

CARBON, OXYGEN AND STRONTIUM ISOTOPES STUDIES OF THE CARBONATE ROCKS OF THE ARAGUAIA BELT, BRAZIL

Moura C.A.V.¹, Costa N.O.², Feio G.R.L.², Nogueira A.C.R.³, Scheller T.², Galarza M.A.^{2,5}, Martins P.S.⁴

1 – Universidade Federal do Pará, Centro de Geociências (CG-UFPA), CP 8608, Belém, Brazil, CEP 66075-900 candido@ufpa.br

2 – CG-UFPA, Curso de Geologia, Belém, Brazil, CEP 66075-900 nivya.costa@gmail.com

3 – CG/UFPA, Pós-Graduação em Geologia e Geoquímica, Belém, Brazil, CEP 66075-900 gilmarafeio@gmail.com

4 – Universidade Federal do Amazonas, Departamento de Geociências, Av. Rodrigo O.J. Ramos, 3000, Manaus, Brazil anogueira@ufam.edu.br

5 – CG-UFPA, CP 8608, Belém, Brazil, CEP 66075-900 scheller@ufpa.br

6 – CG-UFPA, CP 8608, Belém, Brazil, CEP 66075-900 , antogt@ufpa.br

7 – Universidade do Estado do Rio de Janeiro, Pós-Graduação Análise de Bacias pablosimoes15@yahoo.com.br

Keywords: carbonate rocks, stable isotopes, Sr isotopes, Araguaia Belt, Neoproterozoic

INTRODUCTION

The Araguaia belt, located in north-central Brazil, corresponds to the northern portion of the Paraguay-Araguaia belt (Almeida *et al.* 1981). However, as Cenozoic sediments cover the contact between these belts, they have been studied as two distinct geotectonic units. Neoproterozoic glaciations have been recognized in the cratonic cover related to the adjacent Paraguay belt (Alvarenga & Trompette 1992) and $\delta^{13}\text{C}$ negative excursion is well documented in the cap carbonate overlying diamictites (Nogueira *et al.* 2003). In the Araguaia belt, carbonate rocks are associated to very low grade and to amphibolite facies rock units. These carbonate successions are poorly exposed, however, samples from two core of these two successions were recovered from mining companies. These samples were studied isotopically (C, O Sr), in order to constrain the age of deposition of the metasedimentary rocks and to investigate eventual record of Neoproterozoic glaciation in the Araguaia belt.

GEOLOGIC SETTING

The Araguaia belt has a general north-south orientation and is, approximately, 1200 km long and more than 100 km wide. To the east, this belt is covered by Phanerozoic rocks of the Parnaíba Basin, while on the western side, the anchimetamorphic to unmetamorphosed rocks of the belt rest unconformably, or are overthrust, on the rocks of the Amazon craton (Fig. 1). The Araguaia Belt is composed of metamorphosed psammitic and pelitic successions, with minor contributions of carbonatic rocks, mafic and ultramafic rocks, and syn- to late tectonic granitic bodies (Alvarenga *et al.*, 2000). Basement inliers have been recognized in the core of dome-like structures along the eastern side of the northern segment of the Araguaia Belt (Herz *et al.*, 1989). These basement rocks are represented mainly by Archean (2.85 Ga) and Paleoproterozoic (1.85 Ga) gneissic rocks (Moura & Gaudette, 1999).

