CHEMOSTRATIGRAPHY (C, O AND Sr) OF EDIACARAN POST-GLACIAL CARBONATES OF PARAGUAY BELT, MATO GROSSO STATE, BRAZIL

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INTRODUCTION

During the Neoproterozoic the Earth suffered severe climate changes, recorded by enigmatic sequences composed of glacial deposits immediately overlain by carbonate rocks typical of warm climate. At least three glaciations are recognized (Halverson et al., 2005): Sturtian (ca. 725 Ma), Marinoan (ca. 635 Ma), and Gaskiers (580 Ma). Isotopic tools, especially chemostratigraphy, have been widely used to correlate worldwide the successions deposited in this period and to understand the complex depositional environments.

Sediments of the Paraguay Belt record two of the glaciations. The older glaciation corresponds to glacial-marine sediments of Cuiabá Group and Puga Formation that are overlain by platformal carbonates of Araras Group (Alvarenga et al, 2000). The younger glaciation corresponds to tillites and pelites of Serra Azul Formation that overlies the Araras Group carbonates (Figueiredo et al., 2005; Alvarenga et al., submitted).

This work is related to the Neoproterozoic global glaciations and presents a detailed isotopic ($\delta^{13}C$, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$) and chemostratigraphic study carried out on the Ediacaran carbonate succession from Araras Group and Serra Azul Formation, located in the northernmost part of the Paraguay Belt, Mato Grosso, Brazil.

REGIONAL GEOLOGY

The Paraguay Belt is located on the southeastern border of Amazon Craton. It is formed by sedimentary rocks which were deposited on a passive continental margin during the Neoproterozoic Era and deformed by the Brazilian-Pan African Orogeny (Alvarenga and Trompette, 1993; Trindade et al., 2003).

The base of Paraguay Belt is represented by the Cuiabá Group that comprises, from bottom to top, organic-rich shales, dolomites, diamictites, rudstones, sandstones and shales (glaciomarine and turbiditic sediments), according to Alvarenga and Trompette (1992) and Alvarenga et al. (2000). This group is contemporaneous with the Puga Formation and gradates laterally toward the craton region, where the Puga Formation is composed essentially of diamictites. The rocks of this sequence record a glaciation which was correlated to the Marinoan Glaciation (Nogueira et al., 2003; Alvarenga et al., 2004) based on chemostratigraphic studies carried out on post-glacial carbonates.

These glacial rocks are immediately overlain by carbonates of the Araras Group (ca. 1300 m), which is divided into the Mirassol d'Oeste Formation (Nogueira et al., 2003), Guia Formation, and Nobres Formation (Almeida, 1964). The Mirassol d'Oeste Formation is composed of pink cap dolostones (ca. 30 m), characterized by stromatolites, rock tubes and mega ripples. The Guia Formation overlies the Mirassol d'Oeste Formation and chiefly comprises laminated limestones and marls (ca. 250 m) deposited in a deep platform environment. The Guia Formation limestones are overlain by dolostones of the Nobres Formation (ca. 1100 m), which was deposited in a shallow platform environment (Almeida, 1964; Alvarenga et al., 2000).

The Araras Group is overlain by the Serra Azul Formation which contains, from base to top, diamictites (ca. 70 m), brownish laminated siltstone and claystone (ca. 200 m) with intercalations of fine laminated sandstones towards the top of the section (Figueiredo et al., 2004; Figueiredo et al., 2005; Alvarenga et al., submitted). At one location, a limestone bed (12 m) occurs on top of the siltstones. The upper part of the Paraguay Belt is represented by the Alto Paraguai Group, which can be divided into Raizama Formation (rudstones, sandstones and arkoses), and Diamantino Formation (red shales, siltstone and arkoses).

SAMPLING AND ANALYTICAL PROCEDURES

Non metamorphic carbonates from the Araras Group and clastic rocks from the Serra Azul Formation were systematically collected near the town of Nobres, in the state of Mato Grosso, Brazil. The sampling intervals varied from 1.5 to 20 m, according to the field conditions. From the 122 samples collected, 51 were chosen for petrographic studies in order to evaluate grain size, degree of recrystallization, abundance of authigenic and detrital components, presence of stylolites and veins. Samples that did not show evidence of alteration were selected for isotopic analyses. The powder was obtained by microdrilling (1.5 mm diamond drill) a slice of the carbonates sample, which is the mirror of the part used for the thin section. The fine powder (micro-sample of 10-15 mg) was collected on weighing paper.

