ELSEVIER

Precambrian Research 104 (2000) 107–122

Precambrian Research

www.elsevier.com/locate/precamres

Carbon and oxygen isotope profiles across Meso-Neoproterozoic limestones from central Brazil: Bambuí and Paranoá groups

R.V. Santos [a,*], C.J.S. de Alvarenga [a], M.A. Dardenne [a], A.N. Sial [b], V.P. Ferreira [b]

[a] *Instituto de Geociências, Universidade de Brasília, Campus Universitário, Asa Norte, CEP: 70910-900, Brasília, DF, Brazil*

[b] *Departamento de Geologia/NEG-LABISE, Universidade Federal de Pernambuco, Caixa Postal: 7852, CEP: 50732-970, Recife-PE, Brazil*

Received 15 January 1999; accepted 24 April 2000

Abstract

We present carbon and oxygen isotopic data on carbonates along three profiles of the Neoproterozoic Bambuí group in central Brazil. This unit covers an area of more than 300 000 km^2 and comprises carbonate–siliciclastic sediments at the base that grade into siliciclastic sediments towards the top. The Bambuí group overlies by unconformity the Paranoá group, which consists mostly of siltstone, quartzite and minor limestone. The data presented here improve the stratigraphic correlation within the Bambuí basin and show that it evolved in an environment significantly different from that of the Paranoá basin. Our data show large fluctuations of $\delta^{13}C_{PDB}$ in limestones from the Bambuí Group (from +0.8 to +13.5‰) in all the three studied areas. Some of these fluctuations represent stratigraphic markers that can be used as a chronostratigraphic tool within a basin scale. This observation is relevant considering the lack of fossil record and other stratigraphic markers in Neoproterozoic sequences. We also present the first isotopic profiles along the Paranoá–Bambuí transition, which shows that the $\delta^{13}C_{PDB}$ values grade from +1.0‰ in the Paranoá group, to +2.6‰ in the lower portion of the Bambuí group, increasing up to +12‰ in the upper part of this unit. Based on our carbon isotope data, as well as other geological, mineralogical and Nd isotope studies, we argue that the sediments of the Paranoá group were deposited on an open platform that was fully connected to the ocean. On the other hand, the sediments of the Bambuí group were deposited in an epicontinental sea and during a tectonic inversion in a foreland basin at about 790–600 Ma. This unit displays an increased amount of clastic sediments upwards. We argue that the high carbon isotope values observed in limestones and marlstones from the Bambuí group are correlated to worldwide high carbon isotope values reported for the Neoproterozoic. However, we also point out that novel marine conditions induced by the tectonic inversion of the basin may also have contributed to increase the carbon isotopic composition of the Bambuí carbonates. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Neoproterozoic; Carbon isotopes; Oxygen isotopes; Brazil; Bambuí group; Paranoá group

* Corresponding author. Tel.: +55-61-3072078; fax: +55-61-2724286.
E-mail address: rventura@unb.br (R.V. Santos).

0301-9268/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S0301-9268(00)00082-6

1. Introduction

The Neoproterozoic is marked by a global scale occurrence of thick epicontinental carbonate–siliciclastic sequences that encompass glacial events. Chemical and isotopic variations in these sequences have been used to address stratigraphic problems as well as environmental conditions during that time. In particular, carbon isotope studies have indicated significant variations in the organic and inorganic carbon reservoirs during the Neoproterozoic (Knoll et al., 1986; Magaritz et al., 1986; Iyer et al., 1995; Kaufman and Knoll, 1995; Brasier et al., 1996; Hoffman et al., 1998). These variations control the oxygen level of the atmosphere and may be associated with, among other processes, the sulfide–sulfate balance of the oceans and erosion rate of the continents (Veizer et al., 1980; Knoll et al. 1986).

Variations in oxygen and carbon isotope ratios have been reported in Neoproterozoic carbonate sequences worldwide (e.g. Schidlowski et al., 1976; Knoll et al., 1986; Magaritz et al., 1986; Wickham and Peters, 1992; Brasier et al., 1996). Because of the lack of fossils and other stratigraphic markers in these sequences, these isotope variations have also been used as chronostratigraphic tools within a sedimentary basin or even at a larger scale (Kaufman et al., 1993; Kaufman and Knoll, 1995).

Neoproterozoic limestones occur over extensive areas in South America, mainly in central Brazil. In recent years, these rocks have been extensively studied in terms of their sedimentology, lithostratigraphy and mineral occurrences (Alvarenga, 1978; Alvarenga and Dardenne 1978; Dardenne, 1978, 1979; Braun, 1982; Castro, 1997). However, only few studies have addressed the paleoenvironmental meaning of their carbon and oxygen isotopic compositions (Chang et al. 1993; Iyer et al. 1995; Misi and Veizer, 1998). These studies have revealed positive $\delta^{13}C_{PDB}$ excursions in limestones from the Bambuí group, with $\delta^{13}C_{PDB}$ values that range from -6 to up to $+16‰$. Similar Neoproterozoic $\delta^{13}C_{PDB}$ positive excursions have been reported from limestones and dolostones of other continents (Knoll et al., 1986; Fairchild and Spiro, 1987; Kaufman et al., 1991; Wickham and Peters, 1992; Brasier et al., 1996). A detailed isotope study of Neoproterozoic rocks of central Brazil is particularly relevant because these successions are poorly dated and stratigraphic correlation is rather uncertain.

In this study, we sampled in detail Neoproterozoic limestones from three areas of central Brazil that include rocks of the Bambuí group as well as the Paranoá group. We present isotopic profiles from these areas and show that carbon isotopes may be used as reliable stratigraphic markers within the Bambuí basin. We also argue that the extremes in positive carbon isotope values may be related not only to a global process, but also to novel marine conditions induced by tectonic processes.

2. Geologic setting

The Paranoá and Bambuí groups constitute two important Neoproterozoic units in central Brazil (Fig. 1), which on a regional scale are separated by an unconcormity marked by an erosive contact or by diamictites and glacial sedimentary deposits. In some regions, such as in Serra de São Domingos (SSD) area, the Bambuí limestones overly directly the rocks of the Paranoá group, which present a narrow karstified and brecciated horizon indicating an hiatus in the sedimentation (Fig. 2A). In others, the contact between these two units is marked by the presence of diamictites (Jequitaí Formation), a discontinuous unit at the base of the Bambuí Group. At the edges of the basin, the Bambuí and the Jequitaí sediments overly Paleoproterozoic granite-gneiss basement rocks (Fig. 2B).

Sediments of the Paranoá group crop out mainly in central Brazil and consist of mature siliciclastic cratonic sediments that include quartzites with intercalations of metasiltstones with minor lenses of limestones and dolostones.Dardenne and Faria (1985) divided the Paranoá Group into nine lithostratigraphic units, beginning with a paraconglomerate, followed by transgressive and regressive siliciclastic dominated cycles, and ending with pelites and dolostones containing *Conophyton metulum* Kirichenko stro-