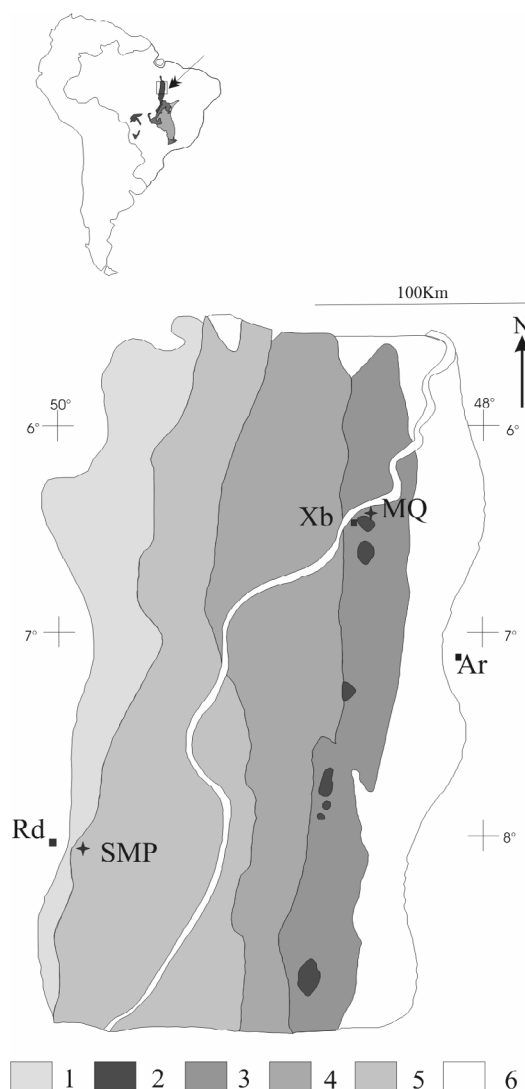


Fig. 1 – Simplified Geologic map of the Araguaia belt. Cities: Redenção (Rd), Araguaia (Ar), Xambioá (Xb). Studied areas: São Martin Prospect (SMP), Marble Quarry (MQ). Geologic units: 1- Amazon craton, 2- Archean and Paleoproterozoic basement gneisses, 3- Estrondo Group, 4- Pequizeiro Formation, 5- Couto Magalhães Formation, 6- Parnaíba Basin.

The metasedimentary rocks of the Araguaia Belt have been assembled in the Estrondo and Tocantins groups (Fig.1). The first unit occurs in the eastern side of the belt and is composed of quartzite and schists with garnet, staurolite and kyanite (Morro do Campo Formation); and feldspathic schist, mica schist, calc-schist, marble and amphibolite (Xambioá Formation). The Tocantins Group lies on the western portion of the Araguaia Belt (Fig.1), and is composed of chlorite schist with minor amounts of phyllite and quartzite (Pequizeiro Formation); and phyllite, slate and subordinated quartzite, meta-arkose and metalimestone (Couto Magalhães Formation) (Alvarenga et al. 2000). Single zircon Pb-evaporation ages around 550 Ma of syntectonic granitic bodies, associated with schists of the Xambioa Formation, dates the peak of the metamorphism in this belt (Moura & Gaudette 1993). Paleontologic data of carbonate rocks of the Couto Magalhães Formation suggest the boundary Neoproterozoic–Cambrian for the deposition of these carbonates (Nogueira et al. 2003).

ISOTOPE GEOCHEMISTRY

Sampling and Analytical Methods

Drill core samples from marbles (Xambioá Formation) and limestone (Couto Magalhães Formation) were collected for Sr, C and O isotope determinations in the Isotope Geology Laboratory of the Federal University of Pará, Brazil (Para-Iso). Petrographic studies, complemented with X-ray diffraction were conducted to investigate the mineralogy and textures of these rock samples. Marble thin sections were stained with alizarine to distinguish calcite from dolomite. Then, calcite was carefully sampled for isotope analysis, in the rock section cut used to make the stained thin section. C and O isotope composition were determined in a Finnigan MAT 252 mass spectrometer after extraction of CO₂ from 100 - 200 micrograms of carbonate using a Kiel III system coupled to the spectrometer. This extraction was done with H₃PO₄ at 70° Celsius. Analysis of the standard NBS-19, during the course of this study, gave average δ¹³C and δ¹⁸O values of 1.93‰ and -2.22‰, respectively. Sr isotope analysis in less than 200 micrograms of sample was conducted in a Finnigan MAT 262, with multicollector in static mode, and the running of the NBS 987 during the course of this study gave ⁸⁷Sr/⁸⁶Sr of 0.710233 ± 18 (n=8). Uncertainties in Sr isotope ratio are given in 2σ.

