

Correlations of some Neoproterozoic carbonate-dominated successions in South America based on high-resolution chemostratigraphy

Correlações de algumas sucessões carbonáticas na América do Sul baseado em quimioestratigrafia de alta resolução

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ABSTRACT: This report reviews and incorporates new elemental and isotope chemostratigraphic data for correlation of Neoproterozoic carbonate-dominated successions in South America (Argentina, Bolivia, Brazil, Paraguay and Uruguay). These thick mixed carbonate/siliciclastic successions were largely deposited in epicontinental basins or accumulated on passive margins on the edges of cratons (e.g. São Francisco, Amazonas, Rio Apa Block, Pampia and Río de la Plata paleocontinents) during extensional events related to the rifting of the Rodinia Supercontinent. From the stratigraphic point of view, these successions occur as three megasequences: glaciogenic, marine carbonate platform (above glaciomarine diamictites or rift successions), and dominantly continental to transitional siliciclastics. In the orogenic belts surrounding cratons, carbonate-dominated successions with important volcanoclastic/siliciclastic contribution have been, in most cases, strongly deformed. The precise ages of these successions remain a matter of debate, but recently new paleontological and geochronological data have considerably constrained depositional intervals. Here, we report high-resolution C, O, Sr, and S isotope trends measured in well-preserved sample sets and mainly use Sr and C isotopes

RESUMO: Esta revisão incorpora novos dados isotópicos e químicos para correlação quimioestratigráfica de sucessões, predominantemente carbonáticas, na América do Sul (Argentina, Bolívia, Brasil, Paraguai e Uruguai). Estas sucessões, depositadas durante eventos de extensão, aparecem como espessos estratos carbonáticos/siliciclásticos em bacias epicontinentais ou foram acumulados sobre margens passivas em bordos de cratons (ex.: São Francisco, Amazonas, Bloco Rio Apa, Pampia e Río de La Plata) como três megasequências: glaciogênica, plataforma marinha carbonática (sobre diamictitos glacio-marinhos) e predominantemente continental siliciclástica. Em cinturões circunjacentes a cratons, sucessões carbonáticas contendo material vulcanoclástico/siliciclástico foram, na maioria dos casos, fortemente deformados. A idade precisa de sedimentação destas sucessões permanece em debate, mas recentes dados paleontológicos e geocronológicos têm consideravelmente restringidos os intervalos de deposição. Neste trabalho, reportamos trends isotópicos de alta resolução de C, O, Sr e S medidos em amostras bem preservadas e usamos principalmente isótopos de Sr e C em consonância com obser-

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in concert with lithostratigraphic/biostratigraphic observations to provide detailed correlations of these successions. The establishing of a high-level and definite chemostratigraphic correlation between Neoproterozoic basins in South America is the main goal of this work.

KEYWORDS: Carbonate successions; correlation; isotope chemostratigraphy; Neoproterozoic; South America.

• *vações litoestratigráficas/bioestratigráficas, para estabelecer correlações detalhadas destas sucessões. Propor uma correlação quimioestratigráfica entre bacias Neoproterozoicas na América do Sul é o principal objetivo deste trabalho.*

• **PALAVRAS-CHAVE:** Sucessão carbonática; correlação; quimioestratigrafia isotópica; Neoproterozoico; América do Sul.

INTRODUCTION

The pioneer C-isotope investigation on Paleoproterozoic carbonate rocks of the Lomagundi province in Africa has evidenced much larger variation of $\delta^{13}\text{C}$ values (Schidlowski *et al.* 1983) than previously known from Phanerozoic carbonate successions (Veizer *et al.* 1980). This finding has raised the possibility that the stratigraphic variation of $\delta^{13}\text{C}$ values could potentially be a tool in stratigraphic correlation. Despite widespread effects of late diagenesis on the isotope record, important isotope events could be demonstrated on a global scale by means of isotope chemostratigraphy (e.g. Knoll *et al.* 1986; Magaritz *et al.* 1986; Holser 1997, to mention a few) as it became evident that contemporaneous, geographically distant marine strata, registered similar isotopic compositions. Chemostratigraphy serves as one of the principal means of intra- and inter-basinal stratigraphic correlation to assemble the Precambrian stratigraphic record from fragments preserved in scattered successions (Karhu *et al.* 2010). Definitely, chemostratigraphy became an important tool for providing a timeline that compensates for the poor biostratigraphic resolution of Precambrian fossils (e.g. Veizer *et al.* 1980; Knoll *et al.* 1986; Magaritz *et al.* 1986; Knoll & Walter 1992; Kaufman *et al.* 1997, 2007; Corsetti & Kaufman 2003; Halverson *et al.* 2005; Sial *et al.* 2015b). Correlations established through chemostratigraphy can be used to comment on climate and biogeochemical changes through time, although the paucity of radiometric constraints on the absolute age of most of extreme isotope excursions leads, sometimes, to debates on their temporal equivalence (e.g. Kaufman *et al.* 1997; Kennedy *et al.* 1998; Calver *et al.* 2004; Allen & Etienne 2008). In the last three decades, the number of studies relying on isotope chemostratigraphy has grown substantially and, in the case of C-isotope stratigraphy, has been applied to metamorphic rocks up to the high grade (Melezhik *et al.* 2005; Nascimento *et al.* 2007; Chigilino *et al.* 2010; Sial *et al.* 2015a) and may retain depositional $\delta^{13}\text{C}$ values in even diagenetically altered carbonates (Kaufman *et al.* 2007).

The first stable isotope laboratory in Brazil was founded in the Center of Nuclear Energy in Agriculture (CENA, University of São Paulo) in 1966. In 1973, the Federal University of Bahia installed a stable isotope laboratory at the Nuclear Geophysics Laboratory of the Research Program

on Geophysics and Geology (PPPG/UFBA) and Petrobras founded another in 1977, at the Center of Research and Development Leopoldo Américo Miguez de Mello (CENPES) in Rio de Janeiro. The widespread use of isotope chemostratigraphy in South America became possible, however, only after the installation of a stable isotope laboratory at the Federal University of Pernambuco (LABISE) in Recife in 1990 and, later on, in three other Brazilian universities (Brasília, São Paulo, and Pará).

C- and O-isotope study of Precambrian successions in Brazil was first performed by Torquato & Misi (1977), who also reported a first cap carbonate characterization (Kaufman *et al.* 2007). Other pioneer chemostratigraphic investigations in Brazil were performed by Torquato (1980), Zaine (1991), Sial *et al.* (1992), Chang *et al.* (1994), Misi & Kyle (1994), Kawashita (1996), Boggiani *et al.* (1996), Chang (1997), Santos *et al.* (2000, 2004), and Sial *et al.* (2000). Zaine (1991) has measured C and O isotope ratios in carbonates of the Tamengo Formation, Corumbá Group, and Boggiani *et al.* (1996) have identified an upper Ediacaran positive $\delta^{13}\text{C}$ excursion, associated to the occurrence of *Cloudina*, which was correlated with the Arroyo del Soldado Group in Uruguay (Gaucher 1999). These studies were followed by systematic chemostratigraphic investigations on the Bambui, Una and Araras groups (Misi & Veizer 1998; Sial *et al.* 2000; Santos *et al.* 2000; Nogueira *et al.* 2003; Alvarenga *et al.* 2004; Misi *et al.*, 2007). Sial *et al.* (2000), Bekker *et al.* (2003), and Maheshwari *et al.* (2010) confirmed the record of the Lomagundi C isotope excursion in South America (Iron Quadrangle in Minas Gerais and Paso Severino Formation in Uruguay). Sial *et al.* (2008) reported, for the first time in South America, the positive carbon isotope excursion (SPICE) from the Steptoean at the Argentine Precordillera and recognized a Sunwaptan negative carbon isotope excursion (SNICE).

An overview on chemostratigraphic correlations of Neoproterozoic carbonate-dominated successions in the South America continent is present here, mainly based on C- and O-isotope chemostratigraphy, updating a preliminary synthesis published by Misi *et al.* (2007) and expanding it to encompass some other Neoproterozoic basins in this continent (Uruguay, Argentina, Paraguay, Bolívia, and northeastern Brazil) (Fig. 1).

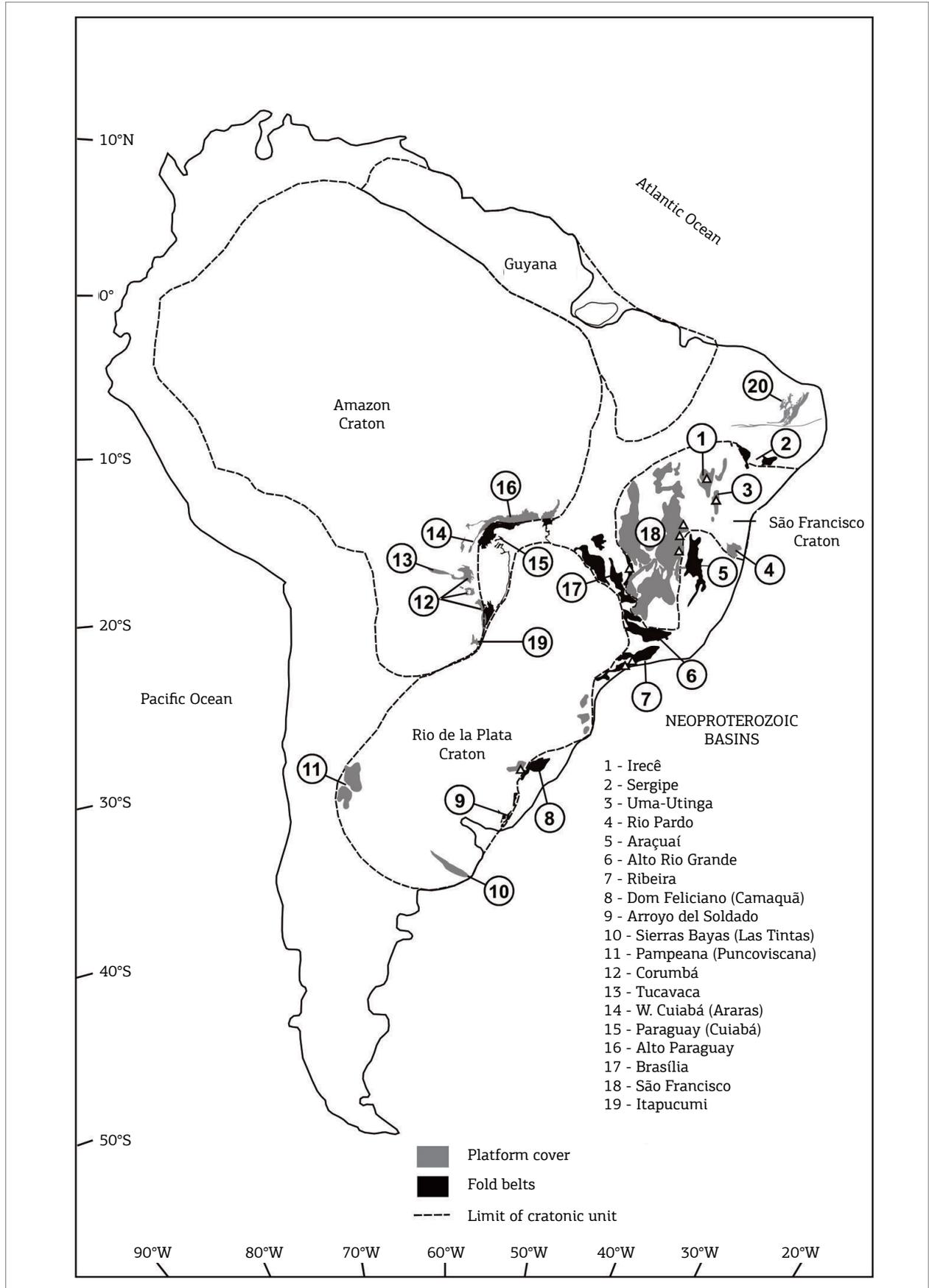


Figure 1. The Neoproterozoic basins of South America (modified from Misi *et al.* 2007).

ANALYTICAL METHODS AND SAMPLE EVALUATION

The majority of the C- and O-isotope analyses plotted here in chemostratigraphic profiles were performed at the Stable Isotope Laboratory (LABISE) of the Federal University of Pernambuco at Recife, although some were also performed at the Universities of Brasília and São Paulo. At the LABISE, CO₂ extraction from carbonates was accomplished by the conventional method of sample reaction with orthophosphoric acid, for 12 hours at 25°C (3 days allowed when dolomite was present), followed by cryogenic cleaning and then by spectrometric analyses in a SIRA II or Delta V Advantage mass spectrometers. Analyses at the University of Brasília or University of São Paulo were performed using the Gas Bench on line with Thermofinnigan Delta V Advantage mass spectrometer. For some stratigraphic sections, strontium isotope ratios were analyzed after concentration by ion exchange chromatography and ⁸⁷Sr/⁸⁶Sr values determined in static mode using a Finnigan MAT 262 seven-collector mass spectrometer at the University of Brasília, or University of São Paulo, as well as other laboratories outside South America.

In evaluation of sample quality, it seems that the most effective parameter is the Mn/Sr ratio, because Sr is preferentially removed during recrystallization of metastable carbonate phases, while Mn becomes enriched during formation of late-stage ferroan calcite cement (Ripperdan *et al.* 1992; Derry *et al.* 1992; Kaufman *et al.* 1993; Knoll *et al.* 1995; Jacobsen & Kaufman 1999). Although Kaufman & Knoll (1995) stated that limestones or dolostones with Mn/Sr < 10 commonly retain near primary δ¹³C abundances, limestones were here considered to be unaltered only when Mn/Sr < 1.5 and δ¹⁸O > -10‰ (VPDB) according to Fölling & Frimmel (2002) criteria. However, each succession should be evaluated separately to assess the nature of isotopic signals, especially for Sr isotopes.

AMAZONIA PALEOCONTINENT

Northern Paraguay Belt

After the end-Cryogenian glaciation, the central region of Brazil was the site of extensive deposition of platformal carbonates of the 1,300-m-thick Araras Group (Fig. 2). This group includes four formations, a basal cap dolostone (Mirassol

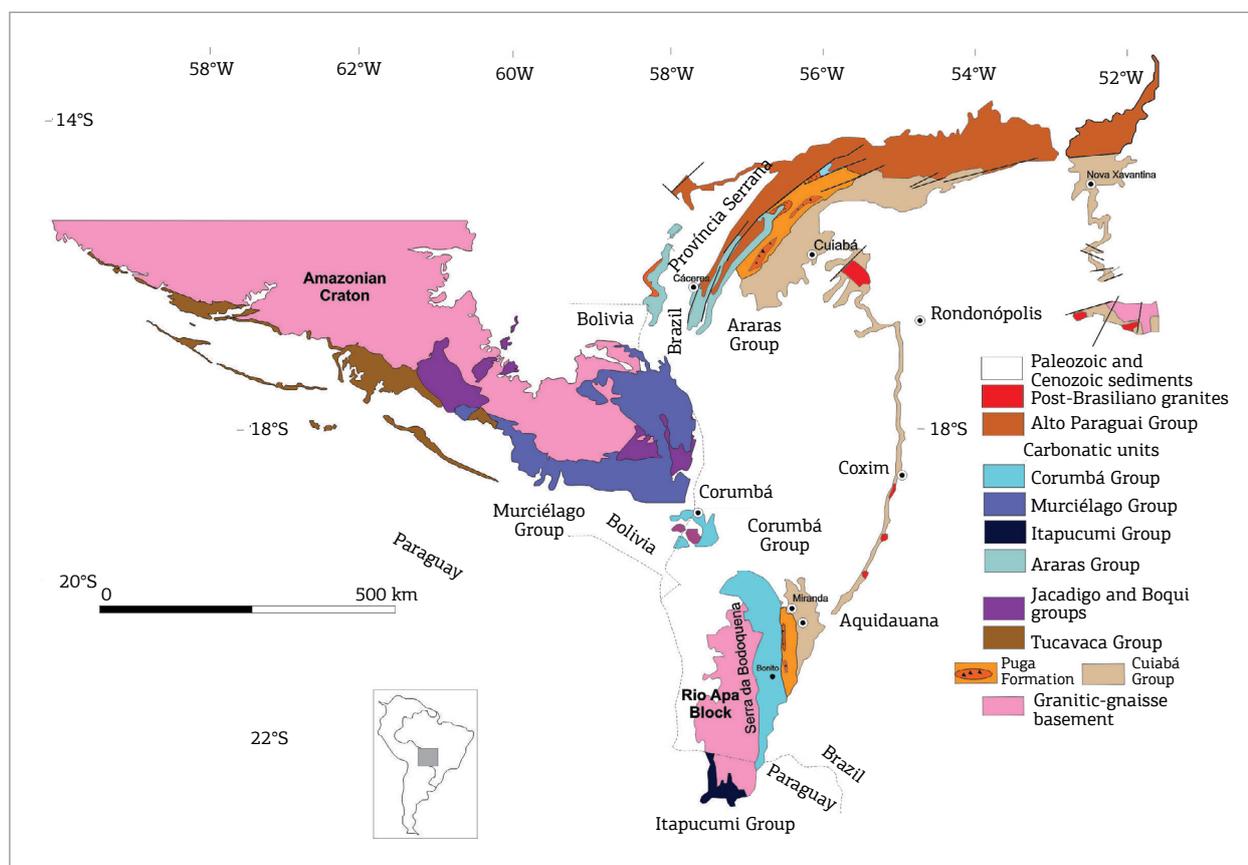


Figure 2. Simplified geological map of the Paraguay Belt showing the areas of outcrop of the Araras, Cuiabá, Corumbá, Itapucumi and the Murciélago groups (modified from Boggiani *et al.* 2010).

d'Oeste Formation), a dark gray laminated lime-mudstone and shale (Guia Formation), and a shallow-water dolostone succession (Nobres Formations) bounded by flooding surface related to an abrupt sea-level rise characterized by a coarsening-upward succession from deep-shale to shallow limestone stromatolites (Pacu Formation).

The basal Mirassol d'Oeste Formation is characterized by laminated dolostone, exhibiting microbialite, wave ripple, and fan-like crystals (Nogueira *et al.* 2003; Nogueira & Riccomini 2006; Alvarenga *et al.* 2008). This 25-m-thick cap dolostone yielded negative $\delta^{13}\text{C}$ values from -10.5‰ to -3.0‰ and $\delta^{18}\text{O}$ values from -8.2 to -1.3‰ VPDB (Nogueira *et al.* 2003, 2007; Alvarenga *et al.* 2004, 2008; Font *et al.* 2006), with high and variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Sr content < 100 ppm) and high Mn/Sr ratios (> 18), interpreted as indication of post-depositional diagenetic alteration (Alvarenga *et al.* 2008). The $\delta^{13}\text{C}$ chemostratigraphic pathway for the basal Ediacaran cap-carbonate (Marinoan) is comparable with $\delta^{13}\text{C}$ stratigraphic profiles worldwide. Marinoan cap-carbonates are described in the São Francisco paleocontinent (Caxito *et al.* 2012; Alvarenga *et al.* 2014), southern Paraguay (Boggiani *et al.* 2003), and Sergipano belts (Sial *et al.* 2010), and in different paleocontinents (Amazonia, Arabia, Arctic, Alaska, Australia, Baltic, Congo, Kalahari, India, Laurentia, Siberia, South China, Mongolia, and West Africa; see Hoffman 2011).

The cap dolostone of the Mirassol d'Oeste Formation is succeeded by transgressive, deep-platformal deposits of dark gray laminated lime-mudstone and shale of the Guia Formation, reaching up to 250 m thick in the middle shelf domain (Nogueira *et al.* 2007; Riccomini *et al.* 2007; Alvarenga *et al.* 2004, 2008, 2011). These transgressive deposits are exposed along more than 200 km from West to East (Alvarenga *et al.* 2008, 2009). Carbon isotope data for rocks of the Guia Formation revealed predominantly negative $\delta^{13}\text{C}$ values, from -3.5 to +0.1‰, and $\delta^{18}\text{O}$ values from -13.5‰ to -6.3‰ (Alvarenga *et al.* 2004, 2008; Figueiredo 2006; Nogueira *et al.* 2003, 2007). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for limestones with higher Sr content (> 750 ppm) and low Mn/Sr ratios (< 0.2) range from 0.7076 to 0.7078 (Alvarenga *et al.* 2008, 2011).

The Nobres Formation consists of a light gray dolostone in a shallow-water succession (900 – 1100 m), showing increasing $\delta^{13}\text{C}$ values from base to top, ranging from -2.2‰ to +2.7‰ in the first hundred meters, while in the upper dolostone $\delta^{13}\text{C}$ values reach +9.6‰ (Fig. 3). $\delta^{18}\text{O}$ values range from -4.7 to -0.1‰ (Pinho *et al.* 2003; Alvarenga *et al.* 2004; Figueiredo *et al.* 2006; Nogueira *et al.* 2007).

A package of about 300-m-thick shale and limestone was recently described as the upper unit of the Araras Group (Souza *et al.* 2012). C-isotope analyses for the uppermost 70 m of stromatolitic limestones include $\delta^{13}\text{C}$ values from

+6.6‰ to +8.9‰, while $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are nearly constant, between 0.7087 and 0.7088 (Souza 2015). The record of the Gaskiers glaciation (Serra Azul Formation) is observed above an erosional surface atop the upper Araras Group, with the Pacu Formation preserved only near the Serra Azul in the eastern part of the North Paraguay Belt (Souza 2015).

Facies distribution, stratigraphy and the $\delta^{13}\text{C}$ stratigraphic profile for the Araras Group match those for the middle Tsumeb Subgroup in Namibia, supporting an Ediacaran age for the Araras Group (Fig. 3). The upper portion of this group shows high $\delta^{13}\text{C}$ values and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, suggesting deposition in the late Ediacaran.

Toward the deeper parts of the basin, carbonate deposition was replaced by fine-grained deposits with low sedimentation rates. Facies and stratigraphic data coupled with C and O isotopes are an evidence of lateral equivalence of the lower units of the Araras Group wherein the Guia syncline, over 250 m thick at the edge of the basin, can be regarded as the break of the carbonate shelf (Alvarenga *et al.* 2004, 2008, 2011). The studied succession in the Guia syncline consists of 150-m-thick black-to-gray lime mudstone and shale with $\delta^{13}\text{C}$ values from -2.5 to -1‰. The $\delta^{13}\text{C}$ stratigraphic profile in this syncline shows a clear correlation with the Guia Formation at the Cáceres region, 250 km away to southwest. At the Cáceres and Nobres region, a thick succession of shallow-water dolostones over 1000 m thick (Nobres Formation) overlies the Guia Formation. The sedimentary rocks of the Guia syncline were deposited in a deeper basin, outside the carbonate shelf, where pelitic sediments are found in its inner portion.

Ca isotopic compositions of post-glacial carbonate successions in central Brazil (Mirassol D'Oeste-Cáceres and Tangará) have been reported by Silva-Tamayo *et al.* (2010). The basal dolostones display $^{44}\text{Ca}/^{40}\text{Ca}$ values between 1 and 0.7‰, while the overlying limestones show a negative Ca-isotope excursion to values around 0.1‰, followed by a positive shift to 2.0‰ values and, then, stabilize upsection to values between 0.6 and 0.9‰. This Ca-isotope secular variation trend is similar to those of Marinoan post-glacial carbonate successions in Namibia, suggesting that the perturbation of the marine Ca cycle was, perhaps, global.

RIO APA CRATONIC BLOCK AND SOUTHERN PARAGUAY BELT: CORUMBÁ GROUP

Corumbá Group

The Corumbá Group is an important stratigraphic unit due to its good preservation, geochronological constraints, and

metazoan fossils in its upper unit, the Tamengo Formation (Almeida 1965; Boggiani, 1998; Gaucher *et al.* 2003; Alvarenga *et al.* 2009; Boggiani *et al.* 2010; Spangenberg *et al.* 2014). This unit bears *Cloudina* and *Corumbella* fossils

associated with volcanic ash levels at the top, which yielded a U-Pb SHRIMP age of 543 ± 2 Ma (Babinski *et al.* 2008).

The 80 – 200-m-thick Tamengo Formation is characterized by black, pure limestone with organic

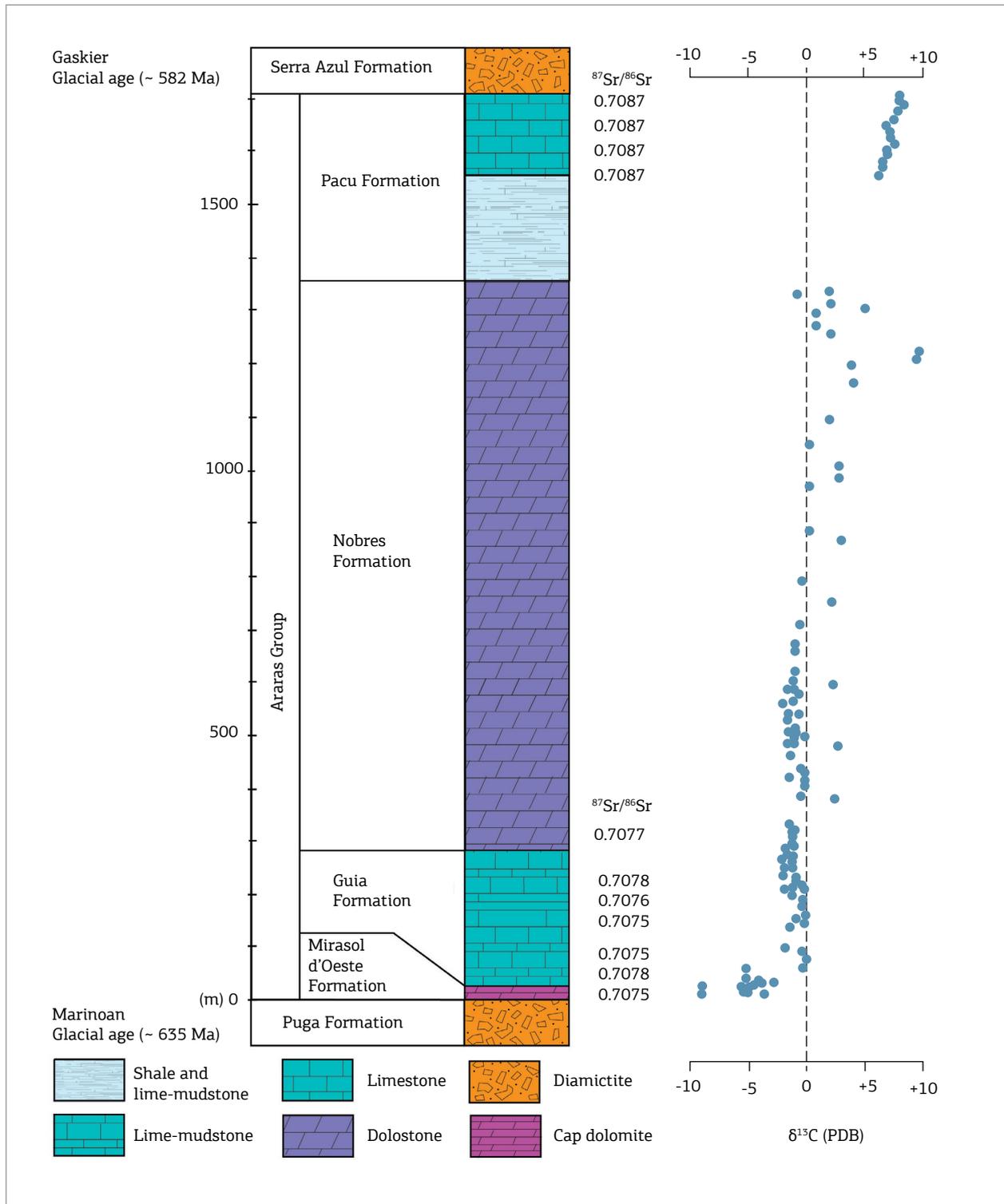


Figure 3. Stratigraphic section and variations of $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ for the Araras Group (data from Nogueira *et al.* 2003, 2007; Alvarenga *et al.* 2004, 2008; Font *et al.* 2006, Figueiredo 2006, Souza 2015).

shale intercalations and rhythmite (black limestone/organic shale), interpreted as deposited in a shelf context (Fig. 4). The metazoan fossils have been observed only in outcrops around Corumbá and Ladário towns, where shallow water conditions prevailed during deposition, attested by hummocky and other cross-bedding structures in grainstones. The Tamengo Formation is the best studied among the units of the Corumbá Group due to its fossil content, C-isotope behavior and the possibility that it may have recorded the Precambrian-Cambrian boundary.

