Ore Geology Reviews 63 (2014) 76–90

Contents lists available at ScienceDirect

Ore Geology Reviews

journal homepage: www.elsevier.com/locate/oregeorev

Review of the geological and geochronological framework of the Vazante sequence, Minas Gerais, Brazil: Implications to metallogenic and phosphogenic models

A. Misi [a,*], K. Azmy [b], A.J. Kaufman [c], T.F. Oliveira [d], A.L. Sanches [a,e], G.D. Oliveira [f]

[a] *Grupo de Metalogênese, Centro de Pesquisa e Pós-Graduação em Geofísica e Geologia da Universidade Federal da Bahia, Campus Ondina–Federação, 40210-340 Salvador, BA, Brazil*
[b] *Department of Earth Sciences, Memorial University of Newfoundland, St. John's, NL A1B 3X5, Canada*
[c] *Department of Geology and Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD, USA*
[d] *Independent consultant, Rio de Janeiro, RJ, Brazil*
[e] *Departamento de Ciências Naturais, Universidade Estadual do Sudoeste da Bahia, Brazil*
[f] *Votorantim Metais, Vazante, MG, Brazil*

ARTICLE INFO

Article history:
Received 8 August 2013
Received in revised form 29 April 2014
Accepted 2 May 2014
Available online 9 May 2014

Keywords:
Vazante Group
Geochronology
Stratigraphic framework
Zn–Pb deposits
Phosphorite deposits

ABSTRACT

The Vazante Group, as originally described, is a thick marine carbonate-dominated succession adjacent to the Brasilia Fold Belt, on the western border of the São Francisco Craton, in south-central Brazil. The sedimentary dolomites of this group contain economically important Zn–Pb and phosphate deposits, but age constraints for the host rocks and mineralization have been controversial. New geochronological data and geological observations have indicated that the upper and middle sections of the Vazante succession belong to a Mesoproterozoic sequence that was thrust over a Neoproterozoic succession correlative with the Bambuí Group. This new stratigraphic framework has significant implications for metallogenic exploration models in both intra-cratonic and passive-margin basins of the São Francisco Craton. Although hosted in Mesoproterozoic units, most of the Zn–Pb mineralization occurred in the Neoproterozoic by circulating hydrothermal fluids during the prolonged breakup of the Rodinia supercontinent. The possibility that an initial stage of mineralization occurred earlier is considered. Phosphorite generation in the Neoproterozoic units is conceivably related to glacial events. The refined stratigraphy combined with a new mineralization model will significantly contribute to the exploration strategy for phosphate and sulfide deposits in the Mesoproterozoic and Neoproterozoic successions of the São Francisco Craton and beyond.

1. Introduction

The Vazante Group, as defined by Dardenne et al. (1998), is a thick marine carbonate-dominated succession adjacent to the Brasilia Fold Belt, on the western border of the São Francisco Craton in south-central Brazil. The sedimentary dolomites of this group contain economically important Zn–Pb and phosphate deposits, but age constraints for the succession have been controversial.

Vazante and Morro Agudo Zn–Pb mines, in the upper section of the Vazante Group, are the largest Zn deposits in South America, with reserves of more than 3 million tons of zinc. Vazante is the largest mine, producing around 170,000 tons of Zn concentrate per year (IBRAM, 2013). The phosphate deposits of Rocinha, Lagamar, in the lower section, are the most important phosphorite mines in South America, ranking among the 200 largest mines of Brazil in 2008. In recent years mine production were, respectively, 261,321 and 250,000 tons/year ROM, with grades ranging from 10 to 15% P_2O_5 (Kulaif, 2009).

Earlier lithostratigraphic comparisons and paleontological observations of *Conophyton* stromatolites suggested that Vazante carbonates belonged to the late Mesoproterozoic or early Neoproterozoic eras, with possible ages ranging between 1.35 and 0.95 Ga (Cloud and Dardenne, 1973; Moeri, 1972). Others researchers, however, suggested a possible correlation of Vazante strata with the Neoproterozoic carbonate platform of the Bambuí Group (ca. 0.9–0.6 Ga), which covers large areas of the São Francisco Craton to the east (Dardenne, 1979; Dardenne, 2000, 2001; Azmy et al., 2001; Misi, 2001). These correlations were based primarily on the similarity of diamictites at the base of both groups (Dardenne, 2000), possibly related to a Sturtian ice age (Azmy et al., 2001; Babinski and Kaufman, 2003; Babinski et al., 2007). In addition, $^{87}Sr/^{86}Sr$ compositions (0.70752 to 0.70794) of high Sr carbonate fluorapatite samples from phosphate deposits of the Rocinha

---

* Corresponding author.
E-mail address: aroldo.misi@gmail.com (A. Misi).

http://dx.doi.org/10.1016/j.oregeorev.2014.05.002
0169-1368/

Formation (lower Vazante) are identical to those of micrites in Irecê (Una Group likely equivalent to the Bambuí Group on the São Francisco Craton; Misi et al., 2007). These observations were consistent with a Neoproterozoic age assignment (Halverson et al., 2010; Misi, 2001; Misi et al., 1997, 2007; Sanches et al., 2007).

However, since the biostratigraphic utility of *Conophyton* as a time-marker is equivocal and Sr isotope compositions are easily reset, radiometric constraints for both the Vazante and Bambuí successions were needed to provide an absolute age for the glacial deposits a-priori assumed to be from the Neoproterozoic Cryogenian Period. Contrary to this expectation, recent geochronological studies of Vazante rocks utilizing Re/Os measurements from organic-rich shales in the upper part of the succession (Azmy et al., 2008; Geboy et al, 2013) coupled with U/Pb detrital zircon analyses (Azmy et al., 2008; Rodrigues et al., 2012) suggest that upper Vazante strata, including two potential glacial diamictites, may belong to the late Mesoproterozoic Era (Geboy et al., 2013). However, data for the lower part of the succession, including the basal glacial diamictite, indicate Neoproterozoic age.

In this paper we propose a new stratigraphic framework for the Vazante sequence (previously called the Vazante Group). The stratigraphic inversion observed results from a thrust fault near the top of the Rocinha Formation that places older rocks atop younger. This redefinition has significant implications for reviewing the metallogenic and phosphogenic models previously proposed, with important consequences for mineral exploration in both intra-cratonic and passive-margin Meso- and Neoproterozoic basins of the São Francisco Craton and other similar geotectonic settings.

2. The geotectonic context of the Brasilia Fold Belt and the Vazante sequences

The Brasília Fold Belt (BFB) lies on the western border of the São Francisco Craton and extends for more than 1000 km along an N–S trend with a width of ~300 km (Fig. 1). The belt is composed of sedimentary and meta-sedimentary rocks, including the following mega-units, according to Dardenne (2000): a) the Paleoproterozoic to Mesoproterozoic Araí and Serra da Mesa groups. The Araí Group is composed of: (i) continental pre-rift (eolian and fluvial) sediments, (ii) rift sequence, including conglomerate, breccias and intercalated volcanic rocks, and (iii) post-rift marine transgressive sediments (carbonates, quartzite). The Serra da Mesa Group consists of a thick sequence of quartzite and micaschist (~1800 m) that, although partially correlated to post-rift sedimentation of the Araí Group, are dominantly Mesoproterozoic in age; b) the Mesoproterozoic Paranoá and Canastra groups (northern and southern segments of the BFB, respectively) consisting of quartzite, pelitic and carbonate rocks metamorphosed in the greenschist facies; c) the Mesoproterozoic to Neoproterozoic Araxá, Ibiá and Vazante groups, in the southern segment of the BFB. The Araxá Group is probably correlated with the Serra da Mesa Group in the northern segment and is composed of micaceous quartzite and micaschists, with volcanic rocks associated. The Ibiá Group is composed essentially of diamictites (basal section), interpreted as glaciogenic, and of calcshists + calciferous phyllite units in the upper section. Diamictite beds have been correlated with the Jequitai Formation of the Neoproterozoic Bambuí Group, and d) the Neoproterozoic Bambuí Group, composed of glaciogenic diamictites + marine carbonates and phyllites. In addition, the BFB contains igneous intrusions and volcano-clastic sedimentary rocks of e) the Paleoproterozoic to Mesoproterozoic Niquelândia, Barro Alto and Canabrava mafic to ultramafic complexes; f) the Mesoproterozoic Juscelândia, Palmeirópolis and Indianópolis volcano-sedimentary sequences, and g) Neoproterozoic synorogenic, late orogenic, and postorogenic granitic and mafic–ultramafic bodies, including the Goiás magmatic arc.

Based on the degree of deformation and metamorphism, Dardenne (1978) and Fuck (1994) have described three geotectonic zones within the BFB from west to east. These zones consist of a western *Internal zone*, which is intensely deformed and metamorphosed to amphibolite facies, a central *External zone*, which is slightly to moderately deformed and metamorphosed, including the Vazante strata, and an eastern *Cratonic zone*, which is only slightly deformed with greenschist to sub-greenschist facies metamorphism, including the Bambuí Group. On the other hand, Marini et al. (1984) described a remarkable E–W lineament (Pirineus lineament) dividing the BFB into two segments, including a *Northern segment* in which the sedimentary rocks are well-preserved and less deformed with very low degrees of metamorphism, and a *Southern segment*, with more intense deformation and metamorphism, including the rock units of the Vazante strata. In the southern segment, the Araxá, Canastra, Ibiá, and Vazante groups were included in a complex imbricated system of nappes and thrusts, which obstructed the recognition of stratigraphic relationships between these rock units and, in some cases, even their internal stratigraphic organization (Dardenne, 1978; Marini et al., 1984).

The seven meta-sedimentary formations of the Vazante Group, as defined by Dardenne et al. (1998) and Dardenne (2000, 2001) are briefly described in structural order below. Sedimentary structures like teepee, columnar stromatolites and ripple marks suggest a normal stratigraphic succession of these rock units. Dardenne (2001) suggested that the total thickness of the Vazante Group was ~5000 m, but thrust faults from the west certainly resulted in stratigraphic repetition. Therefore, the true thickness of these units is only poorly constrained by the available outcrops and cores and will not be considered here (Fig. 2).

2.1. Santo Antonio do Bonito Formation

This unit contains graded quartzite, conglomerates, and intercalated slate beds. Diamictites are characterized by faceted and striated clasts of quartzite, as well as clasts of limestone, dolomite, meta-siltstone and granitoid, all of variable dimensions and floating in a pelitic matrix, which is locally rich in phosphate (Coromandel deposit).

2.2. Rocinha Formation

The unit contains rhythmites with white basal carbonate followed by yellow to reddish slate and meta-siltstone that pass into dark gray, carbonaceous and pyrite-rich slate with fine-grained phosphate laminations and phosphate-rich arenaceous intraclasts. There are two important phosphorite deposits in the Rocinha Formation including the stratigraphically lower Rocinha mine and the overlying Lagamar mine. Other minor phosphate deposits are also present in the formation.

2.3. Lagamar Formation

Basal beds in this interval consist of alternations of conglomerate, quartzite and meta-siltstone with dark-gray limestone clasts, known as the Arrependido conglomerate or Arrependido Member. They are overlain by laminated, brecciated, oncolitic or stromatolitic limestone and dolomite at the top. Stromatolites occur as small mounded bioherms composed of beige to pale pink dolomite, likely constructed from cyanobacterial mats, and as large columns with convex and conical laminations, classified as *Conophyton metula* and *Jacutophyton*. The latter forms were previously used to suggest an age of 1.35 to 0.95 Ga for this formation (Cloud and Dardenne, 1973; Moeri, 1972).

2.4. Serra do Garrote Formation

This unit contains dark-gray to greenish-gray slate and rhythmite with carbonaceous, pyrite-rich slate intercalated with fine-grained quartzite.