The isotopic analyses (C, O and Sr) were carried out at the Centro de Pesquisas Geocronológicas (CPGeo), IGc/USP. The oxygen and carbon analyses were carried out through the digestion of individual samples with H_3PO_4 100% at 25°C for 24 hours (McCrea, 1950). The isotopic ratios of carbon and oxygen in the CO_2 fractions released from the carbonates were measured on an Europa Geo20 mass spectrometer. The precision for both isotope ratios is 0.2‰. The Sr isotopic analyses were carried out through the reaction of part of micro-sample with HCl 0.1N during 1 hour. The sample was then centrifuged and washed three times to obtain the first leached fraction, which was discarded. The sample was then redissolved with HCl 1N for 30 minutes, centrifuged and washed three times to obtain the second leached fraction. The Sr of this second leacheate was purified by standard ionic exchange technique and the isotopic compositions were measured on a VG-354 mass spectrometer.

STUDIED SECTIONS

The four studied lithostratigraphic sections are part of a continuous stratigraphic succession that is ca. 1700 m thick (Figure 1). The beds are subvertical in the study area, near Nobres town, Mato Grosso State, Brazil.

SECTION 1

This section is located ca. 600 m northwest of Copacel II Quarry. At this place occurs diamictites of the Puga Formation made up by sand grain matrix and clasts of granitoid and basic rocks. The diamictites are overlain by limestones of the Guia Formation, but neither the contact is observed nor the first most basal 20 m of the Guia Formation because of the talus deposits. From bottom to top, the basal portion of Guia Formation is made up by black laminated mudstone, gray wave laminate mudstone with black chert nodules, intercalations of mudstone and grainstone, massive black mudstone and gray mudstone with biogenic lamination.

Although the outcrops of this section are non-continuous it was possible to sample a ca. 80 m thick profile with 2.5-20 m intervals.

SECTION 2

This section is located in Copacel II Quarry and is located stratigraphically above section 1, in spite of an interval of ca.50 m between both sections that is missing due to weathering. The middle-upper portion of the Guia Formation is found in this section, comprising thick beds of laminated rich-organic-matter mudstone (3-5 m) that are intercalated with rhythmic mudstone (3-5 m) and lenticular, massive, or irregular laminated mudstone, dolomudstone, or wackestone beds with sharp basal contacts and wavy top contacts (0.5-1.5 m). The rich-organic matter beds contain pyrite agglomerations, black chert nodules and show pelloid and clotty textures. The beds of rhythmite have alternation of light- (microsparry) and dark-gray (micrite) laminae and some fine lenses of packestone produced by slumps.

A ca. 200 m thick sequence was sampled at 4 m intervals in this section.

SECTION 3

This section is located about 100 m southeast of Copacel II Quarry, towards the "Vai quem qué" Range, and is a continuation of section 2. The same intercalations observed in the last section persist for the first 240 m, although the dolomites are recrystallized towards the top of the section. In the last 450 m, we observe a monotonous succession of dolostone that comprises, from bottom to top, crystalline dolostone with incipient primary lamination, dolopackestone, dolograinstone, two conglomeratic arkose beds, dolomudstone, a thick carbonate replaced by silica, dolomudstone with truncated laminations and chert nodules, massive dolomudstone, oolitic dolograinstone, dolowackstone showing turbidite sequences, oncolitic and pelloidal dolograinstone intercalated with primary dolomudstone and, at the very top, stromatolites. This carbonate succession is marked by an erosional contact with the overlying sandstones of the Raizama Formation.

The total thickness of this section is about 690 m with sampling carried out at intervals varying from 10 to 20 m.

SECTION 4

This section is located in the Environmental Reserve of Tocantins Cement Industry. It corresponds to the upper part of the Serra Azul Formation and is formed by ca. 80 m thick red laminated claystone that is overlain by a 12 m thick layer of limestone which is, in turn, covered by 15 m of gray laminated claystone interbedded with fine sandstone layers, grading to sandstones of the Raizama Formation. The limestone bed is composed, from bottom to top, of laminated mudstone, massive mudstone with micro-cut structure filled by wackestone, laminated mudstone with clotty texture, cyclic slump structures and nodular limestone. These limestones were sampling with 1.2-4 m intervals.