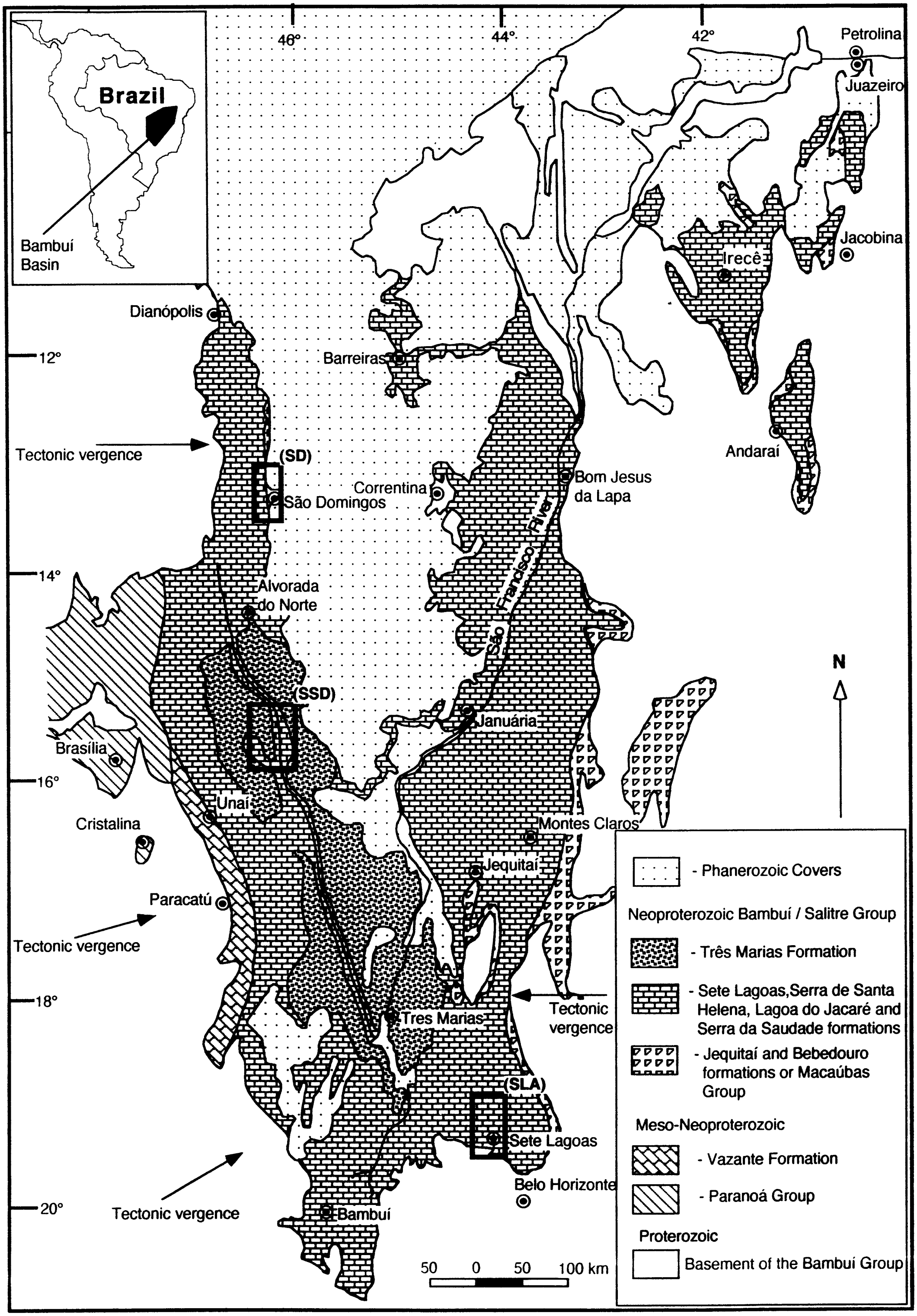

Fig. 1. Geological map showing the distribution of neoproterozoic rocks in central Brazil and sampling locations : SD, SSD, and SLA. After Schobbenhaus et al. (1981).

matolites (Cloud and Dardenne, 1973; Cloud and Moeri, 1973; Dardenne, 1979). In general, this unit can be defined as a Meso-Neoproterozoic shallow marine sedimentary sequence dominated by transgressive events and deposited unconformably over metasediments of the Araí Group

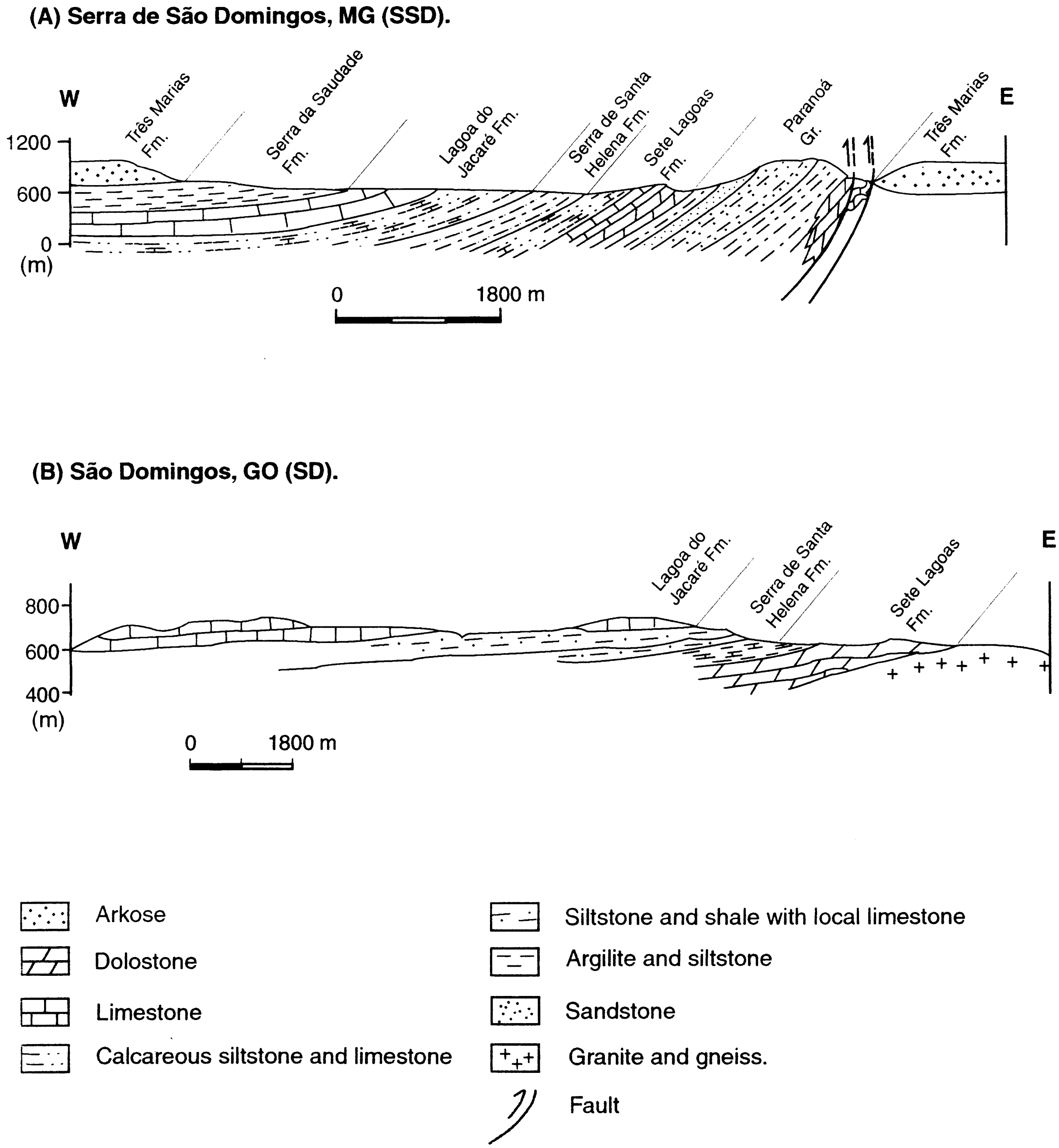

Fig. 2. (A) E-W profile across the SSD redion, showing the general structure of the Bambuí group, that overlies the Paranoá group sediments; (B) E-W profile across the SD region, with the base of the Bambuí group overlying granite–gneiss rocks of the basement.

(1.77 Ga) and prior to diamictites (Jequitaí Formation) at the base the Bambuí Group (Pimentel et al., 1991). After revising the available geochronological and microfossils data from the Paranoá Group, Fairchild et al. (1996) concluded that the best estimate of the age of this unit is 1170–950 Ma. This unit has been interpreted as a passive margin sequence that was deposited at the western border of the São Francisco craton (Dardenne, 1979; Pimentel et al., 1999). Petrographic, chemical and isotopic ($^{147}Sm/^{144}Nd$) studies indicate that the Paranoá sediments were derived from a Paleoproterozoic sialic basement located in the São Francisco craton (Guimarães 1997; Pimentel et al. 1999).

The Jequitaí diamictites consist of clasts supported by a clay-rich matrix with siltstone and sandstone lenses. The clasts include quartz, quartzite, granite, limestone and siltstone. The age of this unit is poorly constrained and falls between 688 ± 69 and 900 ± 2 Ma. While the lower age limit is based on Pb–Pb dating of the Sete Lagoas (SLA) formation limestones (Babinski et al. 1999), the upper age limit is based on U–Pb dating of zircon from basic dikes that cut the underlying siliciclastic sequence (Espinhaço Supergroup Uhlein et al. 1999). Hence, the available data indicate that the Jequitaí glaciation event is probably Sturtian. This unit crops out intermittently at the base of the Bambuí group and, depending of the region, overlies the Paranoá sediments or the granite–gneiss basement (Karfunkel and Hoppe, 1988; Uhlein, 1991; Uhlein et al. 1999). The Bambuí group was deposited during a transgressive phase and after the deposition of the Jequitaí Formation (Dardenne 1979).

