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LAS CUENCAS DEL PROTEROZOICO SUPERIOR EN EL CRATON DE SAN FRANCISCO, BRASIL: "ESTRATIGRAFIA ISOTOPICA" Y EVOLUCION METALOGENICA DE LA CUENCA DE IRECÊ

THE UPPER PROTEROZOIC BASINS OF THE SÃO FRANCISCO CRATON, BRAZIL: ISOTOPE STRATIGRAPHY AND METALLOGENETIC EVOLUTION OF THE IRECÊ BASIN

Aroldo Misi

Instituto de Geociências/PPPG, Universidade Federal da Bahia
Salvador, Bahia, Brazil

INTRODUCTION

Proterozoic basins of the São Francisco Craton in Brazil cover a large area that includes some of the most important mineral provinces, in the states of Minas Gerais, Bahia and Goiás. Iron, manganese, diamond, lead-zinc, barite, fluorite and phosphorite are some of the mineral deposits presently exploited in these basins. This paper reports some partial results of an ongoing research project, focusing the geotectonic and metallogenetic evolution of the Proterozoic basins. The Irecê Basin (upper Proterozoic), in the state of Bahia, is the main object of the present report. Stratigraphic relationships were established by the author and collaborators by field mapping and core studies performed during the course of other projects. Present studies include petrographic investigations supported by cathodoluminescence and scanning electron microscopy, followed by stable isotopic studies of host carbonate sequences and of sulfide and phosphate mineralizations.

SEDIMENTATION

The Irecê Basin is part of an extensive platform developed during the late Proterozoic, on the São Francisco Cráton (Fig. 1). It is dominantly filled by carbonate strata of the Una Group, a correlative

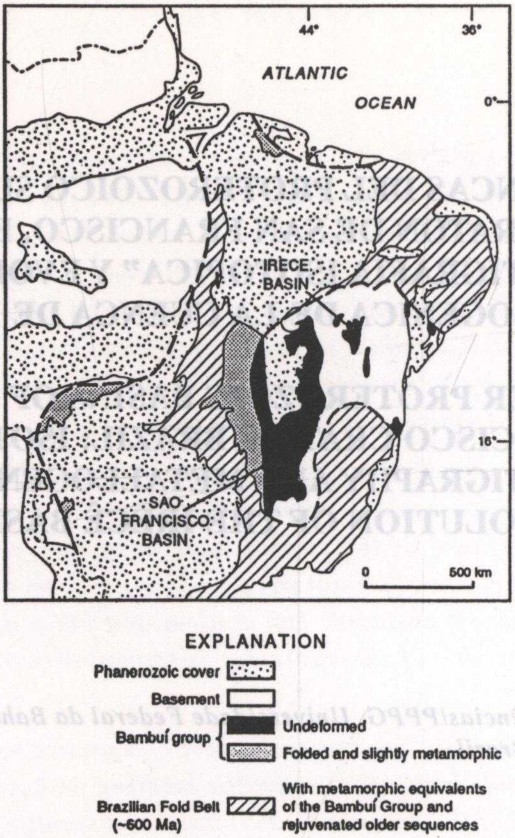


Fig. 1: General geology of the São Francisco Craton. Modified after Dardenne et al. (1986).

of the better known Bambui Group, in the São Francisco Basin. São Francisco and Irecê basins originated by an extensional event aligned NW-SE that commenced at 1.7 Ga., and that also formed marginal rift basins. Tectonic inversion of the marginal basins occurred during Vendian, with development of thrust belts and of the flexure-induced São Francisco foreland basin (Babinski et al., 1989). The Brasiliano (Pan-African) orogeny, at about 600 Ma, is responsible for the present configuration of the basin.

Sedimentation in the Irecê Basin is represented by a basal siliciclastic sequence composed of glaciogenic sediments (diamictites of the Bebedouro Formation), overlain by lacustrine sediments and marine sequences that total several hundreds meters in thickness (Salitre Formation). Two transgressive-regressive cycles are registered in the marine sequences, which are represented by laminated dolomitic limestones and dolostones with mudcracks, stromatolites and calcite/quartz nodules (Units B and B1), followed by argillaceous limestones, shales and siltstones with local lime grainstone lenses, and massive black organic-rich limestone with oolitic and pisolitic textures and current cross-bedding (Units A and A1) (Fig. 2). Rb-Sr age