2.5. Serra do Poço Verde Formation

This is a thick and heterogeneous dolomitic succession composed of (i) oncolitic dolarenites, intra-formational breccia, and dolomitic columnar stromatolites (lower Morro do Pinheiro Member); (ii) medium to dark-gray laminated dolostone with laminar stromatolites and bird-eye structures, with some layers of dolarenites, lamellar breccias and carbonaceous shale (upper Morro do Pinheiro Member); (iii) gray, green and purple siltstone intercalated with pink micritic laminated dolostone with laminar stromatolites and lenses of fine-grained to coarse-grained (conglomeratic) sandstones. The rich zinc silicate (willemite) deposits of Vazante (Vazante mine) are associated with this facies (lower Pamplona Member); and (iv) light gray to pink dolostone with microbialaminite, intercalated with dolarenite, dolomitic breccia

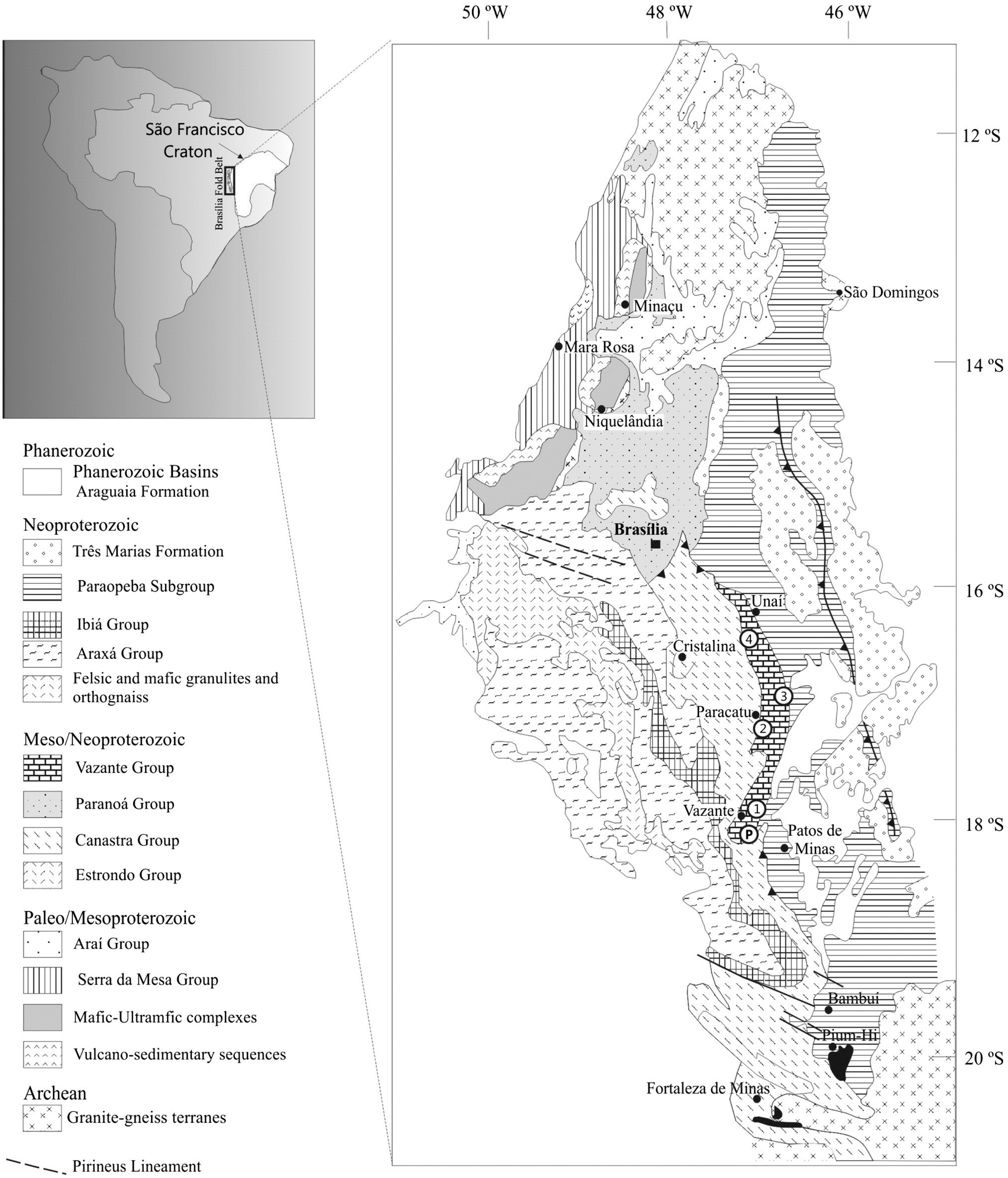
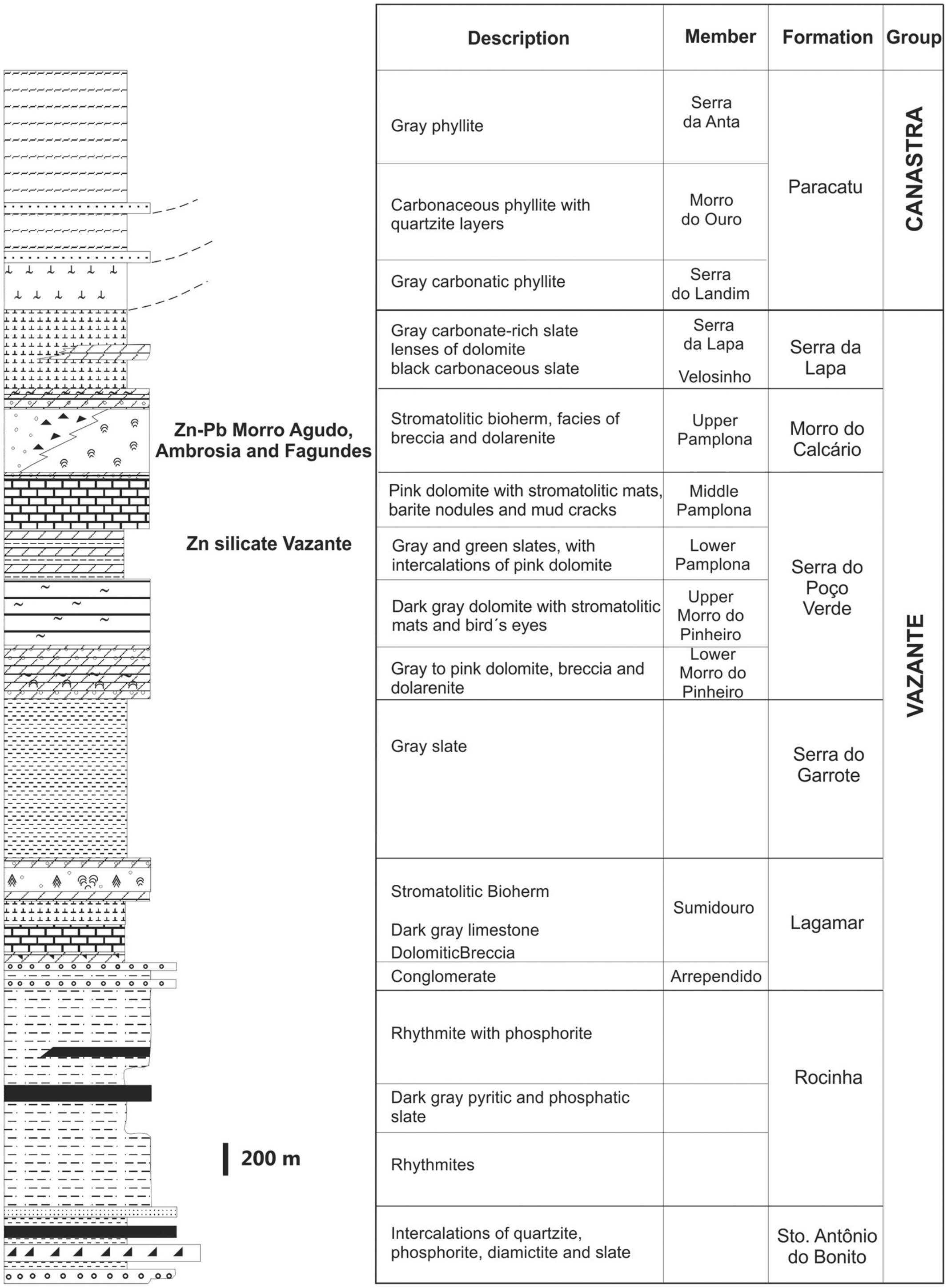


Fig. 1. Simplified geological map of the Brasilia Fold Belt showing the Paleo-Meso-Neoproterozoic units (modified from Marini et al., 1984; Dardenne, 2000; Pimentel et al., 2001; Valeriano et al., 2004). Zn–Pb deposits: (1) Vazante mine (2) Morro Agudo mine (3) Fagundes deposit and (3) Ambrosia deposit. Phosphate deposits: (P) Lagamar, Rocinha, Coromandel.



Description	Member	Formation	Group
Gray phyllite	Serra da Anta	Paracatu	CANASTRA
Carbonaceous phyllite with quartzite layers	Morro do Ouro		
Gray carbonatic phyllite	Serra do Landim		
Gray carbonate-rich slate lenses of dolomite black carbonaceous slate	Serra da Lapa Velosinho	Serra da Lapa	VAZANTE
Stromatolitic bioherm, facies of breccia and dolarenite	Upper Pamplona	Morro do Calcário	
Pink dolomite with stromatolitic mats, barite nodules and mud cracks	Middle Pamplona	Serra do Poço Verde	
Gray and green slates, with intercalations of pink dolomite	Lower Pamplona		
Dark gray dolomite with stromatolitic mats and bird´s eyes	Upper Morro do Pinheiro		
Gray to pink dolomite, breccia and dolarenite	Lower Morro do Pinheiro		
Gray slate		Serra do Garrote	
Stromatolitic Bioherm Dark gray limestone DolomiticBreccia	Sumidouro	Lagamar	
Conglomerate	Arrependido		
Rhythmite with phosphorite		Rocinha	
Dark gray pyritic and phosphatic slate			
Rhythmites			
Intercalations of quartzite, phosphorite, diamictite and slate		Sto. Antônio do Bonito	

Fig. 2. Schematic diagram summarizing the lithostratigraphic framework of the Vazante Group (after Dardenne, 2001). The stratigraphic levels of Zn–Pb and phosphate (P) deposits are marked on the figure.

and columnar stromatolites, along with shale lenses (middle Pamplona Member).

2.6. Morro do Calcário Formation

This unit was previously the Upper Pamplona Member of the "Vazante Formation" in an earlier stratigraphic scheme (Dardenne, 1978). It is composed of stromatolitic dolostones and oolitic to oncolitic dolarenites and dolorudites. Black shale with dropstones and faceted cobbles (diamictites), previously identified as in the basal section of the Serra da Lapa Formation, are also present. This unit hosts the important Pb–Zn mine of Morro Agudo and similar deposits at Fagundes and Ambrosia (Fig. 1).

2.7. Serra da Lapa Formation

The upper interval of the Vazante Group is composed of carbonaceous phyllites and meta-siltstones, dolomite, and quartzite (Madalosso and Valle, 1978). The dolomitic intervals appear as lenses containing laminar

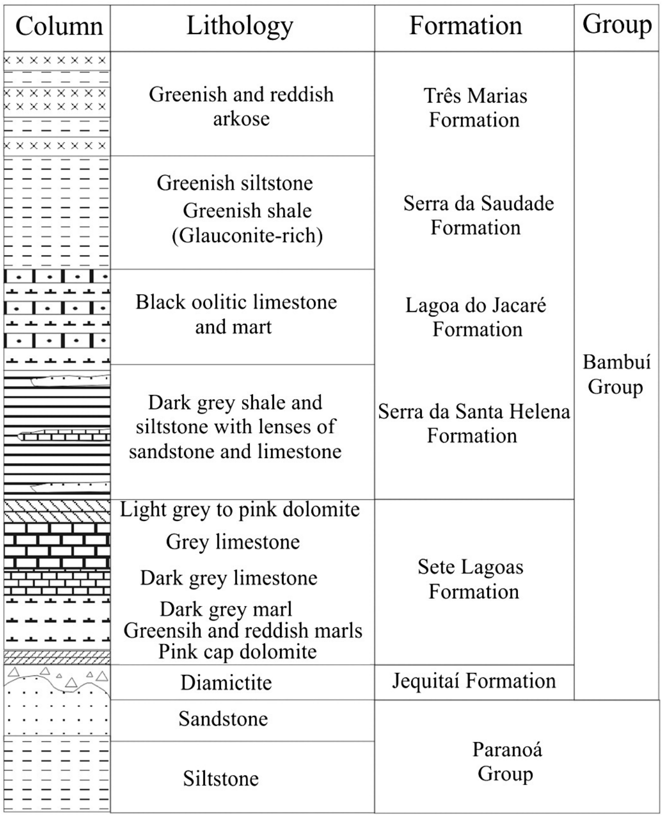


Fig. 3. Stratigraphic section of the Bambuí Group. Not to scale. Modified after Dardenne (2007).

and columnar stromatolites and intraformational breccias interdigitated with pelitic facies.