CHEMOSTRATIGRAPHY

The studied sections comprise a continuous lithostratigraphic succession (Figure 1) that can be chemostratigraphically divided into 8 intervals. Each interval is described below:

INTERVAL I – This interval is correlated to the first 100 m of succession and corresponds to the lowermost limestones of the Guia Formation. The $\delta^{13}C$ values are slightly negative ranging between – 0.76 ‰ to – 0.08 ‰. The $^{87}Sr/^{86}Sr$ ratios show a sudden increase from 0.7075 (base) to 0.7078 (top).

INTERVAL II – This interval is composed of the stratigraphic succession between 150 and 340 m, which is marked by the occurrence of the organic-rich limestones in the upper part of the Guia Formation. Their $\delta^{13}C$ values are between – 1.70 and + 0.03. The $^{87}Sr/^{86}Sr$ ratios are about 0.7077.

INTERVAL III – From 430 to 800 m of the succession, this chemostratigraphic interval is composed of intercalated of limestones and dolostones from the lower part of the Nobres Formation. The $\delta^{13}C$ values became negative (from – 1.34 to – 0.47 ‰) and the $^{87}Sr/^{86}Sr$ ratios (obtained only from the lower part of this interval) are ca. 0.7077, following the pattern observed in the last interval.

INTERVAL IV – This interval corresponds to the 900 to 1070 m of the succession, characterized by dolostones of the middle part of the Nobres Formation with $\delta^{13}C$ values near zero (+0.15 to +0.09 ‰). No Sr isotopic analyses were done on these samples due to their high detrital content.

INTERVAL V – This interval corresponds to the 1200 to 1300 m of the succession and is represented by dolostones of the upper part of the Nobres Formation. The $\delta^{13}C$ values show a strong incursion from +0.43 to +3.97 ‰. No $^{87}Sr/^{86}Sr$ ratios were obtained on these samples.

INTERVAL VI – This interval includes from the sequence from 1300 to 1370 m corresponding to the dolostones of the upper part of the Nobres Formation. These dolostones show positive $\delta^{13}C$ values ranging between +2.15 and +0.57 ‰. An $^{87}Sr/^{86}Sr$ ratio of 0.7085 was obtained from a carbonate sample.

INTERVAL VII – This interval corresponds to limestones that were found on the upper part of the Serra Azul Formation overlying red laminated claystones, from 80 to 84 m of section 3. The $\delta^{13}C$ values are strongly negative with an excursion from – 4.92 to – 7.47 ‰ while the $^{87}Sr/^{86}Sr$ ratio is 0.7088.

INTERVAL VIII – This final interval is a continuation of the previous unit, from 85 to 92 m of section 3. These limestones also show highly negative $\delta^{13}C$ values however with incursion from – 6.53 to – 3.21 ‰. The $^{87}Sr/^{86}Sr$ ratios vary from 0.7086 to 0.7088.

DISCUSSION AND CONCLUSIONS

DEPOSITIONAL ENVIRONMENT

A careful evaluation of the isotopic results obtained during this study, together with sedimentary features observed in the field, permit us to interpret the depositional environment of these rocks. Based on our data, the deposition of Interval I took place during the initial stage of the marine transgression, soon after Puga Glaciation, given the presence of melt water and a slight increase in bioactivity, as evidenced by the C isotopes, and an increase in weathering evidenced by Sr isotopes. This was followed by flooding of the platform during Interval II, indicated by the amount of organic matter reflective of a reducing environment, reduction of bioactivity, perhaps due to low luminosity, and established weathering ratios indicated by Sr isotope ratios. The data obtained on rocks of Interval III suggest that these record the beginning of a marine regression, followed by a slow, gradual increase in bioactivity, as shown by the C isotopes and a stabilization of weathering. The C isotopic values of Interval IV suggest the stabilization of bioactivity or a percolation of fluids through the ca. 170 m thick sequence that formed the crystalline dolostones with the same isotopic composition. The strong $\delta^{13}C$ positive excursion of Interval V is evidence of a significant decrease in bioactivity towards the top of the sequence. The higher values coincide with the appearance of oncolitic occurrences while the lower values coincide with turbidite sequences and detrital fractions, which also indicate the shallowing of the basin. In the Interval VI a new increase in bioactivity is observed. This is supported by the positive excursion of $\delta^{13}C$ values and the constant presence of pellets, oncolites and stromatolites, as well as the more radiogenic $^{87}Sr/^{86}Sr$ ratios, which indicate an increase on weathering rate, possibly related to the Brasiliano Orogeny. The last intervals, VII and VIII, are represented by carbonates deposited after the Serra Azul Glaciation, and their highly negative $\delta^{13}C$ values suggest that they are post-glacial limestones; their $^{87}Sr/^{86}Sr$ ratios are very radiogenic probably due to the evolution of the Brasiliano Orogeny.