The Bambuí Group covers an area of more than 300 000 km^2 over the São Francisco craton. These sediments were deposited in an epicontinental sea, commencing with a carbonate–pelite facies that was followed by siliciclastic sedimentation characterized by immature sediments (Dardenne, 1978; Dardenne 1979; Misi and Kyle, 1994). The base of this unit consists of laminated argillaceous limestones, dolostones, siltstones, stromatolitic dolomite and marlstone (SLA formation). Overlying are rhythmic interbeds of mudstones, siltstones and very fine-grained sandstones of the Serra de Santa Helena Formation, followed by a second carbonate unit with argillaceous limestones, marlstones, shales and siltstones with dark colored lime grainstone lenses (Lagoa do Jacaré formation). The upper portion of the Bambuí group consists of siliciclastic rocks, mainly greenish siltstones and arkoses (Serra da Saudade and Três Marias formations). In contrast to the Paranoá group sediments described above, the Bambuí group siliciclastic rocks are mineralogically and texturally immature sediments, which have been accumulated during the tectonic inversion of a foreland basin (Guimarães 1997). Pb–Pb isochron ages obtained for undeformed carbonate rocks from the SLA formation is 688 ± 69 Ma and is considered as the minimum depositional age of this formation (Babinski et al., 1999). Evidence of the inversion also occurs in the southwestern part of the basin (west of SLA, Fig. 1 and Fig. 3), where conglomerates outcrop associated to a fan delta system that was also related to the tectonic evolution of the foreland basin (Castro 1997). According to Guimarães (1997) and Castro (1997) findings, the tectonic inversion of the basin was related to eastward thrusting movements that, as has been pointed out, affected significantly the sedimentological evolution of the basin. Nd isotope studies also give support for the inversion of the Bambuí basin. They show that the Bambuí group pelites present Nd model ages distinctively younger than those of the Paranoá group sediments, and thus indicate that its sediments were derived from a younger source region (Pimentel et al. 1999).

3. Sampling and analytical methods

We have analyzed oxygen and carbon isotopes along three stratigraphic profiles in central Brazil (Fig. 1): SSD and SLA, both in the State of Minas Gerais, and São Domingos (SD), in the State of Goiás.

Samples from SSD are fresh limestones, dolostones and marlstones, sampled along a 2000 m profile that includes both the Paranoá and Bambuí sediments. The Paranoá sediments consist

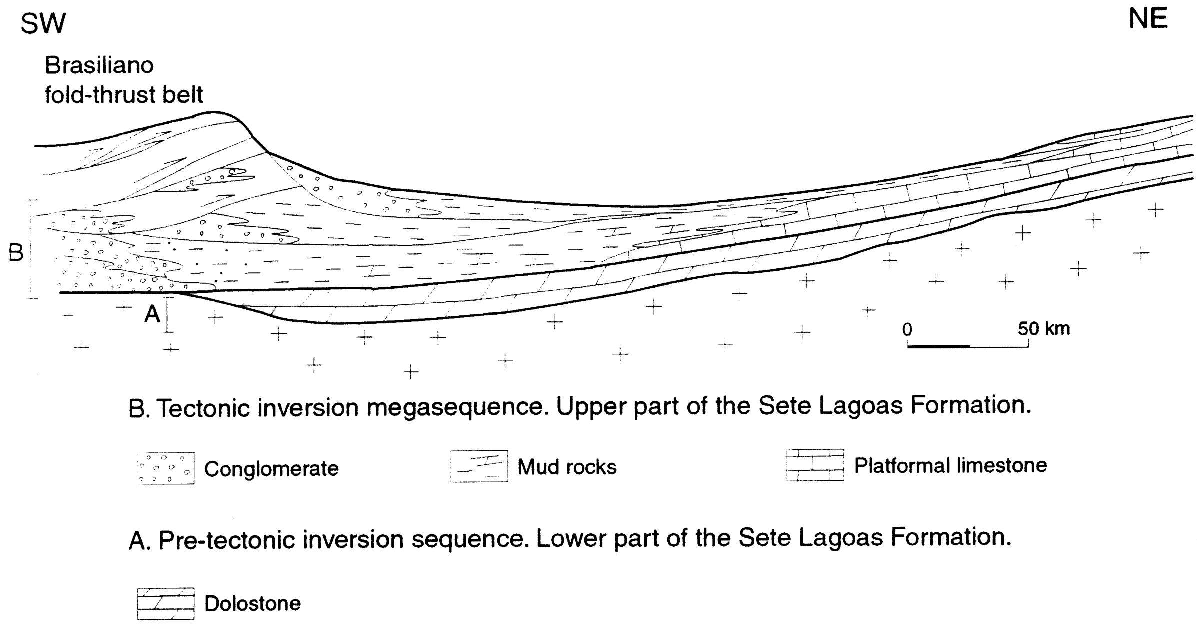

Fig. 3. Geological cross section of southwestern border of the Bambuí foreland basin during the tectonic inversion (after Castro, 1997).

mainly of siliciclastic sediments and minor dolostones with up to 30 m thick stromatolite-bearing dolomite lenses (Fig. 2A). These rocks are overlain by sediments of the Bambuí group, which includes from base to top: limestones, dolostones with stromatolites and marlstones of the Sete Lagoas formation, siltstones of the Serra de Santa Helena formation, siltstones, marlstones and fetid and dark colored limestones of the Lagoa do Jacaré formation. The redish-limestones and dolostones from the base of the SLA formation (cap carbonate) have also been described in other parts of the Bambuí basin and are believed to represent a lithostratigraphic marker which lies directly above glaciogenic diamictites or a narrow karstified and brecciated carbonate horizon (Dardenne 1979; Montes et al. 1981; Guimarães 1996; Alvarenga et al. 1998). In SSD the sediments are progressively more deformed from the top to the base (eastwards) of the sequence due to the SD fault (Alvarenga, 1978). The rocks exhibit no sign of metamorphism or fluid percolation (Fig. 2).

Limestones and dolostones of the SD region overly unconformably Archean (?) granitic and gneissic rocks, as well as Paleoproterozoic (?) metapelites and intrusive rocks of the SD volcano-sedimentary sequence (Fig. 2B). In this area, the base of the Bambuí consists of stromatolitic dolostones and limestones (SLA formation) superposed by siltstone with minor limestone lenses (Serra de Santa Helena formation). Higher up in the stratigraphy are fetid and dark colored limestones of the Lagoa do Jacaré formation. Samples were collected along a 140 m-thick sedimentary sequence that dips 30° westward and presents no signs of metamorphism.

Samples from SLA consist of dolostones, limestones and pelitic rocks that overly granite and gneiss basement rocks. In contrast to previous areas, the lower contact of the Bambuí group is tectonic and marked by intense shearing close to the fault zone, the latter with centimetric veins of calcite and quartz that indicate local carbonate remobilization.

Table 1
Carbon and oxygen isotopes and elemental composition of samples from the SSD profile[a]