3. The glaciogenic units of the Vazante strata

The Vazante strata, regardless of its age, contain diamictite layers at four discrete horizons, and at least three of these contain evidence of glacial transport. These poorly sorted sedimentary deposits occur in the Santo Antônio do Bonito, Rocinha, Morro do Calcário, and Serra da Lapa formations.

Table 1
^{86}Sr/^{87}Sr data of carbonate fluorapatite (francolite) or associated micrite from Lagamar (LG, F), Rocinha (RO) and Irecê (IR).

Sample No	Description	^{87}Sr/^{86}Sr	Sr (ppm)	Mn (ppm)	Mn/Sr
LG 2	Francolite	0.70791	1300	105	0.08
LG AM 10	Francolite	0.70767	2095	ND	ND
LG AM 03B	Francolite	0.70794	2497	ND	ND
F 67 85.2	Francolite	0.70768	ND	ND	ND
F 70 70.8	Francolite	0.70754	ND	ND	ND
F 70 75.0	Francolite	0.70759	ND	ND	ND
F 70 83.95	Francolite	0.70761	ND	ND	ND
RO F 70	Micrite	0.70760	3840	364	0.09
RO AM 09	Francolite	0.70767	5280	38	0.01
RO AM 20A	Francolite	0.70763	6814	ND	ND
RO AM 40	Francolite	0.70776	ND	ND	ND
RO AM 33	Francolite	0.70771	ND	ND	ND
RO AM 38	Francolite	0.70777	ND	ND	ND
IR AM 11	Micrite	0.70752	2384	70	0.03

LG and F — Lagamar.
RO — Rocinha.
IR — Irecê.
Samples LG 2, LG AM 10, LG AM 03B, RO F 70, RO AM 09, RO AM 20A and IR AM 11 were analyzed at Ruhr University, Germany, by J. Veizer (Misi et al., 1997). The other samples were analyzed at the University of Maryland (USA) by A.J. Kaufman.

The lowermost diamictite, which occurs in the basal Santo Antônio do Bonito Formation (Fig. 2) is almost certainly glacial given its wide geographic distribution as well as the heterogeneous composition of its out-sized clasts, some of which are both faceted and striated, floating in a fine-grained pelitic matrix that is locally rich in phosphate. This diamictite is overlain by a thick stromatolitic dolomite and is comparable in composition with diamictites described from the Jequitaí and Bebedouro formations of the Neoproterozoic epicontinental basins of the São Francisco Craton (Misi et al., 2011b) (Figs. 1 and 3).

In the upper Rocinha Formation, a poorly-sorted diamictite layer has been observed with out-sized clasts composed of quartzite, siltstone, argillite and carbonate showing varied sizes and shapes, including some possible faceted stones. No striations have yet been recognized and these thin horizons are intercalated with meta-siltstone/sandstone or glauconite schist. At present the evidence for glaciation at this level should be viewed with caution.

Abundant dropstones and faceted cobbles in black shale of the Morro do Calcário Formation (previously identified as the basal section of the Serra da Lapa Formation by Azmy et al., 2006 and Serra do Poço Verde Formation by Olcott et al., 2005) suggest a glacial origin for this

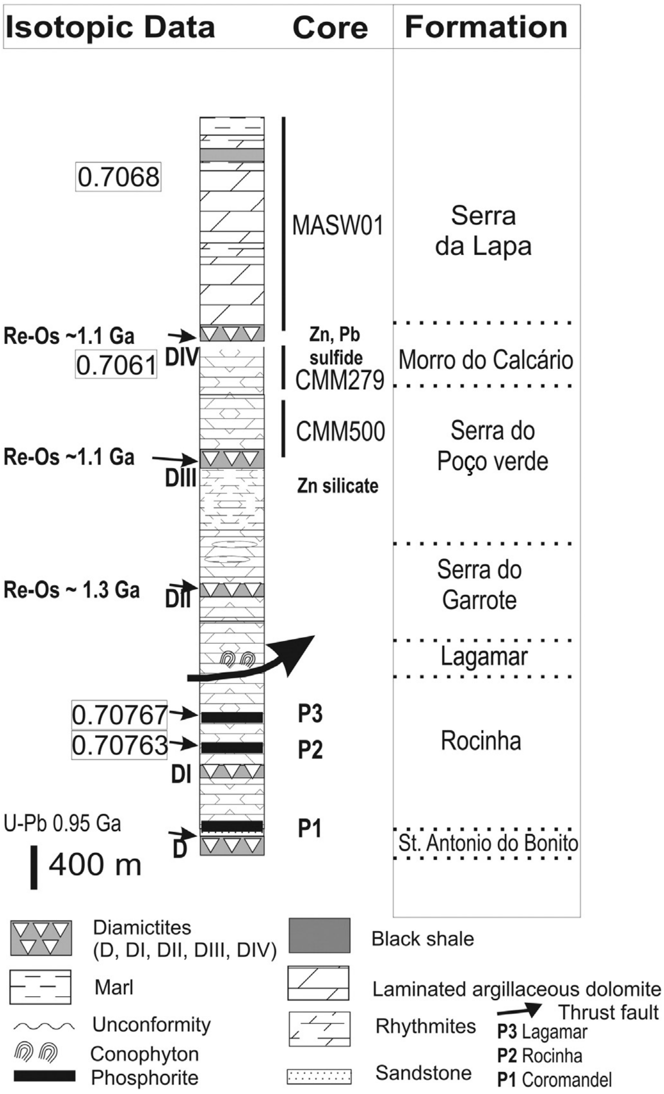


Fig. 4. Re–Os and U–Pb absolute age estimates of organic-rich shales and sandstones along with other isotopic data of the Vazante units: Re–Os ages from Geboy et al. (2013) and Azmy et al. (2008); U–Pb detrital Zr ages, from Azmy et al. (2008) Rodrigues et al. (2008) and Rodrigues et al. (2012)); ^{87}Sr/^{86}Sr signatures of carbonates, from Azmy et al. (2001) and of phosphorites (carbonate fluorapatite), from Misi et al. (1997).

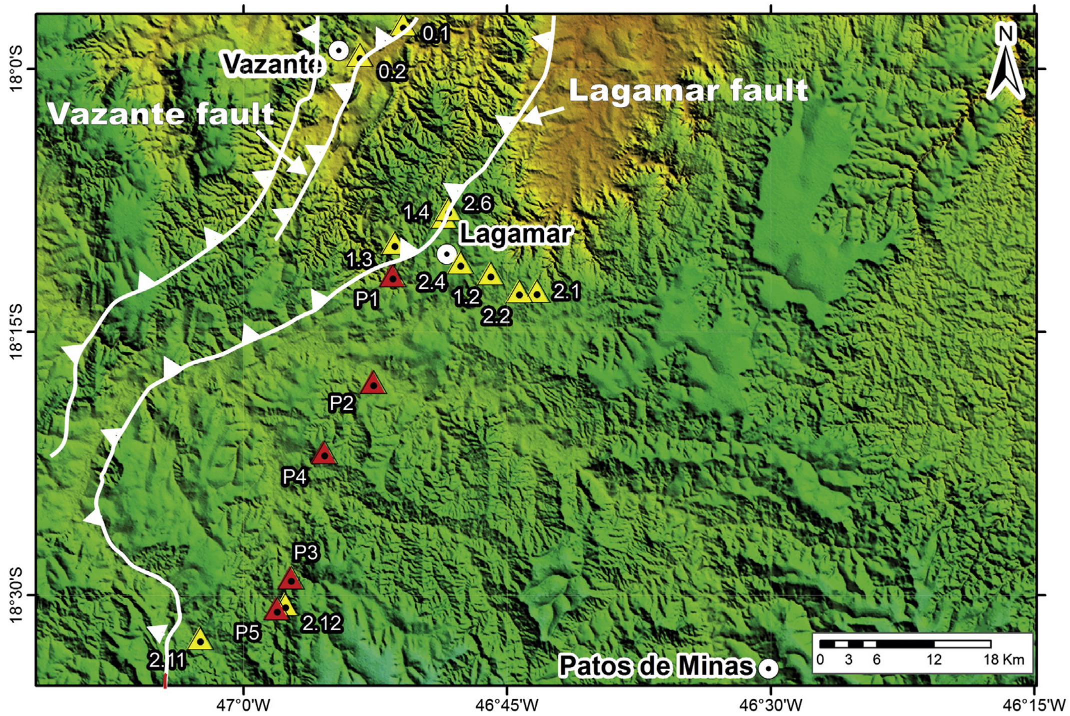


Fig. 5. Outcrops visited and phosphorite deposits near the Lagamar fault, plotted on a digital terrain image (DTM) of the Lagamar sheet. See Table 2 for coordinates and description of the points indicated.

unit. The dropstone-laden shale interval, which extends for >100 km, additionally contains glendonite, a carbonate mineral after ikaite that only forms in sediments at frigid temperatures. Because this unit is sandwiched between carbonate breccia, it was originally interpreted as a syn-glacial deposit (Olcott et al., 2005). Reinvestigation of the sampled cores indicated that the shale might be instead post-glacial in origin, and unconformably overlain by a younger ice age deposit associated with the Lapa Formation (Geboy et al., 2013). Carbon isotope analyses of bedded carbonates above the Morro do Calcário shale in a different core indicated moderately negative $\delta^{13}C$ values of post-glacial cap carbonate lithofacies (Azmy et al., 2001).

The basal Lapa Formation contains carbonate breccia, black shale with dropstones, and quartzite that is Fe-oxide cemented with local accumulations of iron-formation (cf. Derry et al., 1992; Hoffman et al., 1998; Kaufman et al., 1997). Additionally, the muddy carbonate overlying these facies with more than 100 m (thickness) preserves a strong negative $\delta^{13}C$ excursion, which is characteristic of post-glacial cap carbonates in both the early Paleoproterozoic and Neoproterozoic (and perhaps now also the late Mesoproterozoic) intervals (Azmy et al., 2001, 2006; Bekker et al., 2005; Geboy et al., 2013; Hoffman et al., 1998).

4. Correlations

The geotectonic context of the Vazante succession and its correlation with other economically important Proterozoic units in Brazil and worldwide has long been a matter of debate. Some have considered the Vazante sequence to be equivalent to the passive margin Paranoá Group (ca. 1.2 to 0.9 Ga) on the São Francisco Craton (Cloud and Dardenne, 1973; Dardenne et al., 1976; Moeri, 1972), insofar as both preserve a basal paraconglomerate, as well as other similar lithostratigraphic features. Biostratigraphic correlation between the two successions was proposed by Moeri (1972) as well as Cloud and Dardenne (1973) based on the presence of similar stromatolites, including *Conophyton cylindricus* Maslov and *C. metula* Kirichenko. Recently, Geboy et al. (2013) argued for a direct correlation of these units based on the similarity of time-series carbon isotope trends in carbonates (cf. Santos et al., 2000).

On the other hand, different authors (Dardenne, 2000, 2001; Misi, 2001; Misi et al., 2003, 2007; Thomaz-Filho et al., 1998) have suggested a correlation with the younger Neoproterozoic intracratonic succession on the São Francisco Craton (Bambuí Group). The Bambuí Group is floored by glacial diamictites, which are overlain by red cap dolomites depleted in ^{13}C and two shallowing upward carbonate sequences (Fig. 3). This correlation is mainly based on similarities between: (i) the lithology of the Santo Antonio do Bonito (Vazante) and Jequitaí (Bambuí) diamictites at the base of each succession and (ii) the Sr isotope composition of carbonate fluorapatite and micrites of the Rocinha Formation (lower Vazante Group) and of the Salitre Formation (Una Group, correlated to the Bambuí Group) from well-preserved samples (Misi et al., 2007).

