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Chemostratigraphic correlation of Neoproterozoic successions in South America

Aroldo Misi [a,*], Alan J. Kaufman [b], Jàn Veizer [c,d], Kelli Powis [c], Karem Azmy [e], Paulo Cesar Boggiani [f], Claudio Gaucher [g], João Batista G. Teixeira [a], Andreia L. Sanches [a,h], Sundaram S.S. Iyer [i]

[a] *Universidade Federal da Bahia, Centro de Pesquisa em Geofísica e Geologia, Instituto de Geociências, Campus da Federação, 40170-290 Salvador-BA, Brazil*
[b] *Department of Geology, University of Maryland, College Park, MD 20742, USA*
[c] *Department of Geology, University of Ottawa, ON, Canada K1N 6N5*
[d] *Institut für Geologie, Ruhr Universitat, Bochum, Germany*
[e] *Mineralogisch-Petrographisches Institut, Universität Basel, CH-4056 Basel, Switzerland*
[f] *Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil*
[g] *Facultad de Ciencias, Departamento de Paleontologia, Iguá 4225, 11400 Montevideo, Uruguay*
[h] *Departamento de Ciências Naturais, Universidade Estadual do Sudoeste da Bahia, Brazil*
[i] *Department of Physics and Astronomy, University of Calgary, Calgary, AL, Canada*

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Abstract

The Neoproterozoic successions of South America largely accumulated during extensional events associated with the breakup of Rodinia. These units are preserved as thick carbonate and siliciclastic strata in epicontinental seaways and shallow marine environments on passive cratonal margins, which have been intensely deformed in mobile belts surrounding the craton. Volcaniclastic and siliciclastic materials are associated with some of the marginal fold belts. Three mega-sequences are represented in the cratonal area: glaciogenic, carbonate and molasse. At least two transgressive-regressive sea level cycles occurred during the evolution of the carbonate mega-sequence, which lies above iron-cemented glacio-marine diamictite of probable Sturtian age. We report high resolution carbon, oxygen, strontium and sulfur isotope trends from analyses of well-preserved sample sets and use principally strontium and carbon isotopes from the best preserved samples in concert with lithostratigraphic and biostratigraphic observations to provide detailed correlations of the South American Neoproterozoic successions. Lead–zinc deposits, some of which with important metal reserves seem to be restricted to the Sturtian carbonate succession and associated with a sequence boundary at the end of the first transgressive–regressive cycle. Phosphate deposits are found in both Sturtian and Varangerian/Marinoan carbonate successions, above glaciogenic sequences.

Keywords: Chemostratigraphy; Neoproterozoic; Correlation; South America

* Corresponding author.
E-mail address: misi@ufba.br (A. Misi).

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1. Introduction

The theory and application of temporal changes in the isotopic compositions of seawater proxies (i.e. marine carbonates and co-existing organic matter) as a tool for regional and inter-continental correlation, as well as the interpretation of stratigraphic records of environmental, climatic and biological change during Phanerozoic and Precambrian time have blossomed over the past 20 years. This is especially true for the Proterozoic sedimentary record that lacks a robust biostratigraphic framework on which to hang key events in Earth history. Appropriate interpretation of chemostratigraphic data, however, depends on the existence of multiple high-quality stratigraphic sections across depositional basins, and on detailed petrographic and geochemical investigation of alteration in these ancient marginal marine successions.

In this study we present new analyses of $^{87}Sr/^{86}Sr$, $\delta^{13}C$, $\delta^{18}O$ and $\delta^{34}S$ compositions of carbonates and sulfates, in light of previously published data in an attempt to better understand the evolution of Neoproterozoic sedimentary sequences in South America. Coupled with available age constraints, as well as the stratigraphic position of glacio-marine diamictites and fossil horizons, we comment on the geotectonic and sedimentologic evolution of these sequences, including important non-ferrous base metal deposits in Brazil (Misi et al., 1998), and broadly equivalent intervals worldwide.

2. Geotectonic setting and sequence stratigraphy

Neoproterozoic sedimentary basins in South America (Fig. 1) evolved as a consequence of extensional events during the fragmentation of the Rodinia supercontinent between 900 and 600 Ma, and the co-incident closure of the Pan-African–Brasiliano rift (Porada, 1989; Brito-Neves et al., 1999; Condie, 2002; Cordani et al., 2003). The sedimentary sequences deposited during these events are distributed in the following geotectonic settings:

A) Mixed carbonate and siliciclastic strata deposited on tectonically stable cratons, including: (1) the São Francisco Craton (Bambuí and Una groups in the São Francisco, Irecê and Una–Utinga basins, and Rio Pardo Group in the Rio Pardo Basin); (2) the Amazonas Craton and Paraguay Belt (Alto Paraguay, Corumbá, Murciélago, Itapucumi, Tucuvaca, Jacadigo, Boqui, and Araras groups and Araras and Puga Formations and (3) the Rio de la Plata Craton (Arroyo del Soldado and Sierras Bayas groups and Puncoviscana Formation).

B) Intensely deformed mixed carbonate and siliciclastic strata in basins around the stable cratons, including the Cuiabá Group (Paraguay Belt), Ibiá and Vazante groups (Brasília Fold Belt), Miaba, Canudos and Vasa Barris groups (Sergipe Fold Belt), Açungui Group (Ribeira Fold Belt), Macaúbas Group (Araçuaí Fold Belt), and Porongos Group (Dom Feliciano Belt).

C) Mixed siliciclastic and volcaniclastic sediments in basins associated with tectonically active fold belts, including the Bom Jardim, Camaquã, and Fuente del Pluma groups in the Dom Feliciano Belt.

On the stable platforms and passive margin areas large-scale stratigraphic subdivisions are represented by *Glaciogenic*, *Carbonate*, and *Molasse* mega-sequences (Fig. 2). These units are separated from each other by first-order unconformities recognized across South America, but within each of these mega-sequences there are additional parasequence boundaries that may be useful for regional correlation (Misi, 2001). Each of these is reviewed below.

2.1. Glaciogenic mega-sequences

Glaciogenic diamictite and associated lithologies are known to occur in two discrete stratigraphic positions within Neoproterozoic successions of South America, and these most-likely correspond to Sturtian and Marinoan (or Varanger) ice ages worldwide (Evans, 2000). The older Sturtian event (as defined in Australia where the iron-rich Sturt diamictites are found) is radiometrically constrained to between 804 and 650 Ma. Brasier et al. (2000) have pinned down the Sturtian glaciation in Oman to ca. 716 Ma. In Brazil the correlated Sturt equivalent goes by many different names, for example: *Bebedouro*, *Jequitaí*, *Carrancas* and *Macaubas*, in the São Francisco, Irecê and Una–Utinga basins, at the base of the Bambuí and Una Groups; *Santo Antonio do Bonito*, at the base of the Vazante Group (Dardenne, 2001); and *Panelinha* and *Salobro*, at the base of the Rio Pardo Group, and others.

The younger Marinoan (or Varanger) equivalent diamictite in South America is observed only in the context of the Paraguay Mobile Belt and Amazon Craton, where the Puga Formation is in the lowermost section of the Corumbá and Araras groups (de Alvarenga and Trompette, 1992). In South Australia, the base of the newly defined terminal Neoproterozoic Period (Ediacaran) lies immediately above the Marinoan diamictite. This ice age is constrained between ca. 640 Ma (Hoffmann et al., 2004) and the Acraman Impact (578 Ma, Grey et al., 2003).

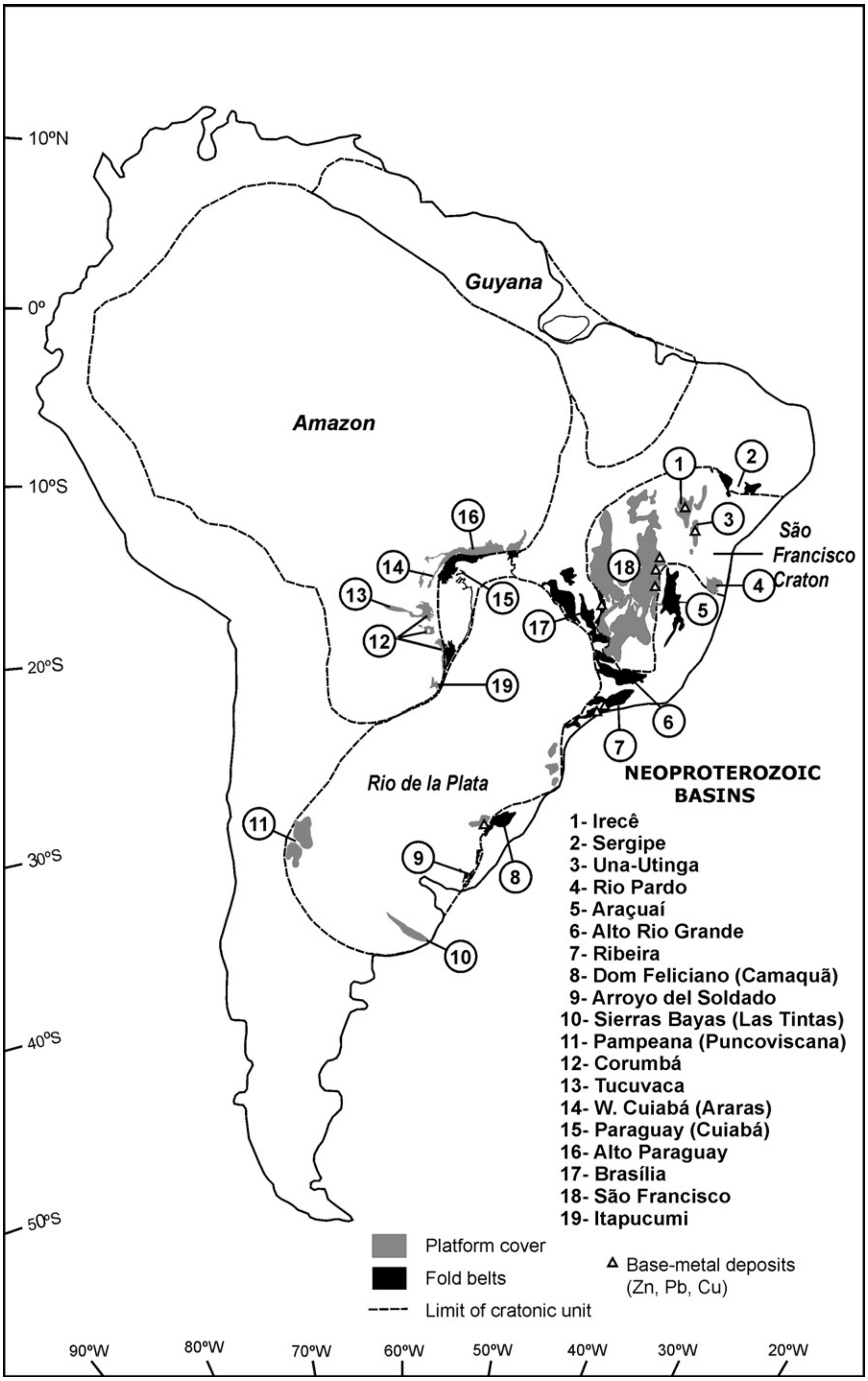


Fig. 1. The Neoproterozoic basins of South America.

2.2. Carbonate mega-sequences

Both the Sturtian and Marinoan equivalent diamictites in South America are overlain by "cap carbonates" (as defined by Kennedy, 1996; Kaufman et al., 1997; Hoffman et al., 1998a,b), as well as a thick succession of mixed shallow marine lithologies. The older of the two carbonate mega-sequences in South America occur in the São Francisco, Irecê and Una–Utinga basins (Fig. 3) and preserves two shallowing-upward sub-sequences representing two transgressive–regressive marine cycles (Dardenne, 1978; Misi, 1978). The zinc–lead deposits of the Vazante, Bambuí and Una groups are associated with this mega-unit, in carbonates above glaciogenic diamictite deposited at the end of the first transgressive–regressive cycle (Misi et al., 1998, 2005). In addition, there are also important deposits of phosphate and fluorite in these broadly correlated carbonates, which contain a variety of stromatolites, known only from Sturtian and older successions: *Conophyton metula* at the base of the Vazante Group (Cloud and Dardenne, 1973; Fig. 4A). and *Jurusania krilov*, at the Unit B1 (Una Group), in the Irecê Basin (Srivastava, 1982; Fig. 4B).