Sample	Lithology	Height (m)	$\delta^{13}C_{PDB}$	$\delta^{18}O_{PDB}$	Mg/Ca*100	Sr (ppm)	Fe (ppm)	Mn (ppm)	Ba (ppm)	Si (ppm)
SD-73	Dolostone	0.00	0.9	−5.6	Nd	Nd	Nd	Nd	Nd	Nd
SD-75	Dolostone	13.00	0.4	−7.8	Nd	Nd	Nd	Nd	Nd	Nd
SD-76	Dolostone	20.00	0.4	−6.7	Nd	Nd	Nd	Nd	Nd	Nd
SD-78	Dolostone	30.00	1.3	−8.8	Nd	Nd	Nd	Nd	Nd	Nd
SD-80	Dolostone	40.00	1.0	−9.9	Nd	Nd	Nd	Nd	Nd	Nd
SD-81	Dolostone	50.00	0.1	−10.4	Nd	Nd	Nd	Nd	Nd	Nd
SD-82	Dolostone	55.00	0.8	−11.3	Nd	Nd	Nd	Nd	Nd	Nd
SD-83	Dolostone	65.00	0.9	−10.3	Nd	Nd	Nd	Nd	Nd	Nd
SD-86	Dolostone	905.00	0.6	−4.3	Nd	Nd	Nd	Nd	Nd	Nd
SD-87	Dolostone	915.00	1.4	−4.3	Nd	Nd	Nd	Nd	Nd	Nd
SD-88	Dolostone	925.00	1.4	−5.5	Nd	Nd	Nd	Nd	Nd	Nd
SD-17	Dolostone	1096.00	2.7	−2.6	28	14	1299	204	30	125
SD-19	Dolostone	1105.70	2.9	−2.7	28	19	1505	203	31	87
SD-23	Dolostone	1115.40	4.1	−1.5	28	30	814	107	32	110
SD-24	Dolostone	1125.10	4.0	−2.2	28	22	996	113	37	118
SD-25	Dolostone	1134.80	2.3	−2.5	27	21	1212	121	39	159
SD-26	Dolostone	1144.50	1.9	−0.2	28	52	596	78	43	99
SD-27	Limestone	1154.20	0.8	−7.5	2	183	1592	140	59	425
MG98-14H	Limestone	1155.00	−0.6	−7.7	Nd	Nd	Nd	Nd	Nd	Nd
MG98-14G	Limestone	1155.80	−0.6	−7.7	Nd	Nd	Nd	Nd	Nd	Nd
MG98-14F	Limestone	1156.60	−0.7	−7.7	Nd	Nd	Nd	Nd	Nd	Nd
MG98-14E	Limestone	1157.40	−2.8	−6.5	Nd	Nd	Nd	Nd	Nd	Nd
MG98-14D	Limestone	1158.20	−3.7	−6.4	Nd	Nd	Nd	Nd	Nd	Nd
MG98-14C	Limestone	1159.80	2.3	−2.4	Nd	Nd	Nd	Nd	Nd	Nd
MG98-14B	Limestone	1160.60	2.2	−2.9	Nd	Nd	Nd	Nd	Nd	Nd
MG98-14A	Limestone	1161.40	−2.4	−5.7	Nd	Nd	Nd	Nd	Nd	Nd
SD-08	Dolostone	1163.90	0.9	−5.9	27	18	8828	594	31	519
SD-09	Dolostone	1173.60	1.2	−7.5	27	11	7418	460	29	470
SD-10	Dolostone	1183.30	1.2	−8.6	27	12	8820	578	31	537
SD-11	Limestone	1193.00	1.7	−6.6	1	187	1026	155	43	120
SD-02	Limestone	1202.70	2.4	−7.6	3	312	851	87	51	327
SD-03	Dol-limestone	1212.40	1.6	−5.6	16	188	1449	71	39	966
SD-04	Limestone	1222.10	2.5	−6.3	7	417	764	52	46	341
SD-O5	Limestone	1231.80	2.2	−6.7	4	427	350	31	36	159
SD-06	Dol-siltstone	1241.50	2.7	−2.5	19	216	1438	70	53	1753
SD-07	Dolostone	1251.20	2.8	−2.7	28	26	973	52	33	184
SD-13B	Dolostone	1260.90	3.1	−3.9	27	26	1003	52	39	1027
SD-14	Dolostone	1270.60	2.4	−2.3	27	41	1058	51	32	495
SE-15	Dolostone	1280.30	2.1	−1.9	28	23	1246	59	34	256
SE-16	Dolostone	1290.00	3.3	−1.7	28	17	805	50	32	99

Table 1 (*Continued*)

Sample	Lithology	Height (m)	$\delta^{13}C_{PDB}$	$\delta^{18}O_{PDB}$	Mg/Ca*100	Sr (ppm)	Fe (ppm)	Mn (ppm)	Ba (ppm)	Si (ppm)
SD-62	Cal-siltstone	1300.00	7.9	−11.3	4	557	6241	223	107	3417
SD-61	Cal-siltstone	1310.00	10.4	−9.4	3	425	7597	398	154	3476
SD-59A	Limestone	1390.00	10.7	−6.9	1	897	999	74	50	240
SD-58	Cal-siltstone	1395.00	12.1	−7.0	1	1553	2357	158	83	949
SD-56	Limestone	1405.00	13.5	−4.6	0	1921	969	69	85	648
SD-31A	Cal-siltstone	1630.00	8.3	−10.1	2	347	5991	588	34	2101
SD-33	Cal-siltstone	1665.00	9.9	−8.8	1	954	4423	1190	62	1609
SD-36	Limestone	1700.00	10.6	−6.9	1	1139	559	29	52	157
SD-38	Limestone	1735.00	10.5	−7.9	1	1677	1454	217	69	149
SD-39	Limestone	1770.00	9.3	−7.9	1	1370	491	43	77	173
SD-43	Limestone	1805.00	9.9	−7.3	1	1173	4376	1234	56	910
SD-46	Limestone	1840.00	10.5	−5.2	0	1358	657	51	63	188
SD-49	Cal-siltstone	1875.00	8.9	−5.4	0	1557	4141	203	62	1174
SD-52	Limestone	1910.00	9.5	−4.5	0	1573	1313	87	60	509
SD-54B	Limestone	1945.00	6.9	−7.3	0	1398	1109	107	67	182

[a] Nd = not determined.

Table 2
Carbon and oxygen isotopes of samples from the SD profile

Sample	Lithology	Height (m)	$\delta^{13}C_{PDB}$	$\delta^{18}O_{PDB}$
DG-1A	Dolostone	5	−2.6	−7.2
DG-1B	Dolostone	7	−1.5	−4.0
DG-02	Dolostone	10	−2.2	−4.4
DG-19	Dolostone	20	−1.0	−4.6
DG-20B	Pinkish dolomite	24	0.2	−2.9
DG-21	Limestone	38	10.2	−10.1
DG-22	Limestone	45	9.8	−2.7
DG-27	Limestone	125	11.6	−7.5
DG-28B	Limestone	130	12.8	−4.6

Most samples for this study were collected at a regular vertical interval of approximately 10–15 m and include dolostones, limestones and marlstones. Carbon and oxygen isotope ratios were obtained after reacting the samples with 100% H_3PO_4 at 25°C for at least 12 h for calcite and for over 3 days for dolomite (McCrea, 1950). The released CO_2 was analyzed by a SIRA II triple collector, dual inlet, VG Isotech mass spectrometer at the University of Pernambuco, and by a Finnigan Delta E mass spectrometer at the University of Brasília. The CO_2 oxygen isotopic compositions were corrected to calcite and dolomite by applying, respectively, the fractionation were factors 1.01025 and 1.01111. The uncertainties of the isotope measurements were 0.2‰ during the period of analyses. Trace element data were obtained after partially reacting the samples with HCl (10%) for 24 h and then analyzing the filtered solution by ICP-AES at the University of Brasília. These analyses are qualitative considering that only a fraction of the samples was dissolved by the acid solution.

4. Results

Oxygen and carbon isotopic compositions of the analyzed samples are displayed in Tables 1–3. Among the three areas, the SSD present the most complete profile because it includes both the upper part of the Paranoá group as well as the whole carbonate sequence of the Bambuí group.

The data from the SSD area reveal an upward increase in $\delta^{13}C$ along the profile, reaching values up to +12‰ (Fig. 4), with carbonates from the Paranoá group within a narrow range of $\delta^{13}C_{PDB}$ (close to 0‰), and $\delta^{18}O_{PDB}$ from −4 to −9‰, while the carbonates of the Bambuí group have a wide range of C and O isotope values. The transition Paranoá–Bambuí is marked by an increase in $\delta^{13}C_{PDB}$, from ∼ +1.0‰ in the Paranoá group to +2.6‰ in the Sete Lagoas Fm, followed by a

Table 3
Carbon and oxygen isotopes of samples from the SLA profile

Sample	Lithology	Height (m)	$\delta^{13}C_{PDB}$	$\delta^{18}O_{PDB}$
AM-1/P2	Limestone	10	3.1	−9.7
AM-2/P2	Limestone	20	3.4	−9.5
AM-3/P2	Limestone	30	3.4	−9.3
AM-4/P2	Limestone	40	2.8	−10.7
AM-5/P2	Limestone	50	3.8	−8.9
AM-6/P2	Limestone	60	3.5	−8.0
AM-1/P1	Limestone	70	10.1	−6.8
AM-2/P1	Limestone	80	9.8	−7.4
AM-3/P1	Limestone	90	8.3	−6.9
AM-4/P1	Limestone	100	10.0	−7.2
AM-5/P1	Limestone	110	10.1	−6.7
AM-6/P1	Limestone	120	9.9	−6.9
AM-7/P1	Limestone	130	9.4	−5.9
AM-8/P1	Stromatolitic limestone	280	10.1	−7.1
AM-9/P1	Stromatolitic limestone	290	10.5	−6.5