5. New Re–Os ages from the Vazante sequence

Until recently there have been no direct radiometric age constraints for the glaciogenic strata of the Vazante sequence, which have led to conflicting correlations. However, utilizing a relatively new geochronometer based on the clock-like decay of Re in organic-rich shale to Os, two recent studies (Azmy et al., 2008; Geboy et al., 2013) of upper Vazante shale horizons from two separate and independent laboratories concluded that at least part of the succession is late Mesoproterozoic in age. Azmy et al. (2008) provided radiometric age estimates of the dropstone-laden Morro do Calcário shale in the upper section of the Vazante Group (previously identified as the Serra da Lapa shale, see Geboy et al., 2013). Obtained ages are between 993 ± 46 and 1100 ± 77 Ma. The age differences are probably related to isochrons constructed from samples with moderately enriched concentrations of Re and Os. Similarly, old Re/Os ages are reported by Geboy (2006) and Geboy et al. (2013) for the pre-glacial Serra do Garrote (1353 ± 69 Ma) and post-glacial Morro do Calcario (1126 ± 57 Ma) shales. Although the isochron ages are not high precise, we have considered other evidences as discussed below and in more detail by Geboy et al. (2013). On the other hand, we should consider that the Re–Os system in organic shale is related to the deposition of the precursor organic-rich sediments under suboxic to anoxic conditions at which seawater Re and Os are highly concentrated in bottom sediments. As pointed out by Geboy et al. (2013), "hydrothermal fluid flow can disturb Re–Os systematics but documented cases of remobilization of Re and Os under such conditions have resulted in erroneously *younger*, not older, ages" (Geboy et al., 2013 p. 210). Therefore, we believe that the upper interval of the Vazante succession with its glacial strata would be late Mesoproterozoic in age.

These radiometric constraints are consistent with U–Pb measurements on detrital zircon in sandstones interspersed throughout the succession (Azmy et al., 2008; Rodrigues et al., 2012). Based on laser ablation ICP-MS U–Pb analyses of zircons in sandstone from the lower Vazante succession, Rodrigues et al. (2012) proposed that the deposition of the original sediments was between 0.78 and 0.94 Ga, i.e., in the Neoproterozoic. On the other hand, their analyses of sandstones in the upper Vazante succession show similar patterns with ages in the Morro do Calcario and Lapa formations ranging between 1.2 (major peak) and 2.2 Ga. The intervening Serra do Garrote Formation had detrital zircons with 2.2 Ga ages (major peaks, max. ages for the sources). These measurements are consistent with a late Mesoproterozoic age for the upper Vazante strata.

Again consistent with an older age for the upper Vazante succession, Pimentel et al. (2001) reported Sm–Nd model ages (T_{DM}) values between 1.7 and 2.1 Ga for detrital meta-sediments. Notably, model ages for the Paranoá Group ($T_{DM} = 2.0$–2.3 Ga) overlap, but may be slightly older, and those for meta-sediments of the Bambuí Group ($T_{DM} = 1.4$–1.9 Ga) are slightly younger. Pimentel et al. (2001) thus suggested that the Vazante succession holds an intermediate stratigraphic position between the Paranoá passive margin basin and the intracratonic basin of the Bambuí Group.

In contrast to the Mesoproterozoic radiometric ages for the middle and upper sections of the Vazante strata, the lower section (Rocinha and Santo Antonio do Bonito formations) preserves evidence for a Neoproterozoic age. In particular, Misi et al. (2007) reported $^{87}Sr/^{86}Sr$ values of ca. 0.70767 from carbonate fluorapatite and 0.70760 from

Fig. 6. Outcrops near the fault line (Lagamar fault): A) Fault line, with the Lagamar carbonates, siltstones and conglomerates of the Lagamar Fm. to the West and laminated siltstone and limestones with phosphorite layers of the Rocinha unit, to the East (point 1.4 on Fig. 5); B) Glauconite schists ("verdetes", point 1.2 on Fig. 5); C) columnar stromatolites (*Conophyton metula*, point 1.3); D) conglomerate with faceted clasts (diamictite, point 2.1); and E) fine laminated beds of phosphorite in pelitic-carbonate lithofacies, Rocinha mine (point P4).

associated micrite of the Rocinha Formation, with extremely high total Sr (>1300 ppm) and low Mn/Sr (0.01 to 0.09) in all of the studied samples, suggesting a high degree of preservation (Table 1). These $^{87}Sr/^{86}Sr$ values are highly comparable with those reported for the Bambuí Group, thus suggesting a possible correlation of these successions. In addition, U–Pb ages of detrital zircon determinations by Rodrigues et al. (2012) and Azmy et al. (2008) from the Santo Antonio do Bonito Formation indicate maximum age of 0.94 Ga. for their source rocks, clearly reinforcing a Neoproterozoic age for the lower section.

If correct, the stratigraphic inversion of older late Mesoproterozoic strata above younger Neoproterozoic strata in the Vazante Group (cf.Dardenne, 2000, 2001; see Fig. 4) is geologically possible only through the presence of an intervening thrust fault, which we have observed in the field beneath the *Conophyton*-bearing carbonates of the Lagamar Formation.

6. A new stratigraphic framework proposed for the Vazante sequence

The stratigraphic framework of the Vazante sequence has evolved significantly since Dardenne (1978) proposed a new stratigraphic mega-unit, called the Vazante Formation, which did not include the basal Santo Antonio do Bonito and Rocinha intervals because these units were severely faulted and difficult to define. Some years later the same author redefined the Vazante Formation as Vazante Group (Dardenne, 2000, 2001), now incorporating the basal intervals below the Lagamar fault (see below). What had been members in the upper section were redefined in ascending order as formations: Lagamar, Serra do Garrote, Serra do Poço Verde, Morro do Calcário, and Serra da Lapa (Fig. 2).

The fault near the Lagamar village (Figs. 5 and 6, Table 2) was identified by Pinho and Dardenne (1994) as a thrust similar to the Vazante fault to the west. The fault line, aligned approximately N45E and N20E in the Lagamar quadrangle, is conspicuous in outcrops and marked by mylonitic foliation (Fig. 6A). A few kilometers to the west, the Lagamar Formation host columnar stromatolites with convex and conical laminations, classified as *Conophytonmetula* and *Jacutophyton* by Moeri (1972) and Cloud and Dardenne (1973) (Fig. 6B). Glauconite facies (Fig. 6C) and diamictite with rounded or faceted clasts of quartzite, siltstone, argillite and carbonates (Fig. 6D) occur closely to the east of the fault line.

The new Re–Os age constraints discussed above and our refined stratigraphic framework strongly suggest that the thrust at the contact between the Rocinha and Lagamar formations is responsible for placing older Mesoproterozoic strata above late Neoproterozoic counterparts. Fig. 7 shows a geological section crossing the fault near Lagamar village (after Dardenne and Freitas-Silva, 1999) modified in view of the new data.

In summary, we suggest that the earlier stratigraphic order of the Vazante strata does not follow a normal succession. The upper section above the thrust fault (Lagamar to Lapa formations) is older than the lower counterpart (Santo Antonio do Bonito and Rocinha formations), thus indicating an older sedimentary sequence of late Mesoproterozoic that thrusts above Neoproterozoic rocks, which can be correlated with the Neoproterozoic Bambuí Group on the São Francisco Craton (Figs. 4 and 8).

7. Metallogenic and phosphogenic events: discussion

Two important events are preserved in Neoproterozoic strata, which are well represented on the São Francisco Craton (Misi et al., 2010; Misi et al., 2011a). These include Zn–Pb mineralization and accumulation of rich deposits of sedimentary phosphate. These events were likely caused by major Neoproterozoic geodynamic processes that are well recognized in equivalent sequences around the world: (i) extensional movements during the break-up of the Rodinia supercontinent and (ii) widespread ice age events documented in all Neoproterozoic basins (i.e., the Snowball Earth hypothesis: Kirschvink, 1992; Hoffman et al., 1998; Hoffman and Schrag, 2002).

7.1. Zn–Pb mineralization

Zn–Pb deposits are being exploited by Votorantim Metais (VM). *Vazante* (26.6 Mt of zinc silicate ore, grading 19.5% Zn, informed by VM geologists) and *Morro Agudo* 23.6 (Mt of sulfide ore, grading 4.6% Zn and 1.9% Pb, idem) and other known deposits like *Fagundes* and *Ambrosia* are hosted by dolarenitic strata restricted to well-defined stratigraphic intervals of the Serra do Poço Verde Formation (*Vazante* mine) and Morro do Calcário Formation (*Morro Agudo* mine). They were previously assumed to be Neoproterozoic in age, matching minor Pb–Zn mineralization in the Bambuí and Una groups. Mineralization is also controlled by a fault system in these deposits (Misi et al., 2005).

Table 2
Outcrops visited and descriptions of the points plotted on Fig. 6.

No	Coordinates		Description
	x	y	
0.1	304082	8013511	Vazante fault (thrust fault): Zn mine of Vazante
0.2	299782	8010253	Vazante fault extension
1.2	313123	7987400	Glauconite schists
1.3	303470	7990512	Dolomite with mounded stromatolites classified as *Conophyton metula*
1.4	308404	7993307	Mylonite: Lagamar fault (thrust fault)
2.1	317782	7985585	Diamictite with faceted clasts of quartzites and pelites
2.2	316020	7985542	Pelites + siltites with few rounded and unsorted clasts
2.4	310113	7988523	Diamictite with faceted clasts + voids of dissolved carbonate clasts (?)
2.6	308853	7994115	Silicified siltites and pelites: Lagamar fault zone
2.11	284442	7948759	Diamictite w/rounded clasts of quartzite, quartz + voids of dissolved carbonate clasts (?)
2.12	292938	7952413	Diamictite w/faceted and striated clasts of quartzites, carbonate, granitoids (Coromandel)
P1	303325	7987104	Laminated phosphorite (L. dos Peixes, Lagamar)
P2	301502	7975869	Laminated phosphorites in pelitic rocks (Fazenda Brejos)
P3	293465	7955190	Laminated phosphorite (Ponte Caida)
P4	296671	7968459	Laminated phosphorite in pelitic and carbonate rocks (Rocinha)
P5	292105	7951952	Phosphorite in pelitic matrix of diamictites (Coromandel)

UTM zone: 23K.
West longitude: 48W.
East latitude: 42W.
Datum: SA 69.

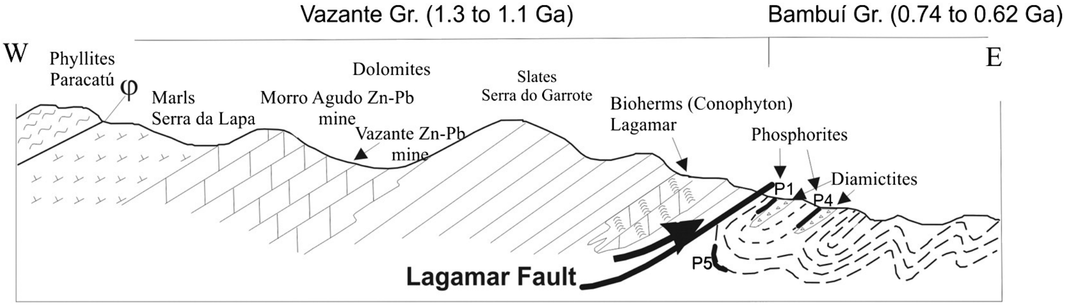


Fig. 7. Schematic geological section West–East, passing by the Lagamar fault. P1 — Lagamar; P4 — Rocinha; P5 —Coromandel. Modified from Dardenne and Freitas-Silva (1999).

During the last 15 years, the Zn–Pb deposits in the Vazante strata have been entirely studied by several researchers, trying to understand their metallogenic evolution processes by using reliable analytical tools (see Misi et al., 2005; Monteiro et al., 2006; Monteiro et al., 2007, and more references therein). The following points are highlighted here concerning the metallogenic processes: (i) Fault and stratigraphic controls of the mineralization in all the deposits are well demonstrated. In Morro Agudo for example, the orebodies are clearly related to a normal fault system; (ii) Pb isotopic data are indicative of upper crustal sources for the metals (Fig. 9A) and S isotopic results are variable, suggesting the participation of more than one sulfur source; and (iii) Fluid inclusion studies indicate between 120 and 250 °C and salinities below 22 wt.% NaCl equiv. for all the Zn–Pb deposits.

More recently, Slezak (2012) and Slezak et al. (2014) presented an interesting study of the Vazante northern extension silicate zinc deposits with new and important analytical data, adding new inputs for understanding the metallogenic process. Slezak (2012) has pointed out some questions that are still open for discussion, regarding the development of an integrated evolution model. From the six topics related by the author, we highlight two (p. 102): (i) what are the ages of the mineralization? and (ii) why the deposits seem to be confined to a specific geological time (hosted in Neoproterozoic to Cambrian carbonate rocks)?