The base of the Corumbá Group is characterized by conglomerate and arkose of the Cadieus and Cerradinho formations, which are restricted to the western border of the Serra da Bodoquena (Almeida 1965; Fig. 4). The deposition of these terrigenous sediments is associated to the development of a rift basin (Boggiani, 1998; Gaucher *et al.* 2003), probably part of a rift system developed in the basement, the Rio Apa Block. The deposition of the Puga diamictite and the manganese/iron formation of the Jacadigo Group are likely associated to the development of this rift system (Urucum Massif; Trompette *et al.* 1998; Walde &

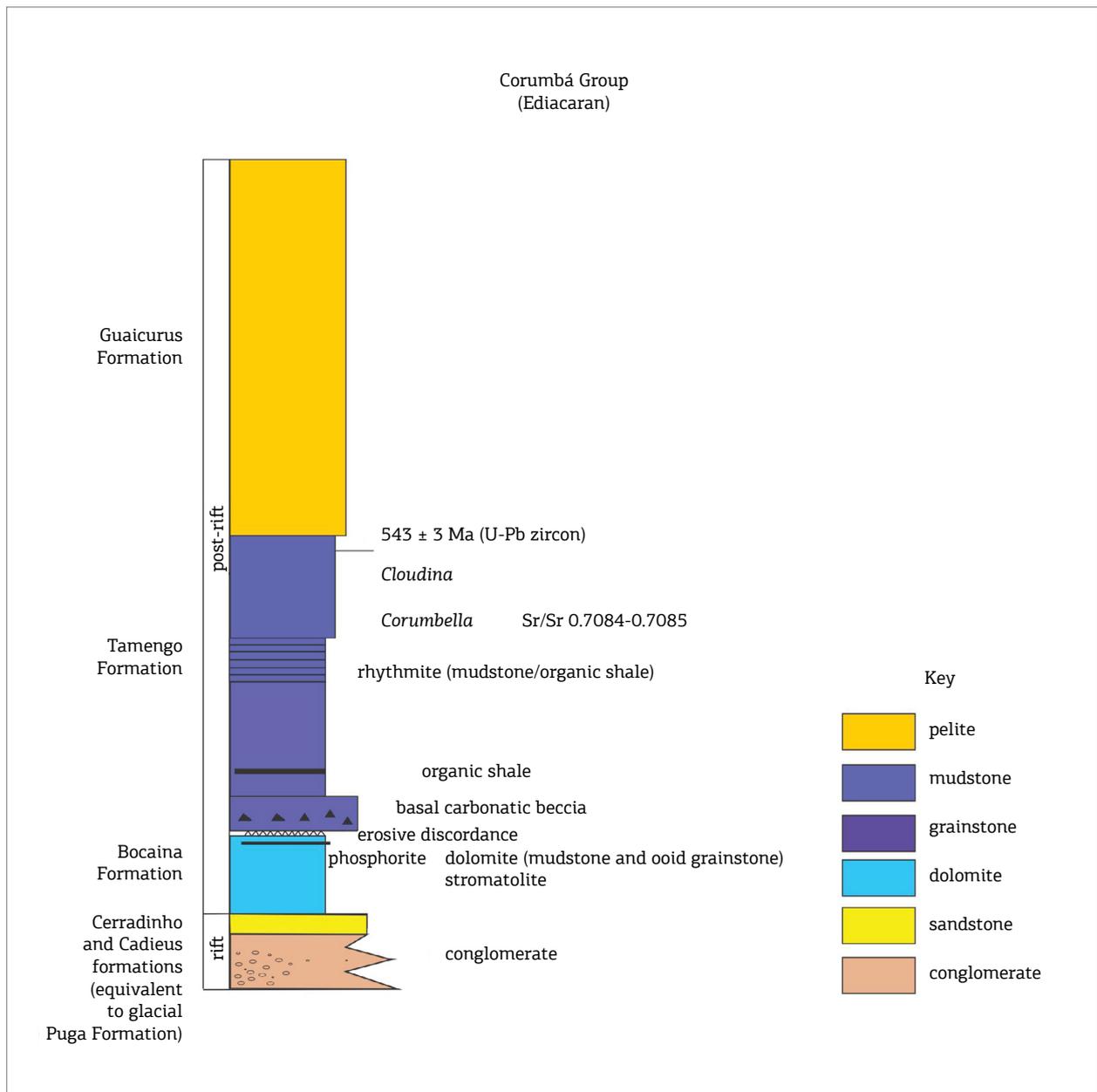


Figure 4. Stratigraphic column of the Corumbá Group, as originally defined by Almeida (1965), with modifications from Boggiani (1998).

Hagemann 2007; Freitas *et al.* 2011). It is worth noting that the Puga Formation was originally described from the southern Paraguay Belt (Maciel, 1959), and is not necessarily time-correlative to the homonymous unit in the northern Paraguay Belt (Alvarenga *et al.* 2011).

The Bocaina Formation is related to thermal subsidence of the Corumbá Basin which promoted shallow deposition under warm water and high-evaporation conditions, responsible of stromatolite proliferation and primary (?) dolomite precipitation. The top of this unit is marked by the occurrence of phosphorite, related to upwelling that testifies the communication with the open ocean (Boggiani *et al.* 1993).

A strong sea-level drop marked the end of deposition of the Bocaina Formation, may be with its exposure, and was responsible for the deposition of an expressive carbonate breccia that defines the base of the Tamengo Formation (Boggiani 1998). This carbonate breccia contains clasts from the Bocaina Formation and from the granite-gneissic basement. The Tamengo Formation records an expressive transgression event contemporaneous to the appearance of metazoan fossils. This formation is overlain by siltstone and shale of the Guaicurus Formation that represents the end of carbonate sedimentation conditions and that probably straddles the Precambrian–Cambrian boundary.

The dolostones of the Bocaina Formation yielded $\delta^{13}\text{C}$ values from zero to $\sim +3\text{‰}$ and $\delta^{18}\text{O}$ VPDB values $\sim -3\text{‰}$ (Boggiani 1998; Fontaneta 2012). Stronger fluctuation of C-isotope values is observed in the Tamengo Formation in which values of $\sim -1\text{‰}$ are common above basal breccias and at about 20 m toward the top, reaching nadir values of -3.6‰ (Boggiani *et al.* 2010; Spangenberg *et al.* 2014). A positive excursion to $+5\text{‰}$ follows, which is associated with the first occurrence of *Cloudina* (Fig. 5). Above the positive C-isotope excursion, the Tamengo Formation is characterized by a plateau of positive values, around $+3\text{‰}$ (Boggiani *et al.* 2010), where some 10 μm -pyrite framboids yielded high positive $\delta^{34}\text{S}$ values, between $+35.9$ and $+43.5\text{‰}$ CDT. Values of $^{87}\text{Sr}/^{86}\text{Sr}$ in the 0.7085 – 0.7086 range characterize limestones of the upper portion of the Tamengo Formation (typical of the Ediacaran–Cambrian boundary).

Carbonate rocks of the top of the Puga Formation diamictite at the Puga Hill in the Paraguay River are interpreted as a cap carbonate. This cap carbonate exhibits rhythmicity of lamination in a deep-red limestone with homogeneous $\delta^{13}\text{C}$ values around -5‰ (Boggiani *et al.* 2003). The deposition of the Puga Formation has been assigned to the early Cryogenian, with youngest detrital zircons yielding ages of 706 ± 9 Ma and 706 ± 12 Ma (Babinski *et al.* 2013).

After about three decades of global chemostratigraphic studies of Neoproterozoic carbonate successions, there is a consensus that negative $\delta^{13}\text{C}$ excursions follow the main

glacial events, identified in Cryogenian cap carbonates, and two Ediacaran negative $\delta^{13}\text{C}$ excursions, one below the first occurrence of skeletal organism (Shuram–Wonoka excursion) and a second one in the Precambrian–Cambrian boundary. One cannot assure that the negative $\delta^{13}\text{C}$ excursion at the base of the Tamengo Formation is a primary feature, since it has not been observed in different sections of this formation, as happens elsewhere (e.g. Oman and Death Valley; Boggiani *et al.* 2010). It is possible that this negative $\delta^{13}\text{C}$ excursion in the Tamengo Formation, associated with black, organic limestone, has resulted from oxidation during deep burial of organic matter. However, positive $\delta^{13}\text{C}$ values in organic limestone in the same stratigraphic position were observed in this formation. This negative $\delta^{13}\text{C}$ excursion is located just below a positive $\delta^{13}\text{C}$ excursion, contemporary with the first occurrence of *Cloudina*. It is of paramount importance in unraveling whether the Shuram–Wonoka C-isotope anomaly is a primary feature or just a diagenetic artifact. If proved to be a primary one, this C-isotope anomaly will encourage further investigation on its relationship with early animal life evolution.

Itapucumí Group, Southern Paraguay Belt

The study of South American Neoproterozoic successions has improved the comprehension of the bioevolutionary, climatic, and geotectonic phenomena coeval with the Rodinia supercontinent rifting. During this time interval, important subsidence cycles took place at the margins of the Amazonian, Pampia, and Rio de la Plata cratons, leading to the deposition of carbonatic and siliciclastic sequences in newly formed basins. These units, as the Corumbá (Brazil), Puncoviscana (Argentina), and Arroyo del Soldado (Uruguay) groups contain important Ediacaran fossils represented by microfossils and skeletal organisms as *Cloudina* sp. and *Corumbella* sp. In this context, the Itapucumí Group is one of the least known Neoproterozoic units (Fig. 6). This group, composed of carbonate and siliciclastic rocks, including ooid grainstones, marls, shales, and sandstones, occurs in northeastern Paraguay as a marginal belt that shows strong deformational pattern at its western edge and forms an almost undeformed sedimentary cover on the Rio Apa cratonic Block, a promontory of the Amazonian Craton (Campanha *et al.* 2010). The Rio Apa Block is delimited at its eastern portion by the Paraguay Belt, a W-vergent thrust-and-fold belt, which is composed of the Ediacaran successions of the Corumbá Group.

The Itapucumí Group is about 400 m thick and comprises siliciclastic rocks of the Vallemí Formation at the base (Fig. 7). These basal layers are composed of immature sandstones interbedded with basalts, covered by an expressive

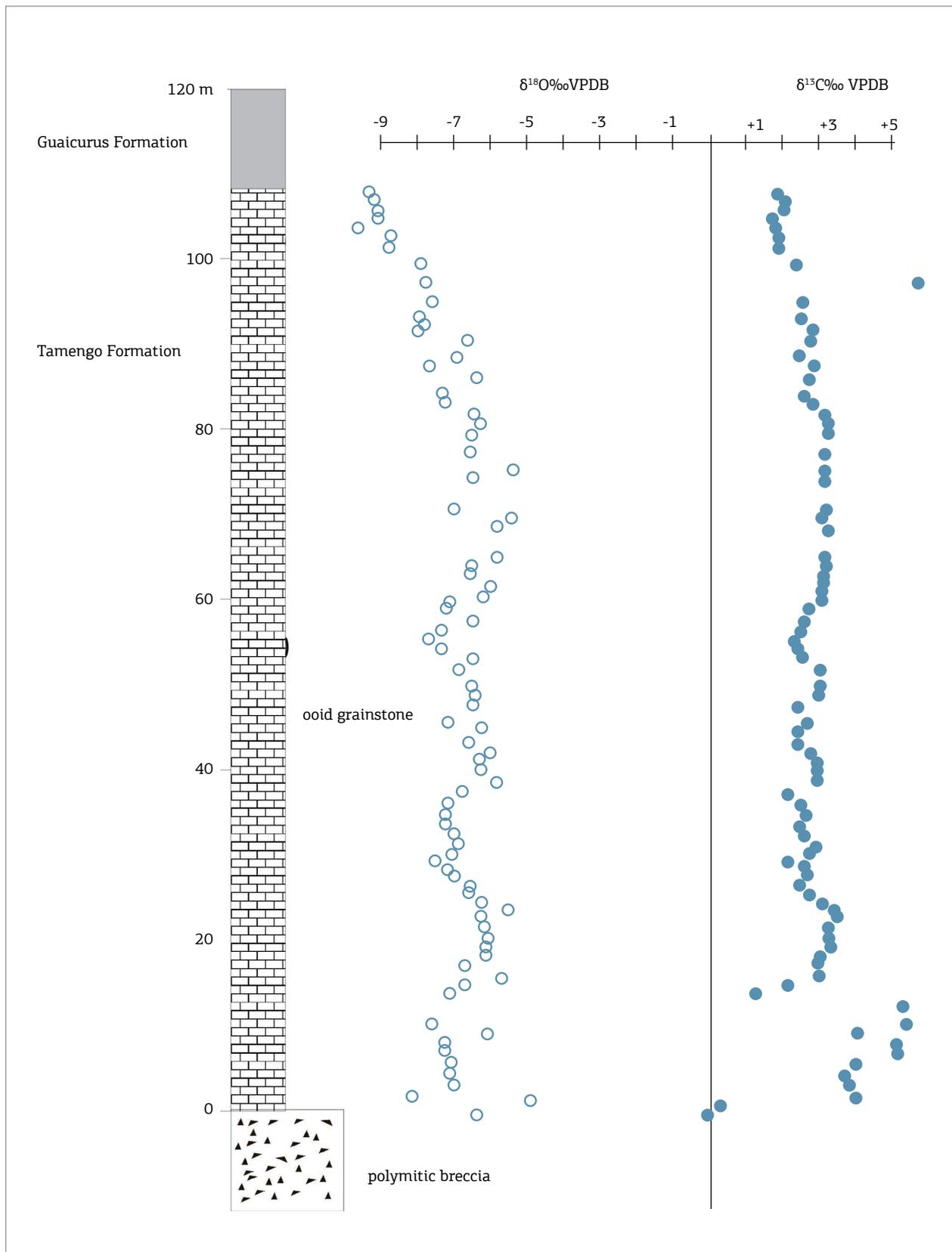


Figure 5. Stratigraphic column and high-resolution chemostratigraphic C and O-isotope data of the Tamengo Formation, Corumbá Group, in the eastern part of Laginha Mine. The contact between the basal breccias and overlying carbonates is faulted and the lower Tamengo Formation is missing (modified from Boggiani *et al.* 2010).

sequence of red beds. This succession is followed by ooid grainstones, microbialites, and dolostones of the Camba Jhopo and Tagatiyá Guazú formations, and capped by dolostones,

marls, and pelites of the Cerro Curuzú Formation (Warren *et al.* 2010; Warren 2011). Close to the Paraguay River, this unit has been metamorphosed in the lower-greenschist facies

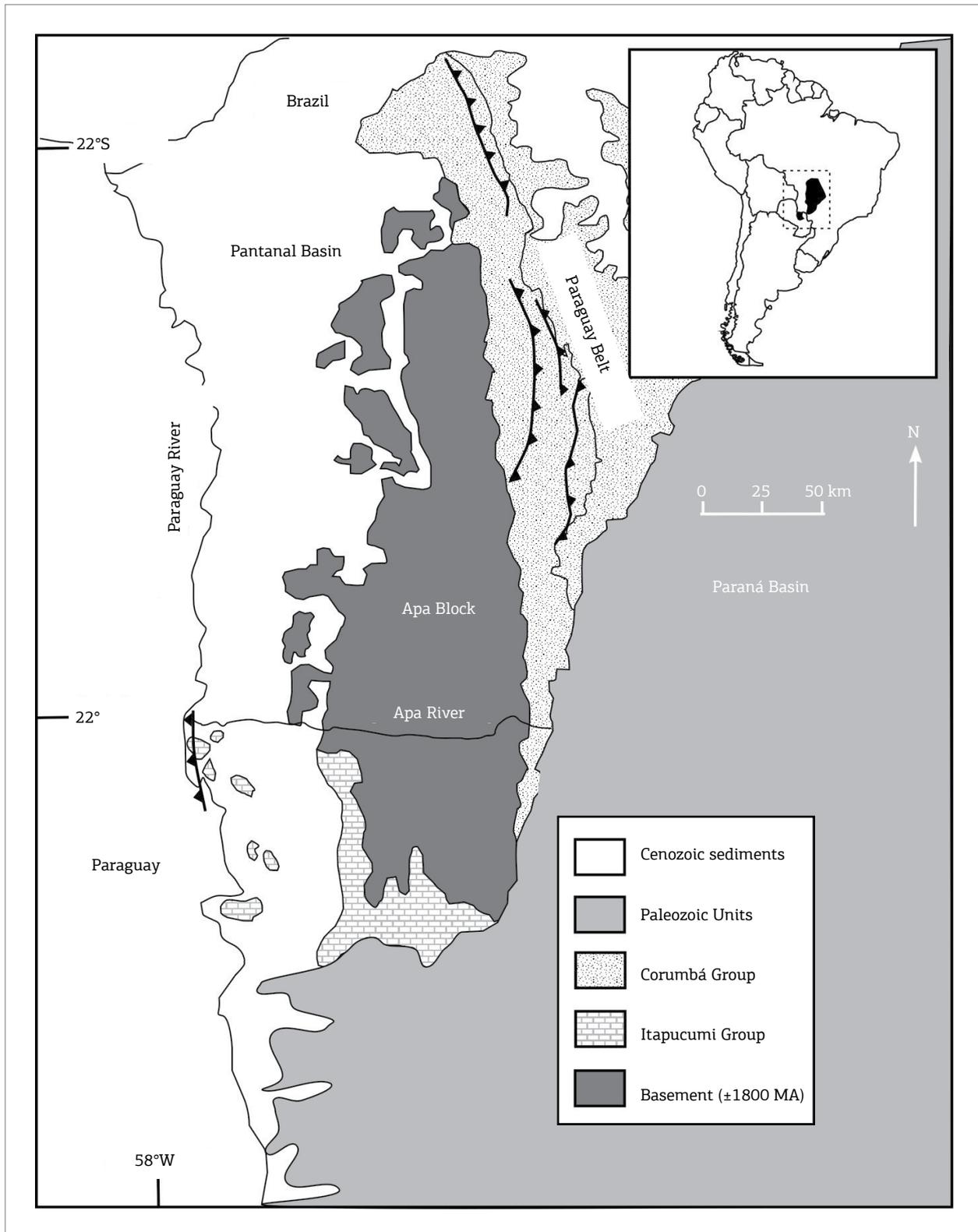


Figure 6. Summary geological map of the area of occurrence of the Apa Block, Itapucumi and Corumbá groups.

and has been intensely deformed, showing E-vergent thrusts and folds, opposite to those of the Paraguay Belt, located in the other margin of the block (Vallemi Belt of Campanha *et al.* 2010). This western Domain of the Itapucumi Group

is characterized by shelf successions of ooid grainstones of the Camba Jhopo Formation, deposited as beach spits and proximal coastal facies. East of these outcrops, the Tagatiya Guazu Formation is not deformed and constitute an extensive

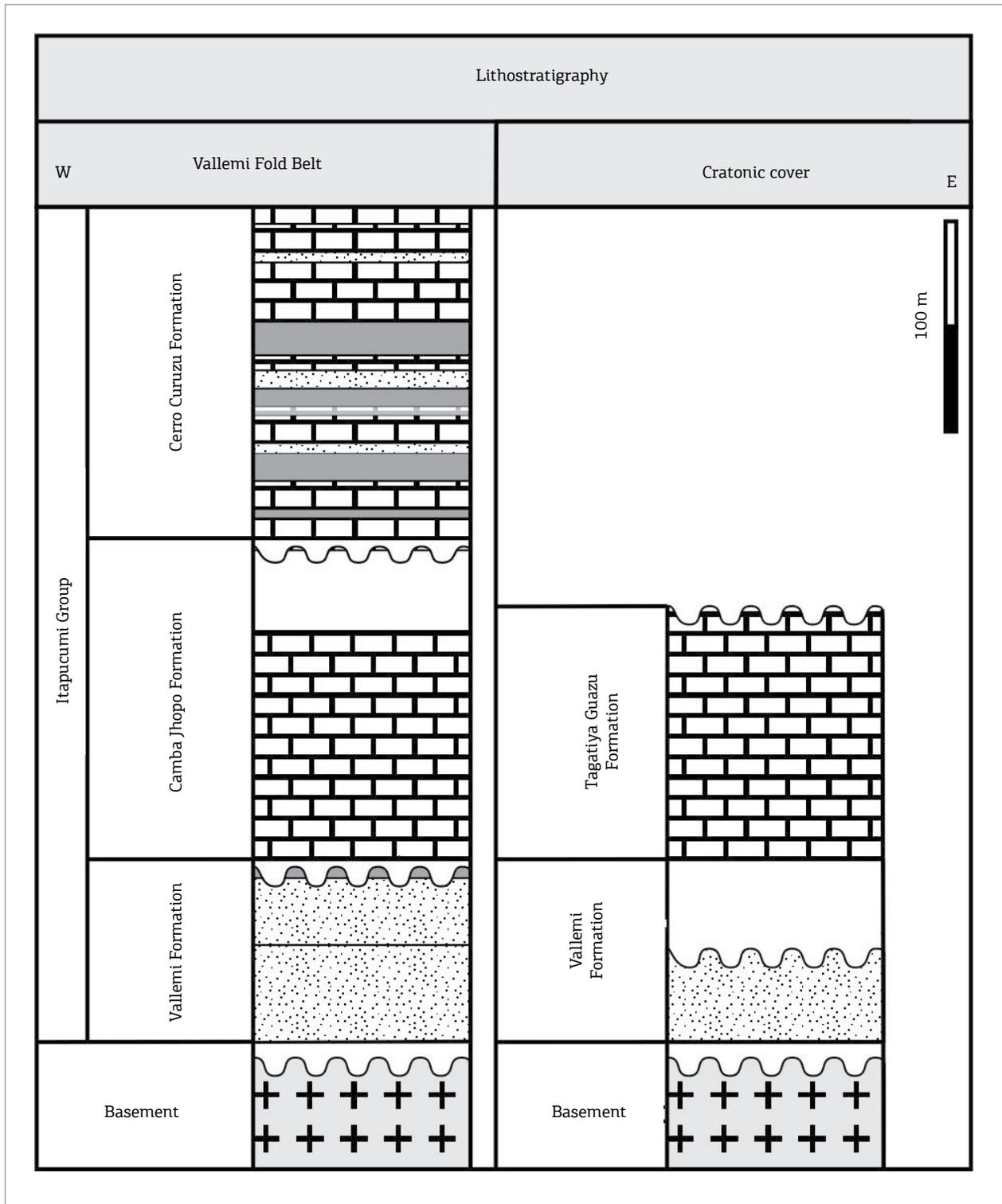


Figure 7. Lithostratigraphy of the Itapucumi Group in the western portion of the Vallemi Belt. Modified from Warren 2011).

cratonic cover comprised by lagoonal facies deposited in inter- to supratidal context, associated with laminated microbialites and thrombolites containing *Cloudina* sp., *Corumbella weneri*, and simple ichnofossils (Boggiani & Gaucher, 2004; Warren *et al.* 2011, 2012). Covering these successions there are pelites, marls, and grainstones of the Cerro Curuzú Formation representing deep-shelf depositional systems with siliciclastic contribution (Warren *et al.* 2010; Warren 2011).

The stratigraphic architecture of the Itapucumí Group successions is similar to that described for the Corumbá Group which is formed by siliciclastic deposits of the Cerradinho, Cadieus, and Puga formations at the base, overlain by carbonate rocks of the Bocaina and Tamengo formations, and pelitic sediments of the Guaicurus Formation at the top. The carbonate units of the Corumbá Group are representative of shallow-water shelf deposits grading into deep-water successions in a transgressive environment, in the same way that lagoon depositional systems grade toward the top to oolitic shoals and coastal bars in the Itapucumí Group. Toward the top of both units, deeper deposits with siliciclastic contribution are representative of retrogradational conditions, which characterizes regional (probably eustatic) sea-level rise. *Cloudina* sp. and *Corumbella weneri* fossils found in the lower portion of the Tagatiyá Guazú Formation attest to a terminal Ediacaran age and the paleoecologic and chronostratigraphic correlation with the Tamengo Formation (Warren *et al.* 2011, 2012).

C-isotope ratios do not show large fluctuations across the Itapucumí Group as commonly observed in Neoproterozoic $\delta^{13}\text{C}$ records (Fig. 8). The Itapucumí carbonate succession yielded positive $\delta^{13}\text{C}$ values, ranging from +0.2 to +3.8‰ (Warren *et al.* 2010; Warren 2011). Levels of microbialites that contain *Cloudina* and *Corumbella* (Tagatiyá Guazú Formation) present average $\delta^{13}\text{C}$ value of +2.45‰ (Warren 2011), supporting the stratigraphic correlation between this unit and the Tamengo Formation in the Corumbá Group. Preliminary $^{87}\text{Sr}/^{86}\text{Sr}$ data of the Camba Jhopo/Tagatiyá Guazú and Cerro Curuzú formations, exhibit mean value of 0.7086, further reinforce this correlation.