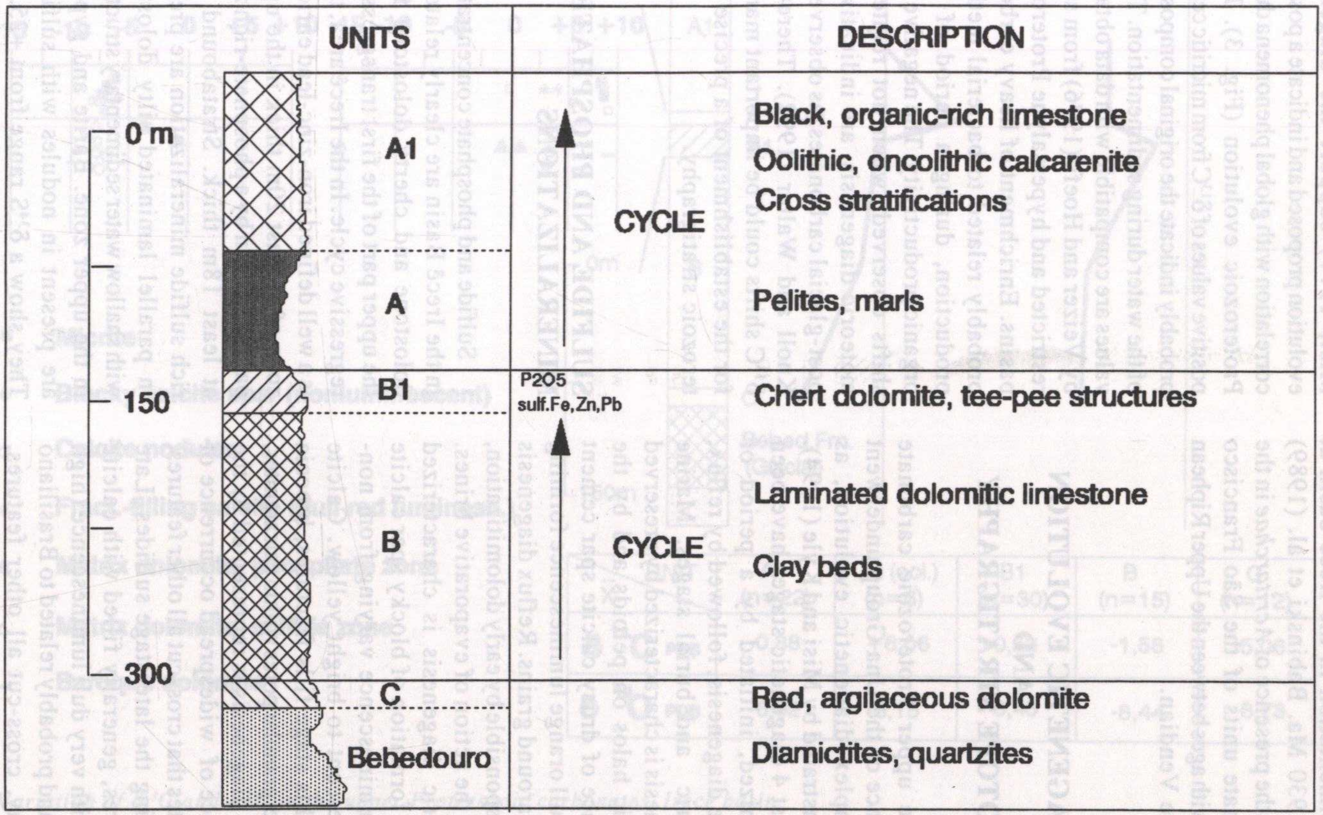


Fig. 2: Transgressive-regressive cycles of the Irecê basin (upper Proterozoic) and the place of sulfide and phosphate mineralization.