In light of the new gechronological constraints, the mineralized host rocks in the Vazante strata are now likely to have been deposited in the late Mesoproterozoic. The mineralization event, however, is interpreted to have occurred during the Neoproterozoic according to Pb–Pb model ages obtained from galenas within these deposits (Cunha et al, 2007) (Fig 9) and other evidences here discussed. The possibility that an earlier mineralization event occurred cannot be discounted considering the presence of (i) mm-scale beds of ultra-fine sphalerite, (ii) silica nodules that deform sphaleritelaminae, and (iii) sulfide replacing sulfate nodules in the uppermost Vazante orebody (N ore body at Morro Agudo mine; see Misi et al., 2005). These observations suggests a syn-diagenetic mineralization event within this interval, although vein sets and pods of sulfide minerals are also present at the same stratigraphic horizon (M ore body), probably representing a new hydrothermal flux. The other ore bodies observed in lower stratigraphic horizons

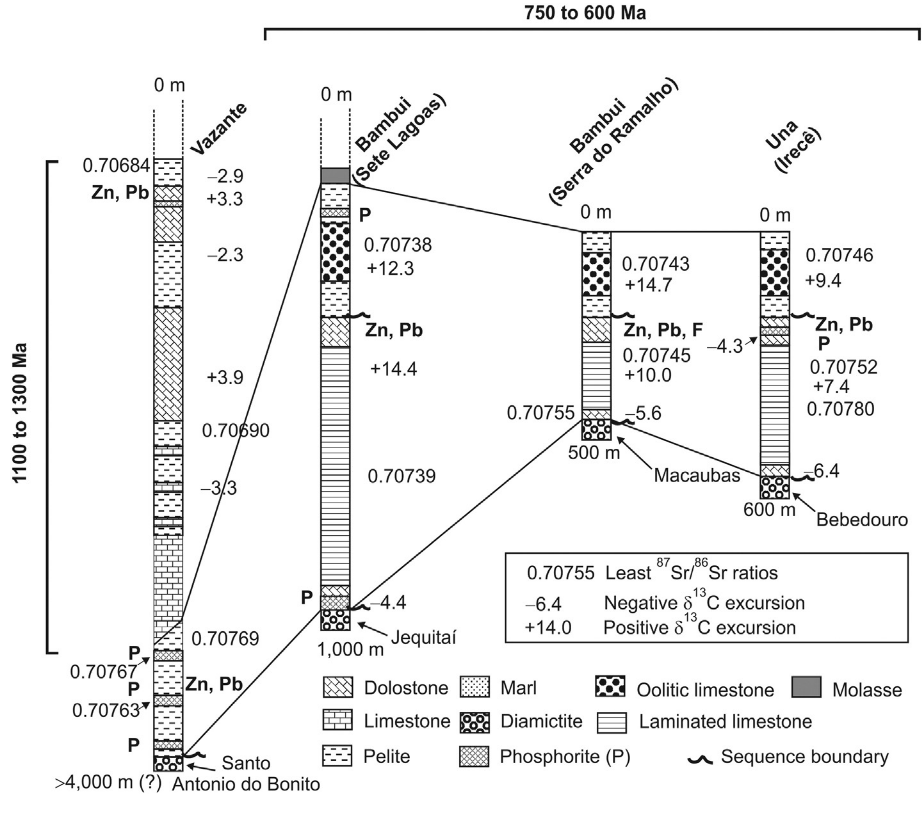


Fig. 8. Proposed correlation of the lower section of the original Vazante Group with the Bambuí and Una groups (Neoproterozoic), in the São Francisco Craton. The upper strata (Mesoproterozoic) are thrusted over the Neoproterozoic successions (see Fig. 4).

of the Morro Agudo mine consist of massive fine- to coarse-grained sulfides (mainly sphalerite) replacing oolitic dolostone beds (JKL orebodies) and of coarse-grained sphalerite and galena cementing breccias (GHI ore bodies). The Pb isotopic composition obtained from 47 galena samples representative of the main types of mineralization in Morro Agudo, Vazante, Fagundes and Ambrosia deposits is distributed in three separate populations (Fig. 9), as demonstrated by Cunha et al. (2007). Population I is represented by the stratiform mineralization of the N orebody. Note that the data from the galena samples of this population ($n = 10$) “present the less radiogenic Pb ratios, probably because this galena is older and was formed during the earlier stages of the mineralization process” (Cunha et al, 2007 p. 392). Accordingly, an earlier work by Freitas-Silva and Dardenne (1997) presented Pb isotope data of 12 galena samples from the Morro Agudo mine, placing the samples in two distinct groups, according to the authors: the first one with model ages of 1.1 to 1.0 Ga and the second group showing galena samples with model ages between 750 to 650 Ma., interpreted by the authors as formed by remobilization processes.

In addition, it is important to consider the δ^{34}S values of the sulfides in the N orebody that are consistently depleted (+2.7 to −8.6‰ VCDT, $n = 12$), contrasting with the highly enriched values in M, JKL and GHI ore bodies (+13.6 to +38.8‰ VCDT, $n = 31$). δ^{34}S values for barite sample range from +14.5 to +44.0‰ VCDT ($n = 15$) (Misi et al., 2005).

In studying the mafic dikes (metabasites) affected by hydrothermal alteration processes and associated to the Zn deposits in the Vazante fault, an important structural control of the mineralization at Vazante mine, Babinski et al. (2005) have demonstrated that: (i) Zircon crystals from the metabasites yield U–Pb ages ranging from 2.1 to 2.4 Ga (age of the Paleoproterozoic basement rocks of the Vazante strata), (ii) titanites separated from the same metabasites show Pb isotope signatures indicating model ages in agreement with those determined for the zinc–lead deposits of the Vazante strata (~700 Ma, Fig. 9B). This suggest “a long lived hydrothermal system related to diagenesis and deformation of the Vazante strata during the Neoproterozoic” (Babinski et al., 2005 p. 293).

Notably there is also a Pb–Zn mineralization (Caboclo deposit) located in the northern border of the Chapada Diamantina, which is hosted in Mesoproterozoic carbonates (dolostones) of the Caboclo Formation (Chapada Diamantina Group) (Franca Rocha and Misi, 1993; Franca-Rocha, 1995; Misi et al., 1999) and fault-controlled. Muscovite samples from hydrothermally-altered limestones spatially associated with the sulfide mineralization have been dated by ^{40}Ar/^{39}Ar techniques. All the muscovite grains yielded very well defined plateau ages varying from 529 ± 3 to 503 ± 3 Ma (Cunha et al., 2003).

Economically important Zn–Pb mineralization that is fault controlled and carbonate-hosted in Mesoproterozoic carbonate strata of the Borden Basin (1260 Ma), Canada, is represented by the Nanisivik deposit (19 Mt with ~10% Zn + Pb) (Turner, 2011). The known sulfide showings are clearly related with faults, fractures, or mafic dykes originated from extensional syn-sedimentary and/or reactivated tectonic events. Olson (1984) reports probable Pb–Pb model ages (galena) of ~700 Ma, approximately coeval with mafic dikes intruding the carbonate strata and Symons et al. (2000) show paleomagnetic evidences of an age of 1095 ± 10 Ma for the mineralization-related recrystalization of dolostone at Nanisivik. In addition, an Ar–Ar Ordovician age (461 ± 2 Ma) has been reported by Sherlock et al. (2004) in orthoclase from hydrothermal alteration zone on the margin of dikes interpreted to have formed by the same event that emplaced the sulfides. Even considering that these ages are uncertain, as pointed out by Turner (2011), a long term metallogenic event seems to have occurred in the Nanisivik deposit.

In summary, in view of the new geological and geochronological constraints, the following considerations are implied: (i) The Zn–Pb metallogenic event in the intracratonic and passive-margin basins of the SFC is mainly of Neoproterozoic age and is related to extensional tectonic events but probably the mineralized event started earlier. The evolution of these sedimentary basins since the Mesoproterozoic and mainly during the Neoproterozoic is marked by a complex polycyclic history during which the extensional events are well represented, especially during the Cryogenian Period (see Brito-Neves and Fuck, 2013). The prolonged breakup process of the Rodinia supercontinent has been remarked by Li et al. (2008) and by Condie (2002), who based this conclusions in well dated sites around the world; (ii) the Morro Agudo, Vazante, Fagundes and Ambrosia deposits, in the upper section of the Vazante sequence, although products of a dominant Neoproterozoic metallogenic event, are hosted by Mesoproterozoic strata that overthrust Neoproterozoic units. Accordingly, these conclusions require modification of the model proposed by Misi et al. (2005) to be consistent with the tectonic and geochronological results (Fig. 10).

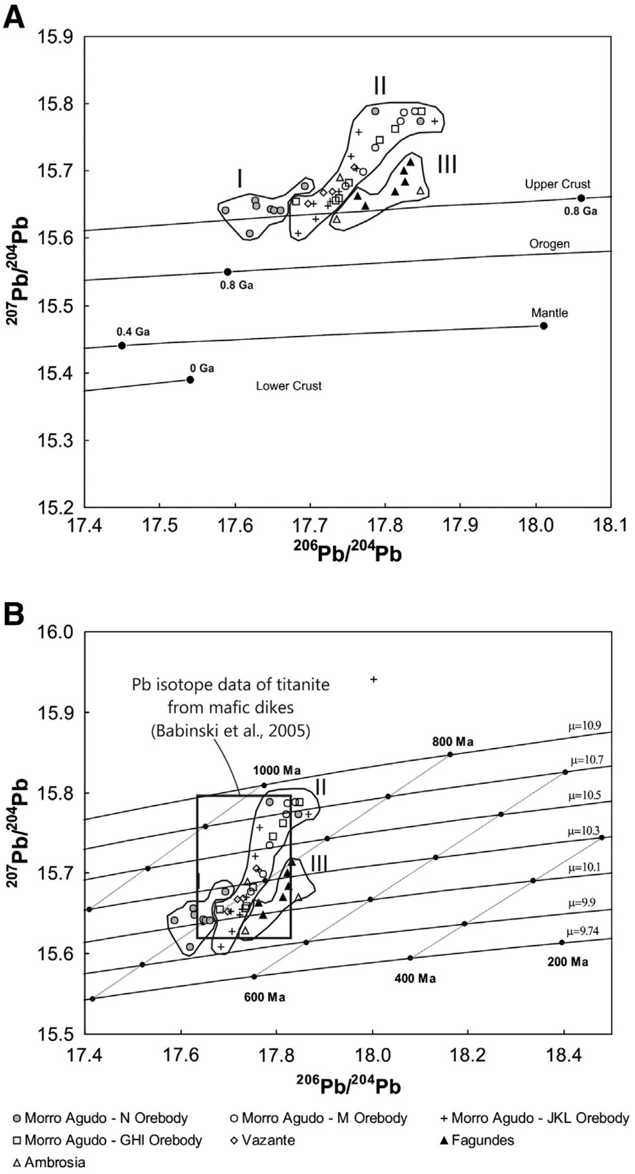


Fig. 9. Lead isotope composition of galena samples from the Zn–Pb deposits of the Vazante successions showing three different populations of data: I — N orebodies at the Morro Agudo mine; II — M, JKL and GHI orebodies at Morro Agudo mine and at Vazante mine; and III — Fagundes and Ambrosia deposits. A) Evolution curves of the plumbotectonic model (Zartman and Doe, 1981). B) Evolution growth curve of Stacey and Kramers (1975). The area plotted on the figure indicates the range of Pb isotope data of titanites from mafic dikes at Vazante mine (Babinski et al., 2005). Modified from Cunha et al. (2007).

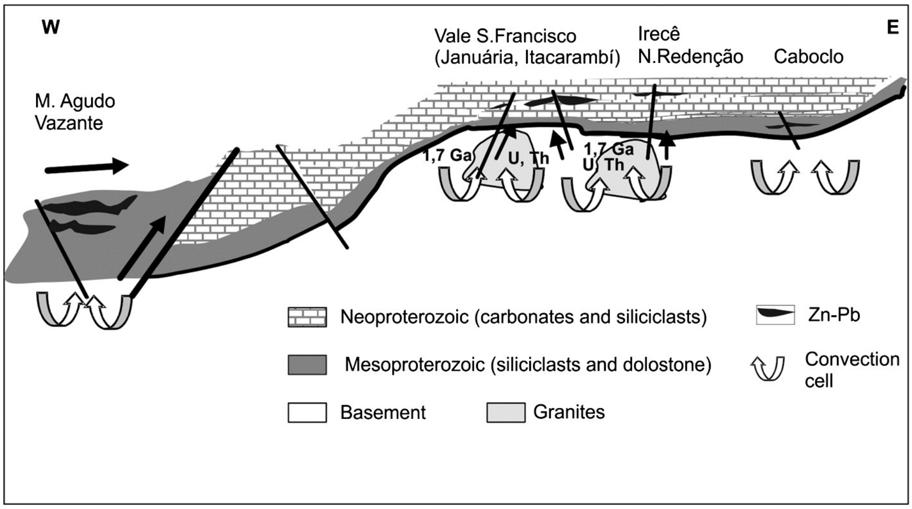


Fig. 10. Simplified metallogenic evolution model for the Proterozoic sediment-hosted Zn–Pb deposits of the São Francisco Craton. Modified from Misi et al. (2005).