Therefore, paleontological, stratigraphical, and isotopic data support the correspondence between the Itapucumí and Corumbá groups, confirming their coeval evolution (Fig. 9). The divergent patterns of tectonic vergence between these two belts could be, perhaps, explained by having the Rio Apa Block acting as a rigid barrier during a Cambrian orogenic event related with the final closure of the Clymene Ocean (Warren 2011; Campanha *et al.* 2010). Alternatively, it could represent a different unit altogether (Poiré, 2014).

Murciélago Group, Tucavaca Belt, Bolivia

Neoproterozoic rocks in Bolivia are found in the Tucavaca Belt, near the town of Santa Cruz de La Sierra, in the southern portion of this country. Litherland & Bloomfield (1981) have summarized a general picture of the geology of the country, McNamee (2001) a model for onset of the Tucavaca Basin, and Pinto-Vasquez (2001), some further details of its geological evolution.

Rocks in the northeastern boundary of the Tucavaca Belt (Fig. 2) are in contact with the Mesoproterozoic basement (Litherland *et al.* 1986) and in its southwestern boundary, are covered by Quaternary sedimentary rocks of the Chaco-Benian Plains regarded as a foreland basin of the Andean Belt. Rocks of the Tucavaca Belt are observed along the railway between the towns of Santa Cruz, in Bolivia, and Corumbá, in Brazil (Hess 1959). Their outcrops can be divided into two groups:

1. one observed near the Bolivia–Brazil boundary, at the Brazilian side, in continuity with the Paraguay Belt that encompasses a thick pack of rocks of the Boquí Group overlain by carbonate rocks of the Murciélago Group, equivalent to the Jacadigo and Corumbá groups of the Paraguay Belt (Chamot 1963); and
2. a second group that corresponds to the Tucavaca Belt, named by Hess (1959), and that extends for over 500 km. These rocks exhibit a NW-SE regional trend, differently from rocks in the Paraguay Belt which are aligned in the N-S direction.

The stratigraphy of the Tucavaca Belt encompasses the Boquí and Tucavaca groups. The Boquí Group is represented by rocks deposited unconformably in a rift basin parallel to the Sunsas Belt, the basement. This group is formed by rocks deposited in three environments:

1. fan-conglomerates of the San Francisco Formation (~2000 m thick);
2. intertidal and lagoonal sediments of the Colmena Formation (~900 m thick); and
3. submarine mudflows of the Cahama Formation (~1,500 m thick).

In the region of Porto Suarez and Mutún, one observes a volcanogenic basal unit below the sequence of rocks included in the Jacadigo Group equivalent to the Cuarrí Formation of the Boquí Group. This volcanic unit has been called Pimienta Formation and the overlying rocks are regarded as tillites. They include other glacial/periglacial deposits as iron and manganese formations (IF) of the Urucum Formation, in the Brazilian side of the Paraguay Belt.

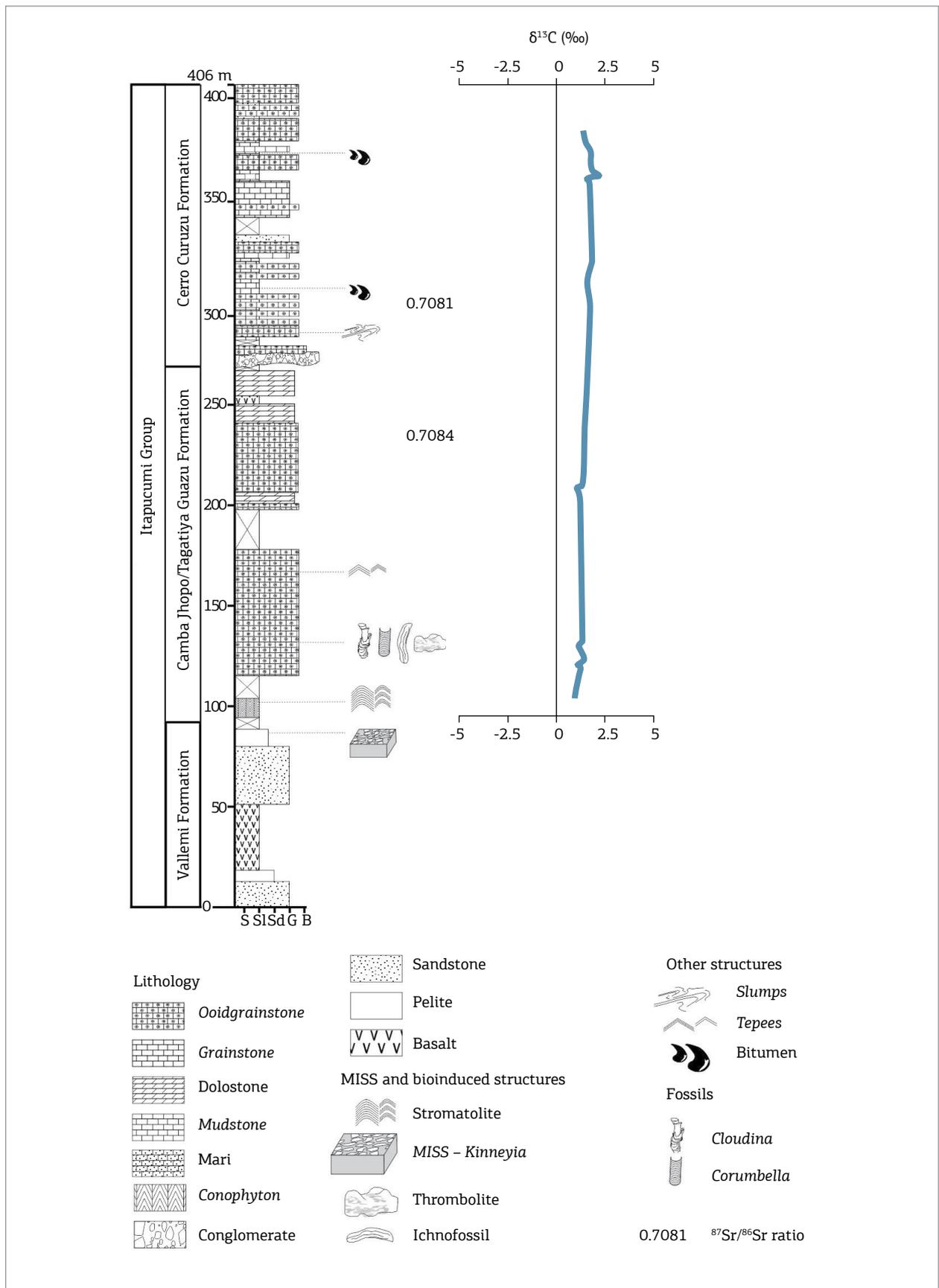


Figure 8. C-isotope chemostratigraphy for the Itapucumi Group (modified from Warren 2011)

The Tucavaca Group has a total thickness of 2,500 m and overlaps the Cahama Formation (youngest unit of the Boquí Group), encompassing a sequence of conglomerates (Pacobilo Formation), finely laminated, gray to pinkish limestones (Pororó Formation), coarse, sometimes micaceous sandstones with rare dropstones (Bocamina Formation). On top of the last one, one observes shales, claystones, and siltites (Pesenema Formation) with intercalations of clastic material (Tarumá Member), metamorphosed at low grade. The Bocamina Formation is stratigraphically correlated to the Motacú (shale and sandstone) and Piococa (arkose) formations that occur in the Tucavaca syncline between the localities of Taperas and Quimóné.

Sandstones and limestones have been identified next to the locality of Murciélago in the region of Porto Suárez, leading to the definition of the homonymous group. The horizontal sedimentary rocks of the Murciélago Group are over 500 m thick and overlap rocks of the Boquí Group. These rocks have been correlated with the Pororó Formation of the Tucavaca Group.

The Tucavaca aulacogen represents a failed rift arm according to Trompette *et al.* (1998) which may mark the boundary between the Río de la Plata and Amazonian cratons (Gaucher *et al.* 2009b). The sedimentary infill of this aulacogen, represented by the Boquí, Murciélago, and Tucavaca groups, correlates with the Jacadigo and Corumbá groups of the southern Paraguay Belt (Avila Salinas 1992), showing that the opening of the Tucavaca Basin took place at approximately 600 Ma (Gaucher *et al.* 2009b). A rhyolite associated with

the Boquí Group in Bolivia (nearby Puerto Suárez) yielded K-Ar age of 623 to 715 Ma (Avila Salinas 1992; Trompette *et al.* 1998). The emplacement of this rhyolite is probably related to continental rifting and, thus, drifting and opening of the Brazilides Ocean in that area is unlikely to have commenced prior to about 600 Ma (Gaucher *et al.* 2009).

Fernández-Ramírez *et al.* (2009) collected stratigraphically seventeen samples of massive limestone and dolostone of the Murciélago Group with horizontal stratification in a continuous profile at a 30-m-high quarry, located between the Roboré town and Santo Corazón village, 4 km from Murciélago. Poorly sorted sandstones and diamictites, stratigraphically below the carbonates of the Murciélago Group were collected at about 1 km to the northeast from the site of collection of the carbonates, following the same road. $\delta^{13}\text{C}$ values for these carbonates are all negative, varying from -0.9 to -1.8‰, and $\delta^{18}\text{O}$ from -4.1‰ to -6.3‰ VPDB (Fig. 10).

SÃO FRANCISCO PALEOCONTINENT AND SURROUNDING BELTS

The Neoproterozoic sedimentary cover of the São Francisco Craton (SFC) is represented by dominant carbonate sedimentation over the cratonic area, deposited in epicontinental (intracratonic) basins. Surrounding the cratonic area, the extensive process of sedimentation provided correlative siliciclastic and carbonate successions

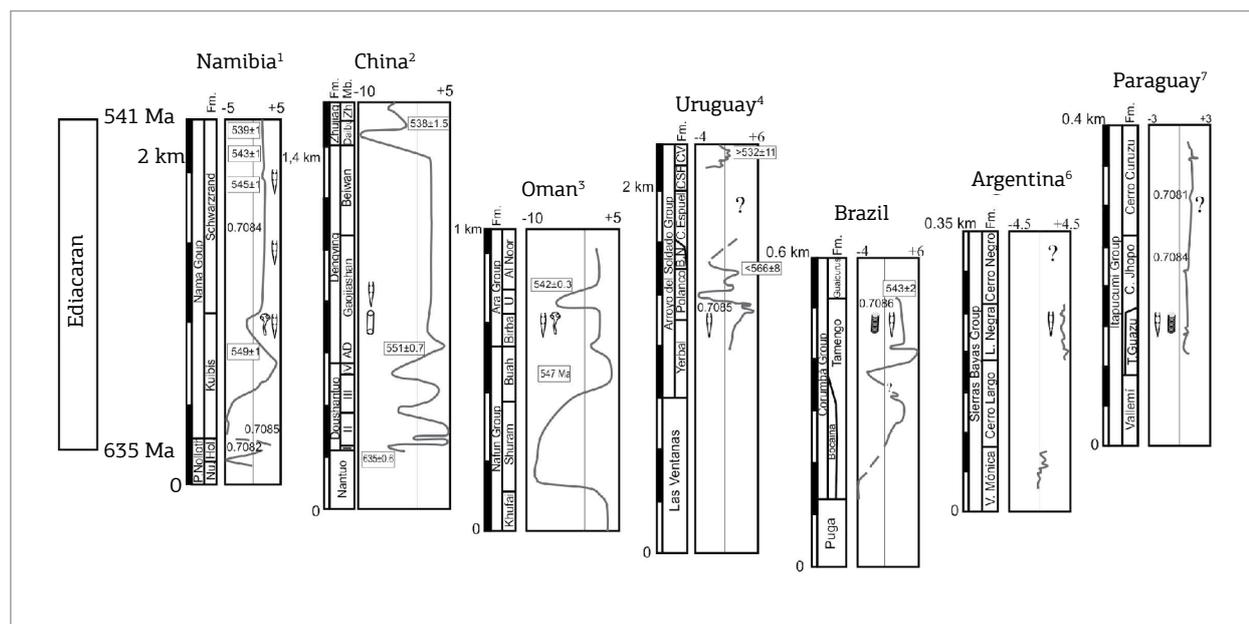


Figure 9. C-isotope chemostratigraphic correlation of the Ediacaran units of the Itapucumi Group with well-known Ediacaran groups worldwide (Namibia, Oman, China, Argentina, Uruguay, Paraguay and Brazil). Modified from Warren *et al.* 2011.

in passive-margin basins present in the Brasília, Araçuaí, Sergipano, Riacho do Pontal and Rio Preto belts, and Rio Pardo Basin (Fig. 11). These belts are marked by intense folding and overthrusting. The intracratonic sedimentary cover is only deformed in the peri-cratonic areas, near the foldbelts. They are preserved in isolated basins and sub-basins in Minas Gerais, Goiás, and Bahia. They include basal assemblages of Paleoproterozoic and Mesoproterozoic ages but here we will restrict the discussion to the Neoproterozoic sedimentary assemblages comprising the São Francisco Supergroup (Alkmim & Martins-Neto 2001; Martins-Neto & Alkmim 2001), which is characterized by a glaciogenic mega-sequence at the base, a carbonate-platform mega-sequence (marine) and a molasse mega-sequence above, separated by first-order unconformities (Misi *et al.*, 2007; Misi *et al.* 2011 and references therein).

Correlations between the stratigraphic successions using parasequence boundaries observed in the different basins and sub-basins, petrographic investigation, and high-resolution chemostratigraphic profiles (mainly $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and

$\delta^{34}\text{S}$), have been suggested by several authors during the last 20 years (Sial *et al.* 2010 and references therein). In the following sections, we will discuss the progress of these studies in the epicontinental (intracratonic) and passive-margin basins (foldbelts).

Neoproterozoic intracratonic basins

The intracratonic successions include the Bambuí Group in the São Francisco Basin (states of Minas Gerais, Goiás and Bahia) and the Una Group in the Irecê, Campinas, Una-Utinga, and Ituaçu sub-basins (Bahia), covering more than 60% of the cratonic area. Despite the proliferation of different names, it is possible to demonstrate the correlation of stratigraphic successions along thousands of kilometers.

A common tectonic evolution is postulated for these basins, during the Neoproterozoic times. Although some authors consider that the sediments have accumulated in foreland basins during compressive tectonic events (e.g. Dardenne 2001, Martins-Neto 2001, among others), others argue in favor of extensional tectonism associated with

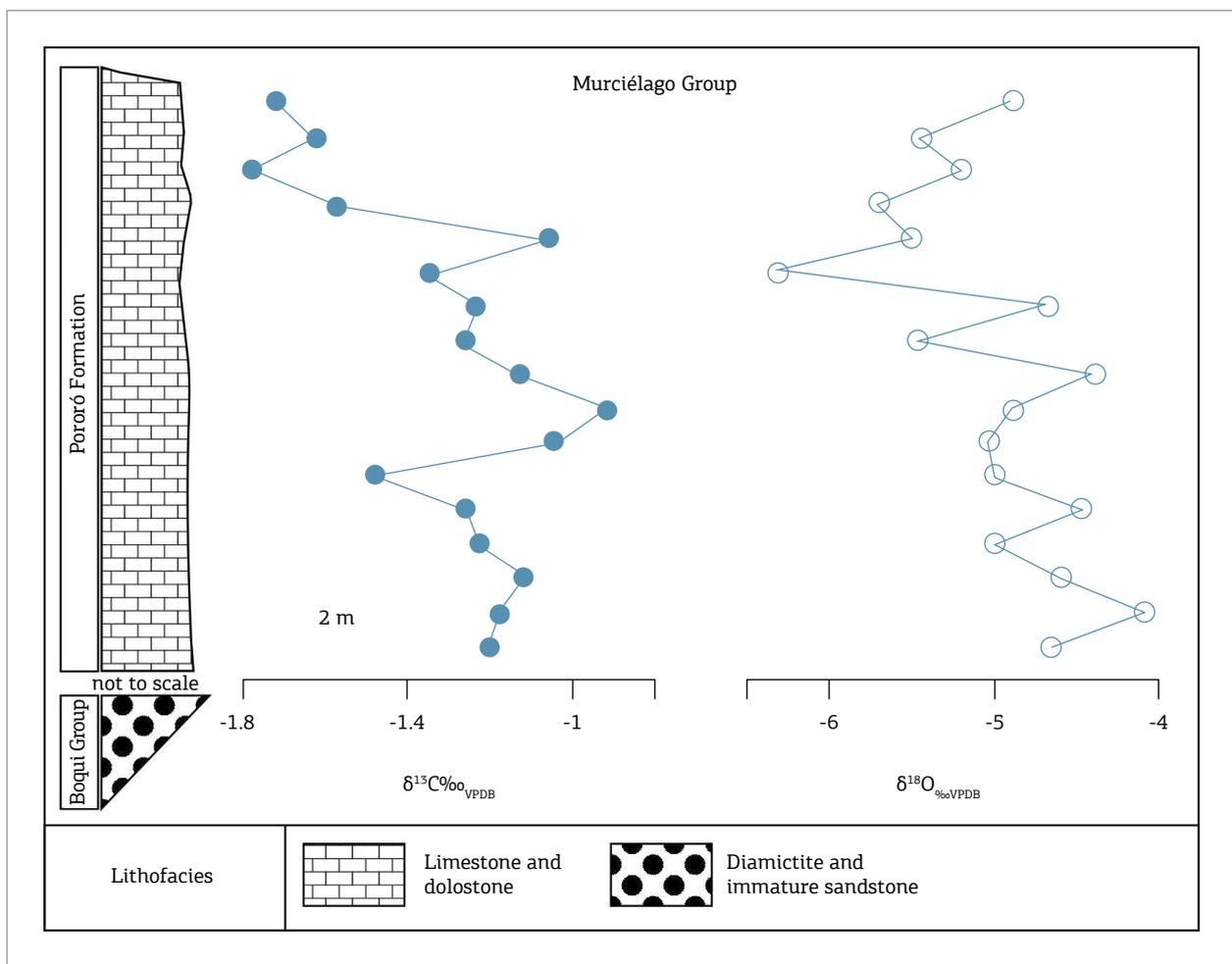


Figure 10. C-isotope chemostratigraphy for carbonates of the Murciélago Group, Bolívia.

glacial diamictites in the basal section (D'el Rey Silva 1999; Misi *et al.* 2011). According to Misi *et al.* (2007), an extensional stage related to the break-up of the Rodinia supercontinent (900 – 600 Ma), responsible for the glaciogenic and marine carbonate mega-sequences, is partially co-incident with the Brasiliano-Pan African orogeny (650 – 500 Ma),

which is responsible for the molasse mega-sequence sedimentation at the upper section. In addition, this collisional stage is determinant of the present structural configuration of the basins, with thrust faults, detachment faults, and verging flexural folds in the peri-cratonic area, including the fold belts (Misi & Veizer 1998). Extensive faults, aligned

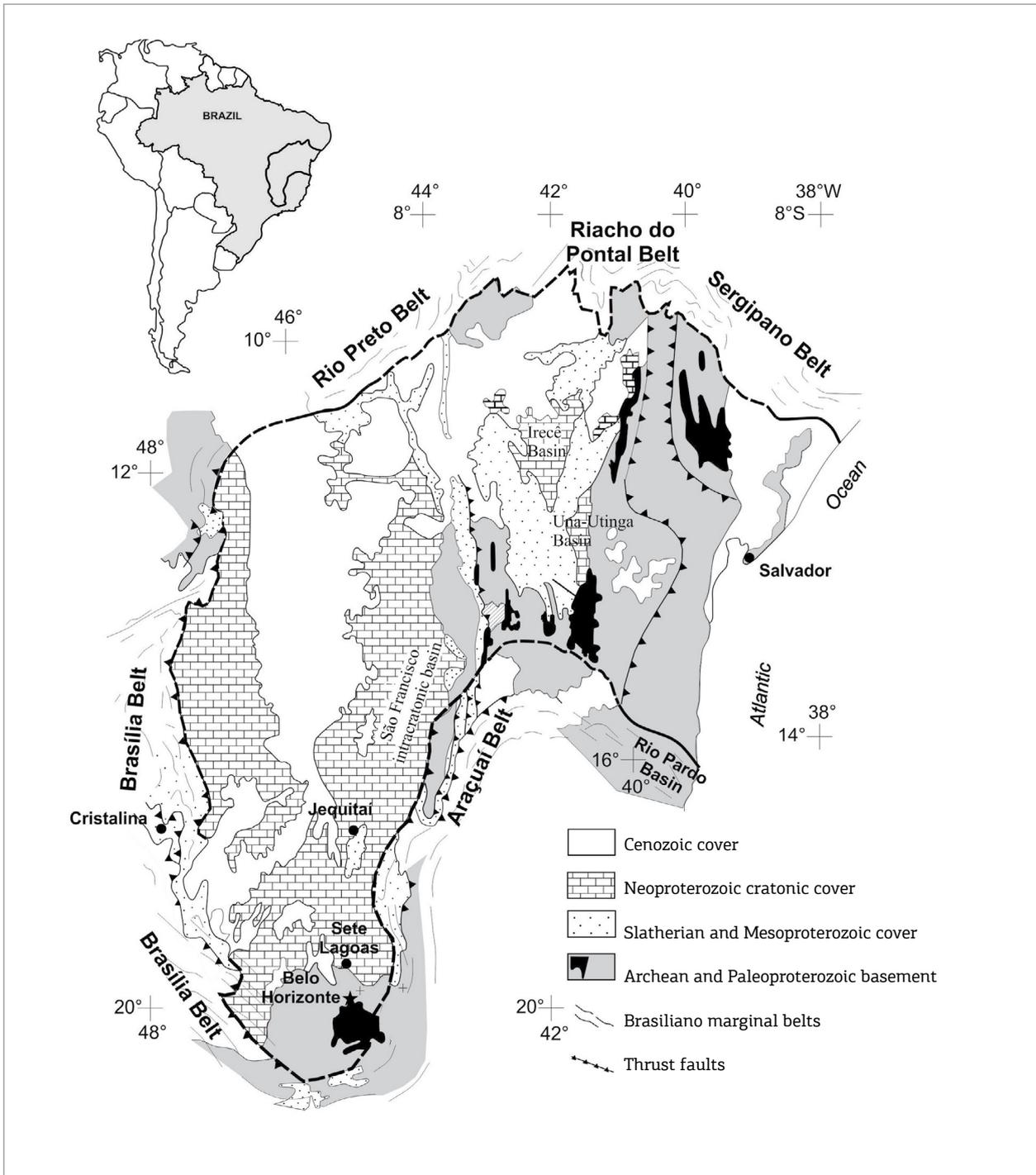


Figure 11. Simplified geological map of the São Francisco craton showing the Neoproterozoic cover and surrounding belts (modified from Sial *et al.* 2010).

NNE-SSW, intersecting the Neoproterozoic cover and the older Proterozoic basement (Alkmim *et al.* 1996; Misi 1999) may represent basement structures reactivated during sedimentation (Misi & Veizer; 1998; Misi *et al.* 2014) (Fig. 11).

Sequence stratigraphy

The Bambuí and Una (São Francisco Supergroup) are formed by carbonate and siliciclastic successions distributed in the following megasequences (Fig. 11):

Glaciogenic

Glaciogenic diamictites are known to occur at least in two stratigraphic positions within Neoproterozoic successions of South America (see Misi *et al.* 2007 and references therein), but in the intratratonic basins of the São Francisco Craton, they are clearly observed only below the carbonate (marine) platform megasequence, represented by the Jeiquitaí Formation (Bambuí Group: São Francisco Basin) and the Bebedouro Formation (Una Group: Irecê, Una-Utinga and Campinas sub-basins). However, Kaufman *et al.* (2008) have

recognized diamictites in association with cap carbonates in Inhaúma district, 25 km from Sete Lagoas, to the East (Sambra Quarry). Although no diamictite has been observed in the area near this quarry, the possibility of correlation with the Inhaúma outcrop is considered in view of the negative $\delta^{13}\text{C}$ shifts measured in the Sambra Quarry (-5‰) as well as in the Inhaúma cap carbonate (-2‰), among others. In the Irecê sub-basin (Una Group), the presence of dolostones in the uppermost section (Unit B1) of the first megasequence showing negative $\delta^{13}\text{C}$ shifts (-4‰, Torquato & Misi 1977), may suggest a discrete glacial event (Fig. 12). No diamictite has been observed.

Carbonate-dominated marine succession

The facies here represented are formed by dolostone, marls, shale, and siltstone. Dardenne (1978, 1979 and 2000) subdivided the Bambuí Group into the following units:

- *Sete Lagoas Formation* – Laminated limestone with dolarenite with teepee structures at the top and red dolostone at the basal section;

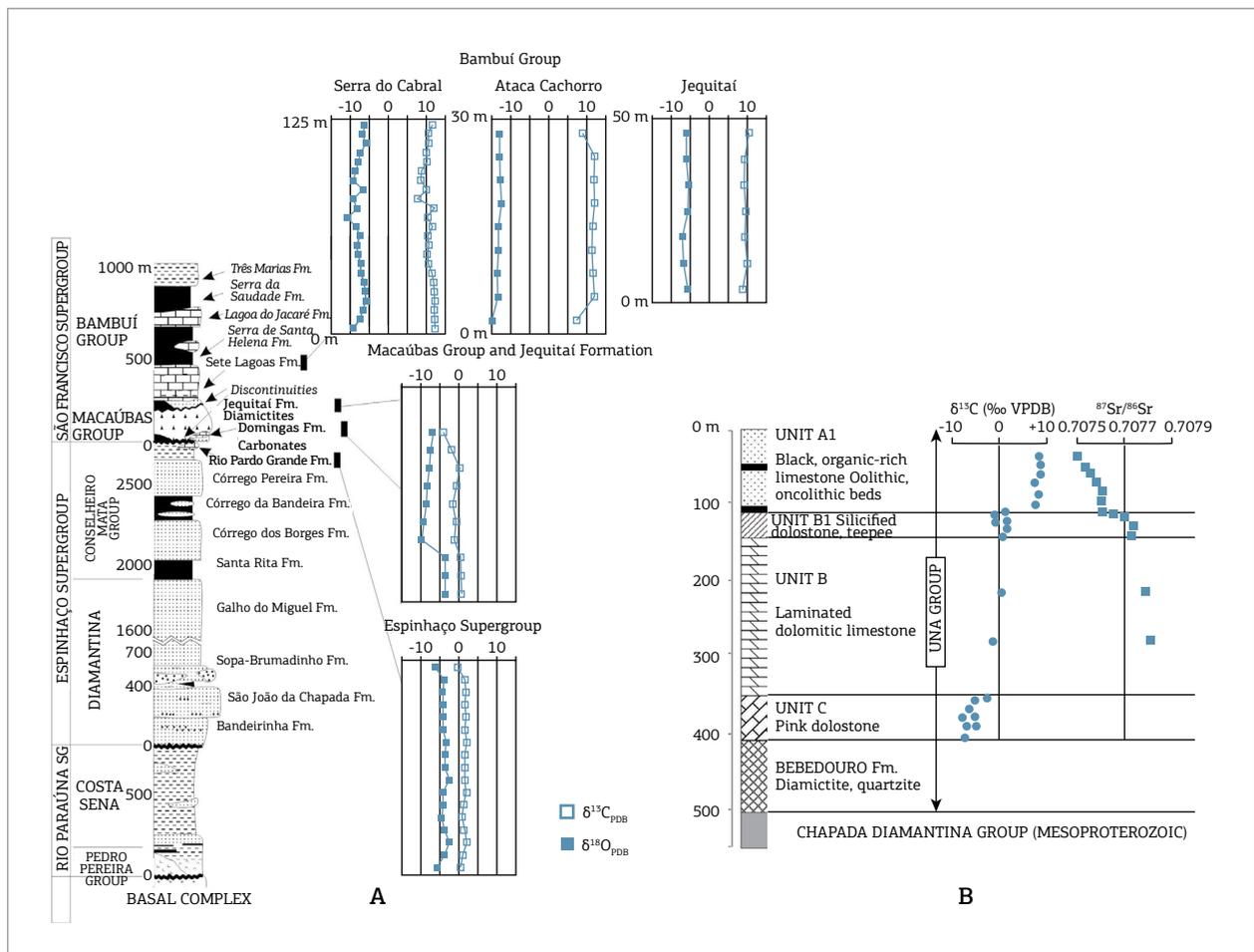


Figure 12. C-isotope chemostratigraphy for the Bambuí (a) and Una (b) carbonate-dominated successions (modified from Santos *et al.* 2000; Misi *et al.* 2011)

- *Serra de Santa Helena Formation* – Marl, siltstones, fine sandstones, and intercalated limestones;
- *Lagoa do Jacaré Formation* – Black, organic-rich intercalated limestone;
- *Serra da Saudade Formation* – Siltstone, pelite, and intercalated limestone;
- The Salitre Formation of the Una Group has been subdivided into five units that correlate with those of the Bambuí Group (Misi *et al.* 2011; Fig. 13).