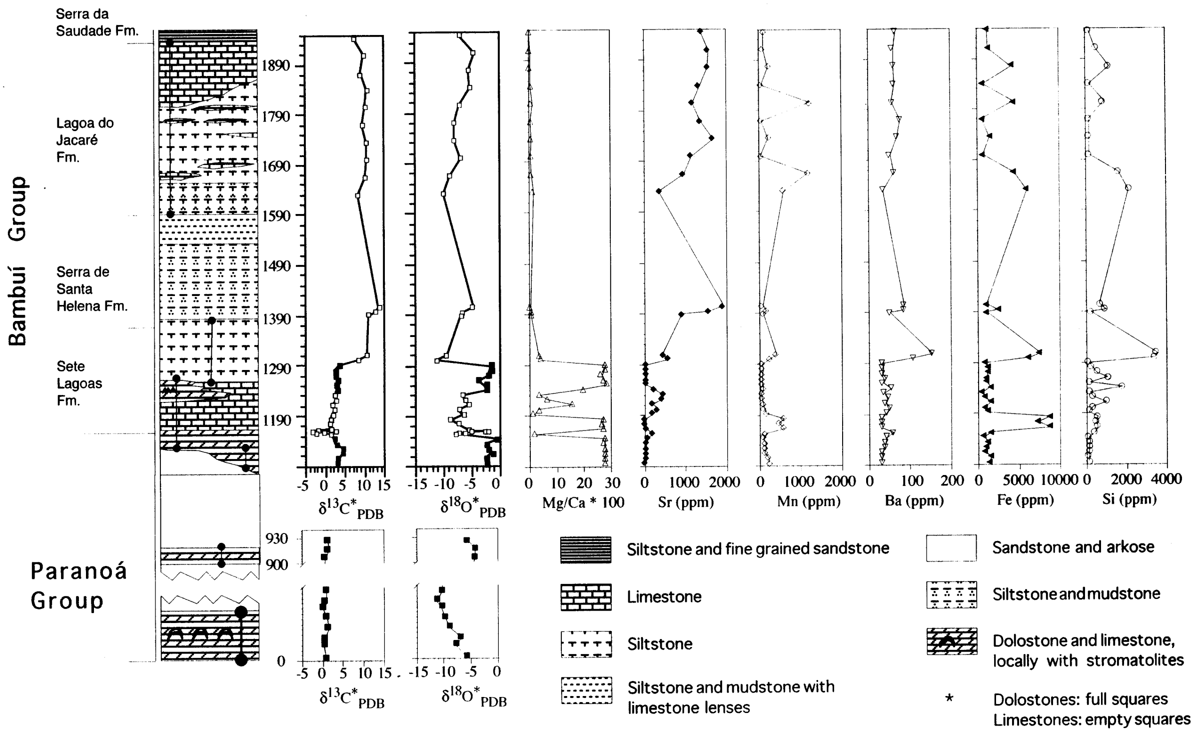

Fig. 4. $\delta^{13}C$ and $\delta^{18}O$ values of limestone along the stratigraphic column of the Bambuí group in the SSD, Minas Gerais state.

steep rise to + 12‰ in the Lagoa do Jacaré Fm. The $\delta^{18}O_{PDB}$ values range between − 11.3 and − 1.5‰, depending on the proportion of carbonate to clastic constituents, and on the mineralogy of the dominant carbonate, with dolomite having higher values than calcite.

The positive $\delta^{13}C_{PDB}$ excursion also marks important changes in mineralogical composition, from dolostones to limestones. As a result, Mg–Ca ratio decreases while Sr and Ba concentrations increase. One also observes large fluctuations in Fe, Mn and Si related to the proportion of carbonate to clastic constituents. The exception is the high Fe values observed at the base of the Bambuí sequence (cap carbonate) that is not accompanied by high Si content.

The profiles from SD (Fig. 5) and SLA (Fig. 6) regions also reveal similar positive $\delta^{13}C_{PDB}$ excursion as observed in SSD. While in SD the $\delta^{13}C_{PDB}$ values shift from − 2.6 to + 12.8‰, in SLA the $\delta^{13}C$ values shift from + 3.1 to + 10.5‰. A $\delta^{18}O_{PDB}$ versus $\delta^{13}C_{PDB}$ plot of all samples of this study shows a wide range of $\delta^{18}O_{PDB}$ values, but only two well defined groups of samples in terms of $\delta^{13}C_{PDB}$ (Fig. 7).

5. Discussion

The isotopic profiles presented here reveal a regional positive $\delta^{13}C_{PDB}$ excursion at the top of the Sete Lagoas Fm. of the Bambuí group. This carbon isotope excursion occurs in all three regions that we have studied and has also been reported in the southeastern part of the basin (Chang et al., 1993; Iyer et al., 1995), indicating that it represents a regional stratigraphic marker for the Bambuí basin. This observation is significant, considering the lack of fossil record and other stratigraphic markers in Neoproterozoic sedimentary sequences. Positive carbon isotope excursions have also been reported in other Neoproterozoic sequences, including South America (Chang et al., 1993; Iyer et al., 1995; Santos et al., 1997), Africa (Kaufman et al., 1991; Saylor et al., 1995; Hoffman et al., 1998), Greenland (Knoll et al., 1986), Siberia (Magaritz et al., 1986), North America (Wickham and Peters, 1992) and China/Mongolia (Lambert et al., 1987; Brasier et al., 1996). In most instances, these $\delta^{13}C_{PDB}$ excursions may be mapped over large areas implying that we are dealing with an oceanographic process that has affected the carbon reservoir at a basinal or a global scale. Examples of such processes include an enhanced burial rate of organic materials that affects the balance between organic and inorganic carbon reservoirs (Scholle and Arthur, 1980; Knoll et al., 1986) or an enrichment of ^{13}C in dissolved carbonate species due to preferential fixation of ^{12}C during photosynthesis in stagnant environments (Schidlowski et al., 1976). Local sedimentological and diagenetic processes may also produce carbonates with high $\delta^{13}C_{PDB}$, as exemplified by environments with strong evaporitic conditions (Stiller et al., 1985; Mees et al., 1998), with methane production related to fermentative processes (Irvin et al., 1977; Whithicar et al., 1986) and direct CO_2 reduction (Whithicar et al., 1986), or having high scales of sulphates reduction accompanied by production of sulphides under anaerobic conditions (Presley and Kaplan, 1968; Nissenbaum et al., 1972; Claypool and Kaplan, 1974; Pierre, 1989). Among the above processes, there is no indication in the Bambuí geologic record that strong evaporitic conditions may have prevailed during formation of these rocks. On the other hand, there is evidence that methanogenic diagenesis and reduction of sulfate may have been locally important, as implied by the occurrence of natural gas (Babinski and Takaki, 1987; Babinski et al., 1989) and local sulfide concentrations (Dardenne, 1978, 1979). Nevertheless, we believe that both methanogenic diagenesis and reduction of sulfate may have been important only at a local scale compared to the lateral extent of the high $\delta^{13}C$ values reported here. Although we have not measured the carbon isotopic composition of coexisting organic matter,

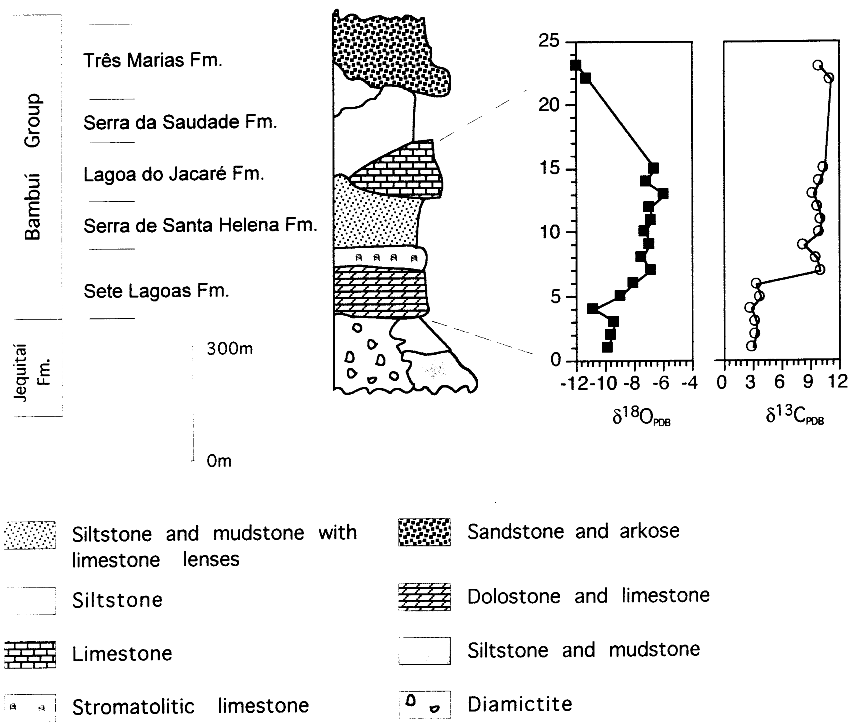

Fig. 5. $\delta^{13}C$ and $\delta^{18}O$ values of limestones along the stratigraphic column of the Bambuí group in SD, Goiás state.