7.2. Phosphate mineralization

In the basal section of the Vazante Group (as originally defined by Dardenne, 2001), there are three phosphorite horizons (Fig. 4): (i) *Lagamar*, an old mine (~5 Mt, 35–38% P_2O_5, Porter Database, 2013) located in the upper section of the Rocinha Formation, in which the phosphorite layers are associated with pink slate, meta-siltstone and clear-gray quartzite; (ii) *Rocinha*, in exploitation (>250 Mt, 12% P_2O_5, Kulaif, 2009), forming centimeter-thick beds intercalated with slate passing laterally to carbonate and glauconite facies in the mid-section of the Rocinha Formation (Fig. 5), and (iii) *Coromandel*, with large deposits associated with slate of the Santo Antonio do Bonito Fm. or replacing pelitic matrix of diamictites in the lower section (Rodrigues et al., 2012).

Studies on stratigraphic correlations and phosphogenesis in the Neoproterozoic successions of the São Francisco Craton (Dardenne et al., 1986; Misi, 1992; Misi and Kyle, 1994; Misi et al., 2010; Sanches, 2012; Sial et al., 2009) have indicated a well-defined stratigraphic control for the recognized phosphate deposits. Fig. 11 shows the distribution of Neoproterozoic phosphorites in the São Francisco Craton. Some of these deposits are spatially related to glaciogenic diamictites, but these relationships are not clearly demonstrated in others (see Sanches et al., 2007). For example, in the Irecê basin until now there is no direct evidence of the presence of glacial diamictites associated with the phosphorite. Nevertheless, a notable $\delta^{13}C$ negative excursion in dolostones of the Unit B1, that hosts the phosphorite horizons (two samples with -4.3 and -4.6‰ VPDB, Torquato and Misi, 1977), along with the presence of ex-aragonite seafloor precipitates in the unit is likely immediately post-glacial in origin (cf. Hoffman et al., 1998).

Carbonate fluorapatite or francolite is the main phosphate mineral associated with the primary phosphorite layers. According to Jarvis et al. (1994), the chemistry and relative stability of francolite lends itself to isotope studies ($\delta^{13}C$, $\delta^{18}O$, $\delta^{34}S$ and $^{87}Sr/^{86}Sr$). In this sense, purified francolites (free from diagenetic carbonate cement) from the Rocinha and Lagamar deposits and from Irecê deposit of the Una Group have been analyzed together with associated micrite for $^{87}Sr/^{86}Sr$ compositions. The best-preserved samples reveal values varying between 0.70752 and 0.70791, which are consistent with global compilations of Sr isotopes from the pre-Marinoan Cryogenian Period (ca. 680 to 635 Ma) (Table 1). In addition, C isotope studies by Misi and Kyle (1994) and Sanches et al. (2007) suggest a suboxic to anoxic environment of phosphorite generation in these deposits, which clearly occurred during an early diagenetic process. In contrast with the incorporation of CO_2 to calcite in oxic zones of normal marine environment, which is almost instantaneous and the fractionation is insignificant, in biogenic phosphates, under reducing conditions (in which free oxygen is absent), CO_2 is added during the transition of the hydroxyapatite to carbonate fluorapatite by a dissolution–reprecipitation process (Jarvis et al., 1994; McArthur et al., 1986). In consequence there is a substantial fractionation of carbon, giving rise to depleted signals of $\delta^{13}C$ (Fig. 12 and Table 3).

Precambrian phosphorites largely occurred after glaciation events during the Paleoproterozoic and Neoproterozoic eras (Papineau, 2010). During post-glacial periods, extensive continental areas were exposed to weathering and erosion, thus providing sources of phosphorus to the marine environment. A post-glacial pulse of oxygen (Halverson et al., 2010) could have also produced a large volume of cold, nutrient-rich water, resulting in a major expansion of organic productivity in the photic zone (Cook and Shergold, 1986). The "iron-redox model" for phosphorite generation, also known as "iron-redox pumping", suggests that ferric oxy-hydroxides scavenge soluble iron dissolved in seawater, and PO_4^{3-} is released from organic matter by microbial decomposition under oxic to suboxic conditions within the top few centimeters of sediment (Jarvis et al., 1994). Particles of $FeOOH \cdot PO_4$ formed along the oxic–suboxic interface are subsequently transferred to the suboxic–anoxic zone where the Eh and pH conditions are adequate to liberate PO_4^{3-} and to form carbonate fluorapatite (francolite). Glauconite is also formed during this process where Fe^{2+}-rich pore water combined with $Si\ (OH)_4$ derived from the dissolution of biogenic opal, together with K^+ and Mg^{2+} ions from seawater, may form glauconite with the aluminosilicate fraction (Jarvis et al., 1994).

The presence of diamictites with faceted clasts in the Rocinha Formation, despite the fact that they have not been widely studied yet, could be an indication of the relationship between glaciation and phosphogenesis. The occurrence of associated glauconite facies is consistent with the current phosphogenic model and suggest a possible correlation with the phosphorites of Cedro do Abaeté, in the Serra da Saudade Formation of the Bambuí Group (Lima et al., 2007) (Figs. 8 and 11).

8. Conclusions

The older (Mesoproterozoic) radiogenic ages consistently measured from the middle and upper Vazante strata above the Rocinha Formation strongly suggest a tectonic contact with the lower section at the base of the Lagamar Formation. Those strata are overthrusted above the Neoproterozoic successions correlated with the Bambuí Group,

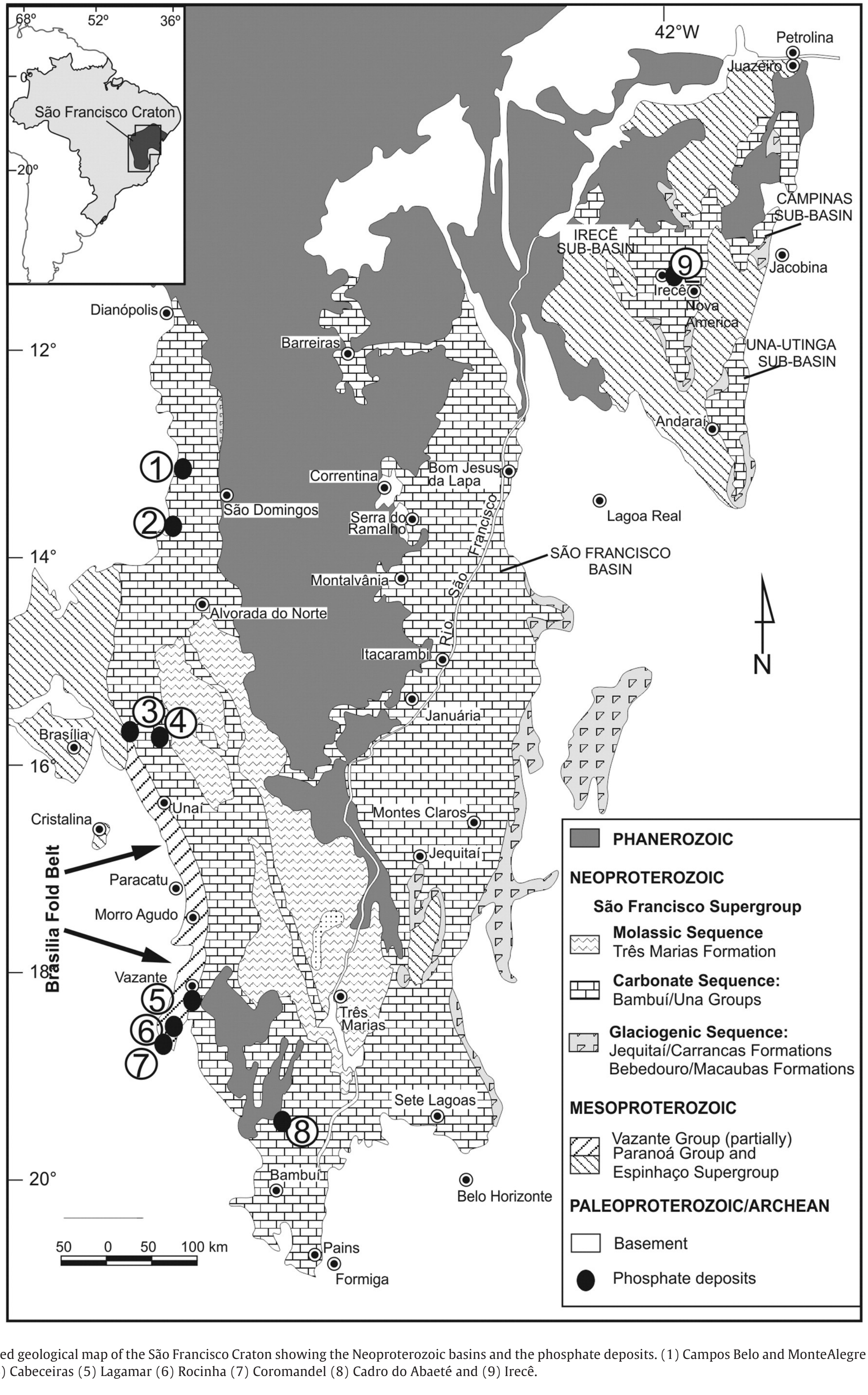


Fig. 11. Simplified geological map of the São Francisco Craton showing the Neoproterozoic basins and the phosphate deposits. (1) Campos Belo and MonteAlegre (2) Nova Roma (3) Formosa (4) Cabeceiras (5) Lagamar (6) Rocinha (7) Coromandel (8) Cadro do Abaeté and (9) Irecê.

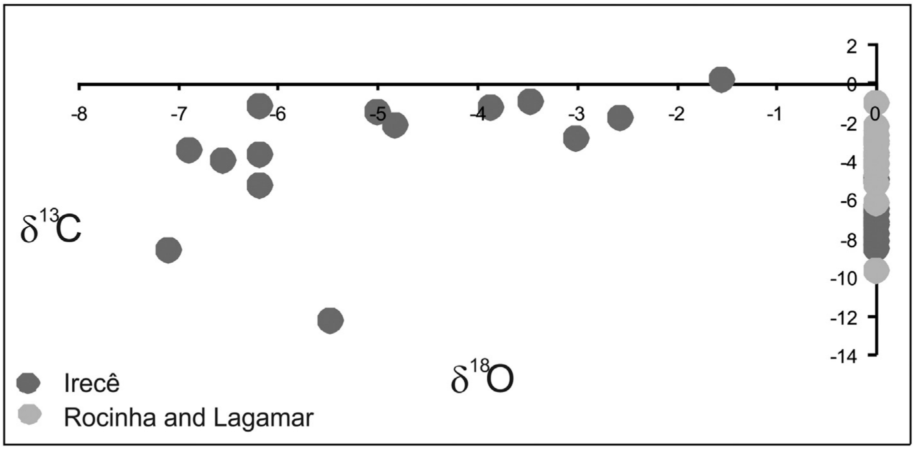


Fig. 12. Plot of $\delta^{13}C$ and $\delta^{18}O$ results from carbonate fluorapatite of Irecê, Rocinha and Lagamar.

probably with the Serra da Saudade Formation, where also glauconite facies are associated with phosphorites.

Metallogenic and phosphogenic events in the São Francisco Craton are both of Neoproterozoic age, although the Zn–Pb deposits in the upper section of the Vazante strata are hosted by Mesoproterozoic units. If correct, this will open new possibilities for the exploration of lead–zinc deposits in other Mesoproterozoic successions of the São Francisco Craton. Phosphorite generation is suggested to occur immediately after the glacial events.

Table 3
Carbon and oxygen isotope data of carbonate fluorapatite from Rocinha, Lagamar and Irecê deposits.