Siliciclastic continental (molasse) succession

Arkose, siltstone, phyllite, and conglomerate form the Três Marias Formation of the Bambuí Group. These facies are related to foreland sedimentation at the end of the Brasiliano orogenesis. According to Brito Neves & Cordani (1991), the contact between the Três Marias Formation and the Bambuí Group is erosional. These facies are not represented in the eastern side of the SFC (Irecê, Una-Utinga and Campinas sub-basins).

Depositional ages: geochronology and isotopic records

Lack of absolute geochronological ages is still a problem. In the absence of datable volcanic rocks, U-Pb ages on detrital zircons have been used during the last 15 years, resulting in controversial data when compared with other methods applied to the same stratigraphic intervals. For example, Pb-Pb model

age of 740 ± 22 Ma (MSWD = 0.66) from well-preserved sea-floor cements in the Sete Lagoas Formation (Babinski *et al.* 2007), considered the most consistent geochronological data until recently, is now contested by recent U-Pb ages of detrital zircon 610 Ma from the same stratigraphic interval, that is, possibly representing the maximum age of the Sete Lagoas Formation (Pimentel *et al.* 2011). On the other hand, U-Pb SHRIMP ages on detrital zircons from diamictites at the base of the Araçuaí Belt give a maximum age of 950 Ma (Pedrosa Soares *et al.* 2000) and from clasts of diamictite from the Bebedouro Formation, central-eastern Bahia, reveal Archean and Paleoproterozoic populations, but the youngest detrital zircon dated 874 ± 9 Ma (Figueiredo *et al.* 2009). The discovery of the Neoproterozoic index fossil *Cloudina sp.* associated with other trace fossils in the Sete Lagoas Formation (lower Bambuí Group) has been reported by Warren *et al.* (2014) who propose, at least for exposures in central eastern Brazil, terminal Ediacaran age (550–542 Ma). Archean to Paleoproterozoic U-Pb SHRIMP ages of detrital zircons from carbonate platform of the basal and mid-sections of the Salitre Formation (Unit B, according to Misi & Souto 1975, correlated to the mid-section of the Sete Lagoas Formation) have been reported by Santana *et al.* (submitted). Besides, they reported detrital zircon from a tuffite layer associated with deep-water mud-lithofacies, and possibly related to active volcanism in the passive marginal basins during mud sedimentation, with a concordia age of 669 ± 14 Ma.

Brasiliano Fold Belt Passive-margin Basin		Intracratonic Basins			Sergipano Fold Belt Passive-margin Basin
VAZANTE GROUP (Formations)		BAMBUÍ GROUP (Formations)	UMA GROUP (Units) (Form.)		VAZA BARRIS/MIABA GR. (Formations)
Mesoproterozoic Units (overthrusted terrain)	Serra da Lapa	Três Marias	-		-
	Morro do Calcário	Serra da Saudade	-		-
	Serra do Poço Verde	Lagoa do Jacaré	A1	Salitre Formation	Olhos d'Água
	Serra da Garrote	Serra de Santa Helena	A		
	Lagamar	Sete Lagoas 3	B1		
		Sete Lagoas 2	B		
Rocinha	Sete Lagoas 1	C			
Santo Antônio do Bonito	Jequitáí	Bebedouro		Ribeirópolis	
					Palestina Simão Dias Group Jacoca

Figure 13. Correlation between the Vazante Group and Vaza Barris/Miaba groups (passive margin basins) and Bambuí, Una, Vazante, Miaba/Vaza Barris (intracratonic basins). Modified from Misi *et al.* (2011).

Despite these controversial ages, the isotopic record for $^{87}\text{Sr}/^{86}\text{Sr}$ in well-preserved carbonates from the intra-cratonic basins of the Bambuí and Una groups (0.7074 to 0.7078), associated with remarkable negative and positive $\delta^{13}\text{C}$ shifts, indicate possible sedimentation age between early Cryogenian and early Ediacaran (720 – 600 Ma) (Fig. 14; data plotted on Fig. 4 of Halverson *et al.* 2010). In this figure, data obtained in Otavi and Lufilian sequences in Africa are considered for correlations, in view of the reliable absolute geochronological data (from associated volcanic rocks) available (see Kaufman *et al.* 2009 and references therein). Lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios observed in cap carbonates of the Otavi Group and Lufilian Arc (0.7066) is probably due to differences in the tectonic and diagenetic evolution of Brazilian and African basins (Kaufman *et al.* 2009).

Kuchenbecker *et al.* (2016) stated that local inputs may control marine $^{87}\text{Sr}/^{86}\text{Sr}$ and not global processes, something which goes against the present knowledge of the Sr system. The high residence time of Sr in the ocean (2.7 Ma) and the relatively high Sr concentration in seawater (7.5 ppm) make a local control highly unlikely (see Jacobsen & Kaufman

1999 and Veizer *et al.* 1999). In fact, the discrepancies that these authors correctly identified arise from a lack of reliable data for much of the Neoproterozoic, and thus a still poorly known global curve for that era. Furthermore, the different preparation methods for Sr isotopes may also contribute to this problem (see Melezhik *et al.* 2001).

Kuchenbecker *et al.* (2016) have mentioned that the Bambuí Basin may have been restricted, but did not mention occurrence of evaporite or extensive black shale deposits as further evidence. The occurrence of cosmopolitan fossils, such as Cloudina, militates against this restricted scenario.

THE NEOPROTEROZOIC SURROUNDING BELTS

The Brasília Belt and Cratonic sedimentary cover

The Brasília Belt is a Neoproterozoic orogen, formed along the western margin of the São Francisco-Congo Craton.

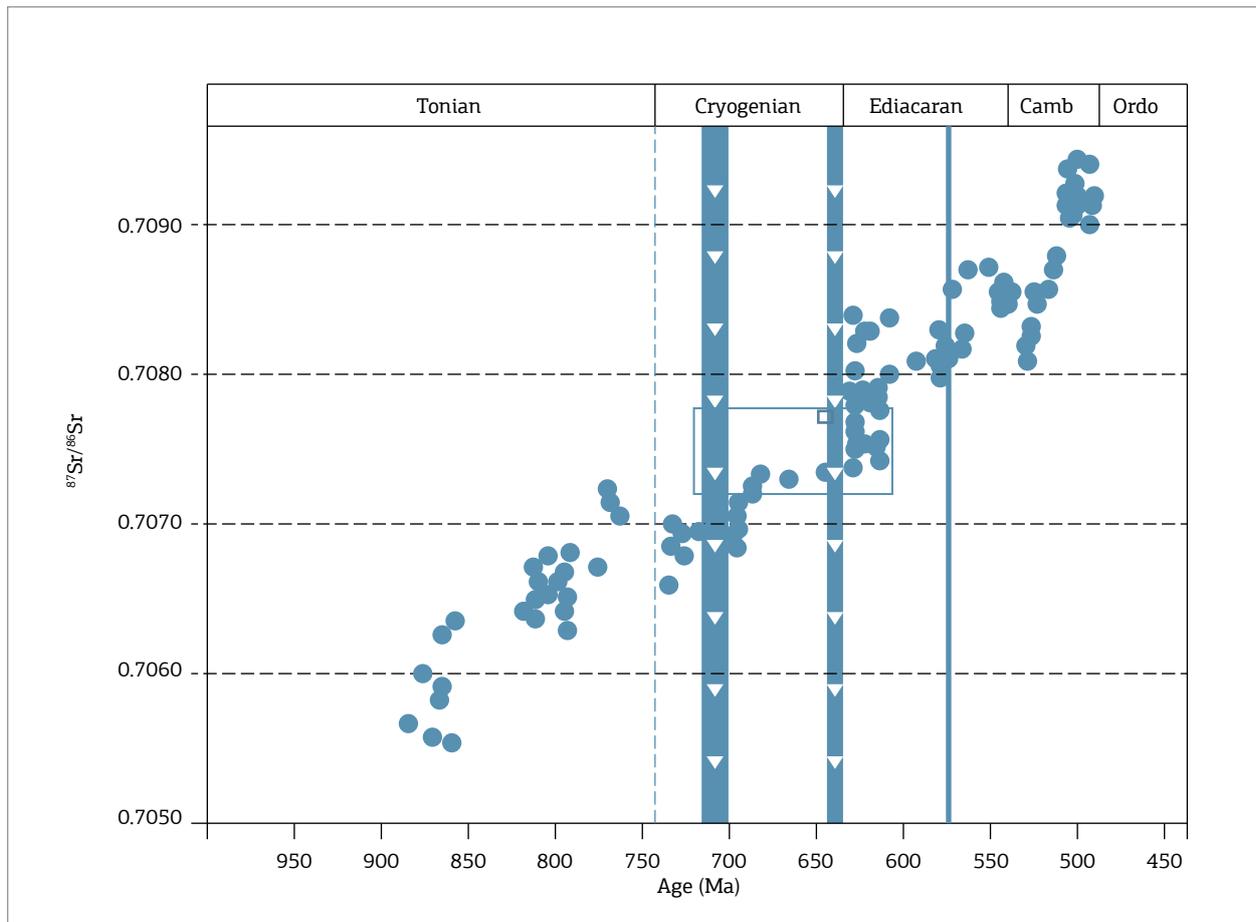


Figure 14. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for carbonates from the Bambuí and Una groups plotted against age on the Fig. 4 of Halverson *et al.* (2010).

Most of the orogen is formed by sedimentary/metasedimentary units, with different tectonic significances and ages. For example, the Paranoá and Canastra groups most likely represent passive margin sequences, the Araxá Group is a fore-arc sequence, and the Bambuí Group which occupies the eastern part of the belt and also covers large areas of the craton, may represent a foreland sequence (Pimentel *et al.* 2011; Fig. 15). The Bambuí Group is represented by

carbonate and siliciclastic sequence overlying glacial diamictes of the Jequitai Formation of unknown age.

The depositional ages of these sequences are still controversial, mostly due to the apparent lack of volcanic layers, as well as the scarce content of diagnostic fossil associations. Pb-Pb whole-rock data for basal carbonates of the Sete Lagoas Formation (base of the Bambuí Group) indicate the depositional age of ca. 740 Ma (Babinski *et al.* 2007), suggesting

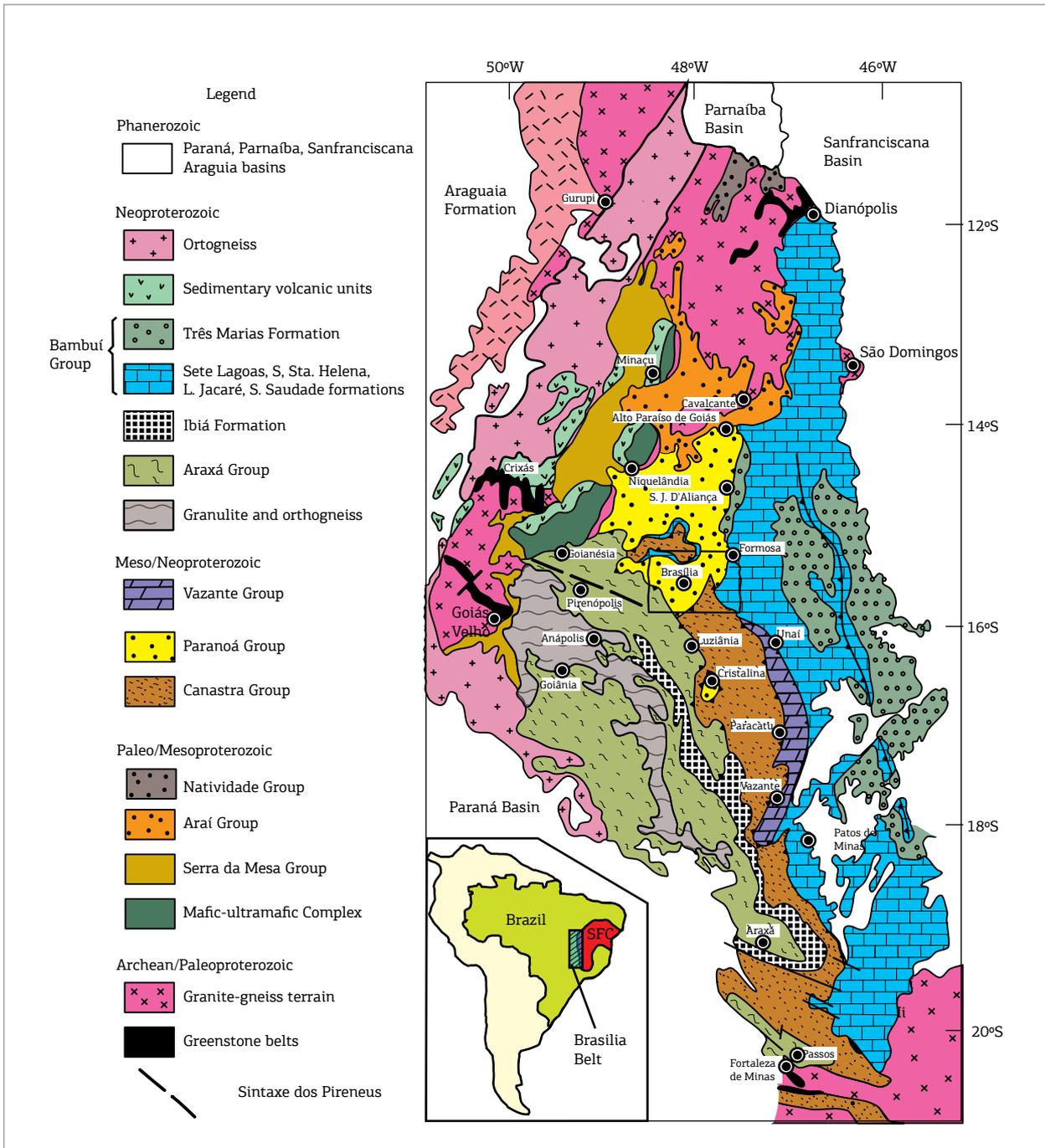


Figure 15. Simplified regional geological map of the Brasília Belt showing the distribution of the Vazante Group (after Marini *et al.* 1984, Dardenne 2000, Pimentel *et al.* 2000; Valeriano *et al.* 2004; modified from Misi *et al.* 2011).

an early Cryogenian or late Tonian age (Shield-Zhou *et al.*, 2016) for the Jequitaiá diamictites which is compatible with C and Sr isotopic data for the cap carbonate. However, metapelites of the upper Sete Lagoas Formation, as well as the rest of the overlying formations of the Bambuí Group, contain zircon grains with important populations with ages of ca. 600 Ma, and even some of these metasediments have a few zircon grains as young as 550 Ma (Pimentel *et al.* 2011, Paula Santos *et al.* 2014) suggesting an Ediacaran age for the unit. Recent paleontological discoveries of Ediacaran fauna in the Sete Lagoas Formation indicate depositional age of ca. 550 Ma (Warren *et al.* 2014), which agrees with the presence of the younger detrital zircon population. This recent data suggest, therefore, that part of the Sete Lagoas Group and the remaining overlying units have depositional ages close to the Precambrian-Cambrian boundary.

Carbonate rocks of the Paranoá and the Bambuí groups have been investigated for their C, O, and Sr isotopic compositions (Santos *et al.* 2000; Alvarenga *et al.* 2007, 2014). Santos *et al.* (2000, 2004) demonstrated that the isotopic patterns vary in the studied profiles, although a general positive excursion is observed toward the upper parts of the Bambuí Group. These authors have shown in the investigated profiles (São Domingos area) a sharp increase in the $\delta^{13}\text{C}$ values at the very top of the Sete Lagoas Formation (+9 to +12‰), a signal which is common to all profiles investigated, representing a regional stratigraphic marker (Santos *et al.* 2000). Carbonates of the underlying Paranoá Group have consistently lower $\delta^{13}\text{C}$ values (normally close to 0‰).

Similarly, carbonates of the Paranoá and Bambuí groups are very different in terms of their $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Values between 0.7056 and 0.7068 are observed in upper carbonates of the Paranoá Group and higher values are recorded in Bambuí carbonates (0.7074 – 0.7080; Alvarenga *et al.* 2014). The C and Sr isotope stratigraphic data indicate very distinct characteristics for these two carbonate sequences. The data for the Paranoá carbonates are consistent with a Tonian sedimentation age, before the first Cryogenian glaciation. On the other hand, carbonate facies and isotope data for the Bambuí carbonates suggest deposition after the second Cryogenian glaciation.

As pointed out by Santos *et al.* (2000), the clear isotopic differences between the Paranoá and Bambuí groups indicate deposition in different paleoenvironments and different kinds of basin. According to these authors, based on the $\delta^{13}\text{C}$ values, it may be postulated that the Paranoá Group sediments deposited on an open-marine platform (passive margin sequence?) whereas the Bambuí sequence formed in a restricted epicontinental sea affected by tectonic events of the Brasília Belt. This is compatible with the tectonic evolution suggested by Pimentel *et al.* (2011) based on

provenance studies of the Brasília Belt. The common presence of Neoproterozoic zircon grains in the Bambuí Group is compatible with the erosion of adjacent Neoproterozoic mountains, in a foreland setting.

Rio Pardo Basin and Rio Preto Belt

The Rio Pardo Basin is located in the southeastern border of the São Francisco craton, between São João do Panelinha and Itapebi villages in Bahia, eastern Brazil (Fig. 16). This basin is divided into two sub-basins, separated by a reverse fault: the southwestern sub-basin was involved in the folding of the Araçuai Belt; sedimentary rocks of the northeastern sub-basin have been deposited on the foreland of this belt on the São Francisco Craton.

The Rio Pardo Group comprehends, from base to top, the following litho-stratigraphic units (Pedreira 1999; Sial *et al.* 2009):

1. Panelinha Formation underlies the other formations of this Group and consists of conglomerate, breccia, greywacke, and arkose. Diamictites with clasts of granulite and volcanics are, perhaps, glacial in origin;
2. Itaimbé sub-group that encompasses the intermediate formations of the Rio Pardo Group, from north to south:
 1. Camacan Formation (pelite, siltite and carbonate rocks);
 2. Água Preta Formation (phylite, sandstone, siltite, slate and carbonate rocks);
 3. Serra do Paraíso Formation (carbonate rocks locally with stromatolites, and quartzite);
 4. Santa Maria Eterna Formation (quartzite, conglomerate and carbonatic intercalations with tepee structures);
 5. finally, turbidites of the Salobro Formation overly discordantly the Camacan Formation and are in tectonic contact with the Água Preta Formation (greywacke, siltite, sandstone, and conglomerate); and
3. Salobro Formation (polymitic conglomerate, greywacke and sandstone). Sedimentary rocks of the Rio Pardo Group have been metamorphosed in the greenschist facies.

Carbonate rocks of the Serra do Paraíso Formation (Rio Pardo Basin) are seen in sharp contact with diamictite/arkose of the São João do Panelinha Formation and same situation with respect to carbonate rocks of the São Desidério Formation (Rio Preto Belt) in relation to the Canabrinha diamictite. It is possible that cap carbonates are present in both cases.

Carbon-isotope stratigraphy of the Serra do Paraíso and São Desidério formations could be useful tool to demonstrate this hypothesis. Only a preliminary C-isotope survey was done on carbonates of the Rio Pardo Basin but the lack of clear stratigraphic control on the analyzed samples preclude further stratigraphic interpretation (Costa

Pinto 1977). C and O isotopes have been analyzed in a total of 173 carbonate samples from the Paraíso and São Desidério formations (Cezario *et al.* 2011) aiming at a high-resolution isotope stratigraphy and elucidating the paleoclimatic issue. At the eastern portion of the Água Branca Range, a section (17 m) on buff dolostone, they found $\delta^{13}\text{C}$ values around -2‰. At the western side of the Agua Branca Range, a section (12 m) of gray limestones in a folded sequence of rhythmites exhibit $\delta^{13}\text{C}$ values from +3.5 to +6‰ and a section to the north of Pau Brasil village (12 m) shows values from +7 to +9‰. A composite C-isotope section is found in Figure 17 and the $\delta^{13}\text{C}$ pathway resembles that observed in successions with basal cap carbonates.

The Rio Preto Belt is located at the northwestern border of the São Francisco Craton (Fig. 18) as an example of an intracontinental belt (Egydio-Silva 1987; Egydio-Silva *et al.* 1989; Andrade Filho *et al.* 1994; Trompette 1994; Sial *et al.*

2009) and is considered a marginal belt forming an extension, to the west, of the Riacho do Pontal and Sergipano belts. These sedimentary successions are an equivalent to those of the São Francisco Supergroup in Bahia. From south to north, the Rio Preto Belt can be subdivided into three structural units:

1. southern unit, region of São Desidério, the sequence begins with limestone with argillaceous intercalations (50 m thick, horizontal layers) and shows no sign of metamorphism or deformation (cratonic domain). This unit was called São Desidério Formation (Egydio-Silva *et al.* 1989) probably equivalent to the Sete Lagoas Formation of the Bambuí Group, Minas Gerais;
2. to the north, inwards the belt, limestones are overlain by clastic rocks that show intercalations of marls and limestones (Serra da Mamona Formation), a sequence probably correlated with the Santa Helena Formation (Egydio-Silva *et al.* 1989);

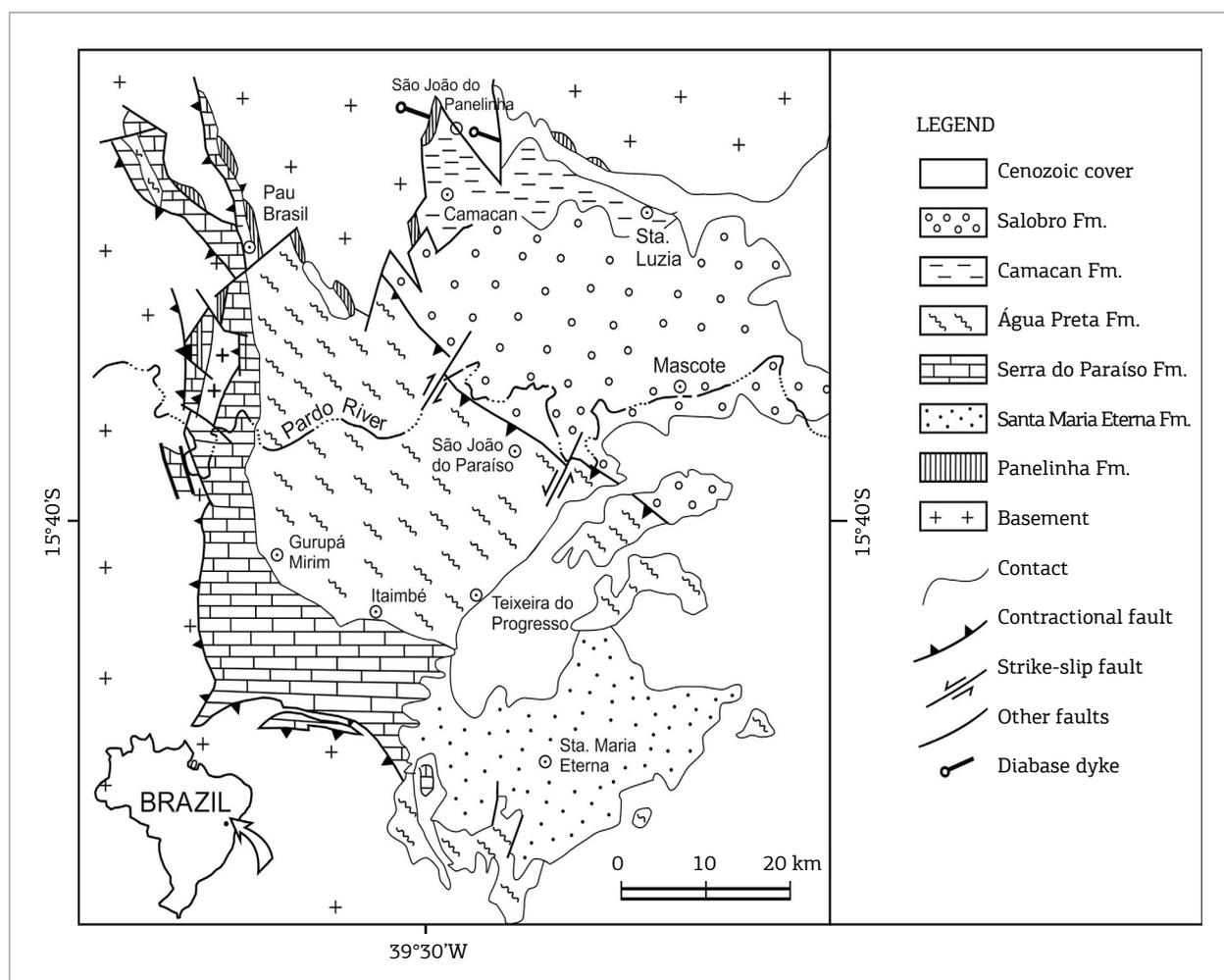


Figure 16. Simplified geological map of the Rio Pardo Basin, eastern São Francisco Craton (modified from Pedreira 1999; Sial *et al.* 2010).

