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$\delta^{13}C$ AND $^{87}Sr/^{86}Sr$ OF PHOSPHORITES FROM NEOPROTEROZOIC SEQUENCES OF THE SÃO FRANCISCO CRATON, BRAZIL: PHOSPHOGENESIS AND CORRELATIONS.

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INTRODUCTION

Phosphate accumulations in the São Francisco Craton are found in both the cratonic non-deformed strata, and in the Brasilia Fold Belt, to the west of the cratonic area. The deposits are stratigraphycally controlled and their formation is probably related to a widespread episode during the terminal Proterozoic Era (Cook and Shergold, 1986). These authors suggested that major phosphogenic event followed a period of glaciation, which "could produce a large volume of cold, nutrient-rich water, resulting in a major expansion of organic productivity in the photic zone following the glacial period".

The phosphorites studied are intimately associated with stromatolites. Nevertheless, most of the stromatolitic structures present in these sequences are not mineralized. This suggests that some other controls or processes might have governed the phosphate concentration in these structures.

We report new analyses of $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ compositions of phosphorites of the Sao Francisco Craton in light of previously published data on associated carbonates, in an attempt to better understand the evolution of Neoproterozoic sedimentary sequences and phosphorite formation. The current study is still in progress.

GEOLOGY AND GEOTECTONIC SETTING

Neoproterozoic sedimentary basins of the São Francisco Craton resulted from extensional events during the fragmentation of the Rodinia supercontinent, between 900 and 600 Ma, and the coincident closure of the Pan-African-Brasiliano rift. The sedimentary sequences deposited during these events are distributed in the following geotectonic settings (Misi et al., 2003; Misi et al., 2005):

A) Mixed carbonate and siliciclastic strata deposited on tectonically stable cratons, represented by the Bambuí Group in the São Francisco Basin, Una Group, in Irecê and Una-Utinga basins, and Rio Pardo Group in the Rio Pardo Basin;

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

Large-scale stratigraphic subdivisions are represented on the stable platforms and passive margin areas by *Glaciogenic*, *Carbonate*, and *Molasse* mega-sequences. These units are separated from each other by first-order unconformities recognized across the Neoproterozoic basins, but within each of these mega-sequences there are additional parasequence boundaries that may be useful for regional correlation (Misi, 2001; Misi et al., 2005 and references).

PHOSPHATE DEPOSITS

Phosphorite deposits are present in the Vazante, Bambuí and Una Groups. They are widespread over a large area and are stratigraphycally controlled (Figures 1 and 2). Coromandel, Rocinha and Lagamar, in the Vazante Group, as well as Campos Belos, Nova Roma, Monte Alegre and Cedro do Abaeté, in the Bambuí Group, are located at the lower section of the carbonate unit immediately above glaciogenic diamictites (Dardenne et al., 1986; Dardenne, 2001). Cabeceiras, in the Bambuí Group, is located at the boundary between the Lagoa do Jacaré and Serra da Saudade Formations (Dardenne et al., 1986). Irecê phosphorites, in the Una Group, occur in dolomitic facies at the top of laminated limestones, equivalent to the Sete Lagoas Formation of the Bambuí Group (Misi and Kyle, 1994).. Three of these deposits – Irecê, Rocinha and Lagamar – are object of the present study.

Fine grained carbonate fluorapatite are concentrated in columnar and laminar stromatolitic structure, in the Irecê area (Una Group). They are close associated to a small sulfide deposit, at the same stratigraphic unit. The presence of resedimented phosphatic clasts in dolostone,

derived from the destruction of columnar structures by currents, among others, suggests that phosphatization is an early diagenetic process (Misi and Kyle, 1994).

Rocinha (and Lagamar) deposits, in the Vazante Group, show microcrystalline carbonate fluorapatite concentrations forming lenses or centimeter-thick beds within carbonate schist (Da Rocha, 1992). There are also phosphate clasts forming grains and angular fragments. The phosphate beds are continuous, although fragmented and folded in some places.