The carbonate mega-sequence above presumed Marinoan-aged diamictites occur in the Corumbá Group (Corumbá Basin), the Araras Group and the Arroyo del Soldado Group in Uruguay (Gaucher et al., 2003a). This mega-sequence evolved similarly to the older example (above) insofar as it contains two transgressive–regressive marine cycles. Phosphate is also concentrated in some carbonates of the Corumbá Basin (Boggiani, 1998, Gaucher, 2000; Gaucher et al., 2003a). These younger beds contain fossil evidence of a 550 million-year-old biota (Fig. 4c, d; Gaucher et al., 2003a).

2.3. Molasse mega-sequences

In Brazil, the older carbonate mega-sequence is interrupted and partially removed at the unconformity beneath molassic infill of the Três Marias Formation. These coarse siliciclastic sediments occur along the border of the São Francisco Craton (Thomaz-Filho et al., 1998) in Minas Gerais state (Brazil). A similar geotectonic history is ascribed to molasse of the Mulden Group, which truncates thick Otavi Group carbonates in northern Namibia (Hoffman et al., 1998a,b and references therein).

The Alto Paraguay Group overlying the younger carbonate mega-sequence in Brazil in the north Paraguay Mobile Belt, was interpreted as a molasse sequence, consisting of cross-bedded sandstone and red shale with siltstone and arkose at the top (Alvarenga et al., 2004). The correlated beds in the Nama Group of Namibia (Grotzinger et al., 1995; Saylor et al., 1998) are similarly truncated by molasse of the Fish River Group.

3. Radiometric age constraints

The scarcity of absolute geochronologic age constraints remains the most challenging problem in the reconstruction of South American Neoproterozoic Earth history. Datable volcanic horizons are generally absent (or have not yet been recognized) in these sedimentary basins, with the rare exception of those developed in tectonically active settings, like the Camaquã, Bom Jardim (Brazil) and Fuente del Puma (Uruguay) groups, in the Don Feliciano Belt. There, SHRIMP analysis of authigenic zircons from the volcano-plutonic magmatic event within the Bom Jardim Group give precise ages of 594±5 Ma, interpreted as magmatic ages (Remus et al., 2000).

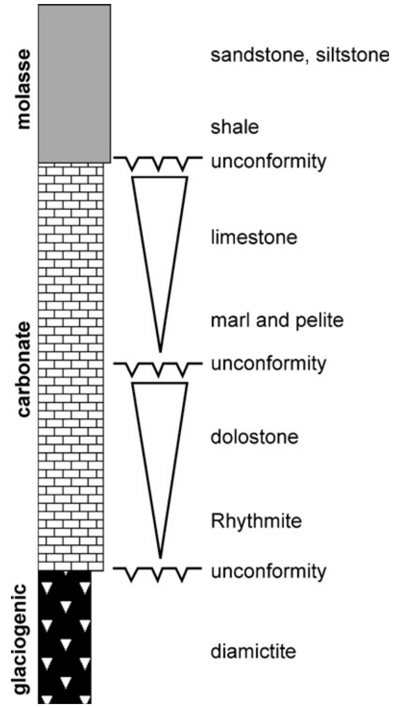


Fig. 2. Composite stratigraphic cartoon showing details of the three mega-sequences including the direction of shallowing and deepening in the two sub-cycles from the carbonate megasequence.

In the absence of volcanics, sediments have been used to provide some age control for these successions on the São Francisco Craton. For example, U–Pb SHRIMP ages on detrital zircons from the diamictite at the base of the Araçuaí fold belt provide a maximum age of this deposit of ca. 950 Ma (Pedrosa-Soares et al., 2000). Alternatively, Rb–Sr determinations on pelitic sediments intercalated with carbonates in the Paraopebas Formation (equivalent to Sete Lagoas+Serra de Santa Helena Formations of the Bambuí Group; Parenti-Couto et al., 1981) suggest ages of 640±15 Ma.. However, the extreme range of $^{87}Sr/^{86}Sr$ of associated carbonate (ca. 0.7109 and 0.7255) suggests that these are unlikely to be depositional ages. Perhaps most promising is new Pb–Pb carbonate ages from spectacularly preserved post-glacial seafloor cements in the Sete Lagoas Formation of the Bambuí Group. Analyses of these carbonates resulted in an 11-point isochron suggesting a depositional age of 740±22 Ma. (MSDW=0.66) (Babinski and Kaufman, 2003).

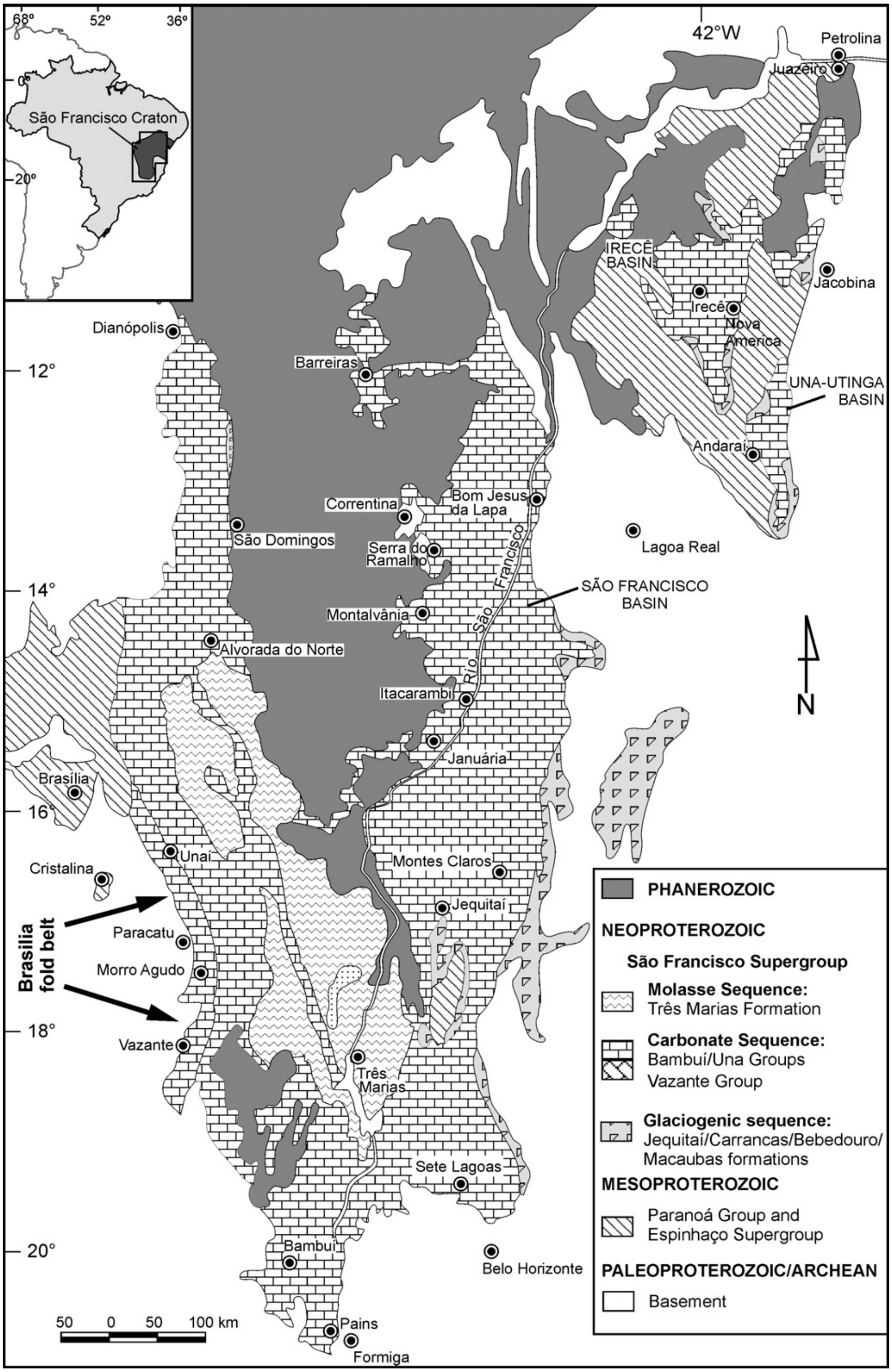


Fig. 3. Simplified geological map of the São Francisco Craton with indication of the Neoproterozoic basins studied.

4. Stratigraphy and isotope composition of the carbonate sequences

The detailed stratigraphy of the South American Neoproterozoic basins reviewed in this report are provided in several publications (e.g. Branco and Costa, 1961; de Almeida, 1965; Miranda et al., 1976; Dardenne, 1979; Misi, 1979; Misi and Kyle, 1994; Boggiani, 1998; Gaucher, 2000; Dardenne, 2001; Gaucher et al., 2003a), although some new observations are highlighted here. Published strontium and carbon isotope data from the same successions were also compiled for this report (Tables 1 and 2; see Torquato and Misi, 1977; Kiang, 1997; Kawashita, 1998; Misi and Veizer, 1998; Boggiani, 1998; Martins, 1999; Sial et al., 2000; Azmy et al., 2001; Gaucher et al., 2003a; Boggiani et al., 2003; Galindo et al., 2004, among others).

Petrographic and geochemical screens were used to evaluate the diagenetic rank of new strontium isotope analyses. Only samples retaining the lowest Mn/Sr

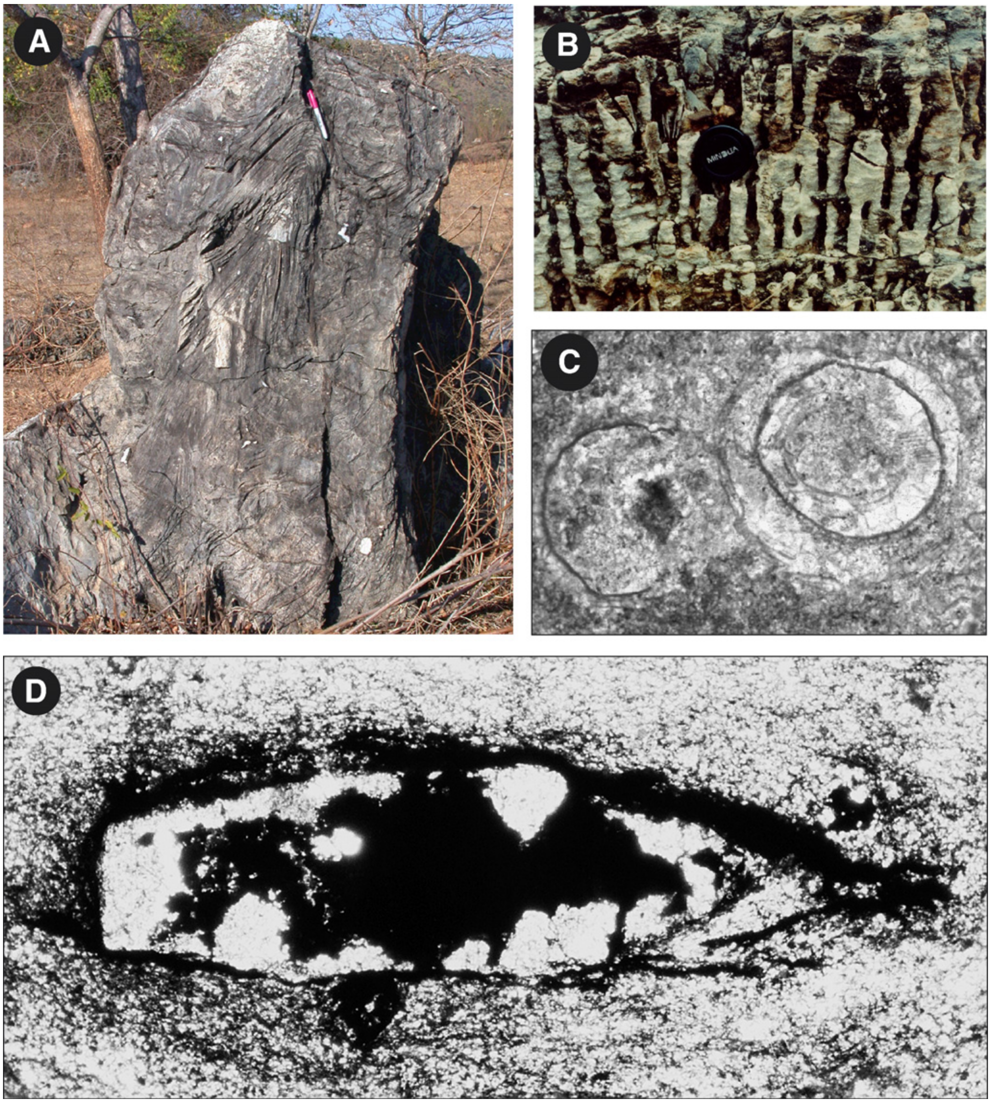


Fig. 4. A) *Conophyton metula* from dolostones of the Serra do Poço Verde Formation, Vazante Group (Cloud and Dardenne, 1973); B) Phosphate–rich columnar stromatolites classified as *Jurusania krilov* (Srivastava, 1982), from dolostone of the Unit B1 (equiv. to upper Sete Lagoas Formation, Bambuí Group), Una Group; C) *Cloudina lucianoi* from tempestites of the Tamengo Formation. Photomicrographs of thin sections, transmitted light; field of view = 1.5 mm (Gaucher et al., 2003a); D) *Cloudina riemkeae* from banded siltstones of the Yerbal Formation, Arroyo del Soldado Group; specimens are preserved hematized and filled with quartz and hematite; transmitted light photomicrograph; field of view = 4 mm (Gaucher et al., 2003a).