Carbonate rocks -Couto Magalhães Formation

Carbonate rocks of Couto Magalhães Formation were investigated in the drill core SMD-08 of the São Martim Prospect (Fig. 1), that recovered a continuous segment of about 20m of black to grey nodular limestone. Pressure solution effects are common and are indicated by shale seams between nodules. Thin beds of intraclastic packstone occur locally. Silt and fine sand (quartz, feldspar and muscovite) and rare pyrite crystals are disseminated in the limestones. Fine-grained sandstone cemented by calcite is interbedded with the limestone upsection.

C-isotope data of the carbonates rocks show mainly, near zero, negative values of δ¹³C (Table 1). The δ¹⁸O data are very negative, mainly lower than -11‰. These highly negative values suggest that remobilization of the oxygen isotopes might have occurred by meteoric water (Kaufman & Knoll, 1999). Diagenetic remobilization with formation of new minerals and recrystallization of the existing minerals, has been documented in rocks of this prospect (Lima et al. 2005). The ⁸⁷Sr/⁸⁶Sr ratio, generally over 0.709, is higher than that expected for the Neoproterozoic seawater, and does not represent the original values of these rocks. Variations of δ¹³C, δ¹⁸O and ⁸⁷Sr/⁸⁶Sr ratio with depth are plotted in figure 2.

Marble – Xambioá Formation

The 100 m thick drill core in the marble shows alternate light gray and dark gray marble beds. Calcite is the most abundant mineral in the light gray beds, and dolomite occurs in minor amounts. On the other hand, dolomite is the most abundant carbonate phase in the dark gray beds. Quartz, white mica, apatite and opaques are the accessory minerals in both dark and light gray marble. Four marble lithotypes were classified based on the proportion between calcite and dolomite: calcitic marble, dolomitic marble, calcitic marble with dolomite and dolomitic marble with calcite.

Carbon and oxygen isotope data are very consistent and show small variation (Table 2). In general, the values of δ¹³C vary between 2.68‰ and -0.26‰. In the calcitic marble they vary from 1.29‰ to -0.26‰, while in the dolomitic marble these values are between 2.68‰ and 0.30‰. The values of δ¹⁸O are negative and situated between -4.82‰ and -6.19‰. In general, they are higher than -5‰, the value suggested by Kaufman & Knoll (1999) as indicative of oxygen remobilization.

The values of the ⁸⁷Sr/⁸⁶Sr ratio are higher in the dark gray marble beds, where it may reach 0.710 (Table 2). However, in the calcite rich light gray beds, the ⁸⁷Sr/⁸⁶Sr ratio is lower, varying from 0.7075 to 0.7078. Figure 3 shows carbon, oxygen and strontium isotope variation with depth in this drill core.

Table 1 – Carbon, oxygen and ⁸⁷Sr/⁸⁶Sr isotope data for carbonate rocks of drill core SMD-08 in the São Martim Prospect, Couto Magalhães Formation.

Depth (m)	δ ¹³ C	δ ¹⁸ O	⁸⁷ Sr/ ⁸⁶ Sr
613.90	-0.06	-13.34	0.709151(49)
615.00	-	-	0.719020(62)
616.75	-0.04	-11.02	0.708232(78)
617.78	0.05	-11.21	0.708639(33)
618.50	-0.54	-11.56	0.709234(50)
621.75	-0.47	-10.71	-
622.50	-0.50	-8.60	0.708673(29)
623.08	-	-	0.709341(28)
623.90	-2.82	-6.65	0.709063(71)
624.95	-2.68	-10.97	0.709452(61)
625.47	-0.75	-11.12	0.709685(18)
628.35	-0.44	-10.36	0.708864(18)
629.00	-0.82	-11.25	0.709320(53)
629.70	-0.04	-11.63	0.709937(20)
631.23	-0.23	-11.69	0.710042(36)
632.51	-0.86	-11.51	0.709295(25)