GLOBAL CORRELATION

The Snowball Earth Hypothesis (Hoffman et al., 1998; Halverson et al., 2005) presumes at least three Neoproterozoic glaciations. The studied succession in the Paraguay Belt contains the record of, at least, two Neoproterozoic glaciations, represented by the Puga Formation (older) and Serra Azul Formation (younger).

In comparing the isotopic results obtained in this study (C and Sr) with those obtained on other successions by different authors, we observe that Araras Group carbonates, which overlie the diamictites of the Puga Formation, present the same isotopic pattern determined on the platform carbonates from the Tsumeb Subgroup, which overlies the diamictites of the Ghaub Formation, in the Namibia (see Halverson et al., 2005). The similarities are observed also between carbonates from the upper part of the Araras Formation and those from the base of the Nafun Group, in Oman. The Ghaub Formation is considered representative of the Marinoan glaciation, which has been precisely dated at 635.5 ± 1.2 Ma (U-Pb age on zircons from volcanic tuffs; Hoffman et al., 2004). The Araras Group has been correlated to the Marinoan Glaciation by Nogueira et al. (2003) based on isotopic data from cap dolostone. Recently, Babinski et al. (submitted) obtained a Pb-Pb isochron age of 627 ± 32 Ma on the cap carbonate from the Mirassol D´Oeste Formation, confirming the post-Marinoan and pre-Gaskiers age of the Araras Group.

The Serra Azul Formation limestones have a very similar isotopic pattern (C and Sr) of that obtained for the upper part of Nafun Group (see Burns & Matter, 1993; Burns et al. 1994, Amthor et al., 2003) and to the upper part of Wonoka Formation, in Australia (see Calver, 2000). These successions are correlated to the Gaskiers Glaciation (Halverson et al., 2005) that has an age of 582.4 ± 0.4 Ma obtained on tuffs from the glacial Gaskiers Formation, in Newfoundland, Canada (dates obtained by S. Bowring and mentioned by MacGabhann, submitted). However, this dated formation does not have cap carbonates, which could permit the comparison of the isotope patterns and confirm (or not) their correlation. As a result, it is not possible to correlate the Gaskiers Formation with other mentioned successions, although many researchers support the hypothesized correlation between them.

In conclusion, our data confirm the existence of two Neoproterozoic glaciations in the Paraguay Belt, Mato Grosso State, Brazil which can be correlated to the

worldwide Marinoan and Gaskiers Glacial Events. The studied carbonates were deposited in a marine environment because their features and isotopic global correlate with other basins. At the moment, this good correlation reinforces the idea of global Neoproterozoic glaciations, but more detailed isotopic and geochronological work is necessary on Neoproterozoic sections.

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RESUMO

Durante o Neoproterozóico a Terra sofreu profundas mudanças climáticas, as quais foram registradas em enigmáticas sucessões compostas de depósitos glaciais recobertos por rochas carbonáticas de clima quente. Estudos recentes mostram que ocorreram, pelo menos, três glaciações neste período, denominadas Sturtiana (ca. 725 Ma), Marinoana (ca. 635 Ma) e Gaskierana (580 Ma). Na tentativa de estabelecer uma correlação global entre as sucessões depositadas neste período, os geopesquisadores têm usado diversas ferramentas, principalmente a quimioestratigrafia isotópica de C, O e Sr. O presente trabalho apresenta um estudo de quimioestratigrafia isotópica (C, O, Sr) de detalhe, realizado numa sucessão carbonática de idade ediacariana da porção extremo norte da Faixa Paraguai, no Estado do Mato Grosso, Brasil.