Table 1
Least radiogenic $^{87}Sr/^{86}Sr$ ratios from Neoproterozoic successions of South America

Sample	Description	Formation	$^{87}Sr/^{86}Sr$	Fe ppm	Sr ppm	Mn ppm	Mn/Sr	Reference
Vazante Group, Brasilia Fold Belt								
KV-60-3	Dolomite	Lapa	0.70684	ND	570	37	0.06	Azmy et al., 2001
LS1	Micritic lms.	Serra do Garrote	0.70690	ND	1469	75	0.05	Azmy et al., 2001
RO F-70	Micritic lms.	Serra do Garrote	0.70760	8500	3840	364	0.09	Misi et al., 1997
LG 2	Carbon. fluorapatite	Lagamar	0.70791	2060	1300	105	0.08	Misi et al., 1997
RO AM 12	Carbon. fluorapatite	Rocinha	0.70766	6612	6080	61	0.01	Misi et al., 1997
Bambuí Group, São Francisco Basin (Serra do Ramalho)								
CA IE-14	Calcite	Lagoa do Jacaré	0.70743	1654	3847	60	0.01	Powis et al., 2001
3.5	Calcite	Sete Lagoas 2	0.70745	199	1733	26	0.01	Powis et al., 2001
SR AM 111	Micritic lms.	Sete Lagoas 1 (lower)	0.70755	370	1590	18	0.01	Misi and Veizer, 1998
Bambuí Group, São Francisco Basin (Sete Lagoas)								
3 H	Black lms.	Lagoa do Jacaré	0.70738	ND	4050	ND	ND	Kawashita, 1998
MF 7-C	Black lms.	Sete Lagoas	0.70739	ND	2050	ND	ND	Kawashita, 1998
Una Group, Irecê Basin								
VML-8bc	Calcite	Unit A1 (Lagoa do Jacaré)	0.70746	123	1224	11	0.01	Misi and Veizer, 1998
IR-AM-11	Micritic lms.	Unit B1 (Upper Sete Lagoas)	0.70752	3013	2384	70	0.03	Misi and Veizer, 1998
VML-3	Micritic lms.	Unit B (Sete Lagoas)	0.70780	42	1717	28	0.02	Misi and Veizer, 1998
Vasa Barris Group, Sergipe Fold Belt								
MS-01 A	Black lms.	Olhos d'Agua	0.70775	ND	1830	ND	ND	Kawashita, 1998
Corumbá Group								
CD-46-M	Limestone	Tamengo	0.70852	ND	1410	ND	ND	Boggiani, 1998
Arroyo del Soldado Group								
PYE-32/I	Limestone	Lower Polanco	0.70780	ND	1380	ND	ND	Kawashita et al., 1999
Itapucumi Group								
VM-160-E	Limestone	Itapucumi	0.70813	ND	7874	ND	ND	Boggiani, 1998
Argentine Precordillera, Sierras Pampeanas								
TAL-6072	Limestone	?	0.70881	ND	1274	93	0.07	Galindo et al., 2004
Caucete Group, Sierras Pampeanas								
SPP-6081	White marble	Angaco	0.70924	ND	504	62	0.12	Galindo et al., 2004
Difunta Correa Sequence, Sierras Pampeanas								
SSP-6090	Grey marble	?	0.70731	ND	758	25	0.03	Galindo et al., 2004
Sierras Baya Group								
25701	Black lms.	Loma Negra	0.70810	ND	320	ND	ND	Kawashita, 1998

ratios (<0.2) and/or the highest Sr concentration (>300 ppm) were used for comparison with published Neoproterozoic trends — in order to make chemostratigraphic age predictions. The lowest $^{87}Sr/^{86}Sr$ values within any interval were considered to most likely reflect depositional conditions. On the other hand, all of the published and new carbon isotope data from fine-grained carbonates (including both limestone and dolomite) were used for intra-basinal correlations (Table 2: see discussion of diagenetic alteration of $\delta^{13}C$ values in marine carbonates in Corsetti and Kaufman, 2003). In addition, the $\delta^{34}S$ compositions of bedded and disseminated sulfate and carbonate associated sulfate (CAS) from the different South American successions were compared. The relative scarcity of bedded sulfates in Neoproterozoic

Table 2
$\delta^{13}C$ shifts from Neoproterozoic successions of South America

Sample	Description	Formation	$\delta^{13}C$ ‰ PDB	Reference
Vazante Group, Brasilia Fold Belt				
KV-60-1	Dolomite I	Lapa	−2.9	Azmy et al., 2001
KV-279-13	Dolomite IV	Morro do Calcário	+3.3	Azmy et al., 2001
KV-500-1X	Dolomite I	Serra do Poço Verde	−2.3	Azmy et al., 2001
KV-244-78	Dolomite IV	Serra do Poço Verde	+3.9	Azmy et al., 2001
LS 1	Micritic lms.	Serra do Garrote	−3.3	Azmy et al., 2001
Bambuí Group, São Francisco Basin (Serra do Ramalho)				
CA-1E-18	Calcite	Lagoa do Jacaré	+14.73	Powis et al., 2001
CA-1E-29	Dolomite	Sete Lagoas 3 (upper)	+10	Powis et al., 2001
3.0	Calcite	Sete Lagoas 1 (lower)	−5.64	Powis et al., 2001
Bambuí Group, São Francisco Basin (Sete Lagoas)				
BH-BM-6d	Micritic lms.	Lagoa do Jacaré	+12.34	Kaufman et al., 2001
BH-BM-1c	Micritic lms.	Sete Lagoas (upper)	+14.45	Kaufman et al., 2001
BH-BM-7b	Dolomite	Sete Lagoas (lower)	−4.38	Kaufman et al., 2001
Una Group, Irecê Basin				
VML-8cc1	Calcite	Unit A1 (Lagoa do Jacaré)	+9.4	Misi and Veizer, 1998
IR-AM-4	Micritic lms.	Unit B1 (Upper Sete Lagoas)	+7.4	Misi and Veizer, 1998
8M-01-F	Dolomite	Unit C (Lower Sete Lagoas)	−6.4	Torquato and Misi, 1977
Vasa Barris Group, Sergipe Fold Belt				
XX	Limestone	Olhos d'Agua (upper)	+10	Sial et al., 2000
XXX	Limestone	Olhos d'Agua (lower)	−4.7	Sial et al., 2000
Corumbá Group				
CO-45-G	Dolomite	Tamengo	+5.5	Boggiani et al., 2003
TMG-8	Dolomite	Tamengo (lower)	−3	Boggiani et al., 2003
PUGA 1	Dolomite	Puga Hill	−5.3	Boggiani et al., 2003
Arroyo del Soldado Group				
CLL-2A	Stromatolitic lms.	Cerro Victoria	−3.48	Gaucher et al., 2003a
CPA-35	Limestone	Cerro Espuelitas	−3.63	Gaucher et al., 2003a
PRJ-14 b2	Limestone	Polanco (upper)	+2.88	Gaucher et al., 2003a
CPA-28D	Dolomite	Polanco (middle)	−2.59	Gaucher et al., 2003a
980305/2	Dolomite	Polanco (lower)	+2.86	Gaucher et al., 2003a

successions worldwide has complicated the job of constructing temporal trends in seawater $\delta^{34}S$ compositions (Strauss, 1993, 1997), requiring a new sea water proxy to be developed. Trace sulfate in carbonate could be in some cases a faithfully record of seawater $\delta^{34}S$ compositions in Neoproterozoic (Hurtgen et al., 2002) and Phanerozoic (Kampschulte and Strauss, 2004) successions. Nevertheless, Shields et al. (2004) demonstrated that this cannot be assumed for certain samples where there is no contemporaneous evaporite or phosphorite data. What is generally known from the Neoproterozoic bedded sulfate record is that through most of the era $\delta^{34}S$ values were close to the modern (ca. +20‰ vs. VCDT) until near the Precambrian–Cambrian boundary when there was a dramatic rise to values near +30‰ and greater. New analyses of CAS in Neoproterozoic post-glacial carbonates in Namibia (Hurtgen et al., 2002), Death Valley, and Brazil reveal wide variations in both sulfate concentration and S isotope compositions, which rise to Neoproterozoic extremes (see below) in these carbonates.

4.1. São Francisco basin (Bambuí Group)

4.1.1. Stratigraphy and age constraints

The early stratigraphic subdivision established by Branco and Costa (1961) for the Bambuí Group in the Sete Lagoas area, near Belo Horizonte, is representative for the entire São Francisco Basin and for the other chrono-correlated sequences in the surrounding areas. Fig. 5 shows a typical section of the Bambuí Group along with resistivity and gamma log profiles obtained

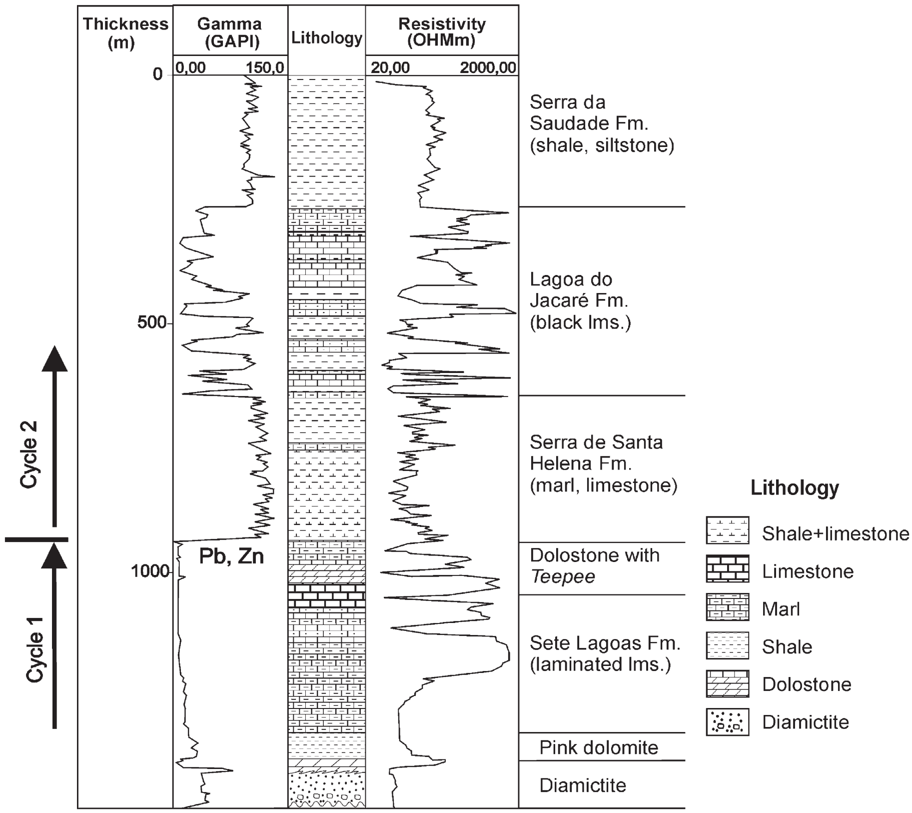


Fig. 5. Typical section of the Bambuí Group with the formal names given by Branco and Costa (1961) along with resistivity and gama log profiles performed in a stratigraphic borehole made by PETROBRAS in the central area of the São Francisco Basin. (Martins et al., 1993). The main Pb–Zn mineralization is at the uppermost section of the first cycle.

from a stratigraphic borehole made by PETROBRÁS in the central part of the São Francisco Basin. From the top to bottom, formations include:

Serra da Saudade: siltstone, pelite and intercalated limestone.