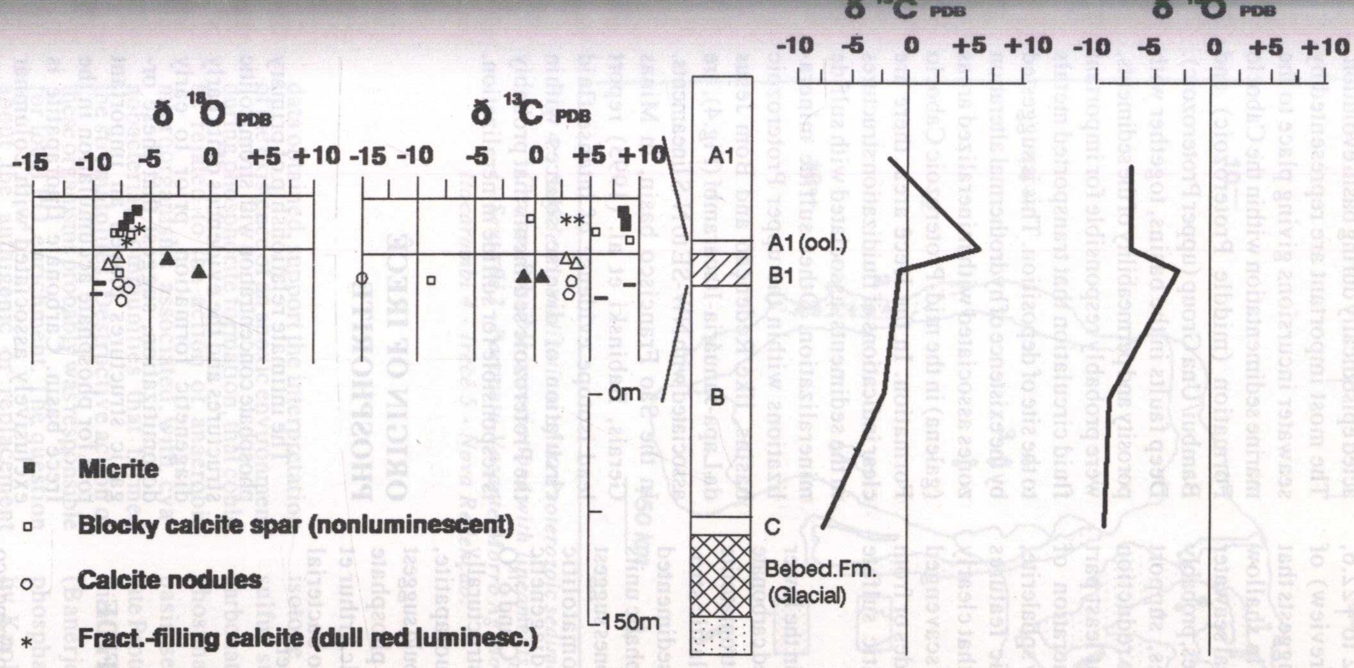
determination on pelitic rocks of the Bebedouro Formation place the beginning of sedimentation in the Irecê basin at about 930 Ma. Babinski et al. (1989) report the presence of *Acritarchae* in the carbonate units of the São Francisco basin with ages between the Upper Riphean and the Vendian.

DIAGENETIC EVOLUTION AND ISOTOPE STRATIGRAPHY

The upper Proterozoic carbonate sequence of the Una Group underwent a complex diagenetic evolution, as demonstrated by Misi and Kyle (1994). At least 4 diagenetic stages have been recognized, initiated by a period of marine diagenesis, followed by reflux, meteoric and burial stages. Marine diagenesis is characterized by preserved micritic halos on peloids and by the presence of drusy calcite spar cement with dull orange luminescence forming crusts around grains. Reflux diagenesis was responsible by early dolomitization, due to the action of evaporative brines. Meteoric diagenesis is characterized by the formation of blocky spar calcite with luminescence varying from non-luminescent to bright yellow. Calcite from this stage fills fractures, breccia and intergranular pores within calcarenites. Burial diagenesis is represented by the presence of widespread occurrence of stylolites that crosscut all other features, including the late-stage sulfides. Late fractures, generally filled with calcite spar with very dull luminescence (high Fe^{2+}), and probably related to Brasiliano orogeny, cross-cut all other features. Veins of iron-rich baroque dolomite are also present. Carbon and oxygen isotope determination of individual cements (Misi and Kyle, 1994), as well as of carbonate units (Torquato and Misi, 1977) support the diagenetic evolution proposed and indicate a possible correlation with global phenomena during Proterozoic evolution (Fig. 3). High positive values of $\delta^{13}C$ from micritic cement probably indicate the original composition of the water during sedimentation. These values are compatible with data obtained by Veizer and Hoefs (1976) from semi-restricted and hypersalyne Proterozoic basins. Enrichment of heavy carbon is probably related to bacterial methane production, during a period of high organic productivity. The negative $\delta^{13}C$ shifts observed, when not related to meteoric diagenesis, are indicative of post-glacial carbonates, as observed by Knoll and Walter (1992). Therefore, $\delta^{13}C$ shifts could be important markers for the establishment of a precise Proterozoic stratigraphy.