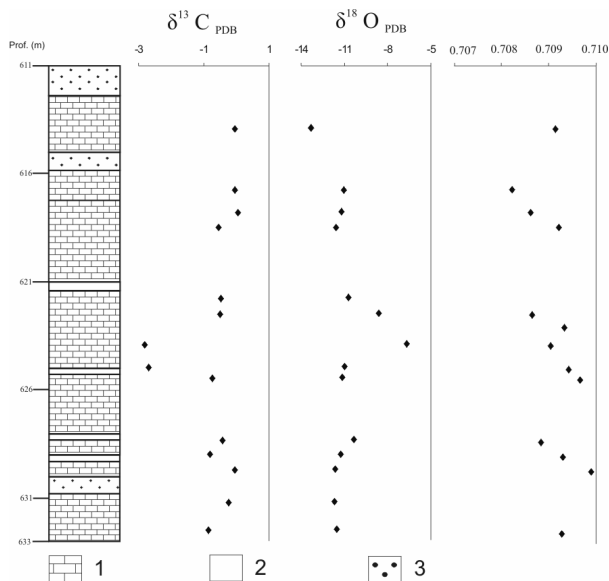


Fig. 2 – Carbon and oxygen isotope compositions, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of carbonate rocks of the drill core SMD-08, São Martim Prospect. 1- Nodular limestone; 2- Intraclastic limestone; 3- Sandstone.

The values of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio are higher in the dark gray marble beds, where it may reach 0.710 (Table 2). However, in the calcite rich light gray beds, the $^{87}\text{Sr}/^{86}\text{Sr}$ are lower, varying from 0.7075 to 0.7078. The isotope variation with depth in this drill core is plotted in figure 3.

Table 2 – Carbon, oxygen and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope data for marble of the Xambioá Formation.

Depth (m)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$^{87}\text{Sr}/^{86}\text{Sr}$
10.82	0.74	-4.82	0.707565(12)
15.87	1.98	-4.83	0.707717(78)
19.00	1.24	-4.31	0.707852(56)
26.67	1.79	-4.93	0.707532(14)
29.69	1.88	-5.02	0.708254(31)
35.53	0.06	-5.76	0.707655(12)
40.45	-0.12	-6.19	0.707663(24)
45.19	-0.26	-6.09	0.707749(11)
52.00	0.04	-5.89	0.707738(15)
56.22	0.30	-4.52	0.708516(17)
64.89	0.54	-6.18	0.707582(13)
70.55	0.76	-6.04	0.707803(26)
76.84	1.29	-5.07	0.707574(21)
80.87	0.61	-4.43	0.708378(19)
83.85	1.76	-2.47	0.710304(13)
87.00	2.68	-2.23	0.709781(58)
92.77	0.62	-2.98	0.709253(14)
98.90	1.42	-4.86	0.710528(07)

DISCUSSION AND CONCLUSIONS

The oxygen isotope data for the marble of the Xambioá Formation indicate very little alteration of the original values. Then, it is assumed that the marble retained its original C-isotope composition in spite of the

amphibolite facies metamorphism affecting the carbonatic rocks. In addition, the values of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the calcitic marble are consistent with the curve of temporal variation of the $^{87}\text{Sr}/^{86}\text{Sr}$ for Neoproterozoic carbonates, for the time interval between the Sturtian and Vendian glaciations, suggested by Jacobsen & Kaufman (1999), figure 4. Plotting the $\delta^{13}\text{C}$ values in the diagram for temporal variation in $\delta^{13}\text{C}$ for Neoproterozoic carbonates suggested by Jacobsen & Kaufman (1999), it is possible to constrain the age of deposition of the original carbonate rocks for times very close to the Sturtian (750-720Ma) and Vendian (575-595 Ma) glaciations (Fig. 5). However, the available data do not permit to select between one of these two glaciations period.