Lagoa do Jacaré: black, organic-rich calcarenite, calcilutite; cross stratified oolitic and pisolitic limestone with intercalated pelite and marl.

Serra de Santa Helena: gray marl, pelite and siltstone with black limestone.

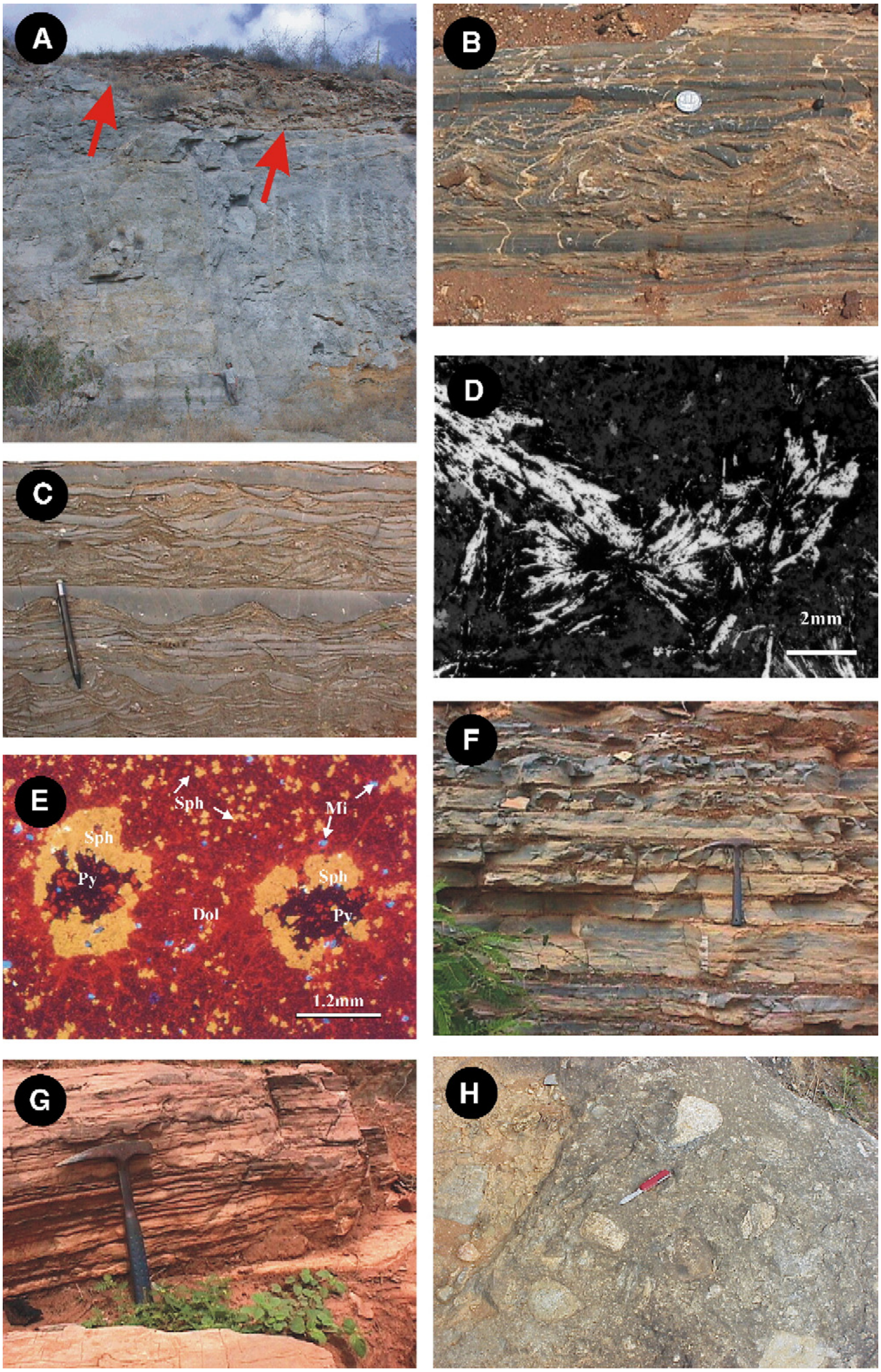
Sete Lagoas: (upper) clear gray dolarenite and dololutite with a variety of stromatolite forms and dessication-related teepee structures; (middle) laminated organic-rich limestone and shale; (lower) red, argillaceous dolomite.

These units were formed during two tectono-sedimentary cycles (Figs. 2 and 6A). The older cycle preserves a shallowing-upward succession beginning with pinkish dolostone (Fig. 6F, G) at the base of the Sete Lagoas Formation atop diamictite in the *Glaciogenic mega-sequence* (Fig. 6H), and ending in evaporitic dolomite, with teepee structures as well as calcite, quartz nodules and sulfide pseudomorphs after sulfate (Fig. 6B–E) at a major erosional surface. The second cycle preserves evidence of a second transgression over the craton with the deposition of marl and pelite of the Serra de Santa Helena Formation, initiating a new shallowing-upward section that ends with the organic-rich oolitic and pisolitic limestone of the Lagoa do Jacaré Formation.

The thickness of the carbonate sequence is variable, and is probably controlled by a basement fault system that was active during sedimentation. Seismic surveys by PETROBRAS in the central area of the basin indicated that the carbonate sediments are up to 1000 m thick (Teixeira et al., 1993). However, outcrop estimates suggest that the carbonate reaches to only 600 m in the Sete Lagoas area (Pedrosa-Soares et al., 1994) and 400 m in the Serra do Ramalho area (Misi, 1979).

4.1.2. Isotope profiles

The most detailed isotopic trends through the Bambuí succession were determined from a high-resolution sampling of core (the 400 m CA 1e BA Geological Survey of Bahia drillhole) and outcrop material in the Serra do Ramalho area (Powis et al., 2001, unpublished). The exceptionally exposed carbonate beds in this part of the basin are well preserved and flat lying. From the base of the succession, $\delta^{13}C$ compositions of Bambuí carbonates



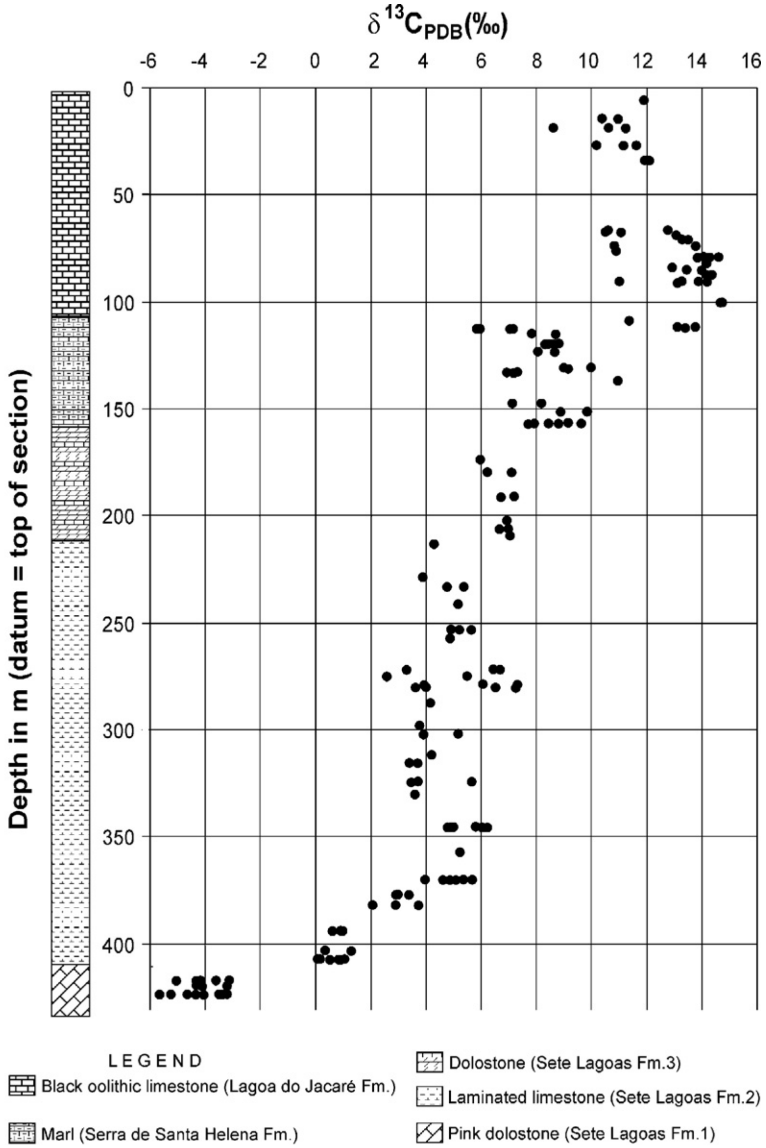


Fig. 7. $\delta^{13}C$ variation along the stratigraphic section of the Bambuí Group at Serra do Ramalho area (Powis et al., 2001, unpublished).

increase steadily upsection from a low of ca. −4.0‰ up to about +13.0‰ near the top (Fig. 7). On the other hand, the $\delta^{18}O$ values of these samples are relatively more scattered and do not exhibit a notable trend upsection, which is expected for variably dolomitized sediments. Similarly, the $^{87}Sr/^{86}Sr$ values of Sr poor dolomite samples are more

Fig. 6. Macro and microscopic features from Sturtian carbonate strata deposited on stable platform basins of the São Francisco craton, Brazil. A) Sharp contact (indicated by arrows) between carbonates of cycle 1 (dolostone, Unit B1) and cycle 2 (black marl + limestone, Unit A, above), Una Group, Irecê basin; these units are equivalent, respectively, to upper Sete Lagoas and lower Serra de Santa Helena formations of the Bambuí Group (São Francisco basin); B) surface exposure during sedimentation of microbial laminites (dolostone and limestone beds) from Unit B1 (equiv. to upper Sete Lagoas Formation, Bambuí Group), Una Group; C) Teepee structures in dolostone of the Unit B1, Una Group; D) radial bladed pyrite aggregates, pseudomorphs after sulfate (gypsum), from Unit B1, Una Group; reflected light photomicrography; E) complex sulfide nodule in dolostone (Dol) of Unit B1 (Una Group), with an inner core of pyrite (Py) surrounded by coarse-crystalline sphalerite (Sph). Sphalerite is also pore-filling crystals in dolostone; cathodoluminescence photomicrograph (Kyle and Misi, 1997) F) Laminated limestone from mid Sete Lagoas Formation (Bambuí Group), São Francisco basin. G) pink to red dolomite, Unit C (equivalent to lower Sete Lagoas Formation, Bambuí Group), Una Group (Irecê basin); h) diamictite of the Carrancas (or Jequitaí) Formation, at the base of the Bambuí Group (São Francisco basin).