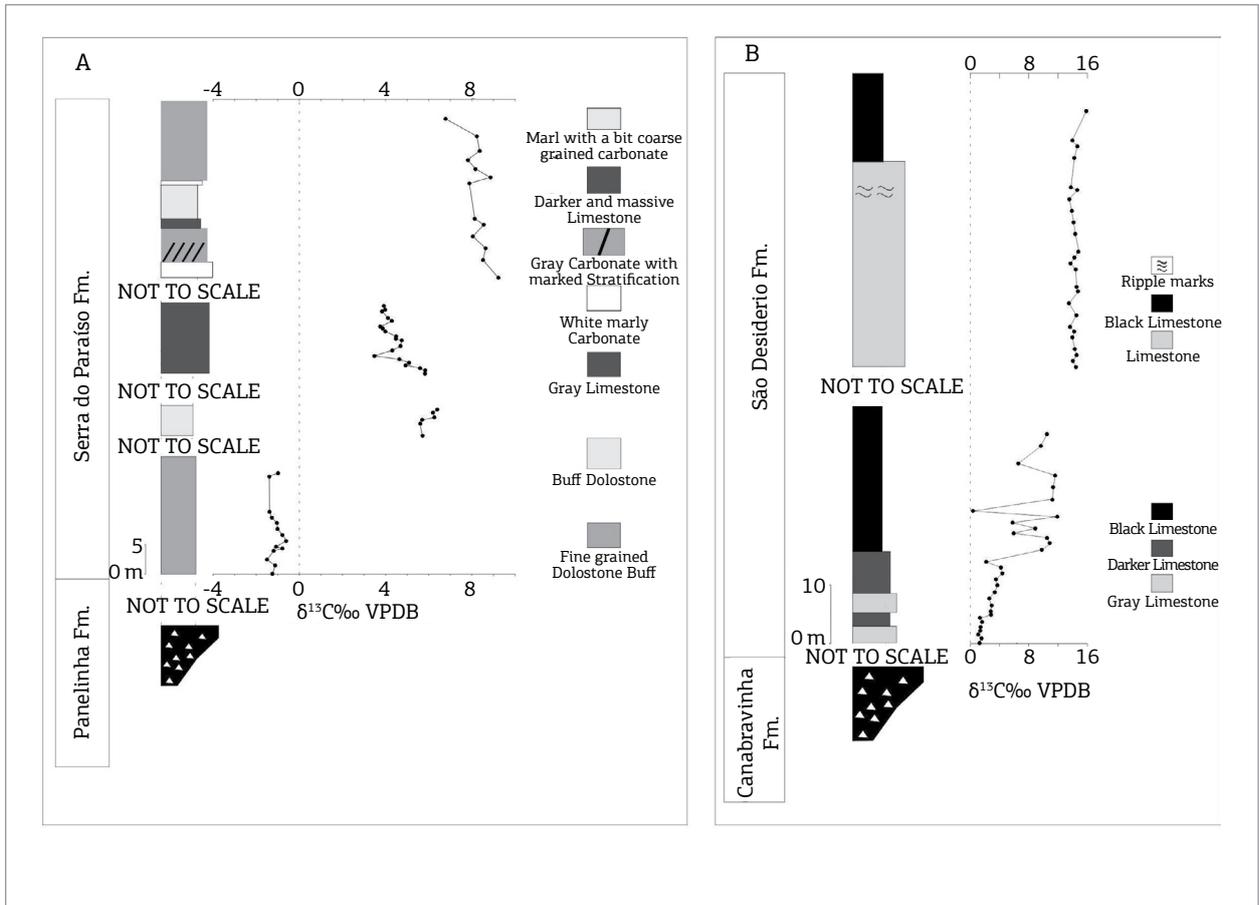


Figure 17. C- and O-isotope chemostratigraphy for successions at the Rio Pardo Basin (A) and Rio Preto Belt (B).

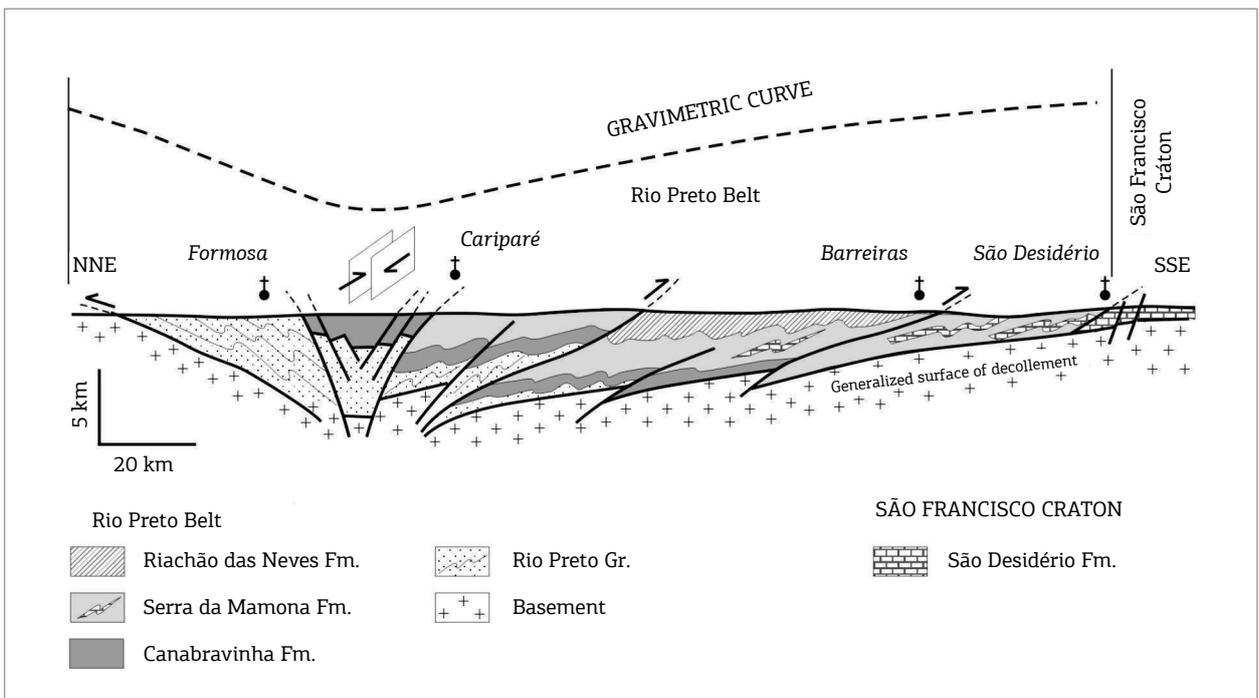


Figure 18. Cross-section for the Rio Preto belt (Egydio-Silva, 1987; Sial et al. 2010).

- north of Barreiras village, limestones are overlain by arkoses, quartzites (locally feldspathic), graywackes, and rare carbonate intercalations (Riachão das Neves Formation). This sequence is considered partially equivalent to the Três Marias Formation of the Bambuí Group (Trompette 1994).

In the central portion of the belt, the Canabrinha Formation is represented by diamictites with pebbles, cobbles, and boulders of gneiss, quartzite, siltstone, marble, and schist. This unit has been correlated to the Jequitaí/ Bebedouro Formation, probably deposited in a glacial marine environment.

In the Rio Preto Belt, continuous chemostratigraphic sections of representative successions of the São Desidério Formation (Cezario *et al.* 2011) were made at:

- Derocal locality about 20 km from São Desidério;
- the Mineração do Oeste Quarry at São Desidério village;
- Sítio Rio Grande about 50 km from São Desidério; and
- Penedo Quarry.

At the Derocal locality, reddish dolomitic argillites display $\delta^{13}\text{C}$ values from +2.5 to +5‰, whereas at the Mineração do Oeste Quarry, limestones yielded $\delta^{13}\text{C}$ values from +1.2 to +2.2‰ in the first 16 m (base to top) changing abruptly up section to values in the +10 to +12‰ range in dark, organic matter-rich limestone. At the Sítio Rio Grande locality, 45 m of limestones were sampled and $\delta^{13}\text{C}$ values vary from +13.5 to +15‰ in the first 30 m (base to top) and from +14 to +16‰ in the upper 15 m, organic matter-rich dark limestone. No negative $\delta^{13}\text{C}$ value has been recorded in these $\delta^{13}\text{C}$ profiles and a composite $\delta^{13}\text{C}$ pathway

is shown in Fig. 17. The C-isotope stratigraphy of the São Desidério Formation approaches that of the top of the Sete Lagoas and Lagoa do Jacaré formations described elsewhere by Santos *et al.* (2000).

Sergipano Belt

The Sergipano Belt is a fold-and-thrust belt located in the northeastern margin of the São Francisco Craton (Fig. 19) that was formed by the continental collision between the Congo-São Francisco Craton and the Pernambuco-Alagoas Massif during the Brasiliano/Pan-African orogeny (Brito Neves *et al.* 1977). It has been interpreted as a geosyncline (Humphrey & Allard, 1968; Silva Filho & Brito Neves 1979) and later as a collage of lithostratigraphic domains (Davison & Santos 1989; Silva Filho 1998) or as a Neoproterozoic belt produced by inversion of a passive margin basin located at the northeastern margin of the São Francisco plate (Del-Rey Silva 1999).

This belt consists, from north to south, of six lithostratigraphic domains separated from each other by major shear zones: Canindé, Poço Redondo, Marancó, Macururé, Vaza Barris, and Estância (Santos & Souza 1988; Davison & Santos 1989; Silva Filho 1998). The Macururé, Vaza Barris, and Estância domains are composed mostly of metasedimentary rocks with metamorphic grade from incipient (or non-metamorphic in the Estância Domain) through greenschist grade, in the Vaza Barris, to amphibolite facies, in the Macururé Domain. Silva Filho & Torres (2002) and Silva Filho *et al.* (2003) have proposed three additional domains: Rio Coruripe, Viçosa, and Pernambuco-Alagoas. Further geological details on all domains of the Sergipano Belt are found in Davison & Santos (1989) and Santos *et al.* (1998).

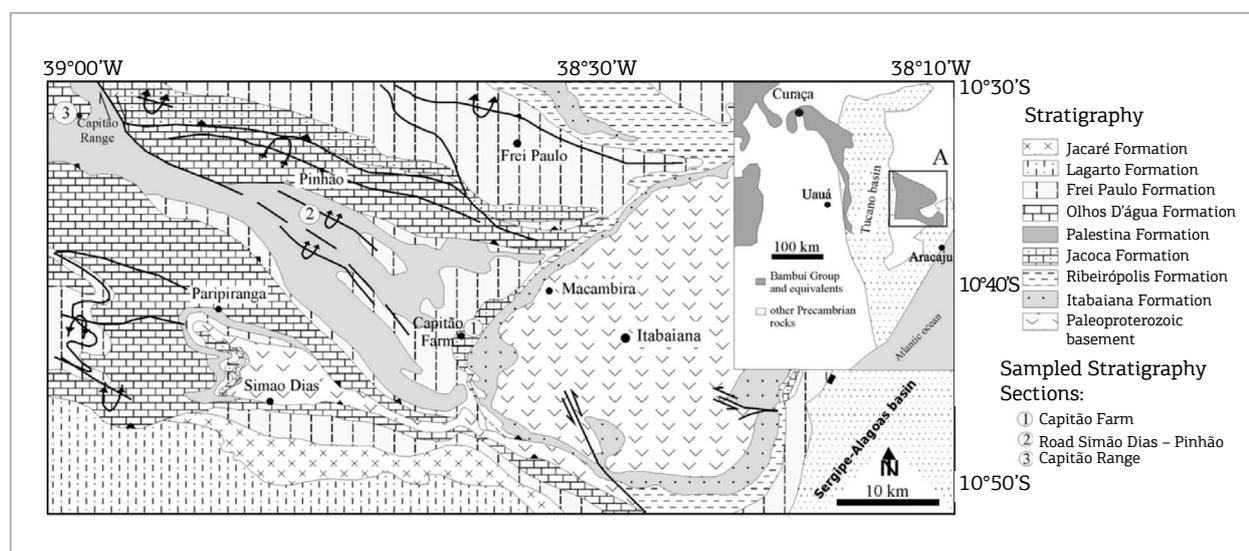


Figure 19. Simplified geological map of the eastern Vaza Barris Domain, Sergipano Belt (modified from D'el Rey Silva, 1999; Sial *et al.* 2010), with the indication of sampled stratigraphic sections in Sial *et al.* (2010).

The Juetê-Acauá, Ribeirópolis-Jacoca, and Palestina Olhos D'Água Formation diamictite-carbonate couplets in the Vaza Barris and Estância domains have been regarded as Neoproterozoic cap carbonates (Sial *et al.* 2000, 2006, 2010). Their relative chronology and correlation with similar cap carbonates in southwestern Gondwana was constrained using carbon- and strontium-isotope chemostratigraphy (Sial *et al.* 2010). Additionally, a preliminary discussion on the use of Hg chemostratigraphy as a potential proxy for volcanism in the study of post-glacial cap carbonates was presented.

Stratigraphic studies on the Vaza Barris and Estancia domains of the Sergipano Belt were pioneered by Humphrey & Allard (1968, 1969) who divided the supracrustal sequences into two groups, Miaba and Vaza Barris, a stratigraphic scheme that was later modified by Silva Filho & Brito Neves (1979) and D'el-Rey Silva (1995, 1999). Among the most relevant modifications, D'el-Rey Silva (1995, 1999) proposed that the Ribeirópolis Formation is older than formerly believed, placing it below the Jacoca Formation. It is assumed here that the Frei Paulo Formation sits on top of the Olhos D'Água Formation as accepted by most authors (Humphrey & Allard 1969; Silva Filho & Brito Neves 1979; Davison & Santos 1989).

The Estancia Group, northern Bahia, comprises the Juetê, Acauá, and Lagarto formations (Silva Filho & Brito Neves 1979). These authors hypothesized that the Juetê and Ribeirópolis formations could be chrono-correlate as well as the Acauá and Jacoca formations, a contention that needs further confirmation.

Two depositional cycles both being represented by a basal continental to shallow-marine siliciclastic megasequence, overlain by a carbonate sequence have been recognized by D'el-Rey-Silva (1995, 1999). These two cycles, with slight modifications, are:

1. Cycle I (Estância-Miaba Group) with a siliciclastic megasequence including the Itabaiana (conglomerate, quartzite, metasilite), Juetê (sandstone, diamictite), Ribeirópolis (silty phyllite, metagreywacke, pebbly phyllite, diamictite) formations, and a carbonate sequence, represented by the Jacoca Formation, stratigraphically equivalent to the Acauá Formation;
2. Cycle II with an upper siliciclastic megasequence (Lagarto-Palmares and Jacaré formations of the Simão Dias Group) overlain by the Vaza Barris Group that comprises diamictites of the Palestina Formation, an upper carbonate megasequence (Olhos D'Água Formation) and the Frei Paulo Formation (pelite and siltstone with rare carbonate rocks). These two megasequences underwent subgreenschistfacies metamorphism which has preserved original sedimentary structures.

The Estância-Miaba Group is well exposed around the Itabaiana and Simão Dias basement domes in Sergipe. The Ribeirópolis Formation is 0 – 300 m thick around this dome and locally reaches thicknesses of about 500 m within the belt. It consists of diamictite, metagreywacke, and quartz-sericite phyllite transitionally overlying quartzite of the Itabaiana Formation. The occurrence of volcanic rocks in this formation, in the west side of the Simão Dias dome, has been reported by D'el-Rey Silva (1995, 1999). Carbonates of the Jacoca Formation are seen in sharp contact on top of the Ribeirópolis diamictite at the Capitão Farm along the Salgado River (western side of the Itabaiana dome). A typical section of the Jacoca Formation starts with a thick layer of laminated gray-to-pink dolostone containing pyrite and chalcopyrite. This is followed upsection by a 3- to 15-m-thick layer of laminated dolostone, and dark gray to black phyllites and about 10-m-thick bed of massive dolostone. This unit is overlain by a 40-m-thick heterolithic sequence of gray limestone and dark-to-dark phyllite and finally by gray dolostone.

At the Capitão Farm, the cap dolostone shows wavy lower contact. Clasts at the top of the diamictite of the Ribeirópolis Formation are concentrated and salient as a result, perhaps, of lithification and erosion prior to cap dolostone deposition. Features suggesting soft sediment deformation were observed in the diamictites and cap carbonates, which may be interpreted as the result of a rapid icehouse to greenhouse transition (e.g. Puga cap carbonate, Amazon Craton; Nogueira *et al.* 2003). Well-developed tubestone stromatolites occur at the dolostone cap carbonate in the Capitão Farm (Sial *et al.* 2010b).

Carbonate rocks of the Acauá Formation overlie either the Juetê diamictite or rest unconformably on basement gneiss. Well-preserved exposures of this contact occur in the western Vaza Barris Domain, between Euclides da Cunha and Bendegó villages, at Patamutê village and at the Serra da Borracha and at Serra da Canabrava (northeastern Bahia). The type locality of the Juetê Formation is at the Juetê River, about 6 km south of Bendegó, where it shows total thickness of about 30 m and is composed of buff sandstone, diamictite (about 15 m thick), and reddish feldspathic sandstone and reddish claystone (Silva Filho & Brito Neves 1979).

The Acauá Formation consists of cap dolostone, limestone (with dolostone dropstones) in proximal sections as seen at the Borracha Range, 20 km west of Patamutê, Bahia, and limestone/dolostone and limestone-shale rhythmites. Continuous sections of the Acauá Formation are exposed at Serra da Borracha and at Serra da Canabrava, as well as Patamutê Creek at Patamutê village and São Gonçalo Farm, about 25 km to the north of Euclides da Cunha village, Bahia (Sial *et al.* 2010b).

Dolostones of the Acauá Formation conformably overlie diamictites of the Juetê Formation, the former showing hummocky and, locally, pseudo-tepee structures. Up section, they pass into a fining and thinning-upward carbonate succession. Diamictites of the Juetê Formation contain clasts of granite, orthogneiss, phyllite, or quartz composition up to 0.5 m in diameter, and locally display Fe-rich claystone beds.

The Olhos D'Água Formation (200 – 1300 m) is composed of interbedded limestones (organic-rich toward the top) and green, calcareous chlorite-schists, and siltyphyllites. It overlies diamictites and pebbly metagreywackes of the Palestina Formation. Marble beds are interbedded with blue to black, fine-grained metalimestone and gray metadolostone. The thick carbonates around the Simão Dias dome pass upward into supratidal-intertidal facies with oolites and wave-reworked sedimentary structures indicating a near-shore environment (D'el-Rey Silva 1995). At the Capitão Range, about 25 km northwest of Paripiranga, Bahia, a 10-m-thick dolostone layer of the Olhos D'Água Formation is in sharp contact with diamictite of the Palestina Formation (metagreywacke with clasts up to 30 cm in diameter) and followed up section by about 50 m of limestone–pelite intercalations. They are in turn overlain by laminated limestone (40 m thick) culminating with a 30-m-thick layer of organic-rich black.

The current geochronological data indicate that the deposition of Jacoca Formation carbonates is younger than 780 Ma and the deposition of the Olhos D'Água Formation carbonates took place after 653 Ma and before 628 Ma (Sial *et al.* 2010).

Detrital zircons from the diamictite of the Juetê Formation, to the north of Euclides da Cunha, are older than 2073 Ma (Oliveira *et al.* 2008) and detrital zircons from sandstones of the Lagarto (on top of the Acauá Formation) and Palmares Formations display ages that cluster around 565 Ma, 582, 633 Ma, 956 Ma, 977 Ma, and 1855 Ma.

The sections chemostratigraphically investigated in the Sergipano Belt by Sial *et al.* (2010) show well-preserved cap carbonates in knife-sharp contact with basal diamictites as known for Neoproterozoic cap carbonates worldwide (e.g. Kennedy 1996; Hoffman & Schrag 2002). Several localities in the eastern and western Vaza Barris Domain fulfill this requirement. Among them, Sial *et al.* (2010) have stratigraphically sampled carbonates of the Jacoca Formation in sharp contact with diamictites of the Ribeirópolis Formation at Capitão Farm. The Acauá Formation overlies with sharp contact diamictites of the Juetê Formation at the Borracha Range, at the Patamutê Creek in the Patamutê village as well as at São Gonçalo Farm in the state of Bahia. Besides, carbonates of the Olhos D'Água Formation in sharp contact with diamictites of the Palestina Formation at the Capitão Range were also sampled.

Several other localities in Sergipe and Bahia offer exposures of carbonate rocks of the Jacoca, Acauá, and Olhos D'Água. Among them, well-preserved carbonate exposures of the Acauá Formation at the Serra da Canabrava and at the Almeida Farm near the Serra da Borracha, and along the road between Euclides da Cunha and Bendengó (Bahia) have been sampled by Sial *et al.* (2010). Besides, continuous outcrops of the Olhos D'Água Formation in the road Rosario-Cocorobó, Bahia, and south of Pinhão village, Sergipe, have been also sampled.

In the eastern Vaza Barris Domain, carbonates of the Jacoca Formation at the Capitão Farm show negative $\delta^{13}\text{C}$ values, mostly between -5 and -4‰ while $\delta^{18}\text{O}$ values are mostly around -8‰ VPDB (Fig. 20). Shallow-marine dolostones of this formation display increasing $\delta^{13}\text{C}$ values, from -6.2 to -4.3‰, interrupted by a sudden decrease to values of -6.7‰ at the base of the overlying deep shelf limestone succession. Such values shift back to values as high as -1.5‰ VPDB in its uppermost portion. The cap dolostones of this formation show relatively limited thickness (a couple of meters or less, especially in more distal sections).

In the western Vaza Barris Domain, detailed C and O isotope chemostratigraphy for the Acauá Formation (São Gonçalo Farm, Borracha and Canabrava Ranges, Patamutê and road Euclides da Cunha–Bendengó) revealed that $\delta^{13}\text{C}$ values tend to group mostly between -5 and -4‰, within the range for mantle values (Hoffman & Schrag 2002). This highlights the role of mantle-derived CO_2 in carbonate deposition in the aftermath of the glacial event represented by diamictites of the Juetê Formation.

At Serra da Borracha hill, $\delta^{13}\text{C}$ values are kept very homogeneous (~ -5‰) for about 165 m. Only about 1 m of shallow marine dolostone is present in the base of the profile (part of the cap dolostones has been eroded away) being followed up section by 30 m of gray fine-grained limestones with dolostones dropstones and limestone-dolostone rhythmites. $\delta^{18}\text{O}$ values for this interval vary gradually from about -12 to about -5‰ VPDB. Such enormous fractionation, if primary, likely resulted from a gradual temperature decrease by the time dolostone-dropstones were deposited. Up section, an interval characterized by boudinaged dolostone-limestone intercalations with plane-parallel lamination is observed indicating below wave-base deposition.

Carbonates at Serra da Canabrava Range show $\delta^{13}\text{C}$ values from -6 to -0.2‰ and a package of light gray fine-grained limestones near the Almeida locality, nearby Canabrava Range, exhibits values from -0.5 to +0.3‰ and seem to be stratigraphically above the carbonate succession at Serra da Borracha. The nearly identical behavior of $\delta^{13}\text{C}$ in the Acauá and Jacoca carbonates opens the possibility that they could have been simultaneously deposited, a contention that finds no support in the Sr isotope behavior as discussed later on.

Marly and dolomitic carbonates of the Olhos D'Água Formation overlying diamictites of the Palestina Formation, near the road Simão Dias-Pinhão (Sergipe), display $\delta^{13}\text{C}$ values as low as -4.7‰ , increasing upsection to a plateau between 0 and 1‰ and finally to another plateau around $+8$ to $+10\text{‰}$. This pattern is observed in the sections at the Capitão Range, at the section in the Rosario-Cocorobó road (Bahia) and between Simão Dias and Pinhão villages (Sergipe). The $\delta^{18}\text{O}$ values in these sections vary from -7 to -11‰ VPDB and $\delta^{13}\text{C}$, from -5 to $+9\text{‰}$ and seem to be

primary regarding the low Mn/Sr and lack of co-variance between $\delta^{13}\text{C}$ and Mn/Sr values (Fig. 20).

A section of the Olhos D'Água Formation near Rosário village, Bahia, shows an intercalation of limestones and siltstones, where the carbonate lenses show variable thickness. These carbonates have been deposited on top of diamictites of the Palestina Formation, the latter comprising pebbles, boulders, and blocks of granite, gneiss, black phyllite, black silexite, greenish quartz, and gray limestones. The $\delta^{13}\text{C}$ values start with slightly negative values ($\sim -2\text{‰}$) and about 10 m from the base, values change dramatically and form a well-defined plateau around $+9\text{‰}$, while the $\delta^{18}\text{O}$ values vary from -10 to -12‰ VPDB.

Strontium isotope ratios have been analyzed in forty carbonate samples from the Sergipano Belt including samples from the Acauá Formation (Borracha, Patamutê, São Gonçalo, Euclides da Cunha) and Olhos D'Água Formation (Rosario and Capitão Hill) in the western Vaza Barris Domain and Jacoca Formation (Capitão Farm) and Olhos D'Água Formation (road Simão Dias-Pinhão) in the eastern Vaza Barris Domain. Typically, carbonate samples with high Sr (> 600 ppm), low Rb (< 10 ppm), low Mn/Sr (< 10), and low Mg/Ca (< 0.2) ratios have been considered for Sr isotope-ratio analysis since usually samples which meet these requirements yield consistent $^{87}\text{Sr}/^{86}\text{Sr}$ Sr ratios. However, when dolomite was the only carbonate present (Mg/Ca around 0.6), consistency of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios was the only selection criterion.

Carbonates of the Jacoca Formation have $^{87}\text{Sr}/^{86}\text{Sr}$ ratio values of 0.7077, 0.7081, and 0.7081 at Capitão Farm. Four analyses of carbonates of the Acauá Formation yielded consistent results at the Borracha Range (two values of 0.7072 and two, 0.7073) but very variable and higher values at the three other localities examined in the western Vaza Barris Domain (all dolostones). Three $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for high-Sr carbonates of the Olhos D'Água Formation in the section near Pinhão village yielded values of 0.7078, 0.7080, and 0.7080. At Capitão Range, carbonates of this Formation have values of 0.7077–0.7081 and from 0.7077 to 0.7082 at the section near Rosario Village. All these $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are within the typical range for late Neoproterozoic seawater (Kaufman *et al.* 1993, 2009).

Therefore, carbonates of the Olhos D'Água Formation from the three localities examined (eastern and western Vaza Barris domains) show nearly the same range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, indistinguishable from that of the Jacoca Formation at the Capitão Farm. However, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the Borracha Range are consistently lower than those for the Jacoca Formation, in contrast with $\delta^{13}\text{C}$ values (all negative) that tend to fall in the same range for these two Formations.

