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Carbon isotopes of Mesoproterozoic–Neoproterozoic sequences from Southern São Francisco craton and Araçuaí Belt, Brazil: Paleographic implications

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Abstract

This paper addresses the carbon isotope variations observed on Mesoproterozoic and Neoproterozoic carbonates from the southeastern part of the São Francisco craton and Araçuaí Belt, Brazil. Carbonates were collected across sections of the Mesoproterozoic Espinhaço Supergroup (Rio Pardo Grande Formation) and of the Neoproterozoic units of the São Francisco basin, including: (i) dolomites and marls of the Macaúbas Group (Domingas Formation); (ii) dolomite pebbles and carbonatic matrix of the diamictites of the Jequitaí Formation; (iii) limestones of the overlying Bambuí Group.

Limestones of the Espinhaço Supergroup present a flat trend of positive $\delta^{13}C_{PDB}$ values (varying between +1 and +2‰), while samples of the Macaúbas Group present an upward trend of decreasing carbon isotopic values (from +0.7 to −4.0‰). The lower $\delta^{13}C_{PDB}$ values of this latter unit were obtained on the upper part of the section. Dolostone pebbles and carbonates in the matrix of the diamictite also present negative $\delta^{13}C_{PDB}$ values (−3.1 and −0.6‰). Except for carbonatic pelites placed above the diamictites, that present $\delta^{13}C_{PDB}$ of +7.7‰, limestone samples of all the sections of the Bambuí Group have $\delta^{13}C_{PDB}$ values above +8‰.

The data presented here reveal significant differences between carbonates from the Espinhaço and Macaúbas Groups, indicating that this latter unit may be correlated with the diamictites from the Jequitaí Formation, as already suggested by previous stratigraphic studies.

The data also reveal the absence of the low positive $\delta^{13}C_{PDB}$ carbonates (below +3‰) frequently present at the base of the Bambuí Group, thus suggesting that the deposition of this unit in the Serra do Cabral and Jequitaí areas took place after the regional positive $\delta^{13}C_{PDB}$ excursion observed in other parts of the basin. Hence, it is proposed that these areas were paleo-highs during the deposition of the lower portion of the Bambuí Group sediments.

Keywords: Carbon isotopes; Neoproterozoic; Mesoproterozoic; Paleogeography; Glaciation; Brazil

Resumo

Este trabalho apresenta novos dados de isótopos de carbono e oxigênio em carbonatos do Mesoproterozóico e do Neoproterozóico do Cráton do São Francisco e da Faixa Araçuaí, Brasil. A área em estudo inclui carbonatos mesoproterozóicos do Supergrupo Espinhaço (Formação Rio Pardo Grande), e rochas carbonáticas neoproterozóicas da Bacia do São Francisco: (i) metadolomitos e metamargas do Grupo

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Macaúbas; (ii) seixos carbonáticos e matriz dos diamictitos da Formação Jequitaí; e (iii) calcários do Grupo Bambuí posicionados sobre os diamicititos da Formação Jequitaí.

Os carbonatos do Supergrupo Espinhaço apresentam valores de $\delta^{13}C_{PDB}$ positivos, variando em sua maior parte entre +1 e +2‰. Por outro lado, as amostras referentes ao Grupo Macaúbas apresentam valores de $\delta^{13}C_{PDB}$ variando entre −4.0 e +0.7‰, sendo que os valores mais negativos estão associados às rochas do topo da seção estudada. Os seixos carbonáticos do diamictito da Formação Jequitaí apresentam valores de $\delta^{13}C_{PDB}$ variando entre −2.1 e −0.6‰, enquanto a matriz possui valores mais baixos entre −3.1 e −2.1‰. Em contraste com os dados mencionados acima, os calcários do Grupo Bambuí, tanto da região de Jequitaí, quanto da Serra do Cabral, apresentam em sua maioria valores de $\delta^{13}C_{PDB}$ acima de +8‰. A exceção são pelitos carbonáticos amostrados diretamente sobre os diamictitos que apresentam valores de $\delta^{13}C_{PDB}$ próximos a +7.7‰.

Os dados obtidos revelam uma diferença significativa na composição isotópica de carbono entre as rochas carbonáticas do Supergrupo Espinhaço e do Grupo Macaúbas. A ausência de calcários do Grupo Bambuí com valores de $\delta^{13}C_{PDB}$ inferiores a +3‰, nas regiões da Serra do Cabral e Jequitaí, sugere que os carbonatos desta unidade depositaram-se após a excursão positiva de $\delta^{13}C_{PDB}$ que ocorre na parte superior da Formação Sete Lagoas. Desta forma, é possível admitir que estas regiões comportaram-se como altos topográficos durante a deposição das rochas carbonáticas da parte inferior da Formação Sete Lagoas, base do Grupo Bambuí.

Palabras chaves: Isótopos de carbono; Neoproterozóico; Mesoproterozóico; Paleogeografia; Glaciação; Brazil

1. Introduction

Proterozoic carbonates present a wide range of carbon isotopic compositions. While positive carbon isotope excursions have been described in Paleoproterozoic (Knoll et al., 1986; Baker and Fallick, 1989; Buick et al., 1998; Melezhik et al., 1999; Lindsay and Brassier, 2002) and Neoproterozoic (Iyer et al., 1995; Kaufman and Knoll, 1995; Magaritz et al., 1986; Santos et al., 2000) carbonate sequences worldwide, Mesoproterozoic carbonate sequences usually have $\delta^{13}C_{PDB}$ values similar to Phanerozoic sequences (Veizer et al., 1980; Buick et al., 1995; Kha et al., 1999). In most instances, these carbon isotope variations have been attributed to global processes, such as glaciation events or other mechanisms that disturb the inorganic and organic carbon reservoirs. Because they have been mapped over large areas, they are probably related to oceanographic processes that affected the carbon reservoir at a basinal or a global scale. Examples of processes that may affect the global carbon cycle include an enhanced burial rate of organic matter 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; Scholle and Arthur, 1980; Knoll et al., 1986; Jasper et al., 1994; Hayes et al., 1999; Rothman et al., 2003; Bartley and Kah, 2004; among others). Negative $\delta^{13}C_{PDB}$ excursions are of particular interest as they appear to be related to major glaciations. Besides recording major environmental changes of the Earth's surface, these isotope variations have also been used as chronostratigraphic tools within a given sedimentary basin or globally (Kaufman et al., 1993; Germs, 1995; Kaufman and Knoll, 1995; Melezhik et al., 1999).