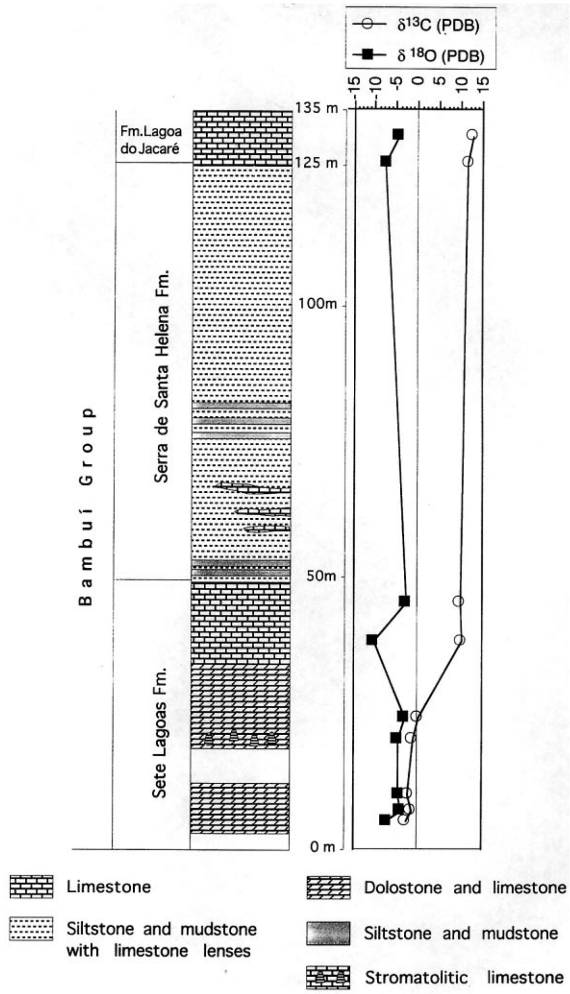

Fig. 6. $\delta^{13}C$ and $\delta^{18}O$ values of limestones along the stratigraphic column of the Bambuí group in SLA, Minas Gerais state.

Iyer et al. (1995) show that the carbon isotopic values for carbonate and organic matter from Bambuí limestones present a high level of stratigraphic co-variation, eliminating diagenesis as the main control of $\delta^{13}C$ fluctuations. Hence, these high $\delta^{13}C$ values are probably the product of large-scale phenomena, such as fluctuation in the relative proportions of inorganic and organic carbon reservoirs or preferential uptake of ^{12}C by photosyntesis due to restricted basinal conditions.

The Bambuí sediments were deposited in an epicontinental basin that, according to Castro (1997) and Guimarães (1997), was affected by thrusting and tectonic processes, which led to the closure of the western margin of the basin, as recorded by the presence of conglomerates and other clastic sediments intercalated with limestones (Fig. 3). These sediments are present within the upper part of the Sete Lagoas Formation and may have been deposited contemporaneously with the positive $\delta^{13}C_{PDB}$ excursion recorded in carbonates from other parts of the basin. Based on this hypothesis, one may argue that the carbon isotopic composition of these rocks may be related not only to the global scale fluctuations in the organic and inorganic carbon reservoirs, but also to the novel restricted marine conditions caused by tectonics. Comparing the high and low $\delta^{13}C_{PDB}$ limestones, the former are dark coloured and fetid. They presumably have higher organic content, as illustrated by the fetid and dark colored calcarenites (grainstones) from the Lagoa do Jacaré formation. Although it is not clear how a stagnant basin may produce a thick sequence of heavy ^{13}C rich limestones, Schidlowski et al. (1976) proposed that the high $\delta^{13}C$ limestones from the Precambrian Lomagundi province, Zimbabwe, were deposited in a stagnant basin. They argue that stagnant water conditions may diminish significantly the carbon exchange rate between the basin and the global CO_2–$H_2CO_3^-$ pool, and because ^{12}C is preferentially removed with the C_{org} fraction, the local carbon pool would be successively enriched in ^{13}C. This interpretation contrasts with the present knowledge of sedimentology and geochemistry of Neoproterozoic carbonate sequences, which argues for the existence of a worldwide positive $\delta^{13}C_{PDB}$ excursions, hence impact on carbon reservoir on a global scale. Recently, Melezhik et al. (1997) concluded that tectonic may have played an important role in the positive carbon isotopic excursion of Paleoproterozoic limestones from the Fennoscandian Shield. They suggest that paleogeographical changes induced by tectonics propitiated climatic and basinal conditions that allowed a high-level of biological productivity, and consequently, the depletion of surface waters in ^{12}C. We believe that the same may also be applied to explain the positive carbon excursion observed in the Bambuí limestones. Hence, besides the global fluctuation in the organic and inorganic carbon reservoirs, we believe that novel restricted marine conditions induced by tectonics were also related to the high carbon isotopic composition of rocks from the Bambuí basin. The relative impact of each of the above processes on the $\delta^{13}C_{PDB}$ values of the carbonates still needs to be evaluated and awaits further detailed studies.

Apart from the positive excursion of $\delta^{13}C$, the Bambuí carbonate sequence also contains reddish to pinkish dolomite horizons (cap carbonate) that have low $\delta^{13}C_{PDB}$ values. In other continents, such as North America (Aitken, 1991; Young, 1992), Australia (Young, 1992; Kennedy, 1996) and Africa (Kaufman et al., 1991; Germs, 1995), this horizon overlies glaciogenic units and usually displays negative $\delta^{13}C_{PDB}$ values that reach − 5‰. For instance, pinkish dolomites overlying glacial deposits in three Neoproterozoic belts of southwest Africa show low carbon isotope values (Germs and Gresse, 1991; Germs, 1995). Similar associations were detailed in Australia by Kennedy (1996), who pointed out that these post glacial carbonates are isolated within siliclastic successions and overly glaciogenic units. Pinkish dolostone and limestone also occur at the base of the Bambuí group and, as for the other Neoproterozoic basins, they usually overly glaciogenic units. In the present study these rocks were described only in SSD region and they have high concentrations of Fe and Mn and low $\delta^{13}C_{PDB}$ values (Fig. 4). Moreover, they overly karstic features, such as dissolution cavities that are filled with a carbonate-cemented sandstone. We believe that these karstic features represent the transition between the Paranoá and Bambuí groups and that they are laterally correlated with diamictites found in other parts of the basin. Low $\delta^{13}C$ pinkish dolostones and limestones were not found in SD and SLA profiles, indicating that the carbonate deposition in these areas postdated the glaciation event described in SSD.

The occurrence of glaciogenic deposits in Neoproterozoic sequences has also been used as a stratigraphic marker with well-defined ages. For instance, Germs (1995) describes glacial events recorded in Neoproteroic sequences from southwest Africa, between 745 and 590 Ma, that can be correlated with comparable successions in South

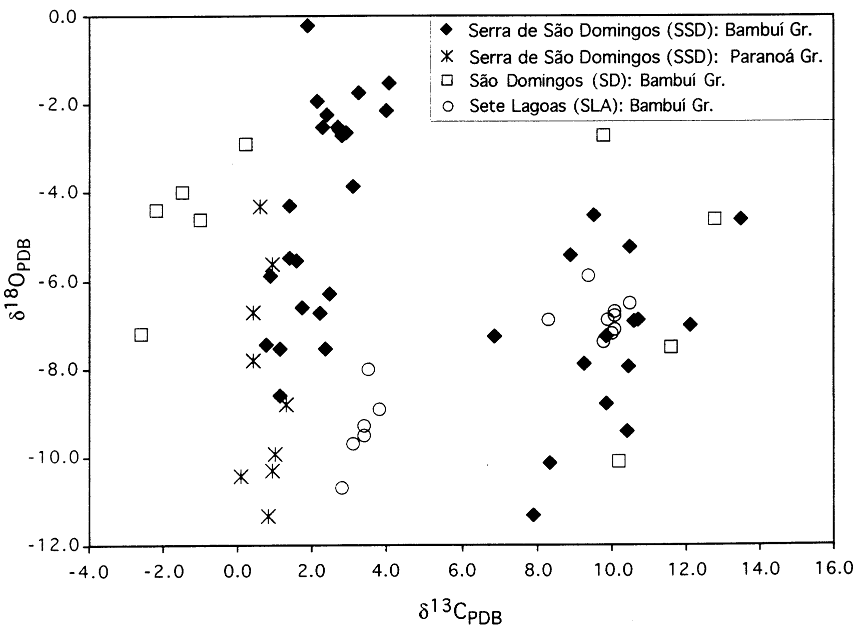

Fig. 7. $\delta^{13}C$ versus $\delta^{18}O$ plot of all studied samples showing two different ranges in terms of carbon isotopic composition.

