST/LHST transition is probably an effect of enhanced bioproduction, as the nitrate reservoir that was built during the EHST was not able to support the high productivity related to high input of nutrients. In this scenario, the input of P due to the enhanced weathering disturbed the normal 16:1 ratio of $[\text{NO}_3^-]:[\text{PO}_4^{3-}]$ on seawater. Consequently, diazotrophic activity rose to restore this ratio (Tyrrell, 1999), which is reflected by low $\delta^{15}\text{N}_{\text{bulk}}$ values (Fig 7.4B). In addition, the restriction likely disturbed the circulation patterns of the basin, decreasing the amount of NH_4^+ that is upwelled and nitrified, making the supply of NO_3^- even shorter. Hence, as the availability of NO_3^- diminished, the energetic costly N_2 fixation became the main path to acquire N. A similar event has been observed in South China and some studies interpreted that the lowering of $\delta^{15}\text{N}_{\text{bulk}}$ values during Ediacaran/Cambrian sections were also linked to low NO_3^- availability (e.g., Cremonese et al., 2014; Chen et al., 2019; Xu et al., 2020). Up section in the LHST, the $\delta^{15}\text{N}_{\text{bulk}}$ values from Arcos rises from 1.6 to 3.4‰, implying that the nitrate reservoir was re-established, but it does not reach the 5.0‰ values reported in the TST.

In Januária, there is not an abrupt shift in $\delta^{15}\text{N}_{\text{bulk}}$ during the transition from the EHST to the LHST as in Arcos, but values present a small shift from 3.4‰ to 2.8‰ near this boundary. However, when one observes the $\delta^{15}\text{N}_{\text{bulk}}$ profile of the LHST of the Januária Section, the most striking feature is the rapid changes of $\delta^{15}\text{N}_{\text{bulk}}$ values, as sometimes they interchange between values around 2.5‰ and 4.0‰, which creates a zig-zag pattern during this interval. These rapid changes suggest that as it happened in the shallow domains of the southern Bambuí sea, in the central part of the basin, shallow domains also faced instability of the superficial nitrate pool during regression, which was compensated by N_2 fixation. Also, the average $\delta^{15}\text{N}_{\text{bulk}}$ of the LHST from Januária (3.2‰, $n = 12$) and Arcos (2.5‰, $n = 6$) is low, which means that even when redox conditions permitted the stability of NO_3^- , the pool was not large and $\delta^{15}\text{N}_{\text{bulk}}$ values still reflect a mix between N_2 fixation and NO_3^- assimilation. It is important to access that in the Januária Section, the fossil *Cloudina sp.* was reported (Warren et al., 2014; Perrella et al., 2017) in the LHST interval. The $\delta^{15}\text{N}_{\text{bulk}}$ values show that even if deep waters were anoxic (Hippertt et al., 2019), superficial waters could intermittently sustain a small nitrate pool, which is important given the fact that major *Cloudina sp.* reports are found in oxic contexts (Bowyer et al., 2017).

The Well 1 LHST record differs from the other two, as no shift in the $\delta^{15}\text{N}_{\text{bulk}}$ values is observed compared to the EHST. Here, the values remain low, but stable, distributed around a plateau of 2.5‰. The stability of $\delta^{15}\text{N}_{\text{bulk}}$ values during the regression stages points that progressive restriction and eustatic fall did not influence the N cycle in the forebulge graben setting as it did in the shallow domains. It also implies that during the regression stage, local controls affected the nitrogen cycle in the forebulge grabens, in spite of sea-level changes. One of the local controls that might have been important in Well 1 is poor water circulation inside the extensional depocenters, which would have prevented the vertical mixing of superficial and intermediate waters and enhanced stratification. Also, if the rates of sinking organic matter are low, this can collaborate to move the redoxcline to shallower depths (Meyer et al., 2016). The values reported for Well 1 section in the entire HST are nearly at the boundary of N_2 fixation and NO_3^- assimilation, which suggests that for this section, anoxia sometimes reached the photic zone, as the nitrate pool was very limited. Importantly, the TOC_{bulk} content of Well 1 during the HST is 3 times higher than the ones from Januária and Arcos section for the same interval. If we consider TOC_{bulk} as a indicative of bioproduction, this can also be one of the local factors that caused the consistent low values of $\delta^{15}\text{N}_{\text{bulk}}$ during the entire Well 1's HST interval.