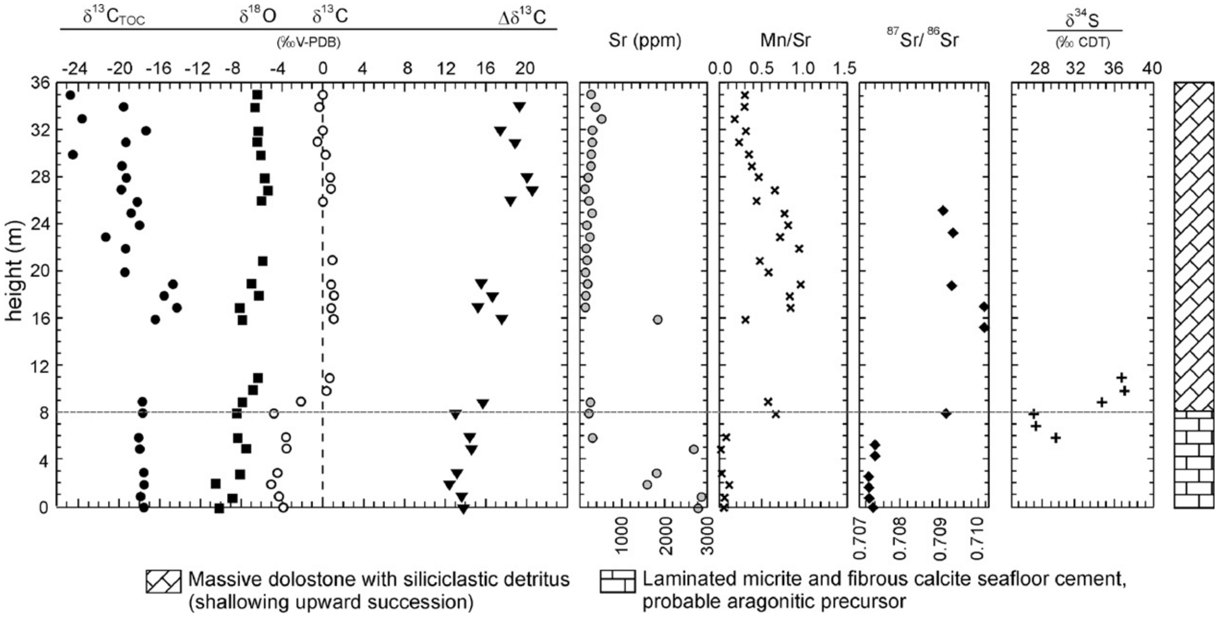


Fig. 8. Covariation of C, O, Sr and S isotopes in the Pedro Leopoldo Facies (base of Sete Lagoas Formation), Bambuí Group, Sete Lagoas, Minas Gerais) (Kaufman et al., 2001).

radiogenic than their Sr-rich limestone counterparts. The least altered limestone samples (Mn/Sr ≤ 0.02) throughout the succession have a narrow range of $^{87}Sr/^{86}Sr$ values between 0.707436 and 0.707507 (Table 1) (*cf.* Misi and Veizer, 1998); the lack of secular variation makes it likely that the Bambuí Group sediments were deposited in a relatively short time interval.

Similar stable isotope trends are recorded in equivalent Bambuí strata in the southern reaches of the São Francisco Basin (see also Torquato, 1980; Kiang et al., 1993; Kiang, 1997; Kawashita, 1998; Santos et al., 2000). For example, basal dolomite of the Sete Lagoas Formation above glaciogenic diamictite is depleted in ^{13}C (−3.9 to −4.4‰) and intercalated limestone has $^{87}Sr/^{86}Sr$ values from 0.70720 to 0.70748. Equivalent Sr isotope values are recorded in beds at the top of the formation, but these are highly enriched in ^{13}C (+12.0 to +14.5‰) (Table 2). In the overlying Serra do Santa Helena and Lagoa do Jacaré formation carbon isotope values remain remarkably high, but the Sr isotope compositions of well preserved limestone samples remain near to 0.7074 (Table 1).

A high resolution study of a post-glaciogenic carbonate in the Sete Lagoas Formation at Sambra Quarry (Kaufman et al., 2001) reveals a sharp carbon isotope shift from negative to positive $\delta^{13}C$ values across an erosional surface that ends an interval of seafloor precipitates (Fig. 8). Above this surface carbonates become more dolomitic, evaporitic, and contain higher abundances of siliciclastic detritus. Over the same interval, $\delta^{18}O$ values appear to co-vary with carbonate ^{13}C abundance; from the base of exposure to the 8-meter mark, oxygen isotope values rise from ca. −10 to −6‰, and then again remain mainly unchanged to the top of the exposure. Organic matter is anomalously enriched in ^{13}C near the base, with $\delta^{13}C$ values between. −18 and −20‰, resulting in remarkably reduced carbon isotope fractionations ($\Delta\delta$) between inorganic and organic phases ranging between 12‰ and 14‰. Concentrations of trace sulfate extracted from carbonate samples at this quarry range between 28 and ca. 900 ppm and the $\delta^{34}S$ values are strongly positive, up to +38‰ CDT. Carbonates higher in the section have generally lower sulfate concentrations, but their sulfur isotope compositions rise to as high as +47.5‰. Variable, but high Sr and low Mn abundances characterize the seafloor cements, which dominate the base of the exposure. These well-preserved limestones exhibit $^{87}Sr/^{86}Sr$ values of ~0.7074, similar to the whole of the Bambuí Group.

Comparison of this data with the Sr isotope age curve constructed by Jacobsen and Kaufman (1999) and additional analyses of Neoproterozoic carbonates worldwide (Shields and Veizer, 2002) suggest that the Bambuí carbonates were deposited somewhere between 750 and 600 Ma. This estimate is consistent with the 740 ± 22 Ma Pb–Pb carbonate radiometric constraint for the basin, which comes from the exceptionally preserved seafloor cements at Sambra Quarry.

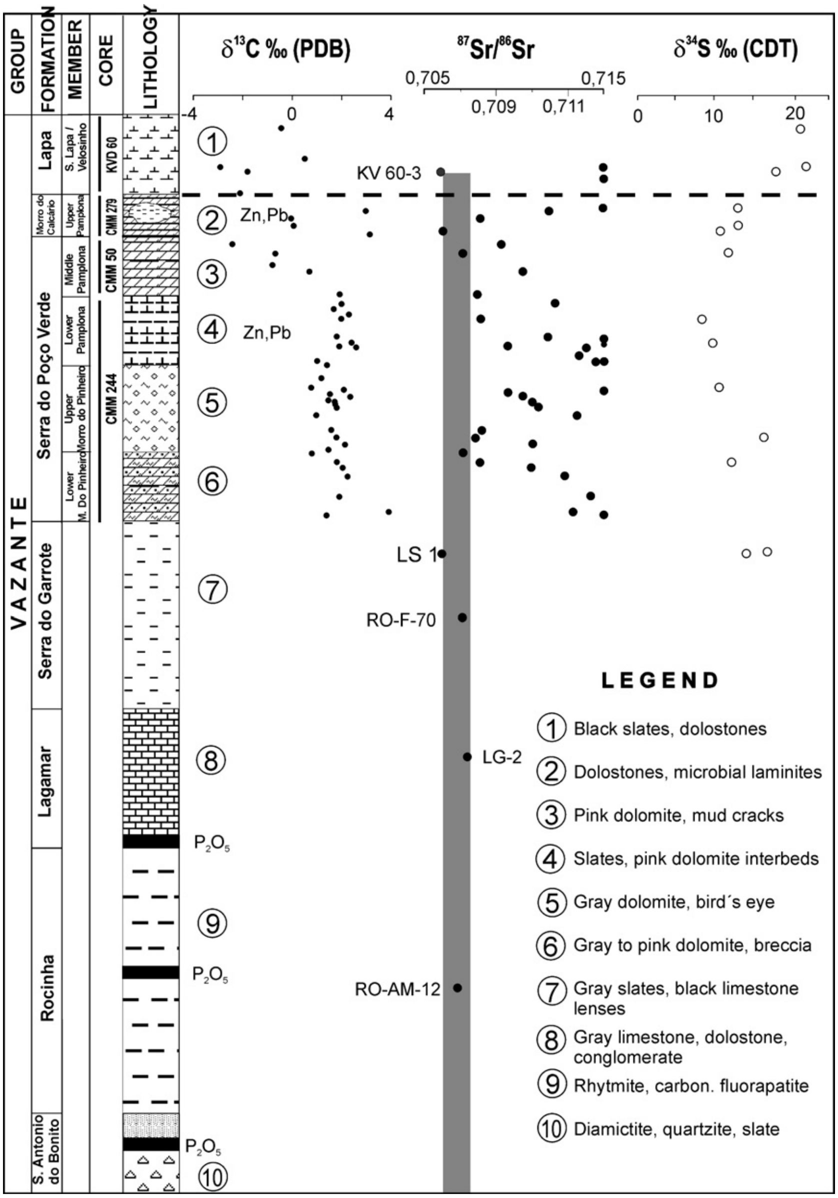


Fig. 9. Variations in $\delta^{13}C$, $^{87}Sr/^{86}Sr$ and $\delta^{34}S$ for dolomites of the Vazante Group. The shaded bar represents the range of the best preserved (lowest) global $^{87}Sr/^{86}Sr$ signals for the Varanger and Sturtian glacial episodes (Fig. 12) (Azmy et al., 2001, modified).

4.2. Brasilia fold belt (Vazante Group)

4.2.1. Stratigraphy and age constraints

The origin and the age of the Vazante Group strata, which contains important Zn–Pb deposits hosted in thick carbonates, has been broadly debated (*cf*. Oliveira, 1998). Early paleontologic and stratigraphic studies, assigned the Vazante Group to the Mesoproterozoic or older Neoproterozoic eras (Cloud and Dardenne, 1973; Pedrosa-Soares et al., 1994), whereas a more recent chemostratigraphic analysis suggests that the Vazante Group may have been deposited during the latter Neoproterozoic Era broadly contemporaneous with Bambuí Group sedimentation (Azmy et al., 2001). However, there are no reliable radiometric constraints for this basin (e.g. Amaral and Kawashita, 1967; Trindade et al., 2004), and stromatolite biostratigraphy is only of limited utility. Fig. 9 shows a general stratigraphic profile for the Vazante Group (Oliveira, 1998; Dardenne, 2000, 2001; Azmy et al., 2001). Shallow water carbonate of the Morro do Calcário Formation (hosting the Pb–Zn deposits) and pelitic sediments of the Lapa Formation are separated by a major incision surface. A strictly lithostratigraphic comparison suggests that these sediments might be equivalent to the lower and upper cycles preserved in the Bambuí Group to the east.

4.2.2. Isotope profile

In an attempt to correlate the Vazante sedimentary succession, Misi et al. (1997) and Sanches et al. (in press), (unpublished data) analyzed fine-grained organic-rich limestone from the Serra do Garrote Formation, and carbonate fluorapatite from the Lagamar and Rocinha formations for their Sr isotope compositions (Table 4). Surprisingly, the total Sr content was extremely high in all samples (>1300 ppm) and Mn/Sr is low, ranging from 0.01 to 0.09, suggesting a high degree of preservation. The $^{87}Sr/^{86}Sr$ ranges from 0.70760 to 0.70791. These values are similar to those reported for the entirety of the Bambuí Group (ca. 0.7074) suggesting possible equivalence of the successions. However, Azmy et al. (2001) analyzed two outcrop samples of high Sr limestone from the Serra do Garrote Formation and one from the Lapa Formation and found values in both units as low as 0.7069, which is lower than anything reported in the Bambuí carbonates.

A high-resolution carbon isotope trend from core samples through the middle to upper Vazante Group, including the Serra do Poço Verde, Morro do Calcário and lowermost Lapa formations, was established by Azmy et al. (2001). This part of the succession is primarily dolomite, and samples representing four different generations of cement were evaluated by petrographic, elemental, fluid inclusion, and isotopic techniques. In summary, Vazante carbonates appear to have been dolomitized during an early fabric retentive episode, followed by the formation of fibrous and equant cements (Dolomites I, II and III) in near surface environments, and a late episode in a deep burial setting that deposited fracture-filling saddle dolomite cement (Dolomite IV) (Azmy et al., 2001). Isotope profiles of $\delta^{13}C$, $^{87}Sr/^{86}Sr$, and $\delta^{34}S$ (from trace sulfate in carbonate) variations were constructed in that study from the analysis of the fabric-retentive dolomitic muds; additional data from the Rocinha, Lagamar and Serra do Garrote formations lower in the Vazante Group (Misi et al., 1997; Sanches et al., in press; Table 4) are also shown in Fig. 9. Moderately negative $\delta^{13}C$ compositions at the base of the Serra do Garrote Formation shift to +3.3‰ at the top of the formation and then increases to a maximum of ca. +4‰ at the base of the Serra do Poço Verde Formation. Above this level $\delta^{13}C$ values hover around +2‰ up to the base of the middle Pamplona Member and then drop to −2.3 ‰ at the top of this unit. Values shift again to a high of +3.9‰ the Morro do Calcário Formation and then shift back to slightly negative in the overlying carbonates of the Lapa Formation.

Given the abundance of breccia and diamictite in the Vazante Group it is plausible that some of the sharp negative $\delta^{13}C$ shifts might be related to either Sturtian or Varanger glaciation (*cf*. Jacobsen and Kaufman, 1999). The two notable negative $\delta^{13}C$ excursions (in the upper Serra do Poço Verde and Lapa formations) not only sit above breccia, but they were also deposited during sea level highstands. If these are glaciogenic deposits, the presence of *Conophyton metula* (Cloud and Dardenne, 1973) in the Serra do Garrote Formation underlying the Serra do Poço Verde carbonates favors the older alternative for this ice age (Azmy et al., 2001). The Lapa event, if glaciogenic, might represent a second Sturtian event (*cf*. Kaufman et al., 1997) or may be part of a much younger Varanger ice age.