Correlation of some Cryogenian and Ediacaran successions in Brazil and Africa, based on lower radiogenic

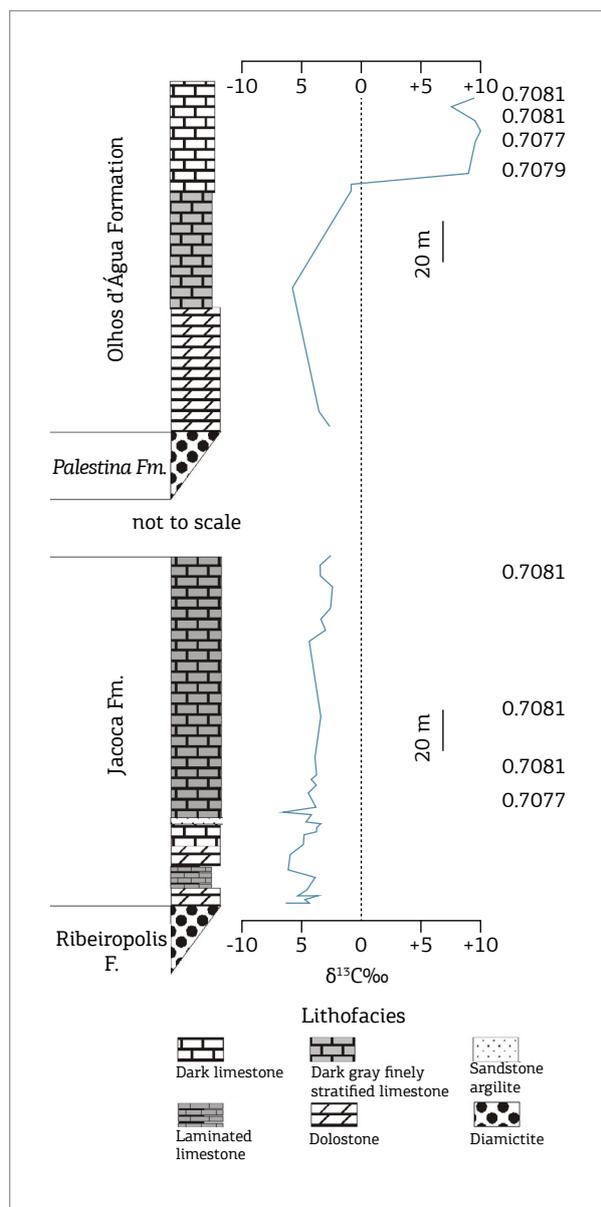


Figure 20. Litho- and composite $\delta^{13}\text{C}$ curve and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for carbonates of the Jacoca (Estância-Miaba Group) and Olhos D'Água formations (Vaza Barris Group). The variation of Sr isotopes also shown in this composite section (modified from Sial *et al.* 2010).

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios (best preserved samples), are summarized in Table 1. Kaufman *et al.* (2009) have compiled $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for limestones in cap carbonates across southwestern Gondwana and they seem to fall consistently within three modes with values near 0.7066, 0.7073, and 0.7081 represented, respectively, by the Rasthof, Maieberg, and Bildah cap carbonates in Namibia and their temporal equivalents. In this scheme of Kaufman *et al.* (2009), $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

for the Acauá Formation carbonates at the Borracha Range (0.7073) approach $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for Sturtian II cap carbonates deposited between 740 and 635 Ma. In addition, similarly to the Maieberg cap carbonate, $\delta^{13}\text{C}$ values at the Borracha Range are all negative. However, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as low as 0.7073 have been reported from Ediacaran, *Cloudina*-bearing limestones in Uruguay (Gaucher *et al.* 2004, 2009) and are also similar to $^{87}\text{Sr}/^{86}\text{Sr}$ values of post-Marinoan

Table 1. Correlation of some Cryogenian and Ediacaran successions in Brazil and Africa, based on lower radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (best preserved samples) available and on carbon isotope shifts. D D D - Glaciogenic diamictites. Sources of information: (1) This work; (2) Sial *et al.* (2010); (3) Sial *et al.* (2000); (4) A.N. Sial (2014, unpublished); (5) Misi *et al.* (2007); (6) Alvarenga *et al.* (2014); (7) Misi & Veizer (1998); (8) Torquato & Misi (1977); (9) Kaufman *et al.* (2010); (10) Jacobsen & Kaufman (1999); (11) Warren *et al.* (2011); (12) Mallmann *et al.* (2007); (13) Oyhantçabal *et al.* (2009); (14) Gaucher *et al.* (2004, 2009b), (15) Gaucher *et al.* (2007); (16) Gómez Peral *et al.* (2007); (17) Bagnoud-Velásquez *et al.* (2013); (18) Gómez Peral *et al.* (2014); (19) Boggiani *et al.* (2010); (20) Santos *et al.*, 2000, (21) Souza (2015), (22) Alvarenga *et al.* (2010); (23) Chigolino *et al.* (2015), (24) Fraga *et al.* (2014) (25) Santana *et al.* (2016), unpublished, (26) Babinski *et al.* (2007), (27) Figueiredo *et al.* (2009).

Period	Seridó Belt (1)	Miaba/ Vaza Barris Group (2,3)	Ubajara Group (4, 22)	Bambui Group (5, 6, 9, 22, 26)	Bambui Group (5, 6, 9, 22, 26)	Una Group (7, 8, 25, 27)	Rio Pardo Basin (1)	Rio Preto Belt (1)
Cambrian								
Ediacaran	Seridó Fm. 0.7078– 0.7081 -5 to +9‰ (1)	Olhos D'Água Fm. Upper 0.7075 (2,3) +10	Frecheirinha Fm. 0.7075 (1) -3.5 to +4‰ (4, 23)	Lagoa do Jacaré Fm. 0.7074 (5) +8 to +12‰ (5)	Lagoa do Jacaré Fm. 0.7074 (5) +8 to +12‰ (5)	Salitre Fm. Unit A1 0.7076 (7) +9.5	Serra do Paraíso Fm (Upper) + 8‰	São Desidério Fm. Upper +12 to +16‰
	Jucurutu Fm. 0.7074– 0.7075 -7 to +10‰ (1)	Olhos D'Água Fm. Lower 0.7077 (2) -5.0 ‰ (3)		Sete Lagoas Fm. Upper 0.7077 (6) -5.0‰ (9)	Sete Lagoas Fm. 0.7077 (6) -5.0‰ (9)	Salitre Fm. Unit B1 0.7075 (7) -4.5‰ (8)	Serra do Paraíso Fm (Lower) -1.0 ‰	São Desidério Fm. Lower +1 to +3‰
Cryogenian		Palestina △ △ △ △ △		Inhauma △ △ △ △ △	Jequitai Fm. △ △ △ △ △		Panelinha Fm. (?)	Canabravimha Fm. (?)
		Jacoca/ Acauá Fm. 0.7072- 0.7076 (2)				Salitre Fm. Unit B 0.7078 (7) -4.4 to +0.3‰ (7) <669 ±14 (25)		
		Jacoca/ Acauá Fm. Lower (cap carb) -5.0‰ (2, 3)		Sete Lagoas Fm. Lower 0.7075 (5) 0.7080 (22) - 4.5 ‰ (5)		Salitre Fm. Unit C (cap carb.) -6.5 ‰ (8)		
		Ribeirópolis Fm. (Jacarecica Fm.) △ △ △ △ △		Jequitai Fm., Macaubas Group △ △ △ △ △ 740 ±22 (26)		Bebedouro △ △ △ △ △ < 874 ±09 (27)		

Table 1. Continued.

Period	Northern Paraguay Belt (21, 22)	Corumbá Group (19)	Itapucumi Group (Paraguay) (11)	Tucavaca Belt, (Bolivia) (1)	Nico Pérez Terrane (Uruguay) (12, 14,15)	Tandilia (Argentina) (16, 18)	Otavi Group (Namibia) (9, 10)	Lufilian Arc (DRC-Zambia) (9)	
Cambrian		Guaicurus Fm.			Cerro Victoria Fm. -3.5 to +0.6‰ (15)				
Ediacaran	Pacu Fm 0.7087	543±2 Tamengo Fm. 0.7084–0.7086 -3.5 to +5.5 ‰ (19)	Cerro Curuzú Fm. (upper) +1.5 ‰ (11)	Murciélago Group -1 to -2‰	Polanco Fm. Yermal Fm. 0.7070–0.7087 -4.5 to +5.5 ‰ (14)	Cerro Negro Fm. -1 to +4.3‰ (18)	Hüttenberg Fm. 0 to +12 ‰ (9)		
	+6.5 to +8.5‰ (21)		Tagatiyá Guazú and Camba Jhopo Fm. (lower) +1.8 ‰ (11) 0.7086 (11)			Loma Negra Fm. 0.7069–0.7087 (16) 0 to +4.5 ‰			
	Nobres Fm -1.0 to +9.6 ‰	Bocaina Fm. -4 to +3 ‰ (19)				Colombo Mb. Δ Δ Δ Δ Δ			Elandshoek Fm. -3 to +8 ‰ (9)
	Guia Fm -5.5 to -0.1‰ 0.7076								
	Mirassol d'Oeste Fm. -8.5 to -3.5 ‰ (22)	Cap carbonate -5‰							
Cryogenian	Puga Δ Δ Δ Δ Δ	Puga (?) Δ Δ Δ Δ Δ	Vallemi Fm. (red beds)				Ghaub Δ Δ Δ Δ Δ 635 ±1 (9)	Petit Conglomerat Δ Δ Δ Δ Δ	
							Ombaatjie Fm. 0.7072 (10)	Kokontuwe 0.7066 (9) -6.2 ‰ (9)	
							Rasthof Fm. 0.7066 (9) -5 ‰ (9)		
							Chuós Δ Δ Δ Δ Δ 746 ±2 (9)	Grand Conglomerat - Δ Δ Δ Δ Δ 760 ±5 (9)	

carbonates in NW Canada, NW Namibia, and SW Brazil (Halverson *et al.* 2007).

The ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the Jacoca and Olhos D'Agua formations are similar to each other (0.7077 to 0.7081), in consonance with values reported for the Marinoan Bildah, Tsabisis, and Bloeddriff cap carbonates, Kalahari Craton. However, $\delta^{13}\text{C}$ values for carbonates of Jacoca Formation at the Capitão Farm are all negative, in contrast with positive values observed in middle and upper sections of the Olhos D'Agua Formation in the eastern and western Vaza Barris domains. On structural grounds, it is known that Jacoca Formation must be slightly older than the

Olhos D'Agua Formation (D'el Rey Silva 1995, 1999) and both have been weakly deformed during the Brasiliano cycle (650 – 600 Ma). Similarities of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of post-Sturtian and post-Marinoan carbonates led Babinski *et al.* (2007) to question the use of Sr-isotope stratigraphy to differentiate and correlate postglacial carbonate successions.

The calcium-isotope record seems to be a true archive of changes in the oceanic Ca isotopic compositions and early Cryogenian $\delta^{44/40}\text{Ca}$ patterns seem to be very different from the Ediacaran ones (Silva-Tamayo *et al.* 2010a, 2010b). Therefore, Ca-isotope stratigraphy appears to be a promising tool to discriminate and correlate Neoproterozoic

postglacial carbonate successions (Kasemann *et al.* 2005; Silva-Tamayo *et al.* 2010a, 2010b).

Stratigraphic changes of $\delta^{44/40}\text{Ca}$ values of the weakly deformed carbonates of the Jacoca Formation, the deformed Cryogenian Sete Lagoas Formation, Minas Gerais, Brazil (740 ± 22 Ma; Babinski *et al.* 2007, but see also discussion above) and Twitya Formation (NW, Canada) are similar, according to Silva-Tamayo *et al.* (2010b), in support of a Cryogenian age. The basal dolostone of the Jacoca Formation displays increasing $\delta^{44/40}\text{Ca}_{(\text{NIST-SRM } 915\text{a})}$ values from 0.3‰ to 2.0‰, followed by a decrease to values averaging 0.8‰ at the top. The overlying limestones display $\delta^{44/40}\text{Ca}_{(\text{NIST-SRM } 915\text{a})}$ values averaging 1.0‰ (Silva-Tamayo *et al.* 2010a).

The basal shallow-marine cap dolostone of the Acauá Formation displays $\delta^{44/40}\text{Ca}_{(\text{NIST-SRM } 915\text{a})}$ values averaging 0.7‰ according to Silva-Tamayo *et al.* (2010a) with a stepwise decrease to values around 0.2‰ at the base of the overlying limestone succession, followed by a rapid increase to 1.0‰ upsection. The Ca-isotope stratigraphic pathway displayed by this cap carbonate, according to these authors, is indistinguishable from those displayed by cap carbonates overlying *ca.* 635 Ma glacial deposits in NW Namibia.

OTHER TERRANES IN THE BORBOREMA PROVINCE

Seridó Belt: Jucurutu and Seridó formations

The Seridó Belt in northeastern Brazil encompasses a metavolcano-sedimentary sequence that was deposited

discordantly on a Paleoproterozoic basement, and has been intensely studied in the last fifty years (Fig. 21). This belt was affected by a strong transpressional deformation, intrusion of voluminous granitic magmas, and reworking by transcurrent structures that imparted an N-NE trend to this belt. The original stratigraphic relationships have been obscured by intense deformation and this led to divergent interpretations of the sedimentation age, stratigraphy, and evolution of the supracrustal rocks, in spite of several geochronological, geochemical, and structural studies (Jardim de Sá *et al.* 1988, 1994; Caby *et al.* 1995; Archanjo *et al.* 2013; Van Schmus *et al.* 2003; Hollanda *et al.* 2015).

Among several stratigraphic schemes proposed for the Seridó Belt, the most commonly used (Jardim de Sá & Salim 1980) includes all metasedimentary rocks of this belt in the Seridó Group. This group is subdivided from base to top into:

1. Jucurutu Formation, composed of a basal conglomerate, iron-formation, marble layers intercalated in gneisses, mica-schist, quartzite, calc-silicate rocks and metavolcanic rocks;
2. Equador Formation, predominantly composed of quartzite with metaconglomerate lenses, which become more abundant toward the top, calc-silicate rocks and paragneisses; and
3. the Seridó Formation, which is made up of metaconglomerate, feldspathic, or aluminous mica-schist with subordinate marble, calc-silicate rocks, paragneiss, basic metavolcanic rocks, and quartzite.

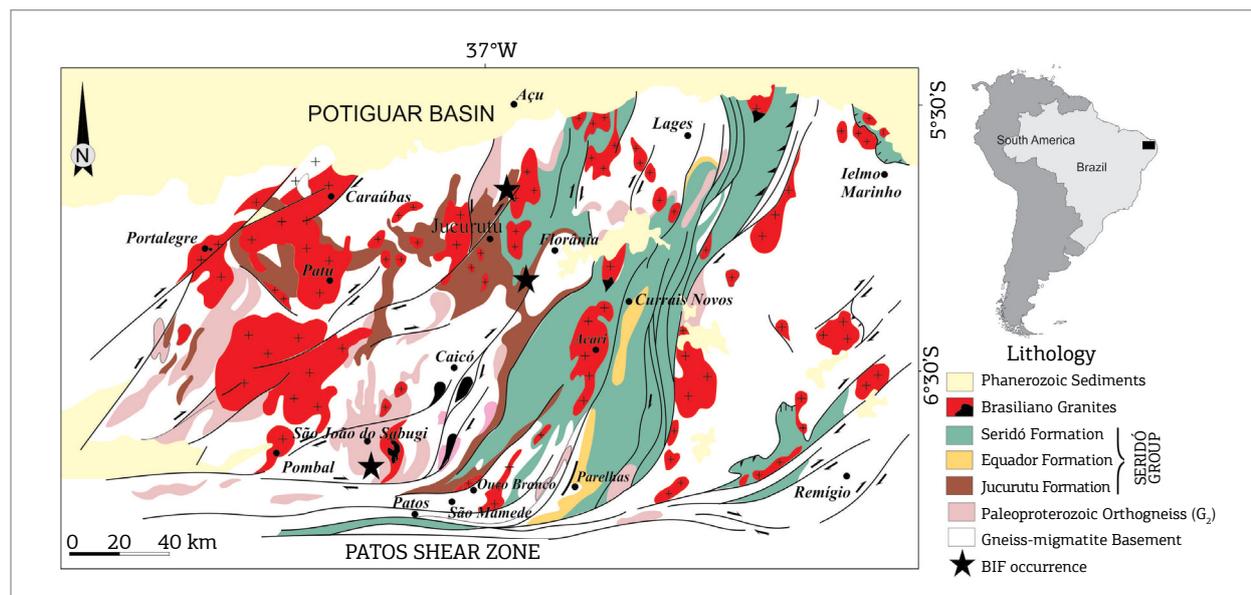


Figure 21. Simplified geological map of the Seridó Belt (after Jardim de Sá, 1994; Angelim *et al.* 2006; modified from Sial *et al.* 2015). Black stars represent locations of BIFs (Bonito iron Mine, Serra da Formiga and Riacho Fundo).

The Equador Formation exhibits variable thickness and can be absent in certain portions of the belt (Jardim de Sá 1994 and references therein). In this scheme, the whole package in the Seridó Belt resulted from a megacycle of sedimentation lacking regional unconformities. The association of iron formation, marble and calc-silicate paragneisses of the Jucurutu Formation could be of shallow-marine environment, although the banded iron formation (BIF) depositional environment could be slope or basinal. The Equador Formation is the siliciclastic component of this shallow-marine association, while mica-schists of the Seridó Formation correspond to a thick package of turbiditic, flyschoid deposits marking the inversion of the basin, according to Jardim de Sá (1994).

A different stratigraphic column was proposed by Cabby *et al.* (1995) in which supracrustal rocks were subdivided into the Jucurutu Group and the overlying Seridó Group with a hiatus (regional unconformity) of deposition between them. Recently reported U-Pb ages of detrital zircons and Nd isotope compositions from the Seridó Group indicate a significant change of sediment provenance during the deposition of sands and conglomerates and the overlying greywacke-pelite sequences (Hollanda *et al.* 2015). According to these authors, this shift in provenance defines an unconformity in the Seridó Group characterized by a metadiamicrite horizon with pebbles and cobbles from the Paleoproterozoic to Archean basement and recycled quartzites of the underlying Equador Formation. The change in provenance is defined by a cryptic internal disconformity that is characterized by a time gap of about 1.0 Ga in the age of the detrital zircons. Nd compositions across this unconformity indicate that the pelites are very radiogenic ($\epsilon\text{Nd}_{\text{present-day}} = -4$ to -11) compared with the sandy deposits ($\epsilon\text{Nd}_{\text{present-day}} = -22$ to -31). The provenance of the metapelites at the top of the metasedimentary succession includes a prominent population of Cryogenian zircons whose youngest grains dated to between 0.64 and 0.62 Ga. According to Hollanda *et al.* (2015), these zircons were deposited in a basin developed on continental basement that preserves remnants of near-shore to terrestrial deposits with no detrital zircons younger than 1.8 Ga. More importantly, Hollanda *et al.* (2015) have raised the possibility that the Equador Formation lies stratigraphically below the Jucurutu Formation and that the Seridó and Jucurutu formations could actually be equivalent stratigraphically.

In the Jucurutu Formation, metric to decametric-scale marble layers, sometimes compositionally banded, are abundant and occur at three stratigraphic levels, one of which is near the base of the succession (Jardim de Sá 1994; Nascimento *et al.* 2007). In the Seridó Formation, marble

layers are less abundant and are only found near the base of this formation (extensional tectonic stage). The lack of carbonates in the latter is due to the tectonic inversion (early compressional stage) in the evolution of the basin (Jardim de Sá 1994). Marble layers intercalated in the Jucurutu Formation are found in the northern, central, southern, and western portions of the Seridó Belt.

Investigation on TDM model ages of metasedimentary rocks (Van Schmus *et al.* 1996) suggests maximum ages between 1.6 and 1.2 Ga for the Jucurutu and Seridó formations. Van Schmus *et al.* (2003) determined U-Pb SHRIMP ages of detrital zircons from a paragneiss (EC-61) of the Jucurutu Formation from its type area, finding a youngest age of 634 ± 13 Ma. These authors also reported an U-Pb SHRIMP age of 628 ± 16 Ma for detrital zircons from the younger Seridó Formation using a mica-schist sample collected near Pedra Preta, state of Rio Grande do Norte. These data suggested that the maximum depositional age for the Jucurutu and Seridó formations is ca. 630 Ma, preceding the peak of metamorphism in the Brasileiro (= Pan-African) orogeny in this region (ca. 600 – 585 Ma; Hollanda *et al.* 2010). However, newly reported U-Pb zircon ages for the Acari granite (577 – 572 Ma) and Santa Luzia migmatite constrain the HT/LP metamorphism of the Seridó to 575 Ma (Archanjo *et al.* 2013).

Depending on the nature of the supracrustal rocks, as well as on the tectonic and metamorphic history of the region, it is difficult to date rocks by radiogenic methods, and C and Sr chemostratigraphy may assist resolve issues such as stratigraphy and sedimentation age (Melezhik *et al.* 2001). In highly metamorphosed regions (e.g. amphibolite facies), as is the case throughout most of the Seridó Belt, the interpretation of depositional patterns of sedimentation, as well as C- and Sr-isotope variations, can be severely compromised. In a preliminary attempt to estimate the age of deposition of carbonate rocks of the Seridó Group (Jucurutu and Seridó formations) using C- and Sr-isotope chemostratigraphy, Nascimento *et al.* (2004, 2007) have examined nine marble layers and proposed a depositional age around 600 Ma.

As part of the meta-volcanosedimentary Seridó Belt, BIFs abound and the couplet formed by BIFs in sharp contact with overlying carbonate rocks of the Jucurutu Formation may represent a record of deposition in the aftermath of one of the Neoproterozoic glaciations. To help addressing this issue, Sial *et al.* (2015a) have examined field relationships, behavior of C and Sr isotopes in carbonates of the Jucurutu Formation, Cr isotopes in BIF and carbonates, and rare-earth elements in both carbonates and BIFs. Six sections were sampled across marble layers of the

Jucurutu Formation, and two drill cores from the Bonito iron Mine have been studied. One of these sections is located at the western flank of the Bonito iron Mine anti-form, about 20 km north of the town of Jucurutu. At this locality, drill cores from boreholes BTO-34 (240 m) and BTO-78 (16 m) of the MHAG Mining Company have been micro-drilled. The $\delta^{13}\text{C}$ shows large variation and in the BTO-34 drill hole, displays values from -12 to -5‰ at the base followed up section by a shift to positive values (+4 to +10‰, Fig. 22). A similar trend is observed for drill core 78, but carbonates at the contact with underlying BIF show a more vigorous $\delta^{13}\text{C}$ fluctuation, with values as low as -12‰ in their lowest portion. No clear correlation exists between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for these samples, except for $\delta^{13}\text{C}$ values below -5‰, which also exhibit the most negative $\delta^{18}\text{O}$ values. Apart from these few samples, $\delta^{13}\text{C}$ values probably represent near-primary isotope signals. Nascimento *et al.* (2004, 2007) found no co-variation between $\delta^{13}\text{C}$ and Mn/Sr ratios or between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for carbonates of the Jucurutu Formation, supporting the primary nature of isotopic signals.

Two sections across marble layers (surface samples) were studied near the town of Ouro Branco (Sial *et al.* 2015a). One of these sections is only 300 m from diamictite outcrops and the other section at about 1 km northwest from this locality. There is no clear stratigraphic relationship between

the Ouro Branco diamictite and these marble layers, which show little variation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ ranging between +8.9 and +9.7‰. As a whole (the two sections), $\delta^{18}\text{O}$ varies from -13.0 to -7.2‰ VPDB.

Sial *et al.* (2015a) studied three sections of marble layers at Serra da Formiga. All show positive $\delta^{13}\text{C}$ values ranging from +2.9 to +8.3‰ VPDB while $\delta^{18}\text{O}$ values vary from -11 to -6.2‰ VPDB. Marble layers associated with BIF at the Riacho Fundo locality display positive $\delta^{13}\text{C}$ values within the 7 – 9‰ interval, a range similar to that observed in a marble layer of the the Jucurutu Formation, at the town of Jucurutu, reported by Nascimento *et al.* (2007).

Marbles of the Jucurutu Formation were metamorphosed up to amphibolites facies, precluding the use of $\delta^{18}\text{O}$ as an indicator of seawater composition. An ample fluctuation of $\delta^{18}\text{O}$ values, from -16 to -3 ‰ VPDB is observed, probably in response to metamorphism or weathering imprint. At the Cruzeiro da Maniçoba locality, near Currais Novos town, basal pink dolostones from the younger Seridó Formation show $\delta^{13}\text{C}$ values around -4‰ and $\delta^{18}\text{O}$ from -16.5 to -12‰ VPDB. Positive $\delta^{13}\text{C}$ values around +9‰ in marbles of the Seridó Formation (e.g. São Mamede) have been reported by Nascimento *et al.* (2007). It became clear to Sial *et al.* (2015a) that the Jucurutu and Seridó Formations exhibit negative $\delta^{13}\text{C}$ values at their base followed upsection by high positive values,

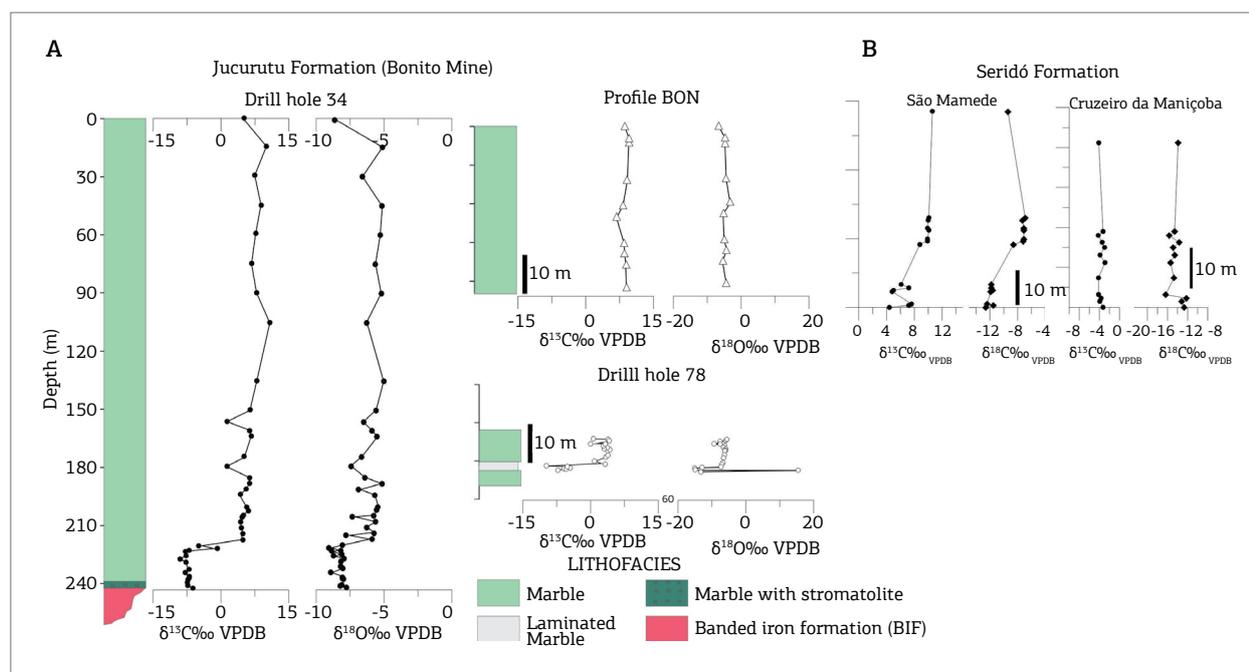


Figure 22. (A) C- and O-isotope chemostratigraphic profiles for marbles of the Jucurutu Formation overlying BIFs at the Bonito iron Mine (drill holes 34 and 78; profile BON corresponds to a section at about the hinge of the antiform of the Bonito iron Mine); (B) C- and O-isotope chemostratigraphic profiles for marbles of the Seridó Formation (São Mamede and Cruzeiro da Maniçoba localities). Modified from Sial *et al.* 2015.

something which was not depicted from the sections studied by Nascimento *et al.* (2007).