Stable isotope studies on Neoproterozoic limestones from the Bambuí Group from central Brazil show a distinct reproducible positive carbon isotope excursion (Chang et al., 1993; Misi and Kyle, 1994; Iyer et al., 1995; Martins, 1999; Santos et al., 2000). Correlation of this excursion across the basin reveals features of the paleogeography of the southeastern São Francisco craton and of the northwestern Araçuaí Belt during the Neoproterozoic. This paper addresses two main points concerning carbonate sequences of southeastern Brazil: (i) the $\delta^{13}C_{PDB}$ variations in Mesoproterozoic and Neoproterozoic sequences; (ii) the paleogeography of the southeast portion of the São Francisco basin. In order to address these points, we have performed a detailed study of carbon and oxygen isotopes in carbonates from the Mesoproterozoic Espinhaço Supergroup and from the Neoproterozoic Macaúbas Group and Jequitaí Formation. We also present carbon and oxygen isotopic compositions of carbonates from the lower Bambuí Group (Sete Lagoas Formation) across three different sections. In addition, Pb isotopes were determined on carbonates from the Macaúbas and Bambuí Groups. The isotopic record of such units indicates that the central-eastern part of the basin was a paleo-high during the deposition of the basal carbonate unit of the Bambuí Group.

2. Geologic settings

The studied area is located in the southeastern part of the São Francisco craton and Araçuaí Belt, east Brazil, and includes both Paleo-Mesoproterozoic and Neoproterozoic units (Fig. 1A). Fig. 1B shows the distribution of its main lithoestratigraphic units: Espinhaço Supergroup, Macaúbas Group, Jequitaí Formation and Bambuí Group.

The Espinhaço Supergroup is a siliciclastic metasedimentary sequence that grades upwards from continental (alluvial-braidplain and aeolian) to shallow marine sediments (Martins-Neto, 2000). Age constraints on the deposition of the sequence are very poor, except for the base of the sequence, in which acid volcanics are dated at 1748±4 Ma (Babinski et al., 1994, 1999a) placing them in the late Paleoproterozoic. Carbonates in the uppermost Rio Pardo Grande Formation (Fig. 2) have been interpreted as

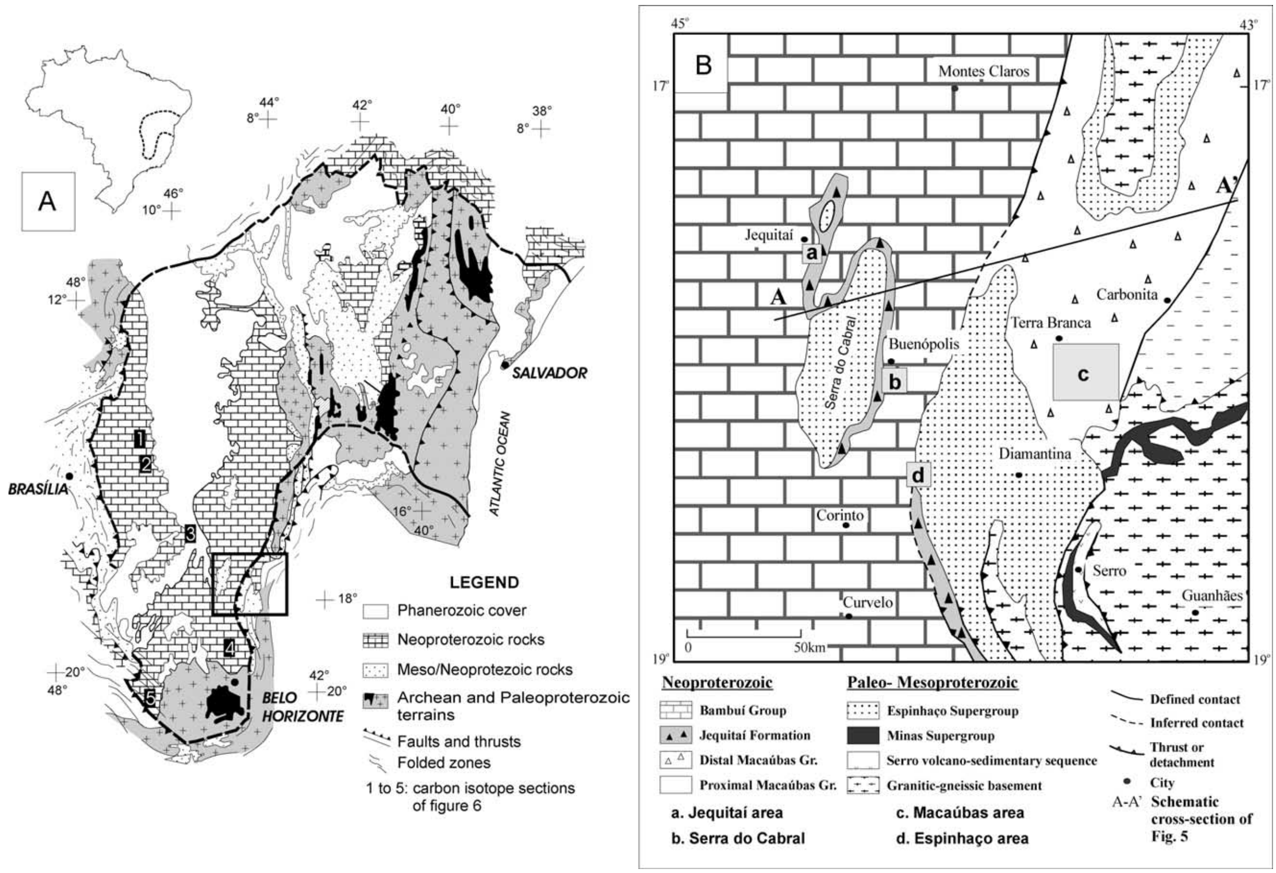

Fig. 1. (A) Geological map showing the distribution of Neoproterozoic rocks in central Brazil (from Alkmin and Marshak, 1998). Square represents area shown in B and numbers correspond to profiles of Fig. 4. (B) Map from the southeastern border of the São Francisco basin showing the areas of this study (from Uhlein, 1991). Studied areas: A, Jequitaí area; B, Serra do Cabral area; C, Macaúbas area; D, Espinhaço area.

shallow marine sequence subjected to sea level oscillations (Dossin and Dossin, 1984; Garcia, 1987; Dupont, 1995). This unit consists of metasiltstones, phyllites, and laminated metamarls, at the base, and fine-grained quartzites intercalated with stromatolitic dolostones, phyllites and metamudstones, at the top. The depositional age of these sediments has not been determined. However, stromatolitic carbonates from the Caboclo Formation that could be correlated to those of the Rio Pardo Grande Formation, were dated at 1.14 ± 0.14 Ga, and it was interpreted as their minimum depositional age (Babinski et al., 1993).