Sample	$\delta^{18}O$ (VPDB)	$\delta^{13}C$ (VPDB)	Description
Irecê:			
Misi and Kyle (1994):			
18.80 C	−6.20	−1.18	Calcite assoc. with fluorapatite
10.92 C	−6.57	−4.01	Calcite assoc. with fluorapatite
19.16 Bc	−7.11	−8.58	Calcite, Irecê phosphorite (>30% P_2O_5)
25.65 Bc	−4.84	−2.18	Calcite, Irecê phosphorite (>30% P_2O_5)
18.80 Bc	−6.91	−3.47	Calcite, Irecê phosphorite (>30% P_2O_5)
10.92 Bc	−5.49	−12.25	Calcite, Irecê phosphorite (>30% P_2O_5)
10.92 D	−3.01	−2.83	Dolomite, assoc. with fluorapatite, Irecê
19.16 Bd	−5.01	−1.51	Dolomite, Irecê phosphorite (>30% P_2O_5)
25.65 Bd	−3.88	−1.28	Dolomite, Irecê phosphorite (>30% P_2O_5)
10.92 Bd	−2.57	−1.76	Dolomite, Irecê phosphorite (>30% P_2O_5)
AM 8 d	−3.48	−0.93	Dolomite, Irecê phosphorite (>30% P_2O_5)
43.42 d	−1.55	0.19	Dolomite, Irecê phosphorite (>30% P_2O_5)
IL 48-(25.65)	−6.20	−5.28	Carbonate fluorapatite
IL 63 (18.80)	−6.20	−3.70	Carbonate fluorapatite
Sanches et al. (2007):			
IL-108 (26.45)	ND	−7.18	Carbonate fluorapatite
IL-39 (7.94)	ND	−6.79	Carbonate fluorapatite
IL-108 (24.20)	ND	−8.18	Carbonate fluorapatite
IL-39 (8.36)	ND	−8.54	Carbonate fluorapatite
IL-80 (28.14)	ND	−4.95	Carbonate fluorapatite
IL-77 (21.95)	ND	−6.50	Carbonate fluorapatite
IL-39 (6.36)	ND	−7.35	Carbonate fluorapatite
IL-77 (20.28)	ND	−7.77	Carbonate fluorapatite
IL-108 (27.89)	ND	−4.94	Carbonate fluorapatite
Rocinha (RO) and Lagamar (LG):			
Sanches et al. (2007):			
RO-AM-20A	ND	−4.59	Carbonate fluorapatite
RO-AM-20B	ND	−3.71	Carbonate fluorapatite
LG-AM-05	ND	−4.16	Carbonate fluorapatite
LG-AM-06	ND	−3.58	Carbonate fluorapatite
RO-AM-22	ND	−5.18	Carbonate fluorapatite
LG-AM-03A	ND	−2.26	Carbonate fluorapatite
LG-AM-04	ND	−3.13	Carbonate fluorapatite
LG-AM-07	ND	−4.11	Carbonate fluorapatite
LG-AM-03B	ND	−9.61	Carbonate fluorapatite
RO-AM-23	ND	−2.70	Carbonate fluorapatite
RO-AM-21	ND	−6.18	Carbonate fluorapatite
RO-AM-38	ND	−1.03	Carbonate fluorapatite
RO-AM-24	ND	−2.99	Carbonate fluorapatite

Acknowledgments

This research has been supported by the National Research Council (CNPq), in Brazil: A. M. received support from projects no. 486416/2006-2 and 306996/2010-3. AJK has been supported by NSF EAR0844270 and NASA Exobiology NNX10AR91G programs in the USA. J. Pinho, N. Signorelli and M.P. Tuller have contributed in discussing our proposals during a workshop of the Project 486416 in Vazante (May, 2009). Excellent contributions to the improvement of the manuscript have been provided by the reviewers Drs. Dwight Bradley and Gema Olivo.

References

Azmy, K., Veizer, J., Misi, A., de Oliveira, T.F., Sanches, A.L., Dardenne, M.A., 2001. Dolomitization and isotope stratigraphy of the Vazante Formation, Sao Francisco Basin, Brazil. Precambrian Res. 112, 303–329.

Azmy, K., Kaufman, A.J., Misi, A., de Oliveira, T.F., 2006. Isotope stratigraphy of the Lapa Formation, Sao Francisco Basin, Brazil: implications for Late Neoproterozoic glacial events in South America. Precambrian Res. 149, 231–248.

Azmy, K., Kendall, B., Creaser, R.A., Heaman, L., de Oliveira, T.F., 2008. Global correlation of the Vazante Group, Sao Francisco Basin, Brazil: Re–Os and U–Pb radiometric age constraints. Precambrian Res. 164, 160–172.

Babinski, M., Kaufman, A.J., 2003. First direct dating of a Neoproterozoic post-glaciogenic cap carbonate. IV South American Symposium on Isotope Geology. Short Papers, vol. 1, pp. 321–323.

Babinski, M., Monteiro, L.V.S., Fetter, A.H., Bettencourt, J.S., Oliveira, T.F., 2005. Isotope geochemistry of the mafic dikes from the Vazante nonsulfide zinc deposit, Brazil. J. S. Am. Earth Sci. 18, 293–304.

Babinski, M., Vieira, L.C., Trindade, R.I.F., 2007. Direct dating of the Sete Lagoas cap carbonate (Bambuí Group, Brazil) and implications for the Neoproterozoic glacial events. Terra Nova 19, 401–406.

Bekker, A., Kaufman, A.J., Karhu, J.A., Eriksson, K.A., 2005. Evidence for Paleoproterozoic cap carbonates in North America. Precambrian Res. 137, 167–206.

Brito-Neves, B.B., Fuck, R.A., 2013. Neoproterozoic evolution of the basement of the South-American platform. J. S. Am. Earth Sci. 47, 72–89.

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

Condie, K., 2002. The supercontinent cycle: are there two patterns of cyclicity? J. Afr. Earth Sci. 35, 179–183.

Cook, P.J., Shergold, J.H., 1986. Proterozoic and Cambrian phosphorites — nature and origin. In: Cook, P.J., Shergold, J.H. (Eds.), Proterozoic and Cambrian phosphorites: Phosphate Deposits of the World, vol. 1. Cambridge University Press, Cambridge, pp. 369–386.

Cunha, I.A., Soares, P.V., Babinski, M., Misi, A., Franca-Rocha, 2003. $^{40}Ar/^{39}Ar$ muscovite ages from hydrothermally altered dolostone hosting the Pb–Ag Caboclo deposit, Bahia, Brazil. IV South American Symposium on Isotope Geology, 2003, Salvador. Short Papers, vol. 2, pp. 731–732 (2003).

Cunha, I.A., Misi, A., Babinski, M., 2007. Lead isotope constraints on the genesis of Pb–Zn deposits of the Neoproterozoic Vazante Group, Minas Gerais, Brazil. Gondwana Res. 11, 382–395.

Dardenne, M.A., 1978. Zonação tectônica na borda ocidental do Cráton São Francisco. Congresso Brasileiro de Geologia, 30, SBG, Recife, pp. 299–308.

Dardenne, M.A., 1979. Les minéralisations de plomb, zinc, fluor du Proterozoique Supérieur dans le Brésil Central. , University of Paris VI, Doctorate thesis 251 p.

Dardenne, M.A., 2000. The Brasilia Fold Belt. In: Cordani, U.G., Milani, E.J., Filho, A.T., Campos, D.A. (Eds.), Tectonic Evolution of South America. 31st International Geological Congress, Rio de Janeiro, pp. 231–263.

Dardenne, M.A., 2001. Lithostratrigraphic sedimentary sequences of the Vazante Group. In: Misi, A. and Teixeira, J.B.G. (org.), 1st IGCP 450 Workshop, Proterozoic Sediment-Hosted Base Metal Deposits of Western Gondwana, Belo Horizonte, Abstracts, pp. 48-50.

Dardenne, M.A., 2007. Lithostratigraphy of the Vazante and Bambuí Groups in the São Francisco craton and the Brasilia Fold Belt. 3rd Symposium on Neoproterozoic-Early Paleozoic Events in southwestern Gondwana, Stellenbosch, South Africa, p. 628.

Dardenne, M.A., Freitas-Silva, F.H., 1999. Pb–Zn ore deposits of Bambuí and Vazante Groups in the São Francisco Craton and Brasilia Fold Belt, Brazil. In: Silva, M.G., Misi, A. (Eds.), Base Metal Deposits of Brazil, MME-Brazil, pp. 75–83.

Dardenne, M.A., Faria, A., Fuck, R.A., 1976. Occurrence de stromatolithes columnaires dans le Groupe Bambuí (Goiás, Brésil). An. Acad. Bras. Ciências 48, 555–566.

Dardenne, M.A., Trompette, R., Magalhães, L.F., Soares, L.A., 1986. Proterozoic and Cambrian phosphorites — regional review, Brazil. In: Cook, P.J., Shergold, J.H. (Eds.), Phosphate Deposits of the World: Proterozoic and Cambrian Phosphorites. Cambridge University Press, Cambridge, pp. 116–131.

Dardenne, M.A., Freitas-Silva, F.H., Nogueira, G.M.S., Campos, J.E.G., 1998. Evolução tectono-sedimentar do Grupo Vazante no contexto da Faixa de Dobramentos Brasilia. Congresso Brasileiro de Geologia, 40, SBG, Belo Horizonte, Anais, p. 26.

Porter Database, 2013. Rocinha, Patos de Minas, Lagamar, Minas Gerais, Brazil. Porter geoconsultancy database. http://www.portergeo.com.au/database/mineinfo.asp?mineid=mn538.

Derry, L.A., Kaufman, A.J., Jacobsen, S.B., 1992. Sedimentary cycling and environmental change in the Late Proterozoic — evidence from stable and radiogenic isotopes. Geochim. Cosmochim. Acta 56, 1317–1329.

Franca Rocha, W.J.S., Misi, A., 1993. Estilo tectônico associado às mineralizações do tipo SEDEX nas coberturas do Proterozoico Médio do Cráton do São Francisco. Simpósio sobre o Cráton do São Francisco. Soc. Bras. de Geologia, 2, pp. 340–343 (Salvador, BA).

Franca-Rocha, W.J.S., 1995. Origem das Mineralizações Sulfetadas nos Sedimentos Mesoproterozoicos da Borda Norte da Chapada Diamantina – BA. (MSc. thesis) , Federal University of Bahia, Brazil (130 pp.).

Freitas-Silva, F.H., Dardenne, M.A., 1997. Pb/Pb isotopic patterns of galenas from Morro do Ouro (Paracatu Formation), Morro Agudo/Vazante (Vazante Formation) and Bambuí Group deposits. South American Symposium on Isotope Geology, Campos do Jordão (SP), Extended Abstracts, pp. 118–120.

Fuck, R.A., 1994. A Faixa Brasília e a compartimentação tectônica na província Tocantins. Simpósio de Geologia do Centro-Oeste. Soc. Bras. Geol., 4, pp. 184–187 (Brasília).

Geboy, N.J., 2006. Rhenium–osmium age determinations of glaciogenic shales, Vazante Formation, Brazil. (M.Sc. thesis) , Univ. of Maryland, College Park, U.S.A.(180 pp.).

Geboy, N.J., Kaufman, A.J., Walker, R.J., Misi, A., Oliveira, T.F., Miller, K.E., Azmy, K., Kendall, B., Pouton, S.W., 2013. Re–Os age constraints and new observations of glacial deposits in the Mesoproterozoic Vazante Group Brazil. Precambrian Res. 238, 199–213.

Halverson, G.P., Wade, B.P., Hurtgen, M.T., Barovich, K.M., 2010. Neoproterozoic chemostratigraphy. Precambrian Res. 182, 337–350.

Hoffman, P.F., Schrag, D.P., 2002. The snowball Earth hypothesis: testing the limits of global change. Terra Nova 14, 129–155.

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

IBRAM, 2013. Votorantim Metais prepara investimento de R$ 500 milhões, Instituto Brasileiro de Mineração, 27/09/2013. http://www.ibram.org.br/150/15001002.asp?ttCD_CHAVE=195996.

Jarvis, I., Burnet, W., Nathan, Y., Almbaydin, F.S.M., Attia, A.K.M., Castro, L.N., Flocoteaux, R., Hilmy, M.E., Husain, V., Qutawnah, A.A., Serjani, A., Zanin, Y.N., 1994. Phosphorite geochemistry: state-of-the-art and environmental concerns. Eclogae Geol. Helv. 87, 643–700.

Kaufman, A.J., Knoll, A.H., Narbonne, G.M., 1997. Isotopes, ice ages, and terminal Proterozoic earth history. Proc. Natl. Acad. Sci. U. S. A. 94, 6600–6605.

Kirschvink, J.W., 1992. Late Proterozoic low-latitude global glaciations: the snowball Earth. In: Schopf, J.W., Klein, C. (Eds.), The Proterozoic Biosphere. Cambridge University Press, Cambridge, pp. 51–52.