America (Alvarenga and Trompette, 1992; Trompette, 1996). The Varangian glaciation, which precedes the appearance of Ediacaran-like fossils, as well as the low $\delta^{13}C$ pinkish limestones, have also been described from sediments in the Paraguay belt (Corumbá group), western Brazil (Boggiani et al. 1997). The $\delta^{13}C$ curve at the base of this unit resembles the one at the base of the Bambuí, where the $\delta^{13}C$ reaches $-5‰$. Nevertheless, based on microfossils (Fairchild et al. 1996) and Pb–Pb dating (Babinski et al. 1999), we suggest that the negative carbon isotope values observed at the base of the Bambuí group in the SSD region is probably related to the Sturtian glaciation.

6. Conclusions

We show that the carbon isotopic composition of limestones and dolostones from the Paranoá and Bambuí groups in central Brazil are quite different. While the values for the Paranoá carbonates do not vary much, the values for the Bambuí carbonates fluctuate by more than 10‰. These differences suggest that the sediments of these two units were deposited in different environmental conditions, as indicated also by their geological features. For instance, the Paranoá sequence comprises mainly mature siliciclastic sediments, with dominant arenites and siltites, and minor carbonates. In contrast, the Bambuí sequence consists of platformal carbonates that grade into siliciclastic immature sediments towards the top, indicating more proximal source areas. Based on the $\delta^{13}C_{PDB}$ values and on the geology of these units, we suggest that the sediments of the Paranoá group were deposited on an open platform fully connected to the ocean, while the sediments of the Bambuí group were deposited on an epicontinental sea influenced by tectonic movements and by restricted marine conditions.

Acknowledgements

We thank the Conselho Nacional de Desenvolvimentos Científico e Tecnológico (CNPq grant 523034/94-6nv) for providing financial support for field work and travel expenses. ANS and VPF would like also to thank PADCT (FADE/PADCT/FINEP 65.930.619-00) for providing financial support to the stable isotope laboratory at the University of Pernambuco (LABISE). We thank A. Kaufman and J. Veizer for constructive reviews.

References

Aitken, J.K., 1991. Two late Proterozoic glaciations, Mackenzie Mountains, northwestern Canada. Geology 19, 445–448.

de Alvarenga, C.J.S., 1978. Geologia e prospecção geoquímica dos Grupos Bambuí e Paranoá na Serra de São Domingos-MG. Master Dissertation, University to Brasília, Brazil, pp. 125.

de Alvarenga, C.J.S., Dardenne, M.A., 1978. Geologia dos grupos Bambuí e Paranoá na Serra de São Domingos, Minas Gerais. Congresso Brasileiro de Geologia, 30, Anais, Recife, Brazil, SBG, Vol. 2, pp. 546–556.

de Alvarenga, C.J.S., Santos, R.V., Cadamuro, A.L.M., Cunha Filho, E.M., 1998. Aplicação de isótopos estáveis ($\delta^{13}C$ e $\delta^{18}O$) nas correlações estratigráficas entre os grupos Paranoá e Bambuí. Congresso Brasileiro de Geologia, 40, Extended Abstracts, Belo Horizonte, Brazil, S BG, pp. 4.

de Alvarenga, C.J.S., Trompette, R., 1992. Glacial influenced sedimentation in the later Proterozoic of the Paraguay belt (Mato Grosso, Brazil). Palaeogeogr. Palaeoclimatol. Palaeoecol. 92, 85–105.

Babinski, M., Chang, H.K., Santos, R.C., 1989. Hydrocarbon occurrence in the Proterozoic São Francisco Basin, Brazil. International Geological Congress, 28, Abstract, Washington, DC.

Babinski, M., Takaki, T., 1987. Ocorrências, origem e classificação dos gases naturais na bacia Proterozóica de São Francisco. Cong. Bras. de Geoquímica, 1, Porto Alegre, Brazil, Vol. 2, 369–377.

Babinski, M., Van Schumus, W.R., Chemale, F., Jr, 1999. Pb–Pb dating and Pb isotope geochemistry of Neoproterozoic carbonate rocks from the São Francisco basin, Brazil: implications for the mobility of isotope during tectonism and metamorphism. Chem. Geol. 160, 175–199.

Boggiani P.C., Sial, A.N., Coimbra, A.M., Ferreira, V.P., 1997. The carbon and oxigen isotope record of Neoproterozoic carbonate rocks of the Paraguay fold belt (central South America). South American Symposium on Isotope Geology, 1, Extended Abstracts, Campos do Jordão, Brazil, Brazil, pp. 57–59.

Brasier, M.D., Shields, G., Kuleshov, V.N., Zhegallo, E.A., 1996. Integrated chemo- and biostratigraphic calibration of early animal evolution: Neoproterozoic-early Cambrian of southwest Mongolia. Geol. Mag. 133, 445–485.

Braun, O.P.G., 1982. Novas contribuições sobre a estratigrafia e os limetes do Grupo Bambuí. Congresso Brasileiro de Geologia, Salvador, Brazil, Vol. 1, pp. 260–268.

Castro, P.T.A., 1997. Os Conglomerados da Borda Sul da Faixa Brasília, Região Centro-Sul do Estado de Minas Gerais: Sedimentologia e Correlações Estratigráficas com as Rochas do Grupo Bambuí. Doctorate Thesis, University of Brasília, Brazil, pp. 230.

Chang, H.K., Kawashita, K., Alkmim, F.F., Moreira, M.Z., 1993. Considerações sobre a estratigrafia isótopica do Grupo Bambuí. Simpósio Sobre o Cráton do São Francisco, 2, Anais, Salvador, Brazil, pp. 195–196.

Claypool, G.E., Kaplan, I.R., 1974. The origin and distribution of methane in marine sediments. In: Kaplan, I.R. (Ed.), Natural Gases in Marine Sediments. Plenum, New York, pp. 99–139.

Cloud, P., Dardenne, M.A., 1973. Proterozoic age of the Bambuí Goup in Brazil. Geol. Soc. Am. Bull. 84, 1673–1676.

Cloud, P., Moeri, E., 1973. Conophyton in the Bambuí Group: what form and age? Geology 1, 127.

Dardenne, M.A., 1978. Síntese sobre a estratigrafia do Grupo Bambuí no Brasil Central. In: Congresso Brasileiro de Geologia, 30, Anais, Recife, Brazil, SBG, Vol. 2, pp. 597–610.

Dardenne, M.A., 1979. Les minéralisations de plomb, zinc, fluor du Protérozoique Supérieur dans le Brésil Central. Doctorate Thesis. Université de Paris VI. Paris, France.

Dardenne, M.A., Faria, A., 1985. Estratigrafia do Grupo Paranoá na Região de Alto Paraíso-GO. Simpósio de Geologia do Centro Oeste: Geologia do Precambriano, 2, Atas, Goiânia, Brazil, pp. 65–69.

Fairchild, I.J., Spiro, B., 1987. Petrological and isotopic implications of some contrasting late Precambrian carbonates, NE Spitsbergen. Sedimentology 34, 973–989.

Fairchild, T.R., Schopf, J.W., Shen-Miller, J., et al., 1996. Recent discoveries of Proterozoic microfossils in the south-central Brazil. Precam. Res. 80, 125–152.

Germs, G.J.B., 1995. The Neoproterozoic of southwestern Africa with emphasis on plataform stratigraphy and paleontology. Precam. Res. 73, 137–151.

Germs, G.J.B., Gresse, P.G., 1991. The foreland basin of the Damara and Gariep orogens in Namaqualand and southern Namibia: stratigraphic correlations and basin dynamics. S. Afr. J. Geol. 94, 159–169.

Guimarães, J.T., 1996. A Formação Bebedouro no Estado da Bahia: faciologia, estratigrafia, e ambientes de sedimentação. Unpublished Master Dissertation, IG-Federal University of Bahia, Salvador, Brazil, pp. 146.