The Macaúbas Group crops out at the western margin of the Araçuaí Belt and overlies stratigraphically metasediments of the Espinhaço Supergroup (Fig. 2). The contact between these two units has been described either as an angular unconformity (Karfunkel and Karfunkel, 1976; Hettich, 1977; Fogaça, 1997) or as an erosive disconformity (Martins-Neto et al., 1997, 2001). The Macaúbas Group presents significant lateral lithofaciologic variations and a stratigraphic position that is still not well defined (Noce et al., 1997; Uhlein et al., 1999). Some authors have correlated it to the Jequitaí Formation (Pflug, 1973; Karfunkel and Karfunkel, 1976; Hettich, 1977; Dardenne et al., 1978; Karfunkel et al., 1984), while others (Uhlein, 1991; Uhlein et al., 1999) argue that it corresponds to the distal facies of the glacial diamictites of the Jequitaí Formation. Carbonates in the Macaúbas Group are placed in the Domingas and Chapada do Acauã formations (Noce et al., 1997). Rocks from the Domingas Formation, which were analyzed in this study, consist of stromatolitic metadolomites and metapelites deposited in a shallow marine environment and are placed stratigraphically below the Jequitaí diamictites (Ramos, 2000).

The glacial diamictites (<100 m thick) of the Jequitaí Formation are overlain by rocks of the Bambuí Group (Fig. 2). They are mainly matrix-supported conglomerates in which the dark-gray and mud-rich matrix presents decimetric siltstone and sandstone lenses. The matrix may also contain sand-size grains and diagenetic carbonate cement (Cukrov, 1999). The clasts of the diamictite include quartz, quartzite, granite, limestone, dolostone and siltstone. Detrital zircon ages recovered from the diamictites give a maximum age of ca. 900 Ma for these rocks (Buchwaldt et al., 1999; Pedrosa-Soares et al., 2000; Pimentel et al., 2002). Based on stratigraphic correlations, these rocks have been related to the Sturtian glacial event (Iyer et al., 1995; Santos et al., 2000; Babinski and Kaufman, 2003; Alvarenga et al., 2004).

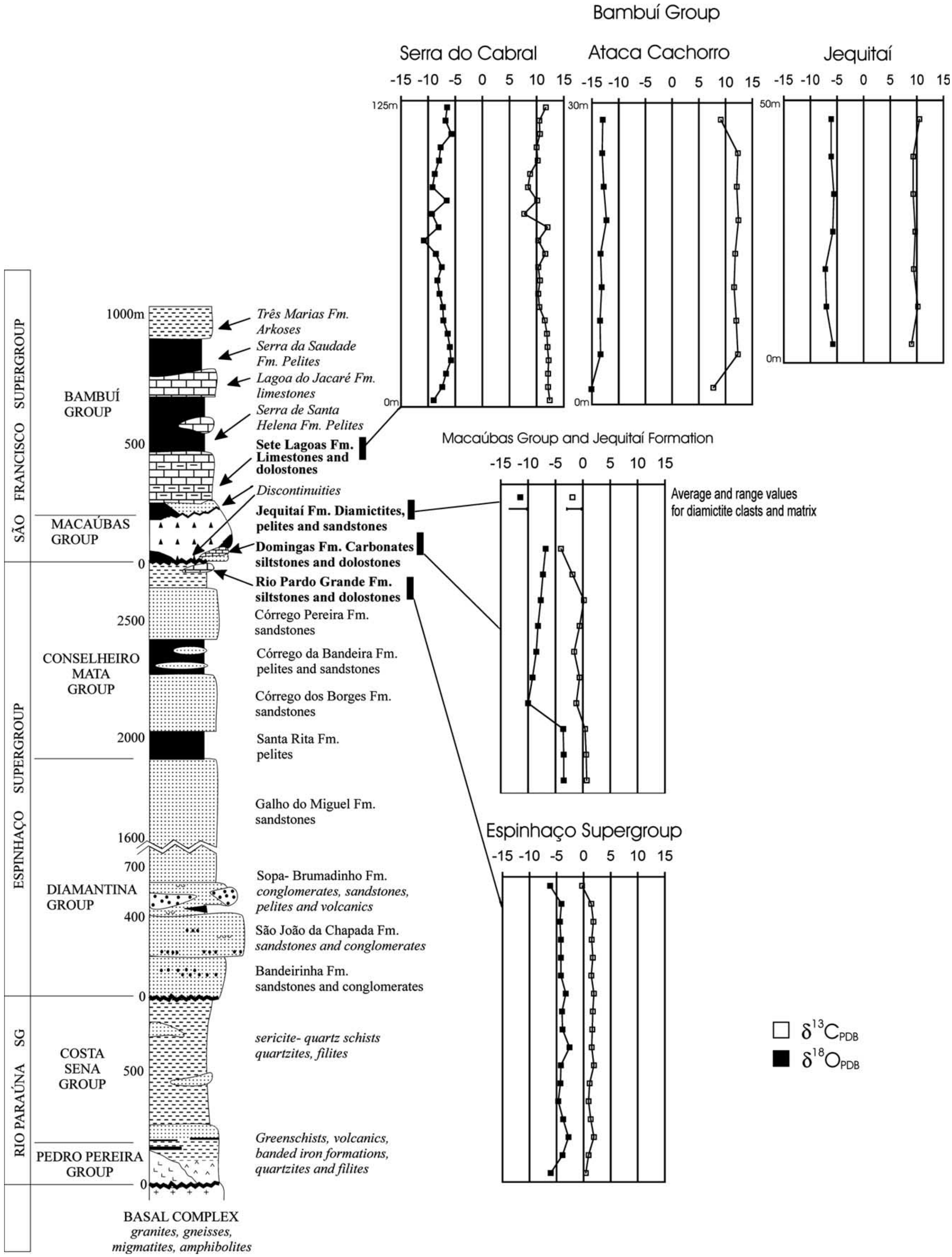

Fig. 2. Carbon and oxygen isotopes variation of carbonates of the Espinhaço Supergroup, Macaúbas Group and Bambuí Group plotted across the stratigraphic section [adapted from Martins-Neto (1998)].

The Bambuí Group is a sedimentary sequence dominated by dolostones and limestones at the base, and siliciclastic rocks at the top (Dardenne, 1978). The lower carbonates overly a variety of rock types regionally, indicating significant depositional hiatus. For instance, in the central part of the basin rocks of the Bambuí Group occur over Archean/Paleoproterozoic gneissic and granitic rocks of the basement, over metasediments of the Paranoá Group and Espinhaço Supergroup (towards the west), and over the diamictites of the Jequitaí Formation. In the present study, carbonates from the Bambuí Group outcrop over laminated marls and diamictites of the Jequitaí Formation, in the Jequitaí area, and over quartzites and rhytmites of the Espinhaço Supergroup in the Serra do Cabral area (Fig. 2). The cap carbonates of the Bambuí Group, collected at the southern part of the basin, have been dated at 740±22 Ma (Babinski and Kaufman, 2003), indicating that these rocks were deposited after the Sturtian Glaciation.