Sulfur isotope analyses of stratiform lenses, irregular bodies and veins of barite from the Morro do Calcário Formation at the Pb–Zn mines of Morro Agudo show $\delta^{34}S$ values ranging widely from +14 to +44‰ ($n=19$) (Table 3). Given the association with mineralized zones, however, these sulfates are unlikely to reflect primary seawater S isotope compositions. Carbonate associated sulfate extracted from various levels in Vazante Group, however, reveal a relatively narrower range of $\delta^{34}S$ compositions. Azmy et al. (2001) report values between +10.8 and +21.3‰ in the Serra do Poço Verde, Morro do Calcário, and Lapa formation carbonates. New analyses of CAS in peritidal pink laminated dolomite from the lower Pamplona Member (Serra do Poço Verde Formation) are significantly more enriched in ^{34}S, with values ranging between +25.2 and +27.3‰ (Varni, 2002; Table 3).

4.3. Irecê basin (Una Group)

The Irecê Basin, a small and apparently isolated basin in the north-central part of the São Francisco craton in Brazil, includes platform carbonates and associated sediments in the Una–Utinga Basin, to the south, and most likely the São Francisco Basin to the west. The sedimentary package in these basins lays unconformable over Mesoproterozoic siliciclastic sediments of the Chapada Diamantina and Espinhaço groups and Paleoproterozoic–Archean rocks of the basement complex.

The Una Group in the Irecê and Una–Utinga basins is composed of five lithologically distinct units (Misi and Souto, 1975; Misi, 1979), which most likely

Table 3
Sulfur isotope data of sulfate minerals and trace sulfates from the Vazante Group (Cunha, 1999; Varni, 2002. Unpublished data)

Sample	Mineral	Description	CAS (ppm)	Unreacted matter (%)	$\delta^{34}S$ ‰ VCDT	Reference
Morro do Calcário Formation (Morro Agudo mine)						
MA N	Barite	white, lenses w/ gal.			25.0	Cunha, I.A. (1999)
MA JK 2c	Barite	veins in dolarenite			23.1	″
MA GHI	Barite	irregular bodies			28.5	″
GHI 1a	Barite	irregular bodies			28.5	″
MA GHI 2	Barite	irregular bodies			26.3	″
MA IC 2c	Barite	stratiform lenticular bodies			21.1	″
MA IC 9c	Barite	irregular bodies			23.8	″
MA IC 21b	Barite	irregular bodies			25.4	″
MA IC 3c	Barite	irregular bodies			23.9	″
MA IC 4c	Barite	aggreg. within sphalerite			25.4	″
MA IC 33c	Barite	irregular bodies			14.5	″
MA IC 15c	Barite	stratiform lenticular bodies			19.6	″
MA IC 16c	Barite	stratiform lenticular bodies			20.8	″
MA IC 34a	Barite	irregular bodies			44.0	″
MA IC 15a	Barite	lenses, stratiform			15.9	″
MA IC 44c	Barite	irregular bodies			18.5	″
MA IC 16c	Barite	stratiform lenticular bodies			31.2	″
MA IC 38c	Barite	irregular bodies			28.6	″
Carmelo	Barite	irregular bodies			23.9	″
Lower Pamplona Member, Serra do Poço Verde Formation						
K01.40.1	tr. sulfate		80.07	11.34	26.4	Varni, M. (2002)
K01.40.2	tr. sulfate		115.21	10.30	27.3	″
K01.40.3	tr. sulfate		100.90	6.13	27.1	″
K01.40.4	tr. sulfate		92.74	11.90	25.2	″
K01.40.5	tr. sulfate		97.98	11.05	25.4	″
K01.40.6	tr. sulfate		78.95	7.92	25.2	″
K01.40.7	tr. sulfate		76.81	9.31	24.4	″
K01.40.8	tr. sulfate		93.54	9.22	26.6	″
K01.40.9	tr. sulfate		46.04	4.71	26.0	″
K01.40.10	tr. sulfate		96.85	15.76	27.2	″

correlate with formations in the Bambuí Group. From top to bottom these include:

Unit A1: Massive black organic-rich limestone with oolitic and pisolitic textures. The presence of current cross-bedding suggests a high energy level during deposition. This unit is likely equivalent to the Lagoa do Jacaré Formation in the São Francisco Basin.

Unit A: Grey, argillaceous limestone intercalated with shale and siltstone, deposited in a relatively deep-water environment. The correlative unit in the São Francisco Basin is the Serra de Santa Helena Formation.

Unit B1: Grey to red dolostone with teepee structures, intraformational breccia, calcite and silica nodules, cross and current-ripple bedding and laminated and columnar stromatolites. These sediments accumulated in a shallow water environment with periodic exposure. Sub-facies of this unit contain black limestone with oolites and pisolites. Phosphate bearing columnar stromatolites and Zn–Pb mineralization are hosted by dolostone of this unit (Misi and Kyle, 1994; Kyle and Misi, 1997), which appears to correlate to the upper reaches of the Sete Lagoas Formation in the São Francisco Basin.

Unit B: Parallel laminated gray limestone and dolomitic limestone, which is broadly equivalent to the Sete Lagoas Formation in the São Francisco Basin.

Unit C: Red to green argillaceous dolostone overlying the Bebedouro Formation. Dardenne (1979) described similar “pink dolomites” at the lowermost section of the Sete Lagoas Formation overlying diamictites of the Macaubas Formation in the São Francisco Basin.

Bebedouro Formation: Iron cemented diamictite and greywacke. The presence of striated pavements (Montes, 1997) and dropstones suggest both a terrestrial and glacio-marine origin for this formation, which is equivalent to the Jequitaí or Carrancas and Macaubas formations in the São Francisco Basin. At the top of the unit the diamictite is overlain by cross stratified arkosic and pyritiferous sandstone that may be fluvial in origin (Misi and Silva, 1996).

4.3.1. Isotope stratigraphy

The first chemostratigraphic studies in South America were performed by Torquato and Misi (1977) on carbonates from the Irecê Basin. These authors analyzed 85 whole-rock samples for carbon and oxygen isotopes through the complete Una Group. Their data reveals a δ^{13}C trend from extreme negative values at the base (Unit C, ca. −6‰) to high positive values up section (Unit A1, ca. +8‰). Misi and Veizer (1998) reproduced these results on micro-samples that were characterized by petrographic and geochemical techniques (Fig. 10). In addition, the least altered samples from this study were used for ^{87}Sr/^{86}Sr determinations. The least radiogenic values ranged from 0.70746 (Unit A1) to 0.70780 (Unit B) (Table 1). Comparison of this Sr isotope data with a compilation of ^{87}Sr/^{86}Sr variations through the latter Neoproterozoic (Jacobsen and Kaufman, 1999) suggests an age of sedimentation between 750 and 600 Ma. Sulfur isotope results from secondary barite and gypsum in carbonates of the Irecê Basin range between +25.3 and +32.8‰ CDT (Kyle and Misi, 1997).

4.4. Corumbá basin (Corumbá Group)

The Corumbá Group in the SE border of the Amazonas Craton, Brazil (Fig. 1) was deposited on a stable continental margin (de Almeida, 1984, Zaine, 1991; Boggiani, 1998; Gaucher et al., 2003a), and includes alternating siliciclastic and carbonate units with a composite thickness of nearly 600 m (Boggiani et al., 2003). Following glaciogenic and glacio-marine deposits of the Puga Formation (de Alvarenga and Trompette, 1992), a siliciclastic-rich deepening-upward sequence was deposited, represented by the Cerradinho Formation. In Puga Hill, at the right margin of the Paraguay River, Boggiani et al. (2003) described pinkish and gray laminated limestone with 12 m thick, immediately above the glaciogenic diamictites (Fig. 11). The Cadiueus Formation, which underlies the Cerradinho Formation, may represent alluvial fan, synrift deposits generated during opening of the Corumbá Basin and/or glacial-outwash fans deposited during retreat of a glacial ice-sheet (Gaucher et al., 2003a). The Cerradinho Formation

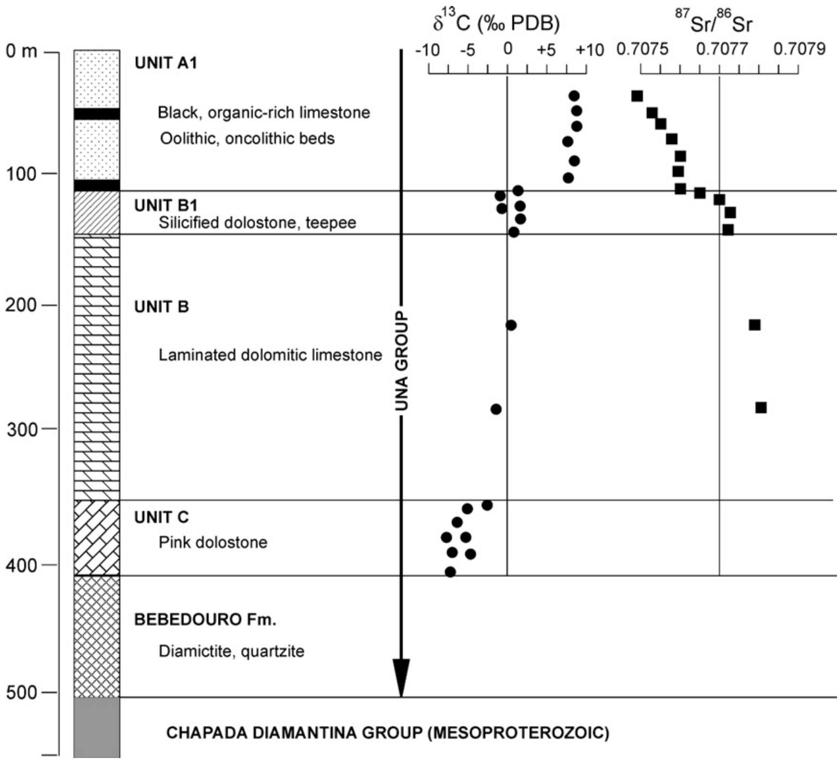


Fig. 10. Stratigraphic variation of δ^{13}C and ^{87}Sr/^{86}Sr in carbonates of the Una Group, Irecê basin, Brazil. Data by Torquato and Misi (1977) and Misi and Veizer (1998): samples from one complete stratigraphic section in the eastern border of the basin.

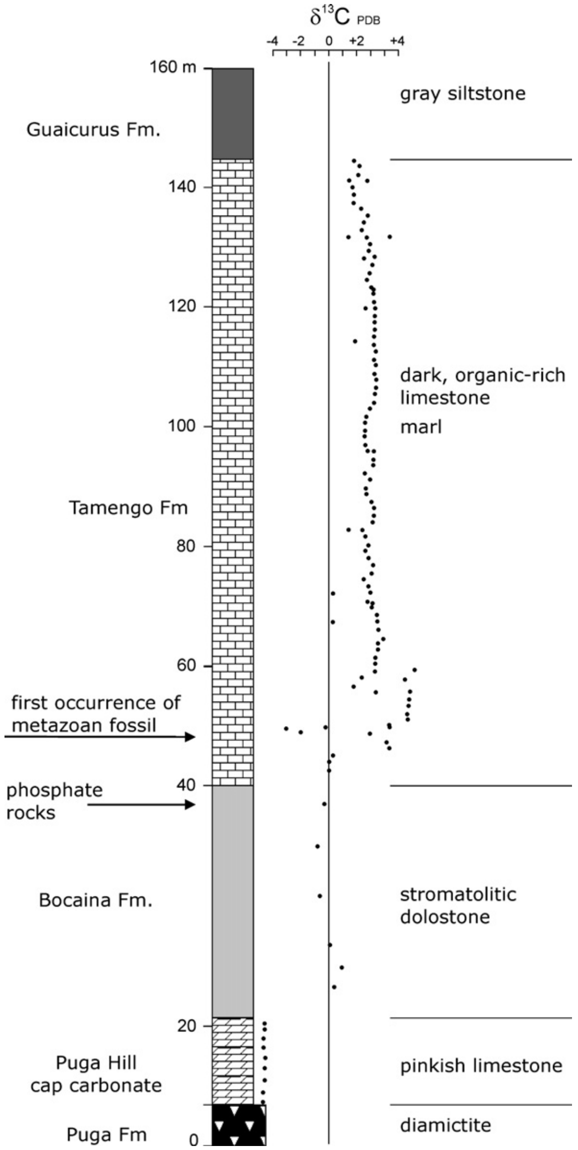


Fig. 11. Composite carbon isotope section of the Corumbá Group, Brazil (Boggiani et al., 2003).