ANALYTICAL RESULTS

Samples of carbonate fluorapatite were analyzed at the University of Ottawa (Canada) and University of Maryland (USA). They were hand-picked from unweathered phosphorites and treated with Silverman solution (Silverman et al., 1952; Kolodny and Kaplan, 1970) to eliminate calcite impurities. Samples were X-rayed and only those that did not show or with very few calcite and dolomite were used for isotope analysis of the carbonate fluorapatite. In addition, samples retaining the lowest Mn/Sr ratios (<0.2) and/or the highest Sr concentration (>700ppm) were used for Sr isotope interpretation. The lowest $^{87}Sr/^{86}Sr$ values within any interval were considered to most likely reflect depositional conditions in most cases. Early diagenetic calcite and dolomite were also analyzed for comparison.

In the Irecê deposits, $\delta^{13}C$ values of carbonate fluorapatite range from -0.19 to -12.25‰ PDB. Early calcite and dolomite associated with carbonate unit hosting phosphate deposits, show dominant positive values from -0.25 to +9.51. Rocinha and Lagamar apatites show $\delta^{13}C$ ranging from -1.03 to -9.61‰ PDB and associated carbonates from Rocinha deposit are between -2.90 and +2.0.

Sr isotope values from phosphorites of Irecê show very high $^{87}Sr/^{86}Sr$ ratios (0.71069 to 0.71586). Nevertheless, well preserved carbonate cements from the same interval – micritic organic-rich limestone with very high total Sr content above 800 ppm and low Mn/Sr ratio of 0.01 - show ratios between 0.70765 and 0.70789. Three samples of Rocinha (2) and Lagamar (1) apatite range from 0.70660 to 0.70910. Micritic organic rich limestone intercalated show similar data, varying from 0.70760 to 0.70886. All the samples are well preserved, with very high total Sr content (above 1700 ppm) and low Mn/Sr ratios (0.09 to 0.56).

DISCUSSION

The broad similarity of lithofacies and mega-sequences, as well as the occurrence of phosphate deposits restricted to a narrow stratigraphic interval in the Vazante, Bambuí and Una groups suggest that these units may be correlative (Misi et al., 2006). The Sr isotope data from well preserved carbonates and apatite from each of these successions support the general correlation and are indicative of seawater composition around 650 Ma. Nevertheless, the lower $^{87}Sr/^{86}Sr$ values of 0.70766 may suggest the possibility that the Vazante succession may be older than the widespread Bambuí sediments. The high $^{87}Sr/^{86}Sr$ values obtained in the Irecê phosphates is probably due to contamination by hydrothermal fluids that formed the sulfide deposits (Fe, Zn, Pb) occurring in the same interval and immediately above the phosphate mineralization.

Carbon isotope data of phosphates reveal sharp negative excursions, as expected in anoxic environments (Fig. 3). Carbonates in these units are moderately enriched in ^{13}C, ranging from positive values of +2.0 and + 9.6‰ in the different sections of Vazante and Irecê. Nevertheless, carbonate fluorapatite from Rocinha and Lagamar deposits, both in stratigraphic units below the Serra do Garrote Formation, give consistent values in the same range of the other successions. Additional chemostratigraphic studies and new radiometric constraints will be necessary, at least for the Vazante Group.