3. Analytical procedures

Carbon and oxygen isotope ratios were obtained on a SIRA II triple collector, dual inlet, VG Isotech mass spectrometer at the University of Pernambuco, and on a Finnigan Delta E mass spectrometer at the University of Brasília after powdered carbonate samples were reacted individually 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 $\delta^{18}O_{PDB}$ was corrected for calcite and dolomite by applying, respectively, the fractionation factors $\alpha_{CO_2\text{–}H_2O}$ 1.01025 and 1.01111. The standard error of the isotope measurements was 0.2‰ during the period of analyses.

Lead isotope analyses were carried out at the Geochronological Research Center of the University of São Paulo, following the analytical procedures described in Babinski et al. (1999b). The carbonates were first crushed into small (ca. 0.1–0.2 cm) pieces, washed with distilled H_2O, and dried. Approximately 500 mg aliquot of sample chips were weighed into a teflon Savillex® beaker. The first leach (L1) was performed with 2 ml of 0.7 N HBr. This L1 was discarded and residual chips were transferred to a Savillex® beaker, washed with H_2O, and dried. For the second leach (L2), 10 ml of 0.7 N HBr was added to the L1 residue and reacted overnight to achieve complete reaction. The solution and residue were transferred to a test tube and centrifuged. The supernate was dried and 0.7 N HBr was added to the residue. Pb was extracted using standard ion exchange techniques, with AG-1X8, 200–400 mesh, anion resin, in HCl–HBr media.

Samples were loaded with silica gel and H_3PO_4 onto Re filaments and the isotopic compositions were determined on a VG 354 multicollector mass spectrometer. Pb isotopic compositions were corrected for a mass fractionation factor of 0.12% amu^{-1} based on analyses of Common Pb Standard NBS 981 performed during and prior to this work. Total Pb blanks were 30–50 pg and have negligible effect on the Pb measured isotopic compositions. Regressions were done using the Isoplot software (Ludwig, 1999).

4. Sample description and results

Carbonate samples of this study were collected from four different stratigraphic units, as shown in Fig. 2: (i) Rio Pardo Grande Formation of the Espinhaço Supergroup; (ii) Domingas Formation of the Macaúbas Group; (iii) Jequitaí Formation; (iv) Bambuí Group.

4.1. Carbon and oxygen isotopes

Samples from the Espinhaço Supergroup area were collected along the boundary between the São Francisco Craton and the Araçuaí Belt, along the road between the villages of Conselheiro Mata and Rodeador, where metapelites and metadolostones of the Rio Pardo Grande Formation are thrusted over marbles of the Bambuí Group (Fig. 1B). Seventeen samples (E11–E48) were collected across a section in which laminated gray metadolostones intercalated with reddish metapelites grade upwards to laminated metadolostones and massive stromatolitic metadolostones (Table 1). In the upper part of the section, these metadolostones are tectonically folded and brecciated. Fig. 2 shows that most samples from the Rio Pardo Grande Formation present a narrow range of carbon (between −0.3 and +1.9‰) and oxygen (between −4.7 and −2.6‰) isotopic values, thus indicating a flat isotopic pattern across the section. Samples E11 and E48 are silicified limestones and present carbon and oxygen isotopic values slightly lower than those above, and probably do not correspond to primary values.

Samples from the Macaúbas Group were collected in the Araçuaí Fold Belt, near the margin of the Jequitinhonha River and consist of deformed carbonatic rocks metamorphosed at the greenschist facies. The sampling was performed across two different stratigraphic intervals of the Domingas Formation (Table 2). The lower interval (M50-a, M50-b and M50-c; Table 2) is an impure gray stromatolitic metadolostone containing quartz and mica grains, and the upper interval (M52-a to M53-d; Table 2) is a metamarlstone with metadolostone lenses. The isotopic data presented in Fig. 2 show a trend of decreasing carbon isotopic values across the section. While the $\delta^{13}C_{PDB}$ values of the lower dolostones range between +0.7 and +0.4‰, the $\delta^{13}C_{PDB}$ values of the marlstone range between −4.0 and +0.2‰ (Table 2). The oxygen isotopic composition of the dolostones (−3.5 to +3.6‰) and the marlstones (−6.8 and −10.0‰) also varied significantly.

The diamictites from the Jequitaí Formation were sampled near the town of Jequitaí, Minas Gerais State. The samples of this unit include five limestone clasts more than 30 cm long and four samples of carbonate-bearing

Table 1
Carbon and oxygen isotopes values of the Espinhaço Supergroup carbonatic samples

Sample	Unit	Description	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O_{PDB}$ (‰)
E11	Espinhaço Sgr.	Laminated and silicified dolomitic marble with stylolites	+0.4	−6.1
E12	Espinhaço Sgr.	Recrystallized dolomitic marble	+0.9	−3.9
E14	Espinhaço Sgr.	Dolomitic marble with prismatic dolomitic crystals that fill secondary posorosity. Presence of stylolites	+1.9	−2.8
E16	Espinhaço Sgr.	Stromatolitic dolomitic marble	+1.3	−3.8
E18	Espinhaço Sgr.	Recrystallyzed dolomitic marble presenting isolated calcite crystals filling the porosity	+0.9	−4.7
E19	Espinhaço Sgr.	Recrystallyzed dolomitic marble	+1.1	−4.3
E21	Espinhaço Sgr.	Stromatolitic dolomitic marble with stilolites	+1.9	−4.2
E26	Espinhaço Sgr.	Recrystallized dolomitic marble	+1.5	−2.6
E27	Espinhaço Sgr.	Recrystallized dolomitic marble. Presence of prismatic dolomite crystal filling voids	+1.6	−3.9
E30	Espinhaço Sgr.	Recrystallized dolomitic marble presenting microspatic and prismatic dolomite crystals	+1.7	−4.0
E31	Espinhaço Sgr.	Recrystallized dolomitic marble presenting microspatic and prismatic dolomite crystals	+1.9	−3.3
E37	Espinhaço Sgr.	Massive dolomitic marble	+1.4	−4.2
E38	Espinhaço Sgr.	Massive dolomitic marble with stylolites	+1.7	−4.2
E42	Espinhaço Sgr.	Recrystallized and laminated dolomitic marble	+1.5	−4.2
E43	Espinhaço Sgr.	Recrystallized dolomitic marble	+1.8	−4.4
E45	Espinhaço Sgr.	Laminated dolomitic marble with stylolites	1.4	−4.1
E48	Espinhaço Sgr.	Deformed and silicified dolomitic marble with calcite crystals filling voids	−0.3	−6.2

matrix (J2–J24 c3; Table 2). Because of the grain size, limestone fragments below 2 mm and the carbonate-bearing matrix cement were sampled together. While the five limestone clasts present $\delta^{13}C_{PDB}$ values ranging between −0.6 and −2.1‰, and $\delta^{18}O_{PDB}$ values ranging between −11.0 and −12.9‰, the four samples of the matrix presented lower $\delta^{13}C_{PDB}$ values ranging between −2.1 and −3.1‰, and $\delta^{18}O_{PDB}$ values ranging between −9.8 and −11.8‰.