SULFIDE AND PHOSPHATE MINERALIZATIONS

Sulfide and phosphate concentrations in the Irecê Basin are clearly related to dolostone and cherty dolostone from the upper part of the first transgressive-regressive cycle. In the Irecê area, there is a well defined iron-zinc-lead enriched zone of at least 20m thick in the upper part, underlain by a phosphate-rich zone at least 18m thick. Stratabound Ag-rich sulfide mineralization are present in parallel laminated silty dolostone with shallow water sedimentary structures in the upper zone. Barite and gypsum are present in nodules with sulfides. They show a $\delta^{34}S$ range from +25.2 to +31.4 per mil CDT (n=7), that could represent seawater composition of Late Proterozoic age (Claypool et al., 1980).



UNIT / $\bar{X}$	A1 (n=22)	A1 (ool.) (n=6)	B1 (n=30)	B (n=15)	C (n=12)
$\delta^{13}C_{PDB}$	-0,88	+6,06	-0,53	-1,58	-5,06
$\delta^{18}O_{PDB}$	-6,92	-6,15	-3,45	-8,44	-8,73

Fig. 3: Variation of $\delta^{13}C$ and $\delta^{18}O$ in the upper Proterozoic carbonates, Irecê basin.
The right side of the stratigraphic column: whole rock determinations represented by average values. Data from Torquato and Misi (1977).
The left side: determinations of individual generations of cements. Data from Misi and Kyle (1994).

The relatively heavy and remarkable uniform $\delta^{34}S$ values (average +21.3 per mil CDT, range of +20.2 to +22.6, n= 18) (Kyle and Misi, in review) of associated sulfide minerals suggests that sulfate reduction processes in shallow sediments modified the original seawater sulfates. Bladed pyrite aggregates, probably pseudomorphs after sulfates, support the interpretation of a sulfate reduction process in the formation of at least part of the sulfides. A late generation of sulfide mineralization, mainly sphalerite, is suggested by petrographic features and uniform isotope values, that clearly indicate that late sulfides scavenged sulfur from pre-existing sulfides or from direct reduction of evaporitic sulfate minerals.

Phosphate concentration, in the lower zone, is composed of fine grained carbonate fluorapatite within columnar stromatolite (mainly), laminar and intraclastic stromatolites. The presence of resedimented phosphatic clasts and of phosphatic units interbedded with barren dolostones suggest that the formation of stromatolitic phosphorite was an early diagenetic process. Limited number of $\delta^{13}C$ and $\delta^{18}O$ determinations from the CO_2 structurally incorporated within the fluorapatite, indicate low $\delta^{13}C$ values. This could suggest an authigenic origin of the phosphate in an anoxic environment (McArthur et al., 1986), probably related to bacterial degradation of organic matter.

METALLOGENETIC EVOLUTION FOR SULFIDE MINERALIZATION

Proterozoic basins of the São Francisco Craton are extensional basins originated from basement ruptures aligned NW-SE, commencing at 1.7 Ga. There are indications that the extensional forces acted episodically during basin evolution. The most important are represented by seawater incursions giving place to the marine sedimentation within the Caboclo Formation (middle Proterozoic) and Bambui/Una Group (upper Proterozoic). Deep faults in the basins, together with porosity and permeability of the sediments, were probably responsible for important fluid circulation that transported metals to the site of deposition. This is suggested by the existence of hydrothermal alteration zones associated with mineralized areas (galena) in the mid-Proterozoic Caboclo Formation. In the Irecê area, there are clear indications of fluidization structures in the sediments, associated with sulfide mineralization. Other sulfide mineralizations within the upper Proterozoic basins, like Redenção and Bom Jesus da Lapa-Januária-Itacarambí (Fig.4), are associated with NW-SE to N-S lineaments. In the São Francisco basin, in Minas Gerais, Babinski et al. (1993) report lead isotope evidence of intense fluid circulation of diverse sources within the Proterozoic sediments that probably is responsible for sulfide mineralization.