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RESUMO

As concentrações de rocha fosfática nas bacias sedimentares Neoproterozóicas do Craton do São Francisco, são encontradas tanto na área cratônica, não deformada, quanto na Faixa Móvel Brasília, a oeste da área cratônica. Os depósitos são estratigraficamente controlados. Neste trabalho são apresentadas novas análises de $^{87}Sr/^{86}Sr$ e ^{13}C visando definir com mais precisão a evolução das seqüências sedimentares e a formação dos fosforitos. A semelhança das litófacies e mega-seqüências bem como a ocorrência de depósitos de fosfato restritos a estreitos intervalos estratigráficos nos Grupos Vazante, Bambuí e Uma. Sugerem que essas unidades podem ser correlatas. Os dados de isótopos de Sr a partir de carbonatos bem preservados e de apatita, provenientes de cada uma dessas sucessões estratigráficas, confirmam as possíveis correlações e indicam composições próximas da água do mar em torno de 650 Ma. Contudo, valores de $^{87}Sr/^{86}Sr$ de 0.70766 poderiam sugerir que as seqüências do Grupo Vazante seriam mais antigas que aquelas do Grupo Bambuí. Os altos valores obtidos no fosfato de Irecê (Grupo Uma) podem ser atribuídos à contaminação por fluidos hidrotermais responsáveis pela formação de concentrações de sulfetos (Fé, Zn, Pb), ocorrendo no mesmo intervalo e imediatamente acima dos fosforitos. De um modo geral, os carbonatos provenientes das unidades estudadas mostram-se moderadamente enriquecidos em ^{13}C tanto em Vazante como em Irecê, variando de +2.0 a +9.6‰.

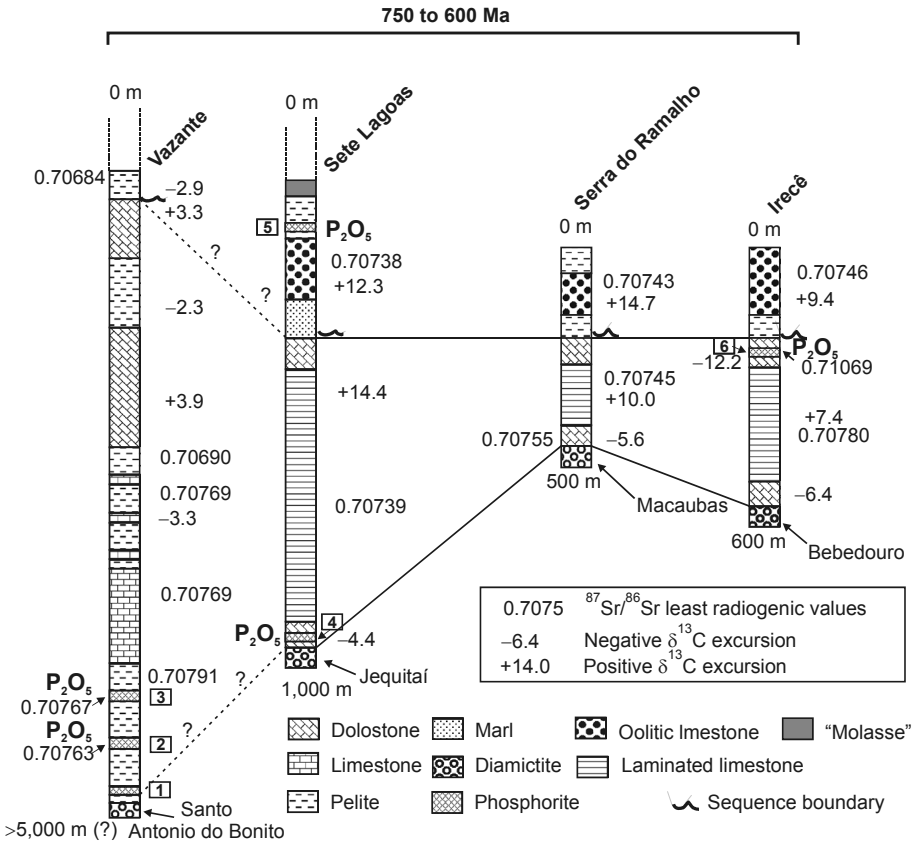

Figure 1 – Correlation between the Neoproterozoic succesions of the São Francisco Craton and phosphorite deposits. 1 – Rocinha 2 – Lagamar 3 – Coromandel 4 –Campos Belos, Nova Roma, Monte Alegre and Cedro do Abaeté 5 – Cabeceiras 6 – Irecê. **Vazante**: Vazante Group; **Sete Lagoas** and **Serra do Ramalho**: Bambui Group; **Irece**: Una Group. From Misi et al. (2006), modified.