Nascimento *et al.* (2007) determined $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for Jucurutu carbonates between 0.7074 and 0.7075 and between 0.7078 and 0.7083 for the Seridó Formation. Sial *et al.* (2015a) analyzed $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in marbles from the Jucurutu Formation at the Bonito iron Mine (10), Ouro Branco (10), Serra da Formiga (3), and Riacho Fundo (2) sections. Samples from the Bonito iron Mine yielded consistent results, between 0.7074 and 0.7075, the same as reported by Nascimento *et al.* (2007) from samples from Jucurutu town (type area). Samples from the Ouro Branco and Serra da Formiga sections yielded values between 0.7074 and 0.7076. Most of the analyzed samples are pure limestones with high Sr contents (up to 3000 ppm) and very low Rb (< 10 ppm), thus the measured isotopic compositions likely represent primary signals. $^{87}\text{Sr}/^{86}\text{Sr}$ values for dolomitic carbonates of the Seridó Formation at Cruzeiro da Maniçoba section obtained in this study are considerably higher (0.7077 – 0.7139) and are less consistent, as expected for dolostones.

Usually, highly metamorphosed carbonates have C and Sr-isotope patterns severely complicated by isotopic re-equilibration due to metamorphic reactions. However, marbles of the Seridó Belt seem to preserve near primary C- and Sr-isotope ratios, as known from other successions up to the high metamorphic grade (Melezhik *et al.* 2008; Chigliano *et al.* 2010). This is probably due to their pure calcitic composition, which determined only very limited metamorphic reactions between different mineral phases. In the particular case of the Jucurutu Formation, Nascimento *et al.* (2007) show that near-primary, unaltered $^{87}\text{Sr}/^{86}\text{Sr}$ values are encountered in samples with $\delta^{18}\text{O} > -15\text{‰}$ VPDB, Sr concentrations > 2000 ppm Sr and Mn/Sr < 0.05. All samples of the Jucurutu Formation that yielded $^{87}\text{Sr}/^{86}\text{Sr}$ values in the range 0.7074 – 0.7076 fulfill these criteria and are interpreted as near-primary.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range observed in the Jucurutu Formation is compatible with values reported for the late Cryogenian (Halverson *et al.* 2005, 2010), although similar $^{87}\text{Sr}/^{86}\text{Sr}$ values also occur in the Ediacaran (to which ferruginous deep-waters were also associated) as registered in *Cloudina*-bearing limestones in Uruguay (Gaucher *et al.* 2009; Frei *et al.* 2011) and Argentina (Gómez Peral *et al.* 2007). One cannot discard, however, that seawater has likely undergone important changes of its $^{87}\text{Sr}/^{86}\text{Sr}$ ratios after major Neoproterozoic glacial events due to input of continental waters from ice melting and strong weathering in continents, blurring the true seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values during deposition of carbonates (Zhao *et al.* 2009).

Recently, chromium stable isotopes in BIFs and iron-rich cherts have been shown to reflect the redox sensitivity of the Cr(III) – Cr(VI) pair in geological and oceanographic processes (Frei *et al.* 2009). Chromium is highly sensitive to the redox state of the surface environment, oxidative weathering processes producing the oxidized hexavalent Cr. Oxidation of the reduced Cr on land is accompanied by isotopic fractionation (Frei *et al.* 2009 and references therein). The isotopic systematic of the chromium cycle including incorporation into BIF has been discussed into details by Lyons & Reinhard (2009). Stable Cr isotopes from BIFs and Fe-chert can track the presence of hexavalent Cr in Precambrian oceans providing a picture of the oxygenation history of the Earth's atmosphere-hydrosphere system as demonstrated by Frei *et al.* (2009). Chromium stable isotopes in Fe-rich chemical sediments deposited during glacial events are suitable for tracing oxygenation of surface environments through Earth's history. Besides, Cr isotopes in carbonates may be useful as a tracer for climate change and for reconstructing the redox state of ancient seawater (Frei *et al.* 2011; Bonnand *et al.* 2013).

Cr-isotope data for late Neoproterozoic BIFs reported by Frei *et al.* (2009) include 755 – 730-Myr-old Rapitan BIF, deposited during the early Cryogenian ('Sturtian') glaciation, the Marinoan-aged Chuos BIF, Namibia, and BIF- and Fe-bearing cherts of the 570 – 550-Ma Yerbal and Cerro Espuelitas formations, Uruguay, deposited well after the Gaskiers glaciation (Frei *et al.* 2009, 2013). BIFs deposited during the late Neoproterozoic record strongly positive $\delta^{53}\text{Cr}$ values ranging from 0.5‰ to 4.9‰. This supports the occurrence of a Neoproterozoic oxygenation Event (NOE) which was accompanied by tectonic upheaval, climatic extremes, and biological innovations (Shields-Zhou & Och, 2011; Och & Shields-Zhou 2012). However, Cr isotope data available for the late Neoproterozoic are limited to a few units, and suggestions for widespread ocean anoxia during the NOE (Shields-Zhou & Och 2011) request further information from the Cr-isotope tracer system.

In an attempt to provide information on the redox state of oceans in the early Ediacaran, Døssing *et al.* (2010) applied Cr isotope systematics to the Jacadigo Group, a glacio-marine succession in central Brazil deposited after 700 Ma (Babinski *et al.* 2013). This group is composed of the Urucum Formation (sandstones) at the base and the Santa Cruz Formation (BIF) at the top. Cr stable isotope measurements on various BIF horizons of the Santa Cruz Formation yielded mostly positive $\delta^{53}\text{Cr}$ values up to +0.9‰, while the Fe-rich glaciogenic diamictites and associated BIF of the likely correlative Puga Formation yielded $\delta^{53}\text{Cr}$ values from to +0.1 to +0.4‰. According to Døssing *et al.* (2010) and Gaucher *et al.* (2015), these

positively fractionated values speak for the occurrence of atmospheric oxygenation pulses during deglaciation stages, which enabled the oxidative weathering and mobilization of trivalent Cr into the oceans.

Sial *et al.* (2015a) have analyzed Cr isotopes in BIFs and overlying carbonates of the Jucurutu Formation. The Cr concentrations of these BIFs are remarkably high compared to other iron formations (e.g. Frei *et al.* 2009), with values between 85 and 400 ppm. The Jucurutu BIFs are also characterized by high-temperature magmatic $\delta^{53}\text{Cr}$ values ($\delta^{53}\text{Cr} = -0.123 \pm 0.102 \text{‰}$; Schoenberg *et al.* 2008; Crowe *et al.* 2013), unlike the other late Neoproterozoic BIFs so far analyzed (Frei *et al.* 2009, 2013; Døssing *et al.* 2010) which all yielded strongly positively fractionated $\delta^{53}\text{Cr}$ signatures. Whereas $\delta^{53}\text{Cr}$ values for BIF from the Bonito iron Mine vary from -0.23 to -0.12‰ (Cr concentration: 85 to 200 ppm), BIF from the Serra da Formiga and Saco Redondo yielded $\delta^{53}\text{Cr}$ values from -0.31 to -0.14‰ (Cr concentration: 110 to 300 ppm). BIFs from the Riacho Fundo locality display the lowest $\delta^{53}\text{Cr}$ values in the interval of -0.42 to -0.14‰ (Cr concentration: 220 to 400 ppm).

At two sections (Saco Redondo and Riacho Fundo), the more negative $\delta^{53}\text{Cr}$ values occur in the top 5 m of section and could be related to the effect of surface weathering, which mobilizes positively fractionated Cr(VI) and leaves negatively fractionated soils behind (Berger & Frei 2013; Frei & Polat 2013; Crowe *et al.* 2013). However, unweathered drill core samples from the Bonito Mine also show negative $\delta^{53}\text{Cr}$ values throughout a 30-m-thick section, between 115 and 146 m depth. It is unrealistic to assume significant weathering for samples at > 100 m depth in a semi-arid area such as the Seridó Belt. Furthermore, other lines of evidence indicate that negative $\delta^{53}\text{Cr}$ values are not the product of weathering, but represent primary features of the Jucurutu BIF, namely:

1. Surface samples yielded essentially the same $\delta^{53}\text{Cr}$ values as those from >100 m deep boreholes, showing that weathering is not the cause of the observed negative Cr isotope ratios;
2. Cr concentrations of the Jucurutu BIF are so high (avg. 220 ppm) that it would necessitate an unrealistic fluid-rock interaction during weathering to change the isotopic composition;
3. If weathering is responsible for the observed negative $\delta^{53}\text{Cr}$ values, overlying carbonates must have suffered similar or even worse alteration. With much lower Cr concentrations in the carbonates (avg. 6 ppm), their isotopic composition should have been altered even more than BIFs. However, they yielded similar or even higher $\delta^{53}\text{Cr}$ values than BIFs, which cannot

be explained if weathering played a significant role in their isotopic composition.

To assess the degree of detrital contamination, Sial *et al.* (2015a) have plotted Sc concentrations for the studied BIFs and marbles samples against $\delta^{53}\text{Cr}$. All samples consistently plot outside the detrital Cr-dominated field for $\delta^{53}\text{Cr}$ (Frei *et al.* 2013), suggesting that the basin was characterized by minimal terrigenous input from the continent. The negative $\delta^{53}\text{Cr}$ values reported by Sial *et al.* (2015a) probably is a record of primary signals, related to hydrothermal vents (see below). Marble samples in the Bonito iron Mine have “normal” Cr concentrations (1 – 3 ppm) and marbles from the Riacho Fundo and Serra da Formiga localities display slightly higher Cr values (4 – 10 ppm). Apart from a few carbonate samples from the Bonito iron Mine which are slightly positively fractionated ($\delta^{53}\text{Cr}$ around -0.05‰), the other samples have unfractionated $\delta^{53}\text{Cr}$ values within the high-temperature magmatic field.

Ubajara Group: Frecheirinha Formation

The Frecheirinha Formation is a carbonate unit about 500 m in thickness whose type area is located near the Frecheirinha town, state of Ceará (Fig. 23), and the best exposures are observed at the quarry of the Companhia Cearense de Cimento Portland, north of the Aprazível village (Chigliano *et al.* 2015 and references therein). The strata exhibit intense ductile deformation recorded by folds with axes with a NE-SW trend and, locally, low-grade metamorphism.

Carbonate rocks are represented by limestones and marly rhythmites in the lower part of the formation, passing into dark gray to gray, fine, laminated, stromatolitic limestones at the top. In the Araticum area, carbonates are composed of fine-grained, calcitic mudstones (grain size: 10 mm) intercalated with organic-rich marls in which microfossils are preserved. On the other hand, in the Angustura Farm region recrystallization of carbonates is evident, and the occurrence of tremolite in these limestones indicates low-grade metamorphic conditions. This metamorphism was probably caused by the intrusion of the nearby Mucambo granite and is not regional in nature.

Chigliano *et al.* (2015) selected the Araticum profile, located between the Frecheirinha and Ubajara villages, for palynological study because of the lower thermal overprint. There, limestone-marl rhythmites occur at the base, which pass into dark gray to black, finely laminated, organic-rich limestones, at the top.

Barroso *et al.* (2014) reported the occurrence of probable soft-bodied Ediacaran fossils in the overlying Jaibaras Group, similar to the White Sea assemblage, which could assure an Ediacaran age to this unit (560 – 542 Ma, Narbonne 2005;

Fedonkin *et al.* 2007). These biostratigraphic relationships can provide a minimum late Ediacaran age for the Frecheirinha Formation, but it needs more detailed study to prove the paleontological affinity of the fossils. The certification of a real relationship with the fossils of the Ediacara fauna needs more investigation.

The age of the Ubajara Group is still uncertain due to the lack of reliable radiometric ages. The minimum age is constrained by the following ages:

1. a Rb-Sr age of 562 ± 19 Ma determined for the Coreaú dike swarm, which crosscuts the sequence (Sial & Long 1987);

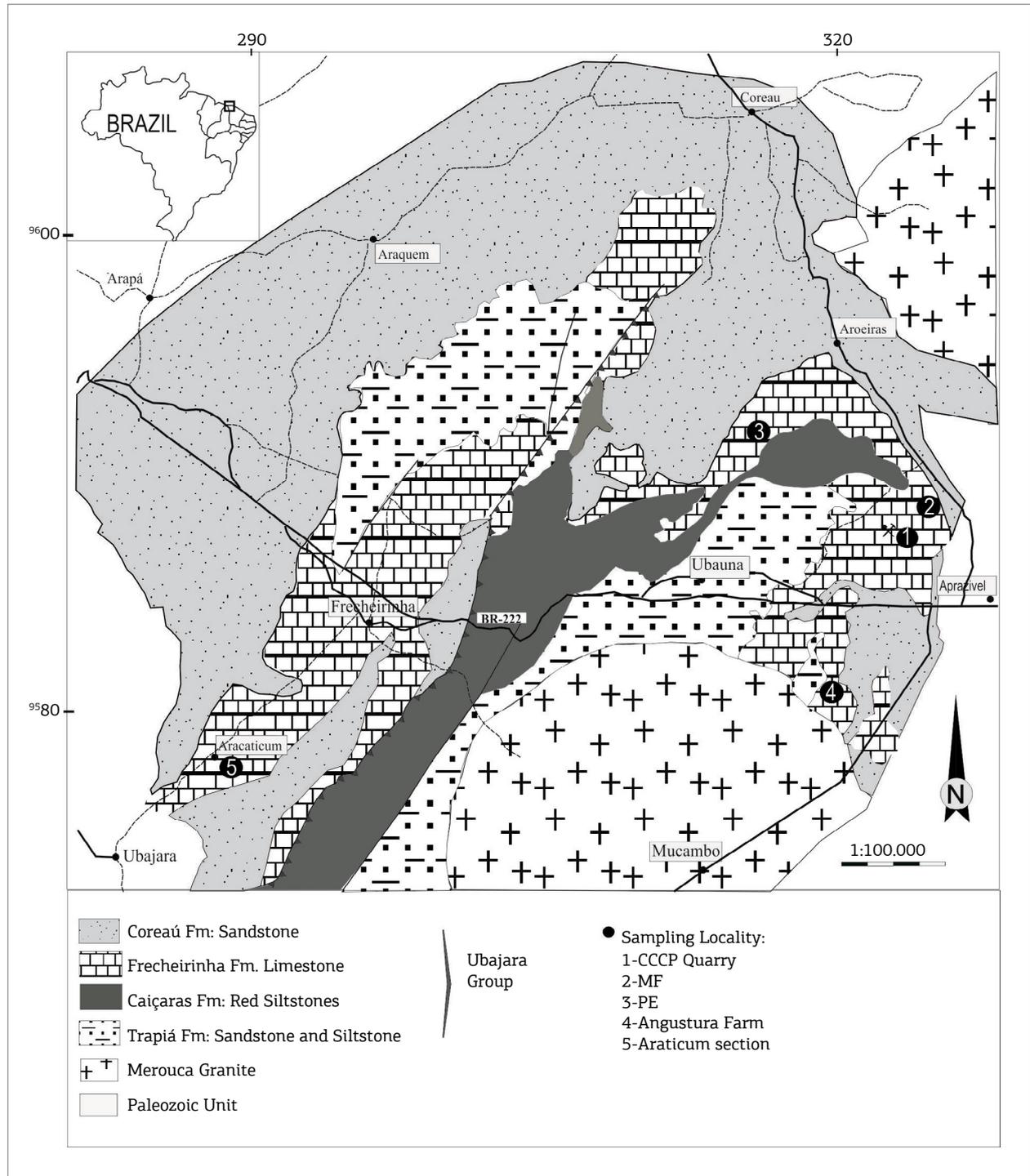


Figure 23. Geological map showing the Ubajara Group and area of outcrop of the Frecheirinha Formation (Araticum Section). Modified from Chiglino *et al.* (2015).

2. the Mucambo granite intrudes the Ubajara Group and yielded a U–Pb crystallization age of 532 ± 7 Ma (Santos *et al.* 2008); and
3. a Rb–Sr age of 540 ± 24 Ma (Sial 1989), a U–Pb age of 532 ± 24 Ma (Fetter *et al.* 2003), and a U–Pb SHRIMP age of 541 ± 5 Ma (Santos *et al.* 2013) for the Meruoca granite, which intrudes the group and develops an important contact aureole. The U–Pb SHRIMP age of 541 Ma is considered the best age estimate for the crystallization of the pluton.

Chemostratigraphic data presented by Chiglino (2013) show negative $\delta^{13}\text{C}$ values of -3.5 ‰ at the base, passing up section into a positive excursion with maximum values of $+3.7$ ‰ (Fig. 24). Corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ values range between 0.7075 and 0.7080 (Sial *et al.* 2003). Especially the Sr isotope ratios, which were obtained from high-Sr limestones (Sr concentration up to 3500 ppm; Chiglino 2013), favor a latest Cryogenian to Ediacaran depositional

age (e.g. Halverson *et al.* 2007). However, latest Cryogenian successions are often characterized by elevated $\delta^{13}\text{C}$ values of up to $+8$ ‰ which drop to negative values before the end-Cryogenian glaciation (Halverson *et al.* 2005). This pattern is not observed in the Frecheirinha Formation. Instead, a plateau around $+3$ ‰ characterizes most of the unit and postdates a negative excursion, similar to that observed for the late Ediacaran Nama and Corumbá groups (Grotzinger *et al.* 1995; Boggiani *et al.* 2010), which also yielded similar acritarchs as the Frecheirinha Formation (Chiglino *et al.* 2015). Likewise, a negative excursion followed by moderately positive values is also observed in the late Ediacaran upper Polanco Formation (Arroyo del Soldado Group, Uruguay), which is also associated to $^{87}\text{Sr}/^{86}\text{Sr}$ values between 0.7070 and 0.7082 (Gaucher *et al.* 2009; Frei *et al.* 2011). Thus, the chemostratigraphic data suggest an Ediacaran age as the most probable depositional age of the Frecheirinha Formation, but so far do not allow a more refined geochronology.

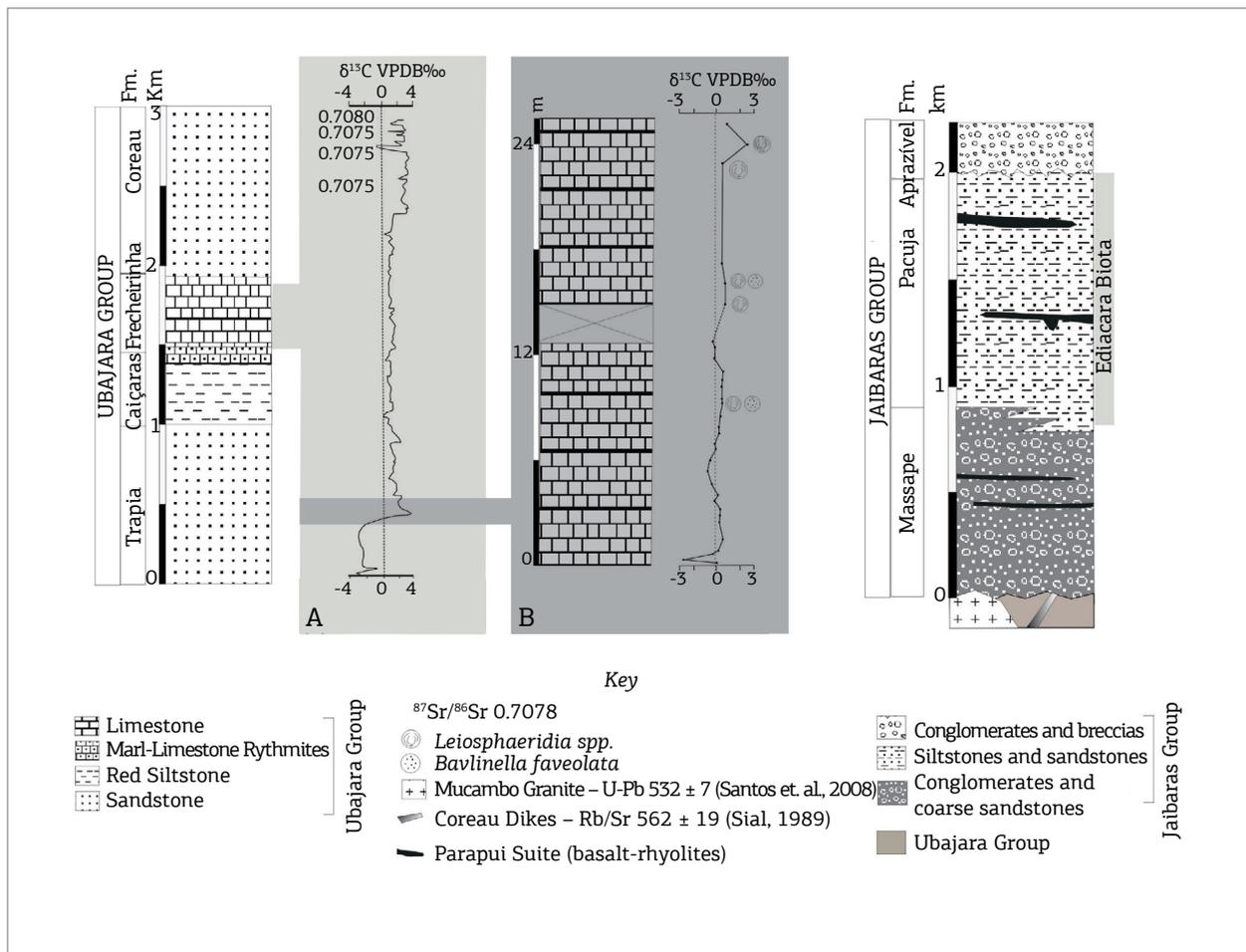


Figure 24. Lithostratigraphy of the Ubajara and Jaibaras groups, showing stratigraphic range of fossils occurring in these units. (A) $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ chemostratigraphy of the Frecheirinha Formation (Sial *et al.* 2003, Chiglino 2013); (B) Detail of the stratigraphic interval sampled (Chiglino *et al.* 2015).

RIO DE LA PLATA CRATON (URUGUAY AND ARGENTINA)

Neoproterozoic carbonate deposits occur both at the eastern and western sides of the Río de la Plata Craton (RPC). Whereas successions deposited at the eastern side are well preserved and largely unmetamorphosed (e.g. Gaucher *et al.* 2008a; Poiré & Gaucher, 2009), carbonates occurring at the western side were strongly deformed and metamorphosed during the Early Cambrian Pampean Orogeny. Due to this fact there is a paucity of chemostratigraphic studies at the western boundary of the RPC; of interest are those of the Puncoviscana Formation (Toselli *et al.* 2012) and carbonates of the Difunta Correa Sequence (Galindo *et al.* 2004). The latter unit may be unrelated to the RPC and only later tectonically accreted (e.g. Ramacciotti *et al.* 2015).

At the eastern side of the RPC, Neoproterozoic sedimentary units crop out in two different tectonostratigraphic terranes (Fig. 25), namely:

1. Nico Pérez Terrane, which crops out mainly in Uruguay, but also in southernmost Brazil. Neoproterozoic successions include the Las Ventanas and Playa Hermosa formations, the Arroyo del Soldado Group and the Marco de los Reyes Formation, and only the two latter units contain carbonates. As will be shown below, all these units are Ediacaran to lowermost Cambrian in age;
2. Tandilia Terrane, in the sense of Bossi and Cingolani (2009) and Abre *et al.* (2014), crops out both in the Tandilia area in Argentina (Buenos Aires Province) and in southern Uruguay. The Neoproterozoic units occurring in the Tandilia Terrane include the Sierras Bayas Group in Argentina, and its likely correlative Piedras Terrane in Uruguay.