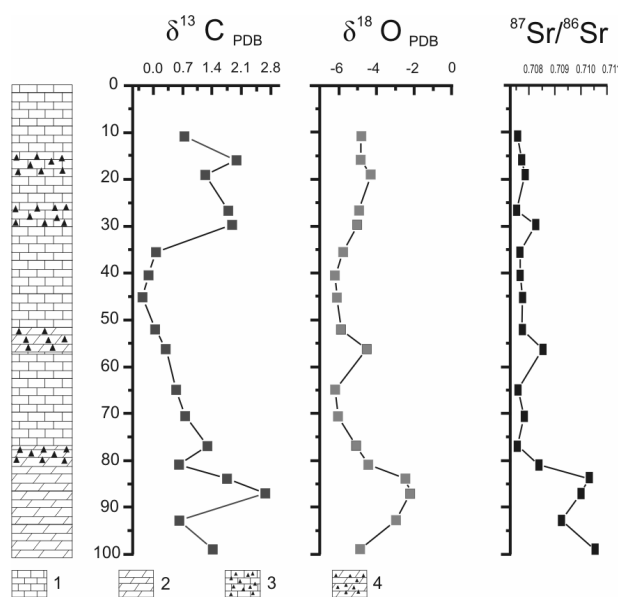


Fig. 3 – Carbon and oxygen isotope compositions and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of drill core samples from marble of the Xambioá Formation. 1- Calcitic marble, 2- Dolomitic marble; 3- Calcitic marble with dolomite, 4- Dolomitic marble with calcite.

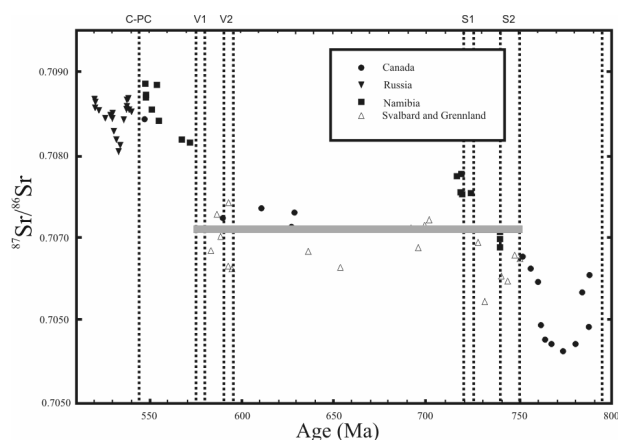


Fig. 4 – Plot of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the drill core samples from marble of the Xambioá Formation in the temporal variation diagram of $^{87}\text{Sr}/^{86}\text{Sr}$ in Neoproterozoic carbonates, proposed by Jacobsen Kaufman (1999).

The $\delta^{18}\text{O}$ data of the carbonate rocks of the São Martin Prospect are highly negative and therefore, altered by meteoric water, probably, during the diagenesis. The values of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio are also too high for the Neoproterozoic seawater and, certainly, were affected by diagenetic processes. Since they do not represent the original values, these Sr-isotope data are useless for geochronological interpretation. However, it is possible that at least some of the $\delta^{13}\text{C}$ of these carbonate rocks are representative of the original values, since there are no correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data. If this is correct, then $\delta^{13}\text{C}$ values, mainly around zero per mil, of carbonates in the São Martin Prospect may be giving one additional clue for the record of Neoproterozoic glaciations in the Araguaia belt.