ORIGIN OF IRECÊ PHOSPHORITE

The intimate relationship of primary phosphate concentration with stromatolitic structures and the evidences of its early diagenetic formation, prior to early dolomitization, suggest that these organic structures played an important role for phosphate accumulation in the Irecê basin. Carbonate fluorapatite is exclusively associated with columnar and laminar stromatolites or with intraclasts derived from these structures. The carbon and oxygen as well as the sulfur isotope

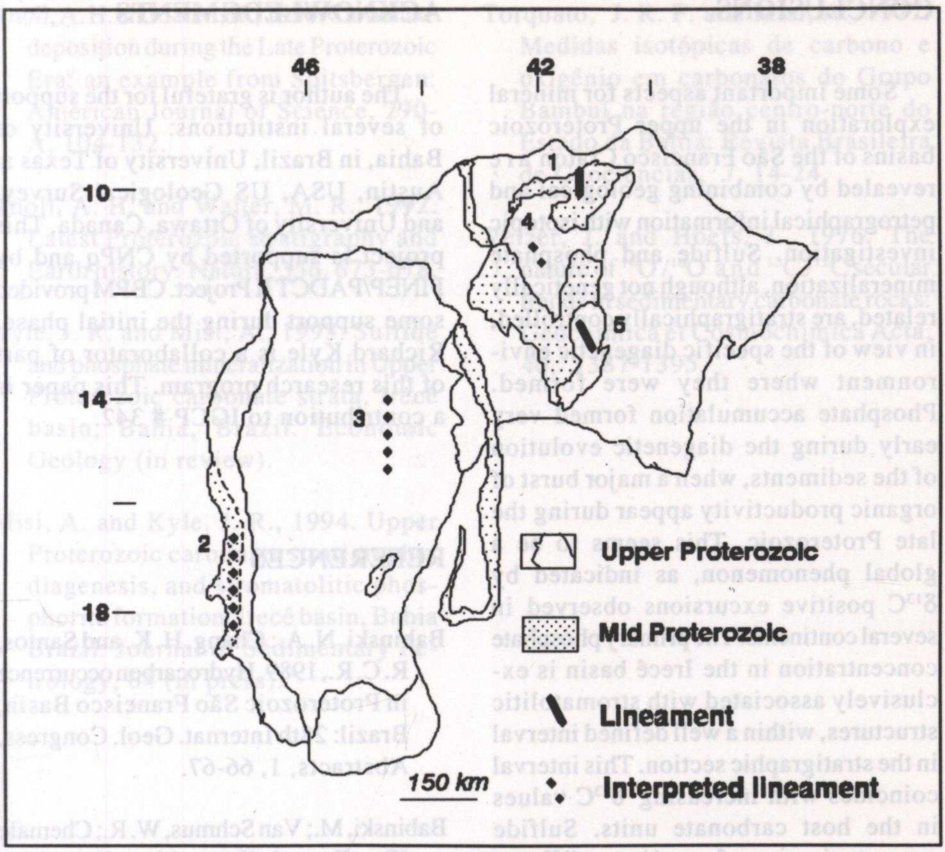


Fig. 4: Sulfide mineralizations of the Proterozoic sedimentary basins of the São Francisco Craton. Possible associations with lineaments related to deep faults. 1 - Sento Sé 2 - Paracatu-Vazante-Morro Agudo 3 - Bom Jesus da Lapa-Januária-Itacarambí 4 - Irecê 5 - Nova Redenção.

data obtained, support the interpretation of the existence of an anoxic environment during phosphorite formation, that could be related to the action of anaerobic microorganisms associated with cyanobacterial communities that formed the stromatolites. Destructive action of these organisms probably was responsible for local PO_4 enrichment. The question about the authigenic or replacement origin of the apatite is still open and can not be solved unless we have more isotope data as, for example, of the sulfur structurally incorporated to the carbonate fluorapatite. By the other hand, phosphate accumulation in the Irecê basin seems to represent an important late Proterozoic event of phosphatization. Similar deposits were discovered in India (Banerjee, 1986) and early diagenetic phosphate mineralization was reported by Knoll and Swett (1990) in the late Proterozoic carbonates of Spitsbergen, East Greenland.