The low availability of NO_3^- observed during the LHST in all sections is also corroborated by episodes of euxinia observed during this interval (Hippertt et al., 2019). Nitrate and sustained euxinia can never coexist because denitrification produces more free energy per mole of carbon than microbial sulfate reduction (MSR), being therefore a preferred respiratory pathway when SO_4^{2-} and NO_3^- coexist. For that reason, nitrate concentrations exert a primary role in the rates of MSR and this mechanism does not take place when NO_3^- is available (Canfield, 2006). However, a form of N acquisition is essential to fuel the production of the organic matter that will be respired by MSR and consequently generate H_2S pool. As this species cannot be NO_3^- , Boyle et al. (2013) argued that intermediate euxinic waters must be coupled to superficial waters in which the main path of the N-cycle is direct N_2 fixation, which is a plausible scenario in the Bambuí geological context.

7.2.3 Oxygenated euphotic zone during the deposition of the second 2nd-order sequence

The sedimentary sequences from the second 2nd-order sequence of the Bambuí Group are considered to be deposited under a fully restricted sea and this interval is marked by very high $\delta^{13}\text{C}_{\text{org}}$ values interpreted to be caused by high methanogenic activity under anoxic conditions (Caetano-Filho et al., 2021). However, the $\delta^{15}\text{N}_{\text{bulk}}$ data from the second 2nd-order sequence points that in this transgression, as in the first one, a nitrate pool was build-up, although smaller and not so stable as the one from TST. Furthermore, samples from this interval do not present a consistent REY pattern, suggesting that freshwater input may have occurred during deposition (Paula-Santos et al., 2020), influencing superficial oxygenation.

In Arcos, $\delta^{15}\text{N}_{\text{bulk}}$ values increase to ~4.0‰ and then return to 2.9‰, while in Januária they are distributed in a plateau around 3.0‰. Even Well 1 section, whose $\delta^{15}\text{N}_{\text{bulk}}$ values were stable during the regression, present higher values during the second transgression. Since $\delta^{15}\text{N}_{\text{bulk}}$ data higher than 2.0‰ can be interpreted as assimilation from a nitrate pool that went through partial denitrification, $\delta^{15}\text{N}_{\text{bulk}}$ values suggest that during the second 2nd-order sequence transgression there was more oxygen dissolved in superficial waters of forebulge grabens than during the HST.

As both transgressions recorded in the Bambuí basal 2nd-order sequences present a rise in $\delta^{15}\text{N}_{\text{bulk}}$ values, which contrast with the regressive tract data, a relationship between transgression and oxygenation has to be considered. In fact, it was suggested that in the Ediacaran Nama Group persistent oxygenation in mid-ramp settings was controlled by basin

hydrodynamics, as data from this unit imply that ventilation was favored by highly energetical flooding events (Wood et al., 2015). Although the tectonic setting of the Bambuí (restricted epicontinental sea) and Nama groups (open sea connected to global ocean) are different, the data presented here show that sea-level changes affected oxygenation and the N-cycle of the former. However, the nitrate pool of the second transgression was not as stable or large as the one from the first TST, which can be inferred by their lower values and also $\delta^{15}\text{N}_{\text{bulk}}$ oscillation, especially in Arcos section. This is probably a response to a heavily stratified water column, as proposed by other studies (Hippertt et al., 2019; Caetano-Filho et al., 2021).

Hence, even if the transgression facilitated the oxygenation of the basin during this stage, the shallow redoxcline caused intense loss of NO_3^- to the atmosphere and this loss was compensated by N_2 fixation, resulting in a mode of $\delta^{15}\text{N}_{\text{bulk}}$ around 3.0‰.