Carbonates of the Sete Lagoas Formation (lower portion of the Bambuí Group) were sampled across three different sections: Ataca Cachorro creek, Jequitaí town and Serra do Cabral. They overlie marlstone and carbonate-rich diamictites, as in the Ataca Cachorro creek and Jequitaí Town section, and quartzites and metapelitic rocks, as in the Serra do Cabral section (Fig. 2). The limestones show only minor deformation and are usually fetid and silicified.

Table 2
Carbon and oxygen isotopes values of the Macaúbas Group and Jequitaí formation samples

Sample	Unit	Description	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O_{PDB}$ (‰)
M50-a	Macaúbas Gr.	Stromatolitic and recrystallized dolomitic marble with stylolites	+0.7	−3.5
M50-b	Macaúbas Gr.	Stromatolitic dolomitic marble with calcite filling voids	+0.6	−3.5
M50-c	Macaúbas Gr.	Stromatolitic dolomitic marble with stylolites	+0.4	−3.6
M52-a	Macaúbas Gr.	Pelitic bearing dolomitic marlstone presenting local concentration of quartz and mica	−4.0	−6.8
M52-b	Macaúbas Gr.	Marlstone with isolated dolomite crystals	−1.9	−7.3
M52-c	Macaúbas Gr.	Calcitic marlstone	−0.6	−8.2
M53-a	Macaúbas Gr.	Banded dolomitic limestone	−1.2	−10.0
M53-b	Macaúbas Gr.	Banded dolomitic limestone	−1.6	−8.5
M53-c	Macaúbas Gr.	Massive limestone	−0.6	−9.2
M53-d	Macaúbas Gr.	Banded dolomitic limestone	+0.2	−7.7
J 2	Jequitaí Fm.	Matrix of the diamictite	−3.1	−11.8
J 3	Jequitaí Fm.	Matrix of the diamictite	−2.1	−9.8
J 4	Jequitaí Fm.	Matrix of the diamictite	−2.2	−10.6
J 5	Jequitaí Fm.	Matrix of the diamictite	−2.6	−10.8
J 24	Jequitaí Fm.	Dolostone clast of the diamictite	−2.1	−11.8
J 24 cg	Jequitaí Fm.	Dolostone clast of the diamictite	−1.8	−12.6
J 24 c1	Jequitaí Fm.	Dolostone clast of the diamictite	−1.9	−12.9
J24 c2	Jequitaí Fm.	Dolostone clast of the diamictite	−0.6	−11.7
J24 c3	Jequitaí Fm.	Dolostone clast of the diamictite	−0.6	−11.0

Table 3
Carbon and oxygen isotopes values of the Bambuí Group limestone samples

Sample	Unit	Description	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O_{PDB}$ (‰)
B 1	Bambuí Gr.	Microcrystalline limestone	+10.5	−6.1
B 2	Bambuí Gr.	Microcrystalline limestone	+9.3	−6.1
B 3	Bambuí Gr.	Microcrystalline limestone	+9.3	−5.6
B 4	Bambuí Gr.	Microcrystalline limestone	+9.7	−5.8
B 5	Bambuí Gr.	Microcrystalline limestone	+9.4	−7.2
B 6	Bambuí Gr.	Microcrystalline limestone	+10.2	−7.0
B 7	Bambuí Gr.	Microcrystalline limestone	+9.0	−5.8
MG98-01A	Bambuí Gr.	Microcrystalline and silicified limestone	+12.3	−13.4
MG98-01B	Bambuí Gr.	Microcrystalline and silicified limestone	+12.0	−13.5
MG98-01D	Bambuí Gr.	Microcrystalline and silicified limestone	+11.6	−13.2
MG98-01E	Bambuí Gr.	Microcrystalline and silicified limestone	+11.8	−13.4
MG98-01F	Bambuí Gr.	Microcrystalline and silicified limestone	+12.4	−12.3
MG98-01G	Bambuí Gr.	Microcrystalline and silicified limestone	+12.1	−12.8
MG98-01H	Bambuí Gr.	Microcrystalline and silicified limestone	+12.3	−13.1
MG98-01I	Bambuí Gr.	Microcrystalline and silicified limestone	+9.1	−13.0
MG98	Bambuí Gr.	Laminated marlstone	+7.7	−15.4
BU04	Bambuí Gr.	Massive limestone	+11.7	−6.5
BU08	Bambuí Gr.	Massive limestone	+10.5	−6.8
BU09	Bambuí Gr.	Massive limestone	+10.6	−5.7
BU10	Bambuí Gr.	Massive limestone	+10.0	−7.7
BU16	Bambuí Gr.	Massive limestone	+10.2	−8.0
BU17	Bambuí Gr.	Massive limestone	+8.8	−8.8
BU18	Bambuí Gr.	Massive limestone	+8.4	−9.2
BU19	Bambuí Gr.	Massive limestone	+10.1	−6.6
BU20	Bambuí Gr.	Massive limestone	+7.7	−9.3
BU21	Bambuí Gr.	Massive limestone	+12	−8.1
BU23	Bambuí Gr.	Massive limestone	+10.3	−10.8
BU25	Bambuí Gr.	Massive limestone	+11.6	−8.6
BU26	Bambuí Gr.	Massive limestone	+10.3	−7.5
BU27	Bambuí Gr.	Massive limestone	+10.6	−8.3
BU28	Bambuí Gr.	Massive limestone	+10.3	−7.9
BU29	Bambuí Gr.	Massive limestone	+10.5	−7.3
BU30	Bambuí Gr.	Massive limestone	+11.5	−7.2
BU31	Bambuí Gr.	Massive limestone	+11.9	−6.4
BU32	Bambuí Gr.	Massive limestone	+12.0	−6.0
BU33	Bambuí Gr.	Massive limestone	+12.2	−5.8
BU34	Bambuí Gr.	Massive limestone	+12.1	−6.7
BU35	Bambuí Gr.	Massive limestone	+12.1	−7.4
BU36	Bambuí Gr.	Massive limestone	+12.4	−9.0

Across most part of the sections, the samples present a flat trend of carbon isotopic variation and high $\delta^{13}C_{PDB}$ values (up to 12.4‰, Table 3). In the Ataca Cachorro area, the boundary between the carbonates from the Bambuí Group and the diamictites from the Jequitaí Formation is marked by a 7 m thick marlstone with intercalations of siltstone and mudstone layers that present $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ values of +7.7 and −15.4‰, respectively. Two of the sections (Serra do Cabral and Jequitaí Town) present $\delta^{18}O_{PDB}$ values ranging between −10 and −5‰, whereas the Ataca Cachorro samples present much lower $\delta^{18}O_{PDB}$ values (between −15.4 and −5.6‰).