conformably passes into carbonates of the Bocaina Formation, or more rarely, directly into the Tamengo Formation (de Almeida, 1965; Boggiani, 1998). The Bocaina Formation is characterized by thick deposits of stromatolitic dolostone that show great lateral facies variation, including phosphorites with up to 34% P_2O_5. The overlying Tamengo Formation is mainly composed of dark, organic rich limestone and marl with occasional *Cloudina* event-accumulations (Zaine, 1991; Boggiani, 1998). The shallow-water carbonate sequences with phosphate concentration "have spread along a larger area, covering the other units including the granitic–gneiss basement" (Boggiani et al., 2003). Finally, carbonates of the Tamengo Formation are concordantly overlain by gray siltstones of the Guaicurus Formation, marking the end of deposition in the Corumbá Basin.The Corumbá Group hosts a rich assemblage of micro-and meso-fossils of broad Vendian age. C*loudina lucianoi* occurs in calcareous storm deposits of the Tamengo Formation (Beurlen and Sommer, 1957; Zaine and Fairchild, 1985; Hahn and Pflug, 1985; Gaucher et al., 2003a). Hahn et al. (1982) reported the occurrence of possible *Scyphozoa* in the Tamengo Formation, erecting the taxon *Corumbella werneri*. *Titanotheca coimbrae*, an agglutinated foraminifer known from Vendian deposits elsewhere in South America, has been found in phosphorites of the Bocaina Formation (Gaucher et al., 2003a). Acritarchs of the genera *Bavlinella* and *Vandalosphaeridium* were first reported from the Corumbá Group by Fairchild and Sundaram (1981), Zaine and Fairchild (1985).

The first systematic paleontological study of the Corumbá Group is due to Zaine (1991). Gaucher et al. (2003a) document a low-diversity palynomorph assemblage with the genera *Bavlinella*, *Soldadophycus* and *Leiosphaeridia* as prominent components of the microflora. Finally, Gaucher (2000) and Gaucher et al. (2003a) describe the vendotaenid *Eoholynia corumbensis* from the lower Guaicurus Formation. Granitogenesis in the Paraguay Belt is mainly confined to the "Metamorphic Brazilides". Post-tectonic granites intruding the Cuiabá Group, such as the São Vicente Granite, yielded ages of 504±12 Ma (K/Ar in biotite: Almeida, 1984). The Cuiabá Group probably represents a lateral equivalent of the Puga Formation. If correct, these dates provide a minimum age constraint for the Corumbá Group.

Tighter age constraints are provided by the remarkable fossil assemblage in the Tamengo Formation, which compare favorably with the world's oldest biomineralized fossils found in Namibia. *Cloudina* (Germs, 1972), for example, is currently regarded as an index fossil of the uppermost Vendian (Grant, 1990). In Namibia and Oman several volcanic ash horizons interbedded with carbonates containing *Cloudina* and related fossils have been identified and dated (Grotzinger et al., 1995; Amthor et al., 2003), thus placing this biozone between about 550 and 543 Ma.

4.4.1. Isotope stratigraphy

Carbon isotope values through the Corumbá Group (Fig. 12) reveal significant temporal variations, ranging from −5.3‰ at the base in carbonate lithofacies to as high as+5.5‰ associated with beds containing the biomineralized metazoans of the Tamengo Formation.

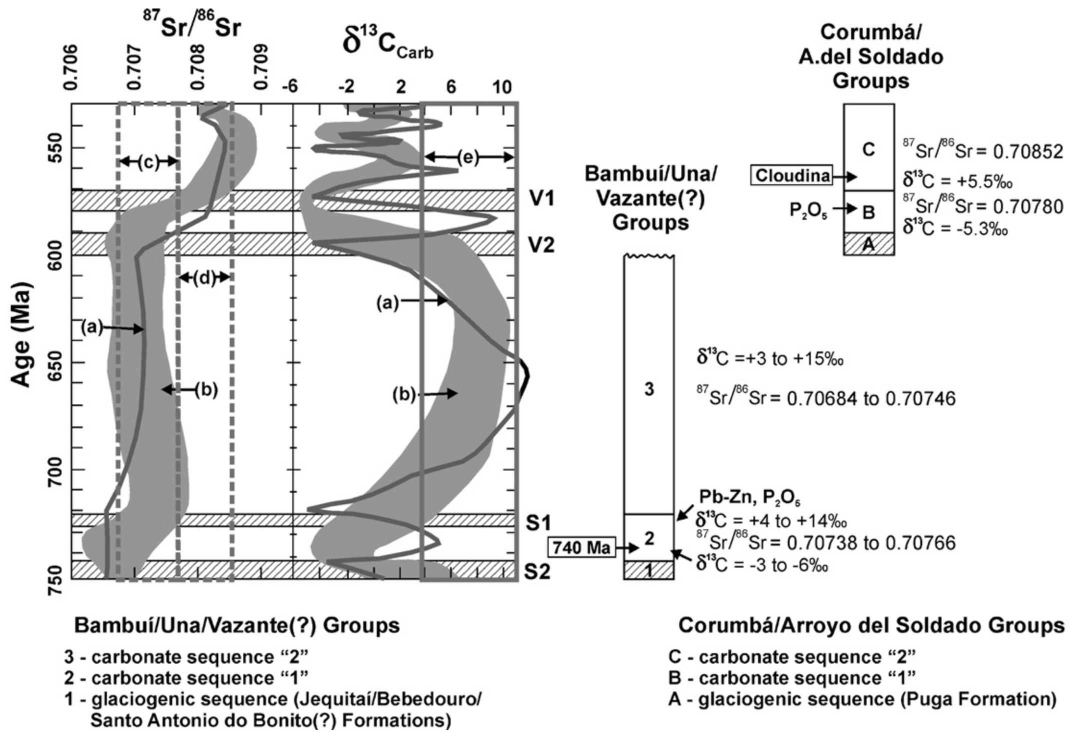


Fig. 12. δ^{13}C and ^{87}Sr/^{86}Sr evolution of Neoproterozoic seawater: (a) Curves obtained by Brasier and Shields (2000), based on data from SW Mongolia, NW Canada and Oman (several sources). (b) Range of seawater variation by Jacobsen and Kaufman (1999), based on data from Siberia, Namibia, Canada, Svalbard and East Greenland. (c) Range of ^{87}Sr/^{86}Sr least radiogenic values in the following groups: Arroyo del Soldado (Lower Polanco Fm.), Cuiabá (Araras Gr.), Vazante, Bambuí and Una Groups. (d) Least radiogenic values of ^{87}Sr/^{86}Sr in the Corumbá Group. (e) Range of δ^{13}C positive excursions in the Groups: Vazante (Morro do Calcário and Serra do Poço Verde Formations), Bambuí (Lagoa do Jacaré and Sete Lagoas Formations) and Una (A1, B1 and B Units). V1, V2: upper and lower Vendian glaciations; S1, S2: upper and lower Sturtian glaciations. At right, possible correlation of the studied sequences with the global curves. The geochronological markers in these sequences are: Vendian fossils (Cloudina) from the Corumbá Group and Pb–Pb isochronic age of carbonates from the Sete Lagoas Formation (740±42 Ma, Babinski and Kaufman, 2003).

Above this horizon δ^{13}C values hover around +3‰ in the exposed section. A second significant negative δ^{13}C interval (down to −3‰) is recorded at the base of the Tamengo Formation, although there is no lithologic evidence for glaciation at this time.

Strontium isotope ratios of well-preserved carbonates rise monotonically through the Corumbá Group from 0.7078 in the Puga Hill post glacial carbonate to 0.7085 at the top of the Tamengo Formation. While the lower ^{87}Sr/^{86}Sr value is comparable with well preserved carbonates in the Bambuí and Una groups, the higher value is consistent with post-Varanger sediments worldwide (Table 1) (*cf*. Kaufman et al., 1997), which is consistent with the paleontologic observations.

4.5. Arroyo del Soldado Group

The Arroyo del Soldado Group in SE border of the Rio de la Plata Craton, Uruguay (Fig. 1) includes a 5 km-thick passive margin platform succession comprising intercalated carbonate, siliciclastic, chert and iron-formation. From base to top, the following formations are distinguished (Gaucher et al., 1998a,b; Gaucher, 2000; Gaucher et al., 2003a, 2004):

Yerbal: up to 1500 m of siliciclastic sediments fining upwards.

Polanco: up to 900 m of bluish gray limestone and dolomite rhythmite.

Barriga Negra: up to 1500 m of conglomerates recording proximal exposure and reworking of platform sediments.

Cerro Espuelitas: ∼1200 m thick succession of intercalated shale, carbonate, and oxide-facies BIF deposited during transgression.

Cerros San Francisco: up to 300 m of quartz arenite and subarkose.

Cerro Victoria: up to 400 m of stromatolitic limestone with trace fossils indicative of lowermost Cambrian age (Sprechmann et al., 2004).

The Yerbal, Polanco, Barriga Negra and Cerro Espuelitas formations host a well-preserved, if depauperate, palynomorph assemblage dominated by *Bavlinella faveolata*, *Soldadophycus bossii*, *Soldadophycus major*, *Leiosphaeridia* spp. and *Lophosphaeridium montanae* (Gaucher et al., 1998a,b; Gaucher, 2000; Gaucher et al., 2003a). This microflora matches the Kotlin–Rovno assemblage of Vidal and Moczydlowska (1997), characterised by low diversity and absence of acanthomorphs and large (>500 μm) sphaeromorphs. Skeletal meiofossils include *Cloudina riemkeae, Titanotheca coimbrae* and *Waltheria marburgensis* (Gaucher and Sprechmann, 1999; Gaucher, 2000; Gaucher et al., 2003a). The uppermost Arroyo del Soldado Group was deposited in the lowermost Cambrian, as shown by trace fossils assigned to *Thalassinoides* isp. by Sprechmann et al. (2004).

The age of the Arroyo del Soldado Group is constrained by a U/Pb SHRIMP age of 633±12 Ma for the Puntas del Santa Lucía pluton (Hartmann et al., 2002), which lies nonconformably beneath the passive margin sediments. Additional radiometric constraints for the Arroyo del Soldado sediments may come from a Rb/Sr study of the 532±11 Ma Guazunambí Granite (Kawashita et al., 1999), which intrudes into the Arroyo del Soldado group, and K/Ar ages ranging between 532±16 and 492±14 Ma for recrystallized pelites belonging to the group (Cingolani et al., 1990; Gaucher, 2000).

4.5.1. Isotope stratigraphy

The first isotopic data for the Arroyo Del Soldado Group was reported by Boggiani (1998) and Kawashita et al. (1999), but later studies by Gaucher et al. (2003a,b, 2004) provide a clear picture of temporal trends through the succession. The succession has moderately enriched $\delta^{13}C$ compositions throughout with notable negative excursions within carbonates of the Polanco, Barriga Negra/Cerro Espuelitas, and Cerro Victoria formations (Table 2). Well preserved basal rhythmites of the Polanco Formation record $^{87}Sr/^{86}Sr$ values between 0.7078 and 0.7082 (Table 1) (Kawashita et al., 1999).

4.6. Other successions

In addition to the successions that have been intensively studied, limited isotopic data from other Neoproterozoic units in South America are considered in the overall correlations. For example, Kawashita (1998) presented Sr isotope data on carbonates in the Vasa Barris Group in the Sergipe Fold Belt on the northeastern border of the São Francisco Craton, Brazil (Fig. 1). The least radiogenic $^{87}Sr/^{86}Sr$ ratio of 0.70775, which comes from black limestone of the Olhos d′Agua Formation, is similar enough to consider the correlation of the Vasa Barris Group with the carbonate platform successions of the Una and Bambuí Groups, to the west and southwest. The Sr isotope equivalence is supported by observed $\delta^{13}C$ variations in the same succession (Sial et al., 2000). These authors report $\delta^{13}C$ values as low as −4.7‰ above diamictites of the Palestina Formation, which increase upsection to values as high as +10‰ at the top of the group (Tables 1 and 2).