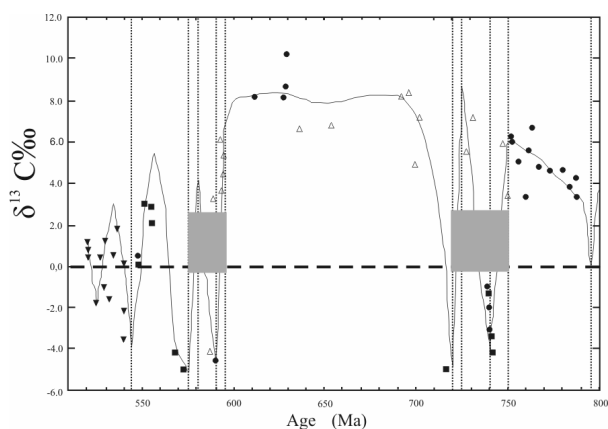


Fig. 5 Plot of the $\delta^{13}\text{C}$ of the drill core samples from marble of the Xambioá Formation in the temporal variation diagram of $\delta^{13}\text{C}$ in Neoproterozoic carbonates, proposed by Jacobsen Kaufman (1999)

It is important to stress that so far, there are no geologic evidences of Neoproterozoic glaciation in the Araguaia belt. These evidences are restricted to the Paraguay belt and its adjacent cratonic cover. However, when the C, O and Sr isotope data presented here are considered together, they show some indications of a relationship between the studied carbonate rocks and the known glaciations events of the Neoproterozoic. If this is true, then, the deposition of the carbonate rocks of the Araguaia belt may have occurred after the Vendian or Sturtian glaciations events. The suggested time interval for the deposition of these carbonate rocks are also constrained by single zircon Pb-evaporation ages in syntectonic granites (~ 550 Ma) and metagabro (817 ± 5 Ma) and, both associated with the rocks of the Xambioá Formation (Moura & Gaudette 1993, Gorayeb et al. 2004). However, if these carbonatic rocks (marble and limestone) are coeval then, based on paleontologic record of Nogueira et al. (2003) for the nodular limestone, the deposition these carbonate successions may have occurred after the Vendian.

ACKNOWLEDGEMENTS

This work was partially funded by CNPq project (Proc. 478173/2003-2), and project PRONEX/CNPq/UFPA (66.2103/1998). The Western Mining Company (WMC) provided the drill core SMD-08, and Mineração Vale do Araguaia Ltda the marble cores used in this study.