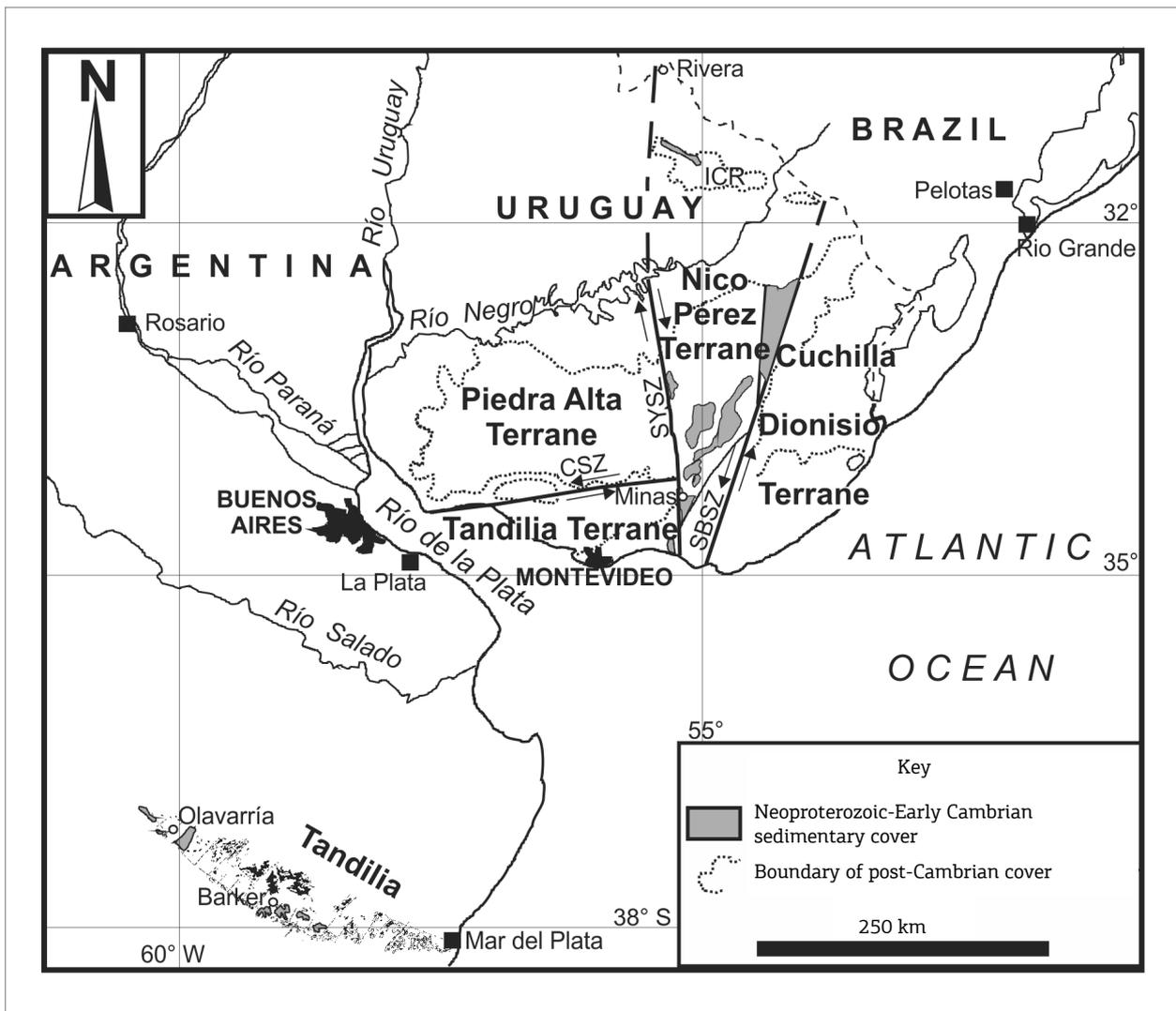


Figure 25. Simplified map of the eastern Río de la Plata Craton, showing outcrop areas of the Arroyo del Soldado Group (Nico Pérez Terrane), Piedras de Afilar Formation and Sierras Bayas Group (Tandilia). Modified from Gaucher *et al.* (2005, 2008a). ICR: Isla Cristalina de Rivera; CSZ: Colonia Shear Zone; SYSZ: Sarandí del Yí Shear Zone; SBSZ: Sierra Ballena Shear Zone.

de Aflar Formation in Uruguay (Pamoukaghlián *et al.* 2014). These units are also largely Ediacaran in age.

Arroyo del Soldado Group (Uruguay)

The opening of the Arroyo del Soldado basin is recorded in the underlying rift deposits of the Las Ventanas and Playa Hermosa formations. The Las Ventanas Formation represents a deepening-upward sequence with conglomerates at the base and middle, passing into sandstones and finally shales with marine acritarchs at the top (Masquelin & Sánchez Bettucci 1993; Blanco & Gaucher 2005, 2014; Gaucher *et al.* 2008b). Basalts occur at the base of the unit and acid volcanics and pyroclastics at the top, representing syngedimentary, bimodal volcanism (Gaucher *et al.* 2008b).

The ages of volcanic rocks allow constraining the deposition of the Las Ventanas Formation between 590 ± 2 Ma and 573 ± 11 Ma (Mallmann *et al.* 2007; Oyhantçabal *et al.* 2009). Glaciogenic diamictites occurring in the lower third have been correlated with the Gaskiers Glaciation (Blanco & Gaucher 2005; Gaucher *et al.* 2008b) which took place at ca. 583 Ma (Bowring *et al.* 2003).

The Playa Hermosa Formation is a deep-water correlate of the Las Ventanas Formation (Pazos *et al.* 2003; Rapalini *et al.* 2015). Its age is constrained between 594 ± 16 Ma (youngest detrital zircon U-Pb age) and 578 ± 4 Ma for intruding magmatic rocks (Rapalini *et al.* 2015), confirming its coeval deposition with respect to the Las Ventanas Formation. Glacially influenced deposits were also described from this unit (Pazos *et al.* 2003).

The Arroyo del Soldado Group (ASG) represents the drift stage after deposition of the rift deposits, comprising a marine platform succession exceeding 5,000 m in thickness. It rests unconformably on top of Archaean to Mesoproterozoic rocks of the Nico Pérez Terrane (Gaucher 2000, 2014). In ascending stratigraphic order, the ASG is made up of the following formations (Gaucher 2000, 2014): Barriga Negra (conglomerates and sandstones), Yermal (sandstones, shale, BIF, and minor dolostones), Polanco (carbonates), Cerro Espuelitas (shales, BIF, and chert), Cerros San Francisco (quartz-arenites), and Cerro Victoria (dolostones).

Detrital zircon U-Pb ages of the lower Barriga Negra Formation provide a maximum age constraint of 566 ± 8 Ma (Blanco *et al.* 2009). *Cloudina riemkeae*, index fossil of the late Ediacaran (Grant 1990; Gaucher & Germs 2009), occurs in the upper Yermal Formation and in the lower-middle Polanco Formation (Gaucher & Poiré 2009a). Trace fossils assigned to *Thalassinoides* were described from the Cerro Victoria Formation, showing that this unit is already Early Cambrian in age (Sprechmann *et al.* 2004). Thus, except for the Cerro Victoria Formation and possibly also the

Cerros San Francisco quartz-arenites, the age of the ASG is late Ediacaran.

Several chemostratigraphic studies were carried out in the ASG, including C, O, Sr, Cr, and Nd isotopes, iron speciation and REE analyses. We summarize in the following main findings of these studies.

Only scarce chemostratigraphic data are available for marls of the upper Barriga Negra Formation, $\delta^{13}\text{C}$ varying between -5.5 and -1.4‰ (Gaucher *et al.* 2004, this work). In the Yermal Formation, $\delta^{13}\text{C}$ values for interbedded dolostones are positive, increasing from 1.2 to 2.2‰ toward the top (Gaucher *et al.* 2004). These values may be interpreted as postdating those of the Barriga Negra Formation, which are all negative. $\delta^{53}\text{Cr}$ values of ferruginous cherts and BIF yielded strongly positive values of up to 5‰ SRM 979 (Frei *et al.* 2013), which are interpreted as reflecting oxygenic weathering in the source area. It is worth noting that these $\delta^{53}\text{Cr}$ values are the highest so far obtained for iron formations (Frei *et al.* 2009).

Due to the pure and uninterrupted carbonates that compose the unit, the Polanco Formation represents a formidable chemostratigraphic archive (Fig. 26). Three positive $\delta^{13}\text{C}$ excursions occur at the base (P_1), middle (P_2), and upper parts of the unit (P_3), reaching 5.5‰ , 2.1‰ , and 4.1‰ , respectively (Gaucher *et al.* 2004, 2009; Frei *et al.* 2011; Fig. B). The intervening negative excursions coincide with regressions, the most prominent being N_1 , which encompasses 200 m of section and drops to nadir $\delta^{13}\text{C}$ values of -4.5‰ (Gaucher *et al.* 2004, 2009b). This negative excursion has been correlated with the Shuram-Wonoka anomaly (Gaucher *et al.* 2009b; Boggiani *et al.* 2010; Frei *et al.* 2011; Gaucher 2014), which ended just before 551 ± 1 Ma (Condon *et al.* 2005). The upper N_2 negative excursion (-2‰ VPDB) marks the top of the Polanco Formation (Gaucher *et al.* 2004, 2009; Frei *et al.* 2011; Fig. 26).

Secular variations can be recognized in the $^{87}\text{Sr}/^{86}\text{Sr}$ curve of the Polanco Formation (Gaucher *et al.* 2009b; Frei *et al.* 2011; Gaucher 2014), which are relevant to determine the precise shape of the global Ediacaran $^{87}\text{Sr}/^{86}\text{Sr}$ curve. Limestones contain in average 1025 ppm Sr, reaching more than 3000 ppm (Gaucher *et al.* 2009; Gaucher 2014). $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.7087 at the base of the Polanco Formation decrease steadily up section, reaching a plateau around 0.7070 in the middle part of the unit (Gaucher *et al.* 2009; Frei *et al.* 2011; Fig. 26). $^{87}\text{Sr}/^{86}\text{Sr}$ analyses are more erratic in the upper part of the unit, but it seems clear that there is a return to higher ratios of 0.7080 – 0.7085 (Gaucher *et al.* 2009; Frei *et al.* 2011). The more than 300 m of section characterized by low $^{87}\text{Sr}/^{86}\text{Sr}$ values encompasses the N_1 negative $\delta^{13}\text{C}$ excursion. On the basis of elevated $\epsilon\text{Nd}(t)$

values in the same carbonates (Fig. 26), Frei et al. (2011) proposed that the fall of $^{87}\text{Sr}/^{86}\text{Sr}$ values may represent a distal hydrothermal signature caused by widespread rifting

elsewhere. A similar pattern is observed between the late Triassic and Late Jurassic, when $^{87}\text{Sr}/^{86}\text{Sr}$ fell between more

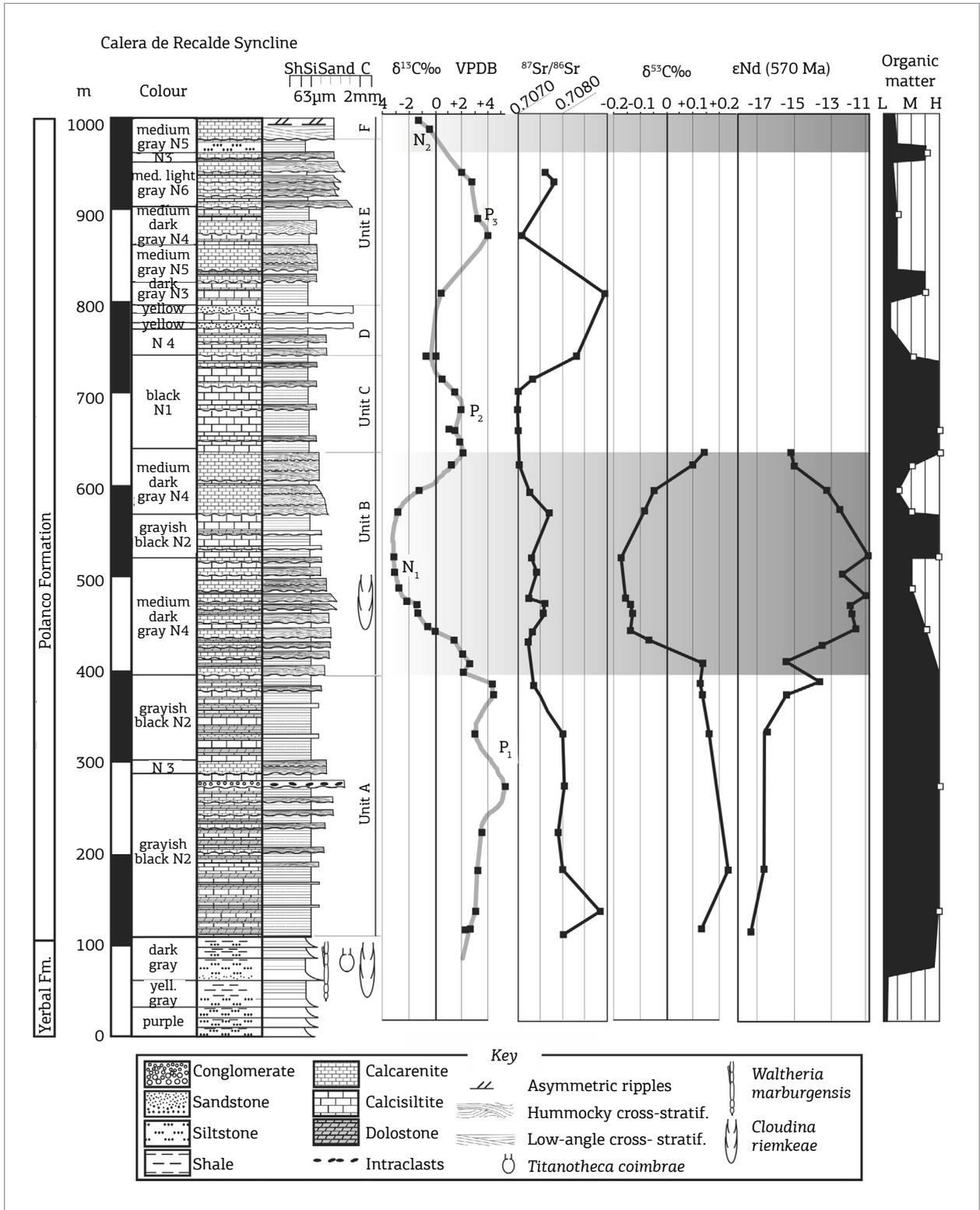


Figure 26. Stratigraphic column of the Polanco Formation at Calera de Recalde Syncline, showing $\epsilon^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\epsilon^{53}\text{Cr}$ and ϵNd data. Modified from Gaucher et al. (2004, 2009b), Frei et al. (2011) and Gaucher (2014).

than 0.7080 and 0.7068 (e.g. Veizer *et al.* 1999), related to the breakup of Pangaea.

Only minor carbonate interbeds occur in the overlying Cerro Espuelitas Formation, which yielded negative $\delta^{13}\text{C}$ values, interpreted as a continuation of the N_2 negative excursion of the upper Polanco Formation (Gaucher *et al.* 2004, 2009). Magnetite BIF of the same unit yielded positive $\delta^{53}\text{Cr}$ values of up to 1.3‰ SRM 979 (Frei *et al.* 2013), thus lower than hematite-bearing BIF of the Yermal Formation. At the top of the ASG, the Cerro Victoria Formation yielded a low-amplitude $\delta^{13}\text{C}$ curve consistent with an earliest Cambrian age (Gaucher *et al.* 2007; Sprechmann *et al.* 2004).

Combined bio- and chemostratigraphic data enabled the correlation at the formational level between the Corumbá and Arroyo del Soldado Groups, and between the latter unit and the Sierras Bayas Group in Argentina (see below). These correlations (Fig. 27) suggest that an extensive carbonate platform covered the eastern RPC in the late Ediacaran and likely continued northwards into the Rio Apa Block (Gaucher *et al.* 2003, 2008a).

Marco de los Reyes Formation (Uruguay)

This unit was erected by Chigolino *et al.* (2010) to include a sedimentary succession occurring in the Nico Pérez Terrane and metamorphosed in the amphibolite facies. The unit comprises dark limestone, BIF, chert, and mica-schist. Limestones yielded $\delta^{13}\text{C}$ values between 4.4 and -3.2‰. Corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ values consistently fall between 0.7070 and 0.7080 for high-Sr limestones (average: 1882 ppm; Chigolino *et al.* 2010). Given that both $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ fall within the range reported for the ASG, a correlation between both units seems probable (Chigolino *et al.* 2010; Bossi *et al.* 2014).

Sierras Bayas Group (Argentina)

The Sierras Bayas Group (SBG) occurs in the Tandilia range in Argentina (Fig. 25). It is an unmetamorphosed, flat-lying, marine sedimentary succession representing a cratonic cover (Poiré 1987; Poiré & Gaucher 2009; Cingolani 2011, and references therein). From base to top the following stratigraphic units are recognized (Fig. 27):

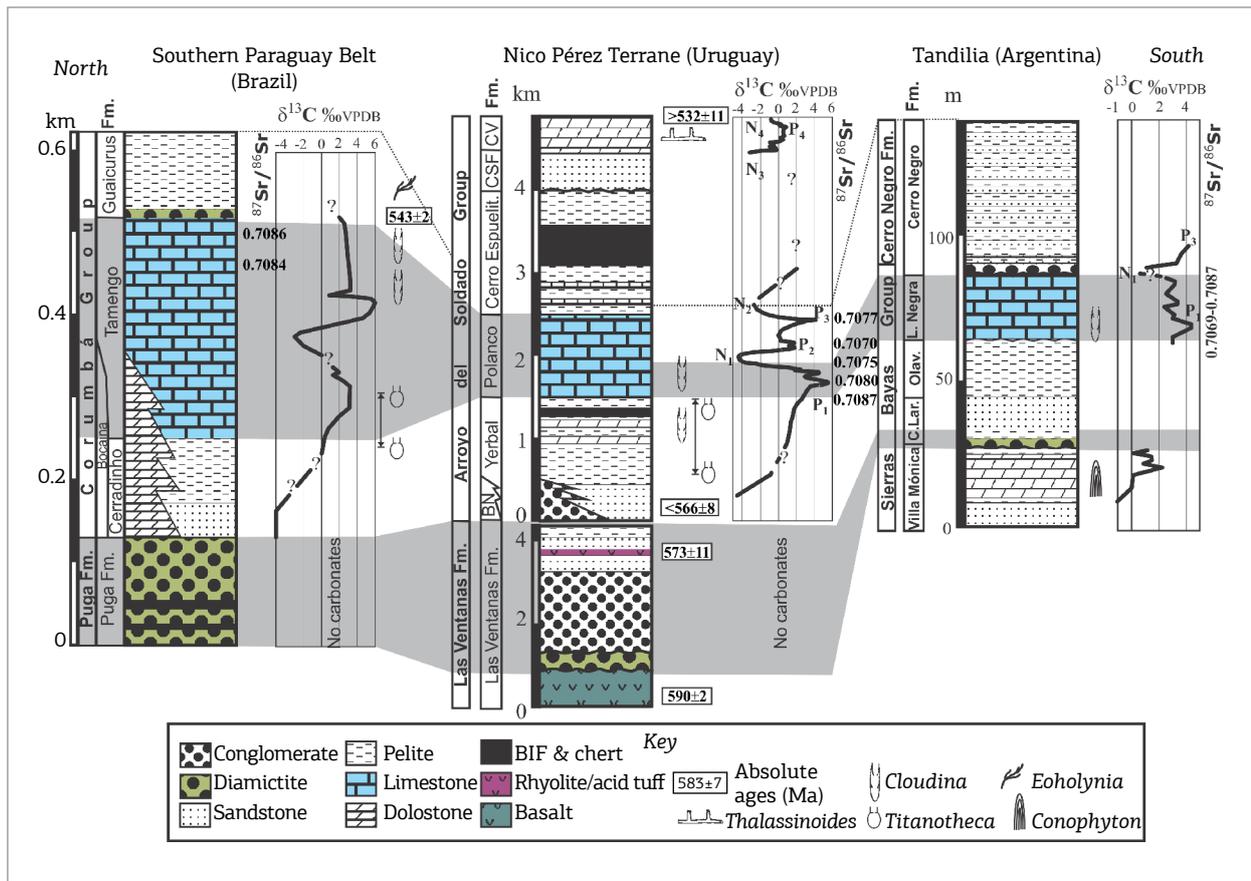


Figure 27. Stratigraphy and correlations of the ASG with the Corumbá Group in Brazil (Gaucher *et al.* 2003; Boggiani *et al.* 2010) and Sierras Bayas Group in Argentina (Gaucher *et al.* 2005; Poiré and Gaucher, 2009), as well as underlying glaciogenic units. Modified from Gaucher (2014). BN: Barriga Negra Fm. CSF: Cerros San Francisco Fm. CV: Cerro Victoria Fm. C.Lar.: Cerro Largo Fm. Olav.: Olavarría Fm. L. Negra: Loma Negra Fm. Sources of chemo- and biostratigraphic data and absolute ages: see text.

1. Villa Mónica Formation: stromatolitic dolostones, minor phosphorite (Gómez-Peral *et al.* 2014).
2. Cerro Largo Formation: cross-bedded quartz-arenite and subordinated shale, with a distinct diamictite unit (Colombo Member) at the base (Poiré & Gaucher 2009).
3. Olavarría Formation: shales, bearing low-diversity acritarchs (Gaucher *et al.* 2005).
4. Loma Negra Formation: *Cloudina*-bearing, fine-grained limestones (Gaucher *et al.* 2005; Gaucher & Poiré 2009a).

The Cerro Negro Formation (shales, sandstones, marls, and minor phosphorite) overlies the SBG with erosional unconformity (Gómez Peral *et al.* 2014, and references therein).

The Colombo diamictite may represent glacially influenced, rift-related deposits (Poiré & Gaucher 2009; Gaucher & Poiré 2009b) which can be correlated to diamictites of the Las Ventanas and Playa Hermosa formations in Uruguay. Rapalini *et al.* (2013) obtained similar paleopoles for both units, supporting this correlation.

Several chemostratigraphic studies were carried out in the SBG and Cerro Negro Formation. The Villa Mónica dolostones are characterized by rising $\delta^{13}\text{C}$ values (-2.2 to 2.2‰) and $^{87}\text{Sr}/^{86}\text{Sr}$ between 0.7069 and 0.7071 (Fig. 27), although the primary nature of the latter remains to be proved (Gómez Peral *et al.* 2007, 2014). The age of the Villa Mónica Formation can so far be regarded as Neoproterozoic, but more analyses are needed to further constrain it.

The Loma Negra Formation is characterized by positive $\delta^{13}\text{C}$ ratios, decreasing up-section from 4.5‰ to near zero (Gómez Peral *et al.* 2007; Bagnoud-Velásquez *et al.* 2013). $^{87}\text{Sr}/^{86}\text{Sr}$ analyses in the same unit yielded ratios between 0.7069 and 0.7087 (Kawashita *et al.* 1999). Taken together, both C and Sr isotope values match those obtained for the lower Polanco Formation of the ASG (Fig. 27).

$\delta^{13}\text{C}_{\text{org}}$ in the Loma Negra Formation varies between -23 and -28‰, with corresponding $\text{D}\delta^{13}\text{C}_{\text{car-org}}$ ranging between 25 and 32‰ (Gómez Peral *et al.* 2007; Bagnoud-Velásquez *et al.* 2013). This is interpreted as reflecting the original fractionation by oxygenic photoautotrophs (Bagnoud-Velásquez *et al.* 2013), which agrees with the reported eukaryotic microbiota dominated by *Leiosphaeridia* (Gaucher *et al.* 2005).

Reported $\delta^{34}\text{S}$ pyrite values (24 – 32.5 ‰ CDT) in the Loma Negra Formation are heavier than $\delta^{34}\text{S}_{\text{CAS}}$ for the same unit (24 – 29 ‰, Bagnoud-Velásquez *et al.* 2013). This “superheavy pyrites” have been interpreted for the coeval Nama Group (southern Africa) as the result of enhanced bacterial sulphate-reduction activity in a low sulphate environment, hinting at low atmospheric O_2 contents in the latest Ediacaran (Ries *et al.* 2009).

As for the Cerro Negro Formation, basal phosphorites yielded negative $\delta^{13}\text{C}$ values around -1‰ VPDB, steadily increasing in overlying marls to a maximum of 4.3‰. This latter positive excursion may match the P_3 excursion of the upper Polanco Formation (4.1 ‰). As a condensed succession deposited in a shallow-water setting, it is not surprising that in the SBG erosional unconformities mark the regressions recorded in the deeper-water ASG, most notably carbonates deposited during N_1 . Acritarchs of the Cerro Negro Formation suggest a late Ediacaran age for the unit (Cingolani *et al.* 1991; Gaucher *et al.* 2005).

CHEMOSTRATIGRAPHIC CORRELATIONS: DISCUSSION AND CONCLUSIONS

It is well known that fossils and U-Pb ages are the most reliable tools in stratigraphic correlation of sedimentary successions. In this way, it is possible that the upper Itapucumí Group, Tamengo, upper Sete Lagoas, Loma Negra, and Polanco formations are all correlative because they host *Cloudina* and, therefore, could be of late Ediacaran age (ca. 560 – 541 Ma). The Frecheirinha Formation hosts an impoverished acritarch biota which points also to a late Ediacaran age.

Limited knowledge of absolute ages among some of the successions discussed in this study represents an obstacle in precise their stratigraphic correlation. U-Pb ages from detrital zircons have been used in cases when datable volcanic rocks are absent. This has led occasionally to controversial interpretations when ages obtained this way are contrasted with those from other methods applied to same stratigraphic intervals. For example, Pb-Pb model age for the Sete Lagoas Formation (740 ± 22 Ma) regarded as acceptable geochronological data until recently (Babinski *et al.* 2007) has been contested by U-Pb age of detrital zircon (610 Ma) from the same stratigraphic interval (Pimentel *et al.* 2011). Furthermore, the presence of *Cloudina sp.* in the the Sete Lagoas Formation suggests a late Ediacaran age, at least for exposures in central-eastern Brazil.

In the absence of fossils and/or radiometric age dating, elemental and isotope chemostratigraphy (e.g. Sr, C, S, Ca, Cr, Mo, N isotopes), in spite of limitations, may represent an important tool in stratigraphic correlation. Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) have been used with this purpose after its suggested monotone rise from Tonian through Cambrian has been proposed (e.g. Halverson *et al.* 2010). One cannot ignore, however, that large $^{87}\text{Sr}/^{86}\text{Sr}$ secular variations, within one same late Ediacaran succession, has been sometimes observed (e.g. from 0.7070 to 0.7087 in

a 900-m-thick, high-Sr limestone section of the Polanco Formation, Uruguay) implying a severe limitation on its use as a stand-alone proxy. If one compares with the more detailed $^{87}\text{Sr}/^{86}\text{Sr}$ Phanerozoic record, characterized by strong $^{87}\text{Sr}/^{86}\text{Sr}$ oscillations (Veizer *et al.*, 1999) the proposed monotone $^{87}\text{Sr}/^{86}\text{Sr}$ rise in the Neoproterozoic is likely an artifact of low sampling resolution.

A tentative correlation of the carbonate-dominated successions in this study, based on available $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ values, is shown in Table 1. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for pure carbonates of the Jucurutu Formation (0.7074 – 0.7075) are equivalent to those found for the early Ediacaran Mirassol D'Oeste Formation in the Paraguay Belt, and Maieberg Formation, Otavi Group (Namibia). According to detrital zircons and intrusions the depositional age of the Jucurutu Formation should be between 634 Ma (youngest zircon) and 591 Ma (Totoró Granite). The Seridó Fm. is younger than 611 ± 7 Ma.

From the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{13}\text{C}$ compilation shown in Table 1, apparently the Cryogenian (circa 720 – 635 Ma; Shields-Zhou *et al.* 2016) is poorly represented among the examined carbonate-dominated successions, except for the Jacoca and Acauá formations, and the end-Cryogenian Palestina, Jequitaí, Bebedouro, and Puga glaciogenic diamictites. There is a possibility that the deposition of the Panelinhas and Cabravinha formations happened at the end-Cryogenian glaciation, but so far there is no radiometric constraint. Despite of the effort

to precise the depositional age of rocks of the Bambuí and Una groups (U–Pb dating, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{13}\text{C}$ and paleontological data), this is still a matter of strong debate, far from being settled. It cannot be totally discarded the possibility that the sedimentation of part of this group happened in the early-to-middle Cryogenian as shown in Table 1.

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