Guimarães, E.M., 1997. Estudo de proveniências e diagênese com ênfase na caracterização dos filosilicatos dos Grupos Paranoá e Bambuí, na região de Bezerras–Cabeceiras, GO. Doctorate Thesis, University of Brasília, Brazil, pp. 270.

Hoffman, P., Kaufman, A.J., Halverson, G.P., Schrag, D.P., 1998. A Neoproterozoic snowball earth. Science 281, 1342–1346.

Irvin, H., Curtis, C., Coleman, N., 1977. Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. Nature 269, 209–213.

Iyer, S.S., Babinski, M., Krouse, H.R., Chemale, F., Jr, 1995. Highly (super 13) C-enriched carbonate and organic matter in the Neoproterozoic sediments of the Bambuí group, Brazil. Precam. Res. 73, 271–282.

Kaufman, A.J., Hayes, J.M., Knoll, A.H., Germs, G.J.B., 1991. Isotopic compositions of carbonates and organic carbon from upper Proterozoic successions in Namibia: stratigraphic variation and the effects of diagenesis and metamorphism. Precam. Res. 49, 301–327.

Karfunkel, J., Hoppe, A., 1988. Late Proterozoic glaciation in Central Eastern Brazil: syntesis and model. Paleogeogr. Palaeoclimatol. Palaeoecol. 65, 1–21.

Kaufman, A.J., Jacobsen, S.B., Knoll, A.H., 1993. The Vendian record of Sr- and C-isotopic variations in seawater: implications for tectonics and paleoclimate. Earth Planet. Sci. Lett. 120, 409–430.

Kaufman, A.J., Knoll, A.H., 1995. Neoproterozoic variations in the C-isotopic composition of seawater: stratigraphic and biogeochemical implications. Precam. Res. 73, 27–49.

Kennedy, M.J., 1996. Stratigraphy, sedimentology, and isotopic geochemistry of Australian Neoproterozoic post-glacial cap dolostones: deglaciation, $\delta^{13}C$ excursions, and carbonate precipitation. J. Sed. Res. 66, 1050–1064.

Knoll, A.H., Hayes, J.M., Kaufman, A.J., Swett, K., Lambert, I.B., 1986. Secular variation in carbon isotope ratios from upper Proterozoic successions of Svalbard and east Greenland. Nature 321, 832–838.

Lambert, I.B., Walter, M.R., Zang, W., Lu, S., Ma, G., 1987. Paleoenvironment and carbon isotope stratigraphy of upper Proterozoic carbonates of the Yangtze platform. Nature 324, 140–142.

Magaritz, M., Holser, W.T., Kirschvink, J.L., 1986. Carbon-isotope events acrros the Precambrian–Cambrian boundary on the Siberian paltform. Nature 320, 258–259.

McCrea, J.M., 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. J. Chem. Phys. 18, 849–857.

Mees, F, Reyes, E., Keppens, E., 1998. Stable isotope geochemistry of gaylussite and nacholite from the deposits of the crater Lake at Malha, northern Sudan. Chem. Geol. 146, 87–98.

Melezhik, V.A., Fallick, A.E., Makarikhin, V.V., Lyubtsov, V.V., 1997. Links between Palaeoproterozoic palaeogeography and rise and decline of stromatolites: Fennoscadian shield. Precambrian Res. 82, 311–348.

Misi, A., Kyle, J.R., 1994. Upper Proterozoic carbonate stratigraphy, diagenesis, and stromatolitic phosphorite formation, Irecê Basin, Bahia, Brazil. J. Sed. Res. A64, 299–310.

Misi, A., Veizer, J., 1998. Neoproterozoic carbonate sequence of the Una group, Irecê basin: chemostratigraphy, age and correlations. Precambrian Res. 89, 87–100.

Montes, A.S.L, Montes, M.L., Dardenne, M.A., 1981. A região da Serra de Jacobina, um paleorelevo ativo durante a sedimentação dos grupos Chapada Diamantina e Bambuí. Simpósio sobre o Craton do São Francisco, Anais, Salvador, Brazil, pp. 79–86.

Nissenbaum, A.C., Presley, B.J., Kaplan, I.R., 1972. Early diagenesis in a reducing fjord Saanich inlet, British Columbia: I. Chemical and isotopic changes in major components of interstitial water. Geochim. Cosmochim. Acta 3, 1007–1027.

Pierre, C., 1989. Sedimentation and diagenesis in restricted marine basins. In: Fritz, P., Fontes, J.C.H. (Eds.), Handbook of Environmental Isotope Geochemistry, V.3 The Marine Environment, A. Elsevier, Armsterdam, pp. 257–315.

Pimentel, M.M., Dardenne, M.A., Viana, M.G., Gioia, S.M.L., Junges, S., Seer, H.J., 1999. Nd isotopes and the provenance of sedimentsof the Neoproterozoic Brasília Belt, central Brazil: Geodimamic implications. South American Symposium on Isotope Geology, 2, Acta, Cordoba, Argentina, pp. 426–429.

Pimentel, M.M., Heaman, R.A., Fuck, R.A., Marini, O., 1991. U–Pb zircon geocronology of Precambrian tin-bearing continental-type acid magmatism in central Brazil. Precam. Res. 52, 321–335.

Presley, B.J., Kaplan, I.R., 1968. Changes in dissolveld sulfate, calcium and carbonate from iterstitial water of near shore sediments. Geochim. Cosmochim. Acta 32, 1037–1049.

Santos, R.V., Alvarenga, C.J.S., Dardenne, M.A., Sial, A.N., Ferreira, V.P., 1997. A carbon isotope stratigraphic marker in the Bambuí Group, Brazil. South-American Symposium on Isotope Geology, 1, Anais, Campos do Jordão, Brazil, pp. 283–285.

Saylor, B.Z., Grotzinger, J.P., Germs, G.H.B., 1995. Sequence stratigraphy and sedimentology of the Neoproterozoic Kuibis and Schwarzrand subgroups (Nama group), southwestern Namibia. Precam. Res. 73, 153–171.

Schidlowski, M., Eichmann, R., Junge, C.E., 1976. Carbon isotope goechemistry of the Precambrian Lomagundi carbonate province. Geochim. Cosmochim. Acta 40, 449–455.

Schobbenhaus, C., Campos, D.A., Derze, G.R., Asmus, H.E., 1981. Geologic Map of Brazil and adjoning ocean floor including mineral deposits. Scale 1: 2 500 000, Ministério das Minas e Energia, Departamento Nacional da Produção Mineral, Brasília, Brazil.

Scholle, P., Arthur, M.A., 1980. Carbon isotope fluctuations in Cretaceous pelagic limestones; potential stratigraphic and petroleum exploration tool. Bull. Am. Ass. Petrol. Geol. 64, 67–87.

Stiller, M., Rounick, J.S., Shasha, S., 1985. Extrem carbon isotope enrichment in evaporating brines. Nature 316, 434–435.

Trompette, R., 1996. Temporal relationship between cratonization and glaciation: the Vendian-early Cambrian glaciation in Western Gondwana. Palaeogeogr. Palaeoclimatol. Palaeoecol. 123, 373–383.

Uhlein, A., 1991. Transição Cráton-Faixa Dobrada: Exemplo do Cráton do São Francisco e da Faixa Araçuai (Ciclo Brasiliano) no Estado de Minas Gerais. Aspectos Estratigráficos e Estruturais. Doctorate Thesis, IG-USP, Brazil, pp. 295.

Uhlein, A., Trompette, R., Alvarenga, C.J.S.de, 1999. Neoproterozoic glacial and gravitational sedimentation on a continental rifted margin: the Jequitaí–Macaúbas sequence (Minas Gerais, Brazil). J. South Am. Earth Sci. 12, 435–451.

Veizer, J., Holser, W.T., Wilgus, C.K., 1980. Correlation of $^{13}C-^{12}C$ and $^{34}S-^{32}S$ secular variations. Geochim. Cosmochim. Acta 44, 579–587.

Wickham, S.M., Peters, M.T., 1992. Oxygen and carbon isotope profiles in metasediments from Lizzies basin; east Humbolt range; Nevada: constrains on mid-crustal metamorphic and magmatic volatile fluxes. Contrib. Mineral. Petrol. 112, 46–65.

Whithicar, M.J., Faber, E., Schoell, M., 1986. Biogenic methane formation in marine and freshwater environments: CO_2 reduction versus acetate fermentation? Isotope evidence. Geochim. Cosmochim. Acta 50, 693–709.

Young, G.M., 1992. Late Proterozoic stratigraphy and the Canada–Australia connection. Geology 20, 215–218.