7.3 The nitrogen cycle and its implications for life and climate systems

The macrofossil record of the Bambuí Group is anomalously scarce when it is compared to other Ediacaran/Cambrian geological units (e.g. Nama Group, Doushantuo Formation), in which most of the phyla appeared. The possible reason has been related to anoxia, euxinia, hypersaline and methane-rich conditions (Hippertt et al., 2019; Caetano-Filho et al., 2021). In addition, $\delta^{15}\text{N}_{\text{bulk}}$ values suggest that the N-cycle, and hence redox conditions were unstable at the basin, which could have affected the evolution of complex forms of life.

The link between oxygenation and the Cambrian explosion has been discussed for more than 60 years (Nursall, 1959). Metazoans can habit environments with low oxygen concentrations and some studies even suggest that the amount of O_2 necessary for their metabolism was achieved much earlier than the first appearance of animals on the fossil record (e.g., Mills et al., 2014). However, poor oxygenated environments cannot support complex life systems or large organisms (Sperling et al., 2013), and concordantly, most of the Ediacaran/Cambrian Fauna is recorded at oxygenated habitats, even if the oxygenation was transient (Bowyer et al., 2017; Wood et al., 2019).

Thus, the redox instability of Bambuí basin may have been one of the drivers of its low macrofauna diversity. In fact, the metazoans reported at the Bambuí Group were found on the Januária's LHST, which is, considering the $\delta^{15}\text{N}_{\text{bulk}}$ values, the most oxygenated section during this stage, although it also presents the most unstable N-cycle (see section 7.2.2). However, the relation between the redox stability and life development is a recent

debate (e.g. Johnston et al., 2012; Wood et al., 2015, 2019; Bowyer et al., 2017) and some argue that instead of jeopardizing animal evolution, redox instability might have helped it, favouring novelties and morphological evolution (Wood and Erwin, 2018; Wood et al., 2019). Moreover, redox conditions control the availability of nitrate, which is the N form preferred by eukaryotes, as they cannot process direct N₂ fixation. In addition, other forms of fixed-N, such as NH₄⁺, are mainly consumed by prokaryotes (Fawcett et al., 2011). Complex and large-celled phytoplankton communities generate food webs that are more effective to transfer nutrients and energy to higher trophic levels (Irwin et al., 2006) and the rise of eukaryotes is linked to the development of metazoans as they have higher energetic demands (Brocks et al., 2017).

The $\delta^{15}\text{N}_{\text{bulk}}$ values from Bambuí Group suggest that nitrate pools were not large or stable, especially during regressions, and this could have affected the large-celled plankton and consequently metazoans. In addition, if a large eukaryote community do not develop and the phytoplankton is dominated by prokaryotes, due to their low mass, the sinking rate of the organic matter particulates is low and the remineralization of this organic matter is faster and occurs within the water column, enhancing anoxia (Lenton et al., 2014).

The relation between nitrate and complex life forms during the Ediacaran-Cambrian transition has been studied mainly in South China (e.g., Xiang et al., 2018; Wang et al., 2018b; Xu et al., 2020; Liu et al., 2020) and although it is not possible to link the Bambuí Group to global trends, due to its isolation, this study brings more data to clarify how the N-cycle operated at that time. It is important to stress that this work does not intend to propose that the episodes of nitrate limitation reported here are the only cause for the hostility of the Bambuí environment. Actually, it is proposed that this is just one of the factors that might have driven the inhospitality of the Bambuí sea, together with others like methane abundance and free H₂S in the water column (Caetano-Filho et al., 2019), which all are an effect of progressive and enhanced restriction of this basin.

Another possible development of the N-cycle in the Bambuí basin is that intense denitrification under low-oxygen conditions might have generated a large quantity of N₂O. Caetano-Filho et al. (2021) suggested that large methane emissions from epeiric seas within Gondwana supercontinent could have affected the global climate, warming the planet and drifting it away from Neoproterozoic ice-house conditions. Accordingly, in this scenario, nitrous oxide, the third most important greenhouse gas after CO₂ and CH₄ (Thompson et al., 2019) might have contributed to this effect. However, this hypothesis needs to be tested by other proxies.