Na região de estudo, ocorrem diamictitos da Formação Puga recobertos por rochas carbonáticas do Grupo Araras, sobre a qual se depositam os diamictitos e carbonatos da Formação Serra Azul, definida neste trabalho. A sucessão carbonática do Grupo Araras apresentou valores de $\delta^{13}C$ variando de – 1,7‰ (base) a + 4‰ (topo) e razões $^{87}Sr/^{86}Sr$ entre 0,7075 (na base) e 0,7084 (no topo). Estes valores são semelhantes àqueles encontrados em outras sucessões carbonáticas Marinoanas. Os calcários da Formação Serra Azul apresentaram um valores de $\delta^{13}C$ entre – 7,5% e – 3,2% e razões $^{87}Sr/^{86}Sr$ de ca. 0,7086, típicas das sucessões carbonáticas Gaskieranas. Os resultados isotópicos obtidos neste trabalho, associados às evidências sedimentológicas, sugerem que na história geológica de deposição da Faixa Paraguai ocorreram, pelo menos, duas importantes glaciações.

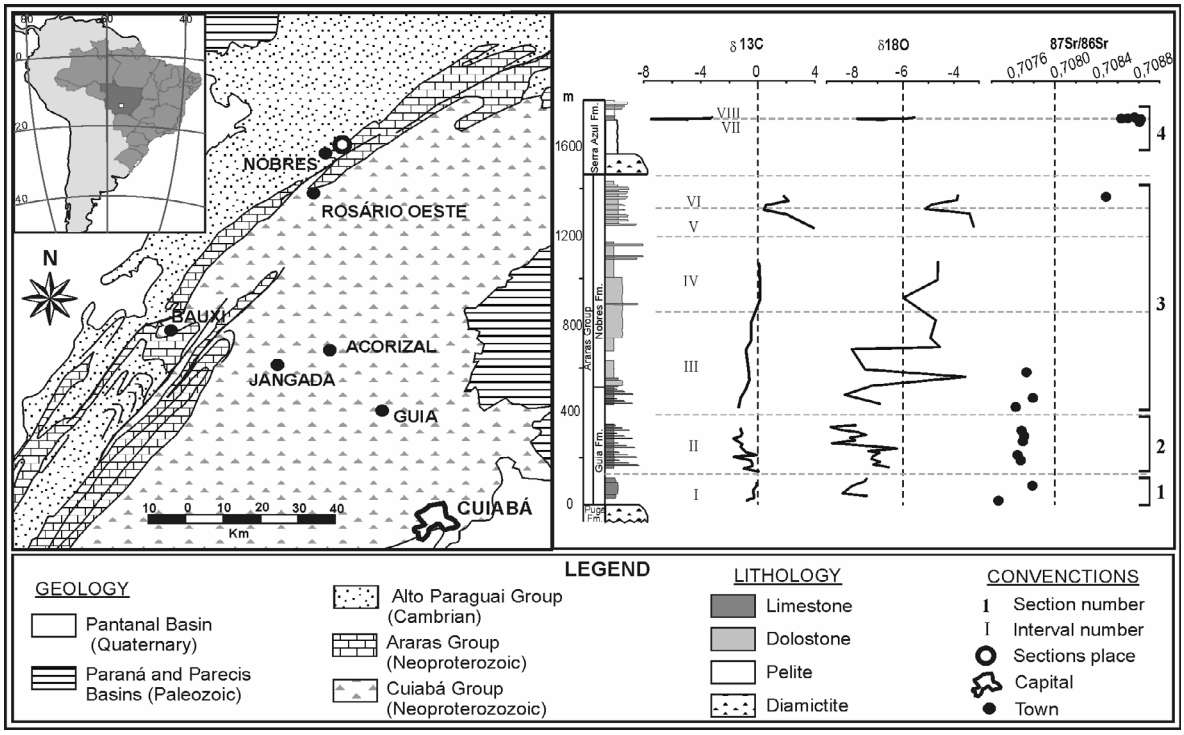

Figure 1: Regional geologic framework and isotopic curves to north Paraguay Belt, with indicated sections and intervals.