4.2. Lead isotopes

Low-grade metamorphic stromatolitic carbonates of the lower interval of the Macaúbas Group were also collected for Pb isotope study in order to get information on the depositional time of these rocks. Twenty samples (M1–M20) were collected on a 10 m high section. Eleven of them were analyzed and their Pb isotopic compositions are slightly radiogenic and do not present much variation (Table 4; Fig. 3), with $^{206}Pb/^{204}Pb$ ratios ranging from 19.1 to 20.8, $^{207}Pb/^{204}Pb$ from 15.86 to 16.03, and $^{208}Pb/^{204}Pb$ from 38.6 to 41.2. On the Pb diagram, the ratios do not form a single linear array, precluding accurate fit to an isochron (Fig. 3). This pattern suggests that the isotopic system was disturbed during the metamorphic event that affected these rocks. However, a regression of the line defined by subset of data indicates an apparent age of ca. 2.5 Ga (Fig. 3), which suggests that Pb from the Archean/Paleoproterozoic basement permeated the carbonates during regional post-depositional fluid flow, as already observed elsewhere in the São Francisco basin (Babinski et al., 1999b; D'Agrella-Filho et al., 2000).

Lead isotope analyses of 10 carbonate samples at the Ataca Cachorro (MG98-1), and three samples from

Table 4
Pb isotope data of the São Francisco basin carbonates, Brazil

Sample	$^{206}Pb/^{204}Pb$	1σ	$^{207}Pb/^{204}Pb$	1σ	$^{208}Pb/^{204}Pb$	1σ
Grupo Bambuí—Ataca Cachorro Creek						
MG98-1A	18.947	0.028	15.756	0.033	38.578	0.033
MG98-1B	18.807	0.020	15.794	0.021	39.194	0.021
MG98-1C	18.533	0.015	15.686	0.016	38.530	0.018
MG98-1D	18.754	0.007	15.797	0.007	39.138	0.007
MG98-1E	18.429	0.005	15.725	0.007	38.756	0.007
MG98-1F	19.303	0.007	15.807	0.008	38.573	0.008
MG98-1G	19.561	0.006	15.808	0.005	39.751	0.005
MG98-1H	19.711	0.007	15.772	0.008	38.620	0.008
MG98-1I	20.208	0.005	15.829	0.006	40.137	0.006
Grupo Bambuí—Palmeira Creek						
MG98-2B	19.280	0.003	15.769	0.003	39.505	0.003
MG98-2D	19.883	0.003	15.791	0.003	39.898	0.003
MG98-2F	18.890	0.006	15.757	0.007	38.969	0.007
Grupo Macaúbas						
M-01	19.497	0.024	15.961	0.025	39.043	0.028
M-02	19.514	0.011	15.894	0.011	38.869	0.011
M-03	19.476	0.024	15.899	0.024	39.033	0.025
M-04	19.368	0.033	15.875	0.031	38.811	0.004
M-05	19.192	0.016	15.911	0.015	38.750	0.017
M-06	19.189	0.020	15.885	0.020	38.773	0.022
M-07	19.093	0.014	15.861	0.013	38.630	0.015
M-08	19.199	0.012	15.906	0.009	38.860	0.009
M-09	19.645	0.007	15.920	0.007	39.299	0.008
M-10	19.807	0.015	15.950	0.015	39.517	0.016
M-20	20.750	0.030	16.027	0.030	41.162	0.031

Isotopic compositions were corrected for a mass fractionation factor of 0.12%/amu, determined through more than 200 measurements of the Common Pb Standard NBS 981. Analytical blanks range from 30 to 50 pg.

the Palmeira (MG98-2) creeks yielded non-radiogenic to slightly radiogenic compositions with $^{206}Pb/^{204}Pb$ ratios ranging from 18.4 to 20.2, $^{207}Pb/^{204}Pb$ from 15.69 to 15.83, and $^{208}Pb/^{204}Pb$ from 38.5 to 40.1. The Pb isotopic compositions present a large spread on the Pb diagram (Fig. 3). However, if a subset of samples were defined an array with an apparent age of ca. 1.9 Ga suggests incorporation of basement derived Pb.

5. Discussion

5.1. Carbon isotopes of the carbonate rocks

The Mesoproterozoic and the Neoproterozoic are marked by differences in the $\delta^{13}C_{PDB}$ values of marine carbonates (Veizer et al., 1980; Buick et al., 1995; Kha et al., 1999). While Mesoproterozoic carbonates are known to have carbon isotope values close to 0‰, $\delta^{13}C_{PDB}$ in Neoproterozoic rocks may have values ranging from −12 to +13‰, or even more (e.g. Knoll et al., 1986; Magaritz et al., 1986; Kaufman and Knoll, 1995; Iyer et al., 1995; Buick et al., 1998; Santos et al., 2000). The low $\delta^{13}C_{PDB}$ values are associated with glaciation events, whereas the high values are usually explained in terms of a high fractional burial of the organic matter that would have enriched the residual carbon reservoirs (Knoll et al., 1986).

The isotopic data presented here also reveal significant differences between the isotopic composition of the Meso- and Neoproterozoic rocks (Fig. 2). The lower part of the stratigraphic column corresponds to the dolostones of the Mesoproterozoic Espinhaço Supergroup that are characterized by a flat pattern of $\delta^{13}C_{PDB}$ values ranging between −0.9 and +1.9‰. Above these rocks, limestones and

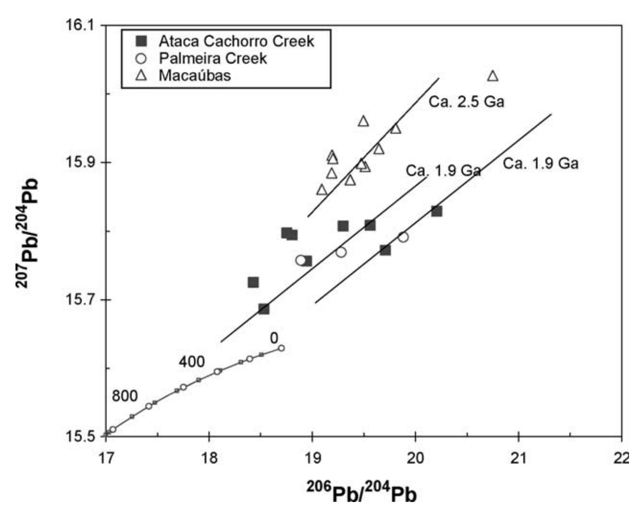

Fig. 3. Pb isotopes on carbonates from the Jequitaí area and from the lower interval of the Macaúbas Group. It also shows the lead growth curve for U–Pb system and isochron across selected data sets.

carbonatic pelites of the Neoproterozoic Macaúbas Group present $\delta^{13}C_{PDB}$ values ranging between −4.0 and +0.7‰. In addition, negative carbon isotope values are also found in the matrix (−3.1 and −2.1‰) and in limestone clasts (−2.1 and −0.6‰) of the diamictites of the Jequitaí Formation. In the upper part of the sequence, limestones of the Sete Lagoas Formation (Bambuí Group) have high $\delta^{13}C_{PDB}$ values (ranging from +7.7 to +12.4‰).