Kulaif, I., 2009. Produto 29 (Agrominerais). Relatório Técnico 53. J. Mendo Consultoria, Ministério das Minas e Energia (MME) (55 pp.).

Li, Z.X., Bogdanova, S.V., Collins, A.S., Davidson, A., De Waele, B., Ernst, R.E., Fitzsimons, I.C.W., Fuck, R.A., Gladkochub, D.P., Jacobs, J., Karlstrom, K.E., Lu, S., Natapov, L.M., Pease, V., Pisarevsky, S.A., Thrane, K., Vernikovsky, V., 2008. Assembly, configuration, and break-up history of Rodinia: a synthesis. Precambrian Res. 160, 179–210.

Lima, O.N.B., Uhlein, A., Britto, W., 2007. Estratigrafia do Grupo Bambuí na Serra da Saudade e geologia do depósito fosfático de Cedro do Abaeté, Minas Gerais. Rev. Bras. Geosci. 37 (4 - suplemento), 204–215.

Madalosso, A., Valle, C.R.O., 1978. Considerações sobre a estratigrafia e sedimentologia do Grupo Bambuí na Região de Paracatu, Morro Agudo - MG. Congresso Brasileiro de Geologia, 30, SBG, Anais, vol. 2, pp. 622–631.

Marini, O.J., Fuck, R.A., Danni, J.C., Dardenne, M.A., Loguercio, S.O.C., Ramalho, R., 1984. As faixas de dobramentos Brasília, Uruaçu e Paraguai-Araguaia e o Maciço Mediano de Goiás. In: Schobbenhaus, C., Campos, D.A., Derze, G.R., Asmus, H.E. (Eds.), Geologia do Brasil. Texto Explicativo do Mapa Geológico do Brasil e da Área Oceânica Adjacente Incluindo Depósitos Minerais. Ministério da Minas e Energias/Departamento Nacional da Produção Mineral, Brasília, pp. 251–303.

McArthur, J.M., Benmore, R.A., Coleman, M.L., Soldi, C., Yeh, H.W., O'Brien, G.W., 1986. Stable isotopic characterization of francolite formation. Earth Planet. Sci. Lett. 77, 20–34.

Misi, A., 2001. Estratigrafia Isotópica das Seqüências do Supergrupo São Francisco, Coberturas Neoproterozóicas do Craton do São Francisco: Idade e Correlações. In: Pinto,C. P. and Martins Neto,M. A. (Org.). Bacia do São Francisco, Geologia e Recursos Naturais, Belo Horizonte: Sociedade Brasileira de Geologia, Núcleo de Minas Gerais v. 1, pp. 67-92.

Misi, A., Kyle, J.R., 1994. Upper Proterozoic carbonate stratigraphy, diagenesis, and stromatolitic phosphorite formation, Irecê Basin, Bahia, Brazil. J. Sed. Res. A 64, 299–310.

Misi, A., Veizer, J., Kawashita, K., Dardenne, M.A., 1997. The age of the Neoproterozoic carbonate platform sedimentation based on ^{87}Sr/^{86}Sr determinations, Bambuí and Una Groups, Brazil. I South American Symposium on Isotope Geology, Campos do Jordão, São Paulo, Brazil, Extended Abstracts, pp. 199–200.

Misi, A., Iyer, S.S.S., Tassinari, C.E.S., Kyle, C.G.G., Coelho, J.R., Franca-Rocha, W.J.S., Gomes, A.S.R., Cunha, I.A., Carvalho, I.G., 1999. Geological and isotopic constraints onthe metallogenic evolution of the Proterozoic sedimenthosted Pb–Zn (Ag) deposits of Brazil. Gondwana Res. 2, 47–65.

Misi, A., Teixeira, J.B.G., Gaucher, C., Remus, M.V.D., Boggiani, P.C., Iyer, S.S.S., 2003. Chemostratigraphic correlation of the Neoproterozoic sequences from South America. V South American Symposium on Isotope Geology, Salvador (Brazil). Short Papers, vol. 1, pp. 368–371.

Misi, A., Iyer, S.S.S., Coelho, C.E.S., Tassinari, C.C.G., Franca-Rocha, W.J.S., Cunha, I.D., Gomes, A.S.R., de Oliveira, T.F., Teixeira, J.B.G., Filho, V.M.C., 2005. Sediment-hosted lead–zinc deposits of the Neoproterozoic Bambui Group and correlative sequences, Sao Francisco craton, Brazil: a review and a possible metallogenic evolution model. Ore Geol. Rev. 26, 263–304.

Misi, A., Kaufman, A.J., Veizer, J., Powis, K., Azmy, K., Boggiani, P.C., Gaucher, C., Teixeira, J.B.G., Sanches, A.L., Iyer, S.S.S., 2007. Chemostratigraphic correlation of Neoproterozoic successions in South America. Chem. Geol. 237, 143–167.

Misi, A., Azmy, K., Kaufman, A.J., Oliveira, T.F., Pinho, J.M., Sanches, A.L., 2010. Metallogenic and phosphogenic events in the intracratonic and passive-margin Proterozoic basins of the São Francisco Craton: the Bambuí/Una and Vazante Groups. VII South American Symposium on Isotope Geology, Brasilia, DF, Extended Abstracts.

Misi, A., Azmy, K., Kaufman, A.J., Oiveira, T.F., Pinho, J.M., Sanches, A.L., 2011a. High resolution chemostratigraphy and Re–Os ages of organic shales of the Vazante Group (Minas Gerais, Brazil): implications for mineral exploration modelling. XIV Congreso Latino Americano de Geologia, Medellin. Memorias, vol. 1, pp. 410–411.

Misi, A., Kaufman, A.J., Azmy, K.A., Dardenne, M.A., Sial, A.N., Oliveira, T.F., 2011b. Neoproterozoic successions of the São Francisco Craton, Brazil: the Bambuí, Una, Vazante and Vaza Barris/Miaba groups and their glaciogenic deposits. In: Arnaud, E., Halverson, G.P., Shields-Zhou, G. (Eds.), The Geological Record of Neoproterozoic Glaciations. Geol. Soc. of London Memoirs, 36, pp. 509–522.

Moeri, E., 1972. On a columnar stromatolite in the Precambrian Bambuí Group of central Brazil. Eclogae Geol. Helv. 65, 185–195.

Monteiro, L.V.S., Bettencourt, J.S., Juliani, C., Oliveira, T.F., 2006. Geology, petrography, and mineral chemistry of the Vazante non-sulfide and Ambrosia and Fagundes sulfide-rich carbonate-hosted Zn–(Pb) deposits, Minas Gerais, Brazil. Ore Geol. Rev. 28, 201–234.

Monteiro, L.V.S., Bettencourt, J.S., Juliani, C., Oliveira, T.F., 2007. Non-sulfide and sulfide-rich zinc mineralizations in the Vazante, Ambrosia and Fagundes deposits, Minas Gerais, Brazil: mass balance and stable isotope characteristics of the hydrothermal alterations. Gondwana Res. 11, 362–381.

Olcott, A.N., Sessions, A.L., Corsetti, F.A., Kaufman, A.J., de Oliviera, T.F., 2005. Biomarker evidence for photosynthesis during Neoproterozoic glaciation. Science 310, 471–474.

Olson, R.A., 1984. Genesis of paleokarst and strata-bound zinc-lead sulfide deposits in a Proterozoic dolostone, northern Baffin Island, Canada. Econ. Geol. 79, 1056–1103.

Papineau, D., 2010. Global biogeochemical changes at both ends of the Proterozoic: insights from phosphorites. Astrobiology 10, 165–181.

Pimentel, M.M., Dardenne, M.A., Fuck, R.A., Viana, M.G., Junges, S.L., Fischel, D.P., Seer, H.J., Dantas, E.L., 2001. Nd isotopes and the provenance of detrital sediments of the Neoproterozoic Brasilia Belt, central Brazil. J. S. Am. Earth Sci. 14, 571–585.

Pinho, J.M.M., Dardenne, M.A., 1994. Caracterização da Falha de Lagamar, NW de Minas Gerais. Abstracts, Brazilian Geological Congress, 38. Sociedade Brasileira de Geologia, Camboriú, SC, pp. 246–247.

Rodrigues, J.B., Pimentel, M.M., Buhn, B., Matteini, M., Dardenne, M.A., Alvarenga, C.J.S., Armstrong, R.A., 2012. Provenance of the Vazante Group: New U–Pb, Sm–Nd. Lu–Hf isotopic data and implications for the tectonic evolution of the Neoproterozoic Brasilia Belt. Gondwana Res. 21, 439–450.

Sanches, A.L., 2012. Fosforitos neoproterozoicos dos grupos Vazante e Una: Origem, Idades e Correlações. (PhD thesis) , Federal University of Bahia, Brazil (157 pp.).

Sanches, A.L., Misi, A., Kaufman, A.J., Azmy, K., 2007. As sucessões carbonáticas neoproterozoicas do Cráton do São Francisco e os depósitos de fosfato: correlações e fosfogênese. Rev. Bras. Geocienc. 37 (4 - suplemento), 182–194.

Santos, R.V., de Alvarenga, C.J.S., Dardenne, M.A., Sial, A.N., Ferreira, V.P., 2000. Carbon and oxygen isotope profiles across Meso-Neoproterozoic limestones from central Brazil: Bambui and Paranoá groups. Precambrian Res. 104, 107–122.

Sherlock, R.L., Lee, J.K.W., Cousens, B.L., 2004. Geologic and geochronologic constraints on the timing of mineralization at the Nanisivik zinc–lead Mississippi Valley-type deposit, northern Baffin Island, Nunavut, Canada. Econ. Geol. 99, 279–293.

Sial, A.N., Dardenne, M.A., Misi, A., Pedreira, A.J., Gaucher, C., Ferreira, V.P., Silva Filho, M.A., Uhlein, A., Pedrosa-Soares, A.C., Santos, R.V., Egydio-Silva, M., Babinski, M., Alvarenga, C.J.S., Fairchild, T.R., Pimentel, M.M., 2009. The São Francisco Palaeocontinent. In:

Gaucher, C., Sial, A.N., Halverson, G.P., Frimmel, H.E. (Eds.), Developments in Precambrian Geology, 16. Elsevier, pp. 31–69.

Slezak, P.R., 2012. Geology, mineralogy and geochemistry of the Vazante Northern Extension zinc silicate deposit, Minas Gerais, Brazil. (Msc.thesis) , Queen's University, Kingston, Ontario, Canada (485 pp.).

Slezak, P., Olivo, G.R., Diniz-Oliveira, G., Dardenne, M.A., 2014. Geology, mineralogy and geochemistry of the Vazante Northern Extension zinc silicate deposit, Minas Gerais, Brazil. Ore Geol. Rev. 56, 234–257.

Stacey, J.S., Kramers, J.D., 1975. Approximation of terrestrial lead isotope evolution by a two-stage model. Earth Planet. Sci. Lett. 26, 207–221.

Symons, D.T.A., Symons, T.B., Sangster, D.F., 2000. Paleomagnetism of the Society Cliffs dolostone and the age of the Nanisivik zinc deposits, Baffin Island, Canada. Miner. Deposita 35, 672–682.

Thomaz-Filho, A., Kawashita, K., Cordani, U.G., 1998. A origem do Grupo Bambuí no contexto da evolução geotectônica e de idades radiométricas. An. Acad. Bras. Ciências 70, 527–548.

Torquato, J.R.F., Misi, A., 1977. Medidas isotópicas de carbono e oxigênio em carbonatos do Grupo Bambui na região centro-norte do Estado da Bahia. Rev. Bras. Geocienc. 7, 14–24.

Turner, E., 2011. Structural and stratigraphic ontrols on carbonate-hosted base metal mineralization in the Mesoproterozoic Borden Basin (Nanisivik District), Nunavut. Econ. Geol. 106, 1197–1223.

Valeriano, C.M., Dardenne, M.A., Fonseca, M.A., Simões, L.S.A., Seer, H.J., 2004. A Evolução Tectônica da Faixa Brasıília. In: Mantesso-Neto, V., Bartorelli, A., Carneiro, D.R.C., de Brito Neves, B.B. (Eds.), Geologia do Continente Sul-Americano: Evolução da obra de Fernando Flávio de Almeida, Beca Ed, São Paulo, Brazil, pp. 575–593.

Zartman, R.E., Doe, B.R., 1981. Plumbotectonics, the model. Tectonophysics 75, 135–162.