CONCLUSIONS

Some important aspects for mineral exploration in the upper Proterozoic basins of the São Francisco Craton are revealed by combining geological and petrographical information with isotopic investigation. Sulfide and phosphate mineralization, although not genetically related, are stratigraphically controlled, in view of the specific diagenetic environment where they were formed. Phosphate accumulation formed very early during the diagenetic evolution of the sediments, when a major burst of organic productivity appear during the late Proterozoic. This seems to be a global phenomenon, as indicated by $\delta^{13}C$ positive excursions observed in several continents. The primary phosphate concentration in the Irecê basin is exclusively associated with stromatolitic structures, within a well defined interval in the stratigraphic section. This interval coincides with increasing $\delta^{13}C$ values in the host carbonate units. Sulfide concentrations were formed in two different stages of the diagenetic evolution. Early sulfides probably formed by the replacement of evaporite nodules and laminae, by the action of sulfate-reducing bacteria. Nevertheless, the main phase of sulfide mineralization originated during late diagenesis. The nature and source of the metal-bearing fluids within the basin are not clear, although its circulation was certainly controlled by deep faults, as well as by porosity and permeability of the sediments: metallic mineralization scavenged sulphur from preexisting sulfides or from direct reduction of evaporitic sulfate minerals, forming Fe-Zn-Pb-Ag sulfide concentrations. Sulfur isotope analysis of sulfates and sulfide minerals support this interpretation.

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REFERENCES

Babinski, N. A.; Chang, H. K. and Santos, R. C. R., 1989. Hydrocarbon occurrence in Proterozoic São Francisco Basin, Brazil: 28th Internat. Geol. Congress, Abstracts, 1, 66-67.

Babinski, M.; Van Schmus, W. R.; Chemale JR., F. and Kawashita, K., 1993. Evolução geológica da porção sul da bacia do São Francisco baseada na geoquímica isotópica de Pb em rochas carbonáticas. In: II Simpósio sobre o Craton do São Francisco, SBG/BA, Salvador, BA. Anais, 185-187.

Banerjee, D. M., 1986. Proterozoic and Cambrian phosphorites - regional review: Indian Subcontinent, in Cook, P. J. and Shergold, J. H., eds., Phosphate Deposits of the World, 1, 70-90.

Claypool, G. H.; Holser, W.T.; Kaplan, I.R.; Sakai, H.; and Zak, I., 1980. The ages curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation: Chemical Geology, 28, 199-260.

Knoll, A. H. and Swett, K., 1990. Carbonate deposition during the Late Proterozoic Era: an example from Spitsbergen: American Journal of Science, 290-A, 104-132.

Knoll, A. H. and Walter, M. R., 1992. Latest Proterozoic stratigraphy and Earth history: Nature, 356, 673-678.

Kyle, J. R. and Misi, A., 1993. Sulfide and phosphate mineralization in Upper Proterozoic carbonate strata, Irecê basin, Bahia, Brazil. Economic Geology (in review).

Misi, A. and Kyle, J. R., 1994. Upper Proterozoic carbonate stratigraphy, diagenesis, and stromatolitic phosphorite formation, Irecê basin, Bahia Brazil: Journal of Sedimentary Petrology, 64 (in press).

Torquato, J. R. F. and Misi, A., 1977. Medidas isotópicas de carbono e oxigênio em carbonatos do Grupo Bambuí na região centro-norte do Estado da Bahia: Revista Brasileira de Geociências, 7, 14-24.

Veizer, J. and Hoefs, J., 1976. The nature of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ secular trends in sedimentary carbonate rocks: Geochimica et Cosmochimica Acta, 40, 1387-1395.

Knoll, A. H. and Swett, K., 1990. Carbonate deposition during the Late Proterozoic Era: an example from Spitsbergen: American Journal of Science, 290-A, 104-132.

Knoll, A. H. and Walter, M. R., 1992. Latest Proterozoic stratigraphy and Earth history. Nature, 356, 673-678.

Kyle, J. R. and Misi, A., 1995. Sulfide and phosphate mineralization in Upper Proterozoic carbonate strata, Irecê basin, Bahia, Brazil. Economic Geology (in review).

Misi, A. and Kyle, J. R., 1994. Upper Proterozoic carbonate stratigraphy, diagenesis, and stromatolitic phosphorite formation, Irecê basin, Bahia Brazil. Journal of Sedimentary Petrology, 64 (in press).

Torquato, J. R. F. and Misi, A., 1977. Medidas isotópicas de carbono e oxigênio em carbonatos do Grupo Bambuí na região centro-norte do Estado da Bahia: Revista Brasileira de Geociências, 7, 14-24.

Veizer, J. and Hoefs, J., 1976. The nature of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ secular trends in sedimentary carbonate rocks. Geochimica et Cosmochimica Acta, 40, 1387-1395.