The carbon isotopic compositions of dolostones from the Espinhaço Supergroup are comparable to those found in other carbonate units of the same time interval. For instance, Santos et al. (2000) have shown that carbonates from the Paranoá Group also present a narrow range of carbon isotopic composition, with $\delta^{13}C_{PDB}$ values ranging between +0.4 and +1.3‰.

Carbonates from the Macaúbas Group present an upward trend of decreasing carbon isotopic values (from +0.2 to −4.0‰). While the samples from the lower part of the section present a narrow range of carbon isotopic composition and values similar to those found in the Espinhaço Supergroup, the samples from the upper part of the section present carbon isotopic values similar to those found in the carbonatic matrix and in the limestone clasts of the Jequitaí diamictite. Hence, it is possible that the limestone clasts and the carbonate matrix found in the diamictites were, at least in part, derived from the carbonate lenses of the Domingas Formation. Indeed, detailed carbon isotopic profiles across limestone sequences placed below Sturtian diamictites in Namibia also show an upward negative trend (Halverson et al., 2003), thus indicating that the passage from the platformal environment to the glacial environment was accompanied by a perturbation of the carbon cycle.

The limestones from the Bambuí Group are stratigraphically above the diamictites of the Jequitaí Formation (Fig. 2). The flat trends of high carbon isotopic values observed across the three sections are quite similar and indicate that the high positive $\delta^{13}C_{PDB}$ values have a significant lateral continuity. It should be emphasized that these high values are comparable also to those found in other parts of the basin, such as Sete Lagoas, Montalvânia, Serra de São Domingos and São Domingos areas (Chang et al., 1993; Iyer et al., 1995; Martins, 1999; Santos et al., 2000). In contrast to the carbon values, the $\delta^{18}O_{PDB}$ from these rocks are more variable, ranging from −15.4 to −5.7‰ (Fig. 2). The lower values were found in the Ataca Cachorro section in which the limestones are usually silicified and extensively recrystallized. We argue that these rocks, which are placed at the base of the Bambuí Group, were affected by pervasive meteoric water percolation accompanied by silica-rich fluids. However, in spite of the diagenetic effect, the carbon isotopic values were not significantly affected.

The boundary between the Bambuí carbonates and the upper Jequitaí diamictites is well preserved in the Jequitaí section. The data indicate that this boundary is also accompanied by an abrupt change in the carbonate carbon isotopic composition. The carbon isotopic values are mostly negative in the diamictites, positive in the carbonatic pelites (+7.7‰), and highly positive in the limestones (up to +12.4‰).

In contrast to the carbon isotopes, the Pb isotopic ratios determined on carbonates from two different geological units were strongly affected by post-depositional processes, which did not allow determination of the depositional age. However, apparent ages of 2.5 and 1.9 Ga obtained on samples from Macaúbas and Bambuí Groups, respectively, could suggest that fluids carrying Pb from the basement may have percolated these carbonates, as already detected in other regions of the basin (Babinski et al., 1999b; D'Agrella-Filho et al., 2000). The isotopic ratios determined on these carbonates could either represent the isotopic fingerprint of the fluid, or most probably the mixture of radiogenic crustal Pb from the basement and non-radiogenic Pb generated by low U/Pb ratio Neoproterozoic carbonates (which did not allow production of radiogenic Pb). If the latter assumption is correct, a large amount of Pb from the basement was incorporated into the carbonates from the Macaúbas Group, or the basement that underlies these carbonates is older (Archean) than the basement (Paleoproterozoic; 1.9 Ga) of the carbonates from the Ataca Cachorro and Palmeira creeks region.

5.2. Paleogeographic significance of the $\delta^{13}C$ values across the Sete Lagoas Formation

Positive carbon isotope excursion in the Neoproterozoic has been related to global perturbation of the carbon cycle that lead to major fluctuations of the organic and inorganic carbon reservoirs. These fluctuations represent global features in the sedimentary records that may be used as stratigraphic markers (Knoll et al., 1986; Magaritz et al., 1986; Baker and Fallick, 1989; Iyer et al., 1995; Kaufman and Knoll, 1995; Buick et al., 1998; Melezhik et al., 1999; Santos et al., 2000; Lindsay and Brassier, 2002). Carbonate carbon isotopic profiles from other sections of the Bambuí Group (Fig. 4), that are located at the south and north of the studied area, present a well-defined positive carbon isotope excursion in which the $\delta^{13}C_{PDB}$ may reach values as high as 16‰ (Iyer et al., 1995; Santos et al., 2000). This positive carbon excursion was also found in other parts of the basin and can be described as a regional stratigraphic marker that can be traced over more than 1000 km (Iyer et al., 1995; Martins, 1999; Santos et al., 1997, 2000).

In contrast to the areas mentioned above, the carbon isotope values across the three sections of the Bambuí Group in Serra do Cabral and Jequitaí regions indicate the absence of the low positive $\delta^{13}C_{PDB}$ carbonates that are found regionally at the base of this unit (Fig. 4). Hence, based on isotope stratigraphic correlation, we argue that these carbonates are stratigraphically above the positive carbon isotope excursion observed in other parts of the basin (e.g. Serra de São Domingos; Santos et al., 2000).