In Argentina, survey level carbon isotopic studies have been carried out by Gómez-Peral et al. (2003) in the Sierras Bayas Group. According to these authors, carbonates in the Loma Negra and lower Cerro Negro formations preserve moderately positive $\delta^{13}C$ values, ranging between +2.8 and +4.5‰. The carbon isotope composition of co-existing organic matter lies between −27.1 and −28.1‰. Kawashita (1998) reports $^{87}Sr/^{86}Sr$ ratio of best preserved samples from this succession of around 0.70810. These values are similar to those obtained for the lower Polanco Formation of the Arroyo del Soldado Group (Gaucher et al., 2003a, 2004) and the Tamengo Formation (Boggiani et al., 2003).

Galindo et al. (2004) present new isotopic data from carbonate rocks of the Western Sierras Pampeanas of Argentina. Despite the absence of stratigraphic sections of the Neoproterozoic/Cambrian sequences studied – Precordillera, Caucete Group, Filo del Grafito and Difunta Correa – the Sr isotopic data are conformable with those of the Corumbá and Arroyo del Soldado groups (Table 1).

5. Chemostratigraphic correlations: discussion and conclusions

Lacking adequate radiometric and robust chronometric constraints, this report attempts to correlate the widely separated Neoproterozoic successions of South America primarily by Sr isotope stratigraphy. The use of Sr isotopes as a correlation tool, however, requires that robust secular trends known from well preserved samples, can be tied to key biological or climatic events, and have been calibrated against time (*cf.* Jacobsen and Kaufman, 1999). Insofar as many Neoproterozoic successions are dominated by dolomite, and that these have all seen variable degrees of diagenetic alteration, locating appropriate well-preserved limestone samples for $^{87}Sr/^{86}Sr$ determinations is difficult. In general, we rely on the lowest value within a unit as being most representatives of seawater compositions, and have greatest confidence when multiple closely-spaced samples record similar values.

The global compilation used for comparison in this report is largely based on analyses of exceptionally preserved seafloor cements that occur in carbonates atop diamictite. However, the ongoing controversy regarding the number of discrete ice ages in Neoproterozoic time (Kaufman et al., 1997; Kennedy et al., 1998; see also Prave, 1999; Corsetti and Kaufman, 2003) complicates the construction of a Sr isotope age curve. The compilation of Jacobsen and Kaufman (1999) (Fig. 12) assumes the presence of four glaciations, but the "cap carbonates" that mark two of these events (the younger Sturtian and older Varanger) have very similar Sr isotope compositions (ranging between 0.7068 and 0.7072). In contrast, the older Sturtian carbonates have lower $^{87}Sr/^{86}Sr$ values (<0.7066) and the younger Varanger caps have higher $^{87}Sr/^{86}Sr$ values (>0.7080). Some of these controversies were also discussed by Brasier and Shields (2000), who present a carbon and strontium isotope compilation assuming the existence of four glaciations (Fig. 12). The obtained curves, based on data from SW Mongolia, NW Canada and Oman (from several sources), are in general similar to that obtained by Jacobsen and Kaufman (1999), except that the older Sturtian glaciations are bracketed by $^{87}Sr/^{86}Sr$ isotope signatures of ca.0.7067 and followed by extremely positive $\delta^{13}C$ values of >+10‰. The younger glaciations are followed by $^{87}Sr/^{86}Sr$ values rising from 0.7072 to 0.7078 and by $\delta^{13}C$ values of ca. +8‰ PDB (Brasier and Shields, 2000).

Better radiometric constraints and more robust stratigraphic datasets from well-preserved carbonate rocks are necessary to ultimately provide a Sr and a carbon isotope database on which correlations worldwide can be hung.

Nonetheless, based on the existing compilations and on $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ data from well preserved samples (Tables 1, 2 and 4), we propose correlations of the Neoproterozoic successions of South America. Given the range of $^{87}Sr/^{86}Sr$ values in the Corumbá and Arroyo del Soldado limestones (0.7078 to 0.7086) (Table 1) these units appear to be younger than all of the remaining basins (consistent with the presence of *Cloudina* and other biomineralized fossils in these deposits (Boggiani, 1998; Gaucher et al., 2003a). However, the similarity in $^{87}Sr/^{86}Sr$ between the younger Sturtian and older Varanger caps (see above) makes it difficult to evaluate which ice age these diamictites might belong, and the possibility remains that the lower portions of these successions (with $^{87}Sr/^{86}Sr$ near 0.7078) are equivalent to the Bambuí Group and equivalent sediments throughout South America. At present it is not known if significant unconformities separate the fossiliferous horizons and the diamictites in the Corumbá and Arroyo del Soldado basins. On the other hand, carbon isotopic compositions of these successions are not overly enriched in ^{13}C, like those in the Bambuí Group (Table 2), which is consistent with a post-Varanger age for these successions outside of the Sao Francisco Craton (*cf.* Smith

Table 4
Sr and C-isotope data from micritic limestone and carbonate fluorapatite of the Vazante Group (Misi et al., 1997; Sanches et al., in press. Unpublished data)

Sample	Description	$\delta^{13}C$ ‰ PDB	$^{87}Sr/^{86}Sr$	Fe ppm	Sr ppm	Mn ppm	Mn/Sr
Serra do Garrote Formation							
RO F-61-79	Black micritic lms.	−2.1	0.70869	11420	1670	556	0.33
RO F-61-81	Black micritic lms.	ND	0.70886	13040	3240	468	0.14
RO F-70-70.6	Black micritic lms.	2	0.70760	8500	3840	364	0.09
RO AM 01	Black micritic lms.	1	0.70769	7790	2670	678	0.25
Lagamar Formation							
LG 2	Carbon. fluorapatite	ND	0.70791	2060	1300	105	0.08
LG AM 03b	Carbon. fluorapatite	ND	0.70794	ND	2497	ND	–
LG AM 10	Carbon. fluorapatite	ND	0.70767	ND	2095	ND	–
Rocinha Formation							
RO AM 03	Black micritic lms.	−0.4	0.70786	12330	2370	566	0.24
RO AM 04	Black micritic lms.	−2.9	0.70769	12460	2910	808	0.28
RO AM 06	Black micritic lms.	−1.4	0.70772	11050	1930	1080	0.56
RO AM 09	Carbon. fluorapatite	ND	0.70767	6340	5280	38	0.01
RO AM 12	Carbon. fluorapatite	ND	0.70766	6610	6080	61	0.01
RO AM 20a	Carbon. fluorapatite	ND	0.70763	ND	6814	ND	–

et al., 1994; Kaufman and Knoll, 1995; Kaufman et al., 1997).

On the Sao Francisco craton (Fig. 3) the broad similarity of lithofacies and mega-sequences, as well as the occurrence of Pb–Zn mineralization restricted to a narrow stratigraphic interval in the Vazante, Bambuí, and Una groups suggests that these units may be correlative. According to Misi et al. (1998, 2000, 2005), all the Pb–Zn deposits of the Neoproterozoic successions are restricted to the sequence boundary atop the first Sturtian carbonate sequence (cycle 1) or immediately below this boundary (Figs. 12 and 13). The common attributes observed in these deposits, including their association with a fault system and with evaporative facies, the sulfur isotope composition of sulfides and sulfates and the fluid inclusion data (salinities and homogenization temperatures) suggest that the same metallogenic event concurred for the formation of these deposits (Misi et al., 2005).

The new Sr isotope data from each of these successions presented in this study (ranging from 0.7074 to 0.7079) (Tables 1 and 4) supports the general correlation of the Vazante, Bambuí and Una successions. Carbon isotope data from the three successions also reveals sharp negative excursions associated with post-glacial carbonate lithofacies and/or evidence of rapid transgression. Otherwise, carbonates in these units are moderately to extremely enriched in ^{13}C, ranging from high values of +3 to +14‰ in the different sections (Table 2). Proposed correlations of the South American successions discussed here are shown in Figs. 12 and 13.

Consideration of previously published data (Azmy et al., 2001) paints a somewhat different picture. For example, outcrop samples of Serra do Garrote Formation limestone with high Sr contents from that study yield consistently low $^{87}Sr/^{86}Sr$ values of ca. 0.7069, which are quite similar to a limestone sample taken from core material of the Lapa Formation (~0.7068) immediately overlying the Morro do Calcário Formation. These lower $^{87}Sr/^{86}Sr$ values (*cf.* Jacobsen and Kaufman, 1999) suggest the possibility that the Vazante succession may, in fact, be older than the widespread Bambuí sediments.

Carbon isotope data further supports this alternative correlation. Whereas the organic-rich Bambuí carbonates reveal remarkable enrichments in ^{13}C (>+9 and up to +16‰; Iyer et al., 1995), which are also found in immediately pre-Varanger successions in Svalbard and East Greenland, Namibia, and arctic Canada (Knoll

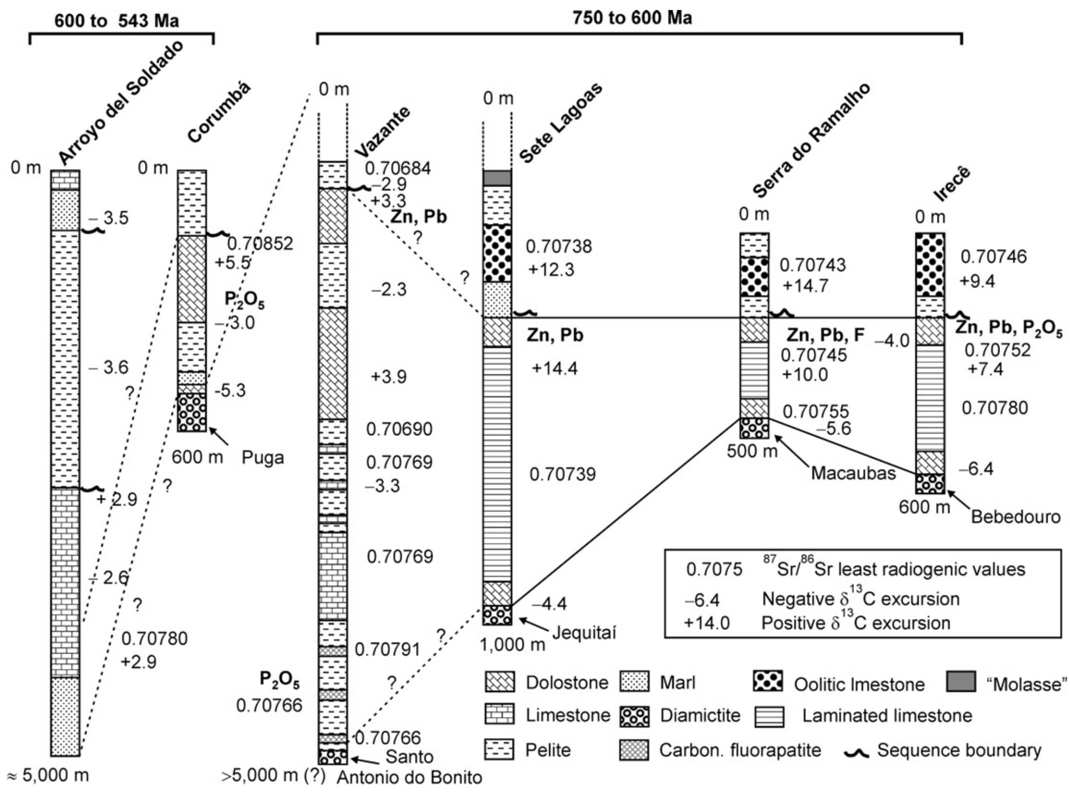


Fig. 13. Proposed correlation between the Neoproterozoic successions studied.

et al., 1986; Kaufman et al., 1991; Narbonne et al., 1994; Kaufman et al., 1997), stratigraphic trends in the Vazante Group indicate values of no greater than +3.3‰ at the base of the thick dolomitic succession. If correct, this alternative correlation has important implications to the timing of Pb–Zn mineralization. Two metallogenic events, instead of one, could have occurred during (and after) the deposition of the Sturtian carbonate sequences. Additional chemostratigraphic studies and new radiometric constraints will be necessary to sort out these discrepancies.

The formation of phosphate deposits throughout the Neoproterozoic interval has important economic significance. Phosphate concentrations, probably related to replacement of organic structures during early diagenetic stages (Misi and Kyle, 1994), are found in both the Sturtian and the Varangerian/Marinoan carbonate successions. These phosphogenic events could be attributed to the high organic productivity following periods of glaciation.

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