8 CONCLUSIONS

The $\delta^{15}\text{N}_{\text{bulk}}$ data obtained on carbonates from the Bambuí basin help to elucidate how was the redox structure of this basin and how the biogeochemical cycle of nitrogen operated in this setting. Three sections were analyzed, Januária within the Januária High Domain paleohigh and the other two within the Sete Lagoas High Domain, Well 1 and Arcos sections, representing a forebulge graben and paleohigh respectively.

Eustatic variations seems to exert control in the Bambuí N-Cycle. During the first transgression (TST), in all the sections $\delta^{15}\text{N}_{\text{bulk}}$ values rise from $\sim 2.0\text{‰}$ to $\sim 5.0\text{‰}$, depending on the section, which can be explained as a rise of the nitrate reservoir and hence oxygen levels where most of the primary production occurs (i.e., euphotic zone). The rise of oxygen levels observed here was also tracked by other geochemical proxies. Then, as the regression begins (EHST), $\delta^{15}\text{N}_{\text{bulk}}$ values point to a stable nitrate reservoir.

As the restriction of the Bambuí increases due to the advance of orogenic fronts and also eustatic fall (LHST) the NO_3^- stability is disturbed. This disturbance is evidenced by a negative excursion observed in the transition of Arcos EHST to LHST and by constant oscillations in the $\delta^{15}\text{N}_{\text{bulk}}$ values of Januária section. Low $\delta^{15}\text{N}_{\text{bulk}}$ values observed in the LHST of both sections are interpreted as the result of N_2 fixation using Mo as cofactor. This mechanism is energetically costly, thus, it only occurs in the absence of other forms of fixed N, which implies that the NO_3^- reservoir diminished during this period (i.e, anoxic conditions might have reached the euphotic zone). At this time, other geological proxies indicate that the input of nutrients in the basin was very high and this could have made nitrate a limiter of primary production, forcing N_2 fixers to compensate for low NO_3^- levels. However, the behavior of $\delta^{15}\text{N}_{\text{bulk}}$ values is different during deposition of rocks from Well 1 section, as in the regression its values are distributed around a plateau of 2.5‰ . This shows that the N-cycle in a forebulge graben setting of the Bambuí basin had a different response to eustatic changes when compared to the shallow domains. Although $\delta^{15}\text{N}_{\text{bulk}}$ values are stable in such tectonic setting, they are low, implying that nitrate was not the dominant form of fixed N, even during the initial regression. The persistence of $\delta^{15}\text{N}_{\text{bulk}}$ signals reflecting N_2 direct fixation in the HST of Well 1 might be an effect of enhanced anoxia in this scenario, probably due to inefficient circulation inside the graben.

Finally, data of samples from the second 2nd-order transgression show that the nitrate pool was re-established in all sections, but at this time, oxygenation was not as effective as it was during the first transgression and N_2 fixation played a more important role here than it

did during the first TST, maybe because of the restriction of the Bambuí basin at this stage.

Summing up, the Bambuí data show that the N-cycle of the basin operated mainly between periods in which N_2 fixation and NO_3^- assimilation intercalated as the dominant path of the biogeochemical cycle of nitrogen, which can be interpreted in terms of more or less oxygen available within superficial waters. Values that are inside the N_2 fixation range are reported in the LHST, while transgressions point to the establishment of nitrate pools. It is important to stress that even when $\delta^{15}\text{N}_{\text{bulk}}$ data indicates the nitrate assimilation, except for Arcos' TST, values are lower than the ones recorded in the modern ocean, which implies that O_2 concentration in Bambuí seawater was not as in the modern ocean.

Many geochemical data from this basin suggest anoxic conditions in bottom waters even in shallow environments, which is corroborated by $\delta^{15}\text{N}_{\text{bulk}}$ signatures since even when oxygenated conditions are observed, the redoxcline was likely shallow, suggesting a strongly stratified basin. In addition, since nitrate is a very important nutrient for eukaryotes and they are necessary to fuel higher trophic levels, its depletion in some intervals might be one of the factors that drove the hostile conditions for metazoans. This is due to their energetic need, and also because light plankton takes more time to sink, which intensifies anoxia as this organic matter is not buried into sediments, but is remineralized within the water column. Furthermore, large N_2O emissions in epeiric seas in the Gondwana supercontinent due to enhanced denitrification may have affected the global climate.

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