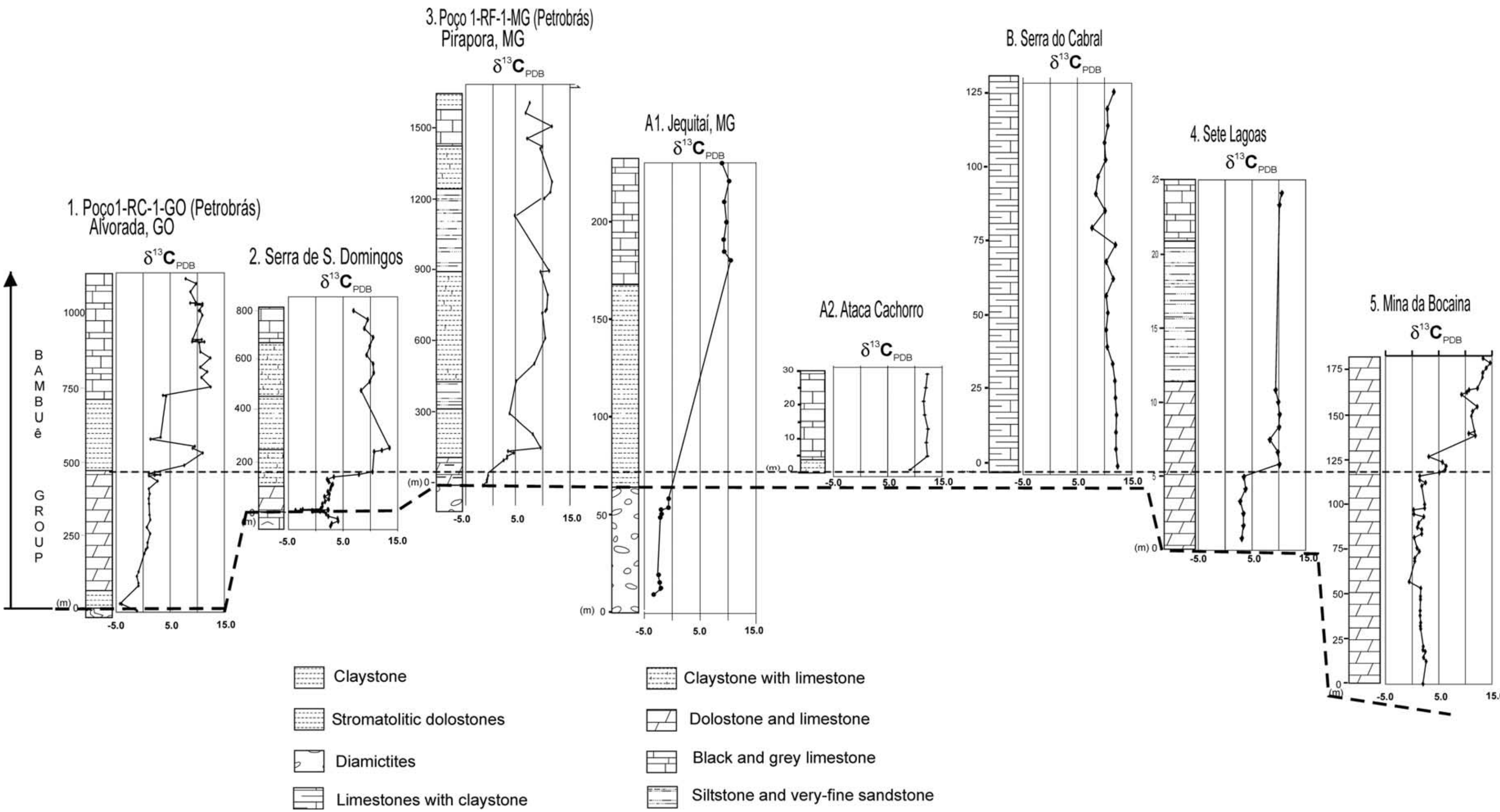

Fig. 4. Carbon isotope variations of the Bambuí Group with the representation of the positive $\delta^{13}C_{PDB}$ excursion mark. 1, Alvorada (1-RC-GO) log according to Martins (1999); 2, Serra de São Domingos log according to Santos et al. (2000); 3, Pirapora (1-RF-1-MG) log according to Chang (1997); 4, Sete Lagoas log according to Santos et al. (2000); 5, Mina da Bocaina log according to Martins (1999); A1, A2 and B this paper. Locations of the logs are shown in Fig. 1.

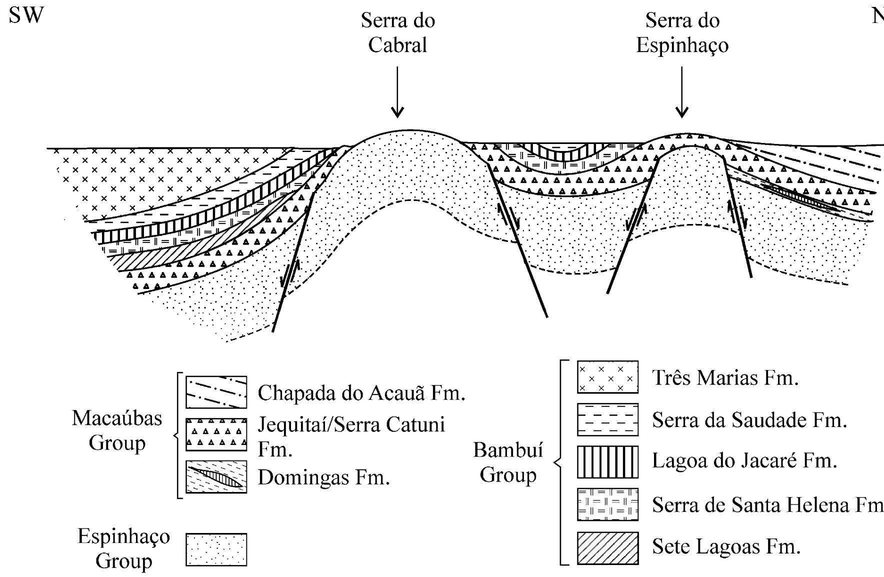

Fig. 5. Schematic paleogeographic interpretation of the Bambuí sedimentation. See Fig. 1 for location of the cross-section.

Considering that this positive carbon isotope excursion represents a basinal stratigraphic marker, the absence of the low positive $\delta^{13}C_{PDB}$ carbonates may be related either to faulting or to a gap in sedimentation. The first possibility is unlikely because there is no tectonic evidence that could account for the absence of these low positive $\delta^{13}C_{PDB}$ limestones. Hence, we argue that they were not deposited in the area of Jequitaí, thus indicating that this region was a paleo-high during the deposition of the Sete Lagoas Formation. This hypothesis is also supported by the high $\delta^{13}C_{PDB}$ values of the marlstones that overly the diamictites, indicating that the positive carbon isotope values were already present before the deposition of the carbonates of the Bambuí Group. Fig. 5 is a cartoon that shows a possible scenario during the deposition of the Sete Lagoas Formation, in which the area of Jequitaí and Serra do Cabral were a regional WNW paleo-high extending to the west of Jequitaí.

6. Conclusions

The carbon isotopic compositions of the Meso- and Neoproterozoic carbonates from the São Francisco Craton and Araçuaí Belt are significantly different. Mesoproterozoic Carbonates from the Espinhaço Supergroup have $\delta^{13}C_{PDB}$ values close to 0‰, while carbonates from the Neoproterozoic Bambuí Group present values as high as 12‰. The isotope data also suggest that the Neoproterozoic Macaúbas Group, which underlies the Bambuí Group, presents an upward trend of decreasing carbon isotopic values and that the carbonates from the upper portion of the studied section were probably reworked during the glaciation, as suggested by the negative $\delta^{13}C_{PDB}$ dolostone clast found in the diamictites.

The data presented here indicate that on a regional scale the Bambuí sedimentary sequence was deposited over an irregular substrate characterized by rocks of different ages. They also show that the southeastern portion of the São Francisco basin was a paleo-high that may have extended to the west of the Jequitaí region. This interpretation is based on the regional distribution of the positive carbon isotope excursion of the Bambuí Group carbonates.

Pb isotope compositions determined on carbonates did not show a large spread on the Pb diagram and did not form a linear array, demonstrating that the isotopic system was disturbed by post-depositional processes. Although, fluids may have disturbed the Pb isotopic system, there is no evidence that it affected the carbon isotope ratios of the carbonates.

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