REFERENCES

- Almeida F.F.M., Hasui Y., Neves B.B.B., and Fuck R.A. 1981. Brazilian structural provinces; an introduction. *Earth Science Review* 17: 1-29.
- Alvarenga C.J.S. & Trompette R. 1998. Glacially influenced sedimentation in the Late Proterozoic of the Paraguay belt (Mato Grosso, Brasil) *Paleogeography, Paleoclimatology, Paleoecology*, 92: 85-105.
- Alvarenga C.J.S., Moura C.A.V., Gorayeb P.S.S., Abreu F.A.M. 2000. Paraguai and Araguaia belts. In: U.G. Cordani, E.J. Milani, A. Thomaz Filho, D.A. Campos eds. *Tectonic Evolution of South America*. p 183-193.
- Gorayeb P.S.S, Moura C.A.V., Calado W.M. 2004. Suite Intrusiva Xambica: um magmatismo toleítico neoproterozóico pré-tectônico no Cinturão Araguaia.. In: XLII Congresso Brasileiro de Geologia, ARAXÁ. Anais do XLII Congresso Brasileiro de Geologia. Belo Horizonte : SBG, 2004. v. 1. p. 35-35
- Herz N., Hasui Y., Costa J.B.S., Matta M.A.S. 1989. The Araguaia Fold Belt, Brazil: A reactivated Brasiliano-Pan-Africano cycle (550 Ma) geosuture. *Precambrian Res.*, 42: 371-386.
- Jacobsen S.B. & Kaufman A.J. 1999. The Sr, C and O isotopic evolution of Neoproterozoic seawater. *Chemical Geology*, 161:37-57.
- Kaufman A.J. & Knoll A.H. 1999. Neoproterozoic variations in the C-isotopic composition of seawater: stratigraphic and biogeochemical implications. *Precambrian Res.*, 73:27-49.
- Lima A.D.P., Villas R.N, Moura C.A.V., Neves M.P., Kotschoubey B., Osborne G.A. 2005. Estudos isotópicos (Pb) microtermométricos na zona de sulfetos estratiformes do Alvo São Martin, NW do Cinturão Araguaia. I Simpósio Brasileiro de Metalogenia, Gramado (RS), CD-ROM
- Moura C.A.V. & Gaudette H.E. 1993. Evidence of Brasiliano/Pan-African deformation in the Araguaia belt: Implication for Gondwana evolution. *Revista Brasileira de Geociências*, 23, 117-123.
- Moura C.A.V. & Gaudette H.E. 1999 Zircon Ages of the Basement Orthogneisses from the Northern Segment of the Araguaia belt, Brazil. In: A.K. Sinha (Editor), *Basement Tectonic* 13, Holanda, Kluwer Academic Publishers. p 155-178.
- Nogueira A.C.R., Hidalgo R., Petri S., Truckenbrodt W., Gorayeb P.S.S., Osborne G.A. 2003. Neoproterozoic-Cambrian Carbonate-Siliciclastic deep-Sea deposits and microfossils of the Araguaia Belt, Southeastern Amazonian craton, Brazil. 3rd. Latinamerican Congress of Sedimentology, Brazil. Abstracts, p. 229-230.
- Nogueira A.C.R., Riccomini C., Sial A.N., Moura C.A.V. Fairchild T.R. E.L. 2003. Solt-sediment deformation at the base of the Neoproterozoic Puga carbonate (southwestern Amazon craton, Brazil): Confirmation of rapid icehouse to greenhouse transition in snowball Earth. *Geology*, 7:613-616.

RESUMO

Estudos isotópicos (C, O, $^{87}\text{Sr}/^{86}\text{Sr}$) foram realizados em mármore e calcáreo do Cinturão Araguaia, situado na porção central do Brasil, para limitar a idade de deposição das rochas metassedimentares e para investigar a presença de eventuais registros de glaciações do Neoproterozoico nestas rochas carbonáticas. Estes estudos foram realizados em amostras coletadas em dois furos de sondagens realizados nestas suções carbonáticas. A razão $^{87}\text{Sr}/^{86}\text{Sr}$ (0,7075 – 0,7078) no mármore calcítico da Formação Xambioá é compatível com aquela do oceano no Neoproterozoico. Os valores de $\delta^{18}\text{O}$ (-4.82‰ and -6.19‰) indicam uma pequena, ou a ausência, de remobilização diagenética e, portanto, os valores originais de $\delta^{13}\text{C}$ (1.29‰ to -0.26‰) desse mármore calcítico podem ter sido preservados. Estes dados sugerem que a deposição desta sucessão carbonática ocorreu após as glaciações do Vendiano ou Sturtiano. No entanto, eles não permitem determinar em qual destes dois períodos. Os valores da razão $^{87}\text{Sr}/^{86}\text{Sr}$ para o calcáreo da Formação Couto Magalhães estão bem acima dos valores sugeridos para o oceano no Neoproterozoico. Além disso, estes calcáreos mostra valores acentuadamente negativos de $\delta^{18}\text{O}$, geralmente menor que -11‰, indicando remobilização durante a diagênese. Contudo, a ausência da correlação entre os isótopos do C e O, e os valores bastantes consistentes de $\delta^{13}\text{C}$, principalmente em torno de zero per mil, sugerem que alguns dos dados isotópicos de C podem representar valores originais. Neste caso, os isótopos de carbono viriam corroborar com a hipótese de que as sucessões carbonáticas do Cinturão Araguaia podem ter sido depositadas depois de eventos glaciais.