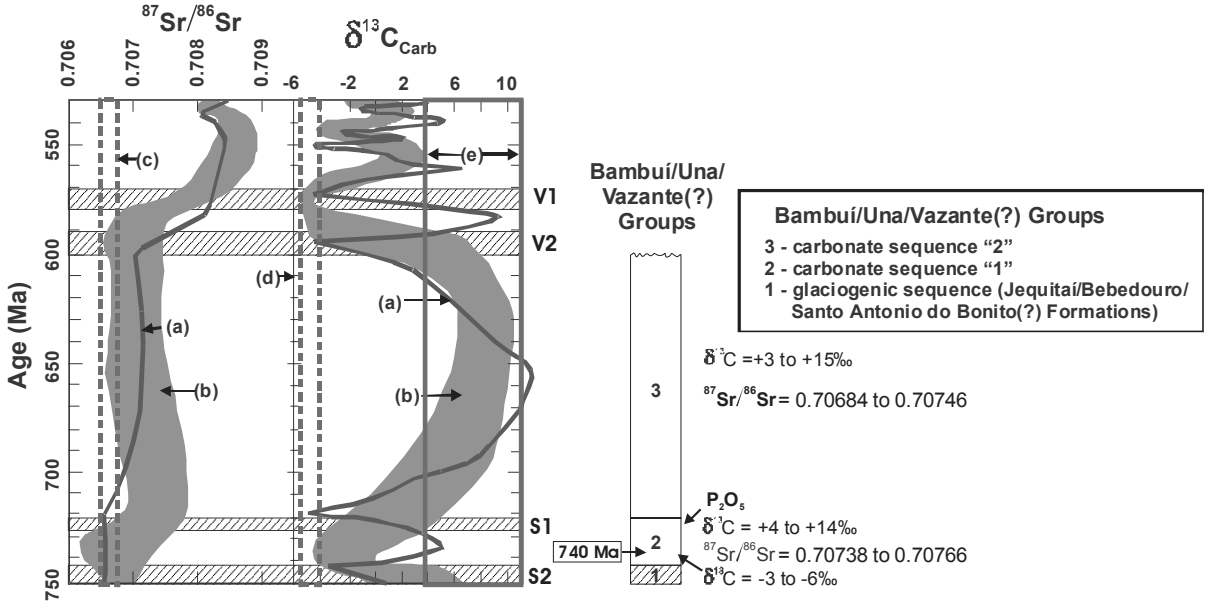

Figure 2: $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ evolution of Neoproterozoic seawater: **(a)** Curves obtained by Brasier and Shields (2000), based on data from SW Mongolia, NW Canada and Oman (several sources). **(b)** Range of seawater variation by Jacobsen and Kaufman (1999), based on data from Siberia, Namibia, Canada, Svalbard and East Greenland. **(c)** Range of $^{87}Sr/^{86}Sr$ least radiogenic values in the Vazante, Bambuí and Una Groups. **(d)** Range of dominant negative excursions of phosphates in the Vazante and Una Groups. **(e)** Range of $\delta^{13}C$ positive excursions in the Groups: Vazante (Morro do Calcário and Serra do Poço Verde Formations), Bambuí (Lagoa do Jacaré and Sete Lagoas Formations) and Una (A1, B1 and B Units). **V1**, **V2**: upper and lower Vendian glaciations; **S1**, **S2**: upper and lower Sturtian glaciations. At right, possible correlation of the studied sequences with the global curves. A possible geochronological mark are Pb-Pb isochronic ages of carbonates from the Sete Lagoas Formation, Bambui Group (740 ± 42 Ma, Babinski and Kaufman, 2003). From Misi et al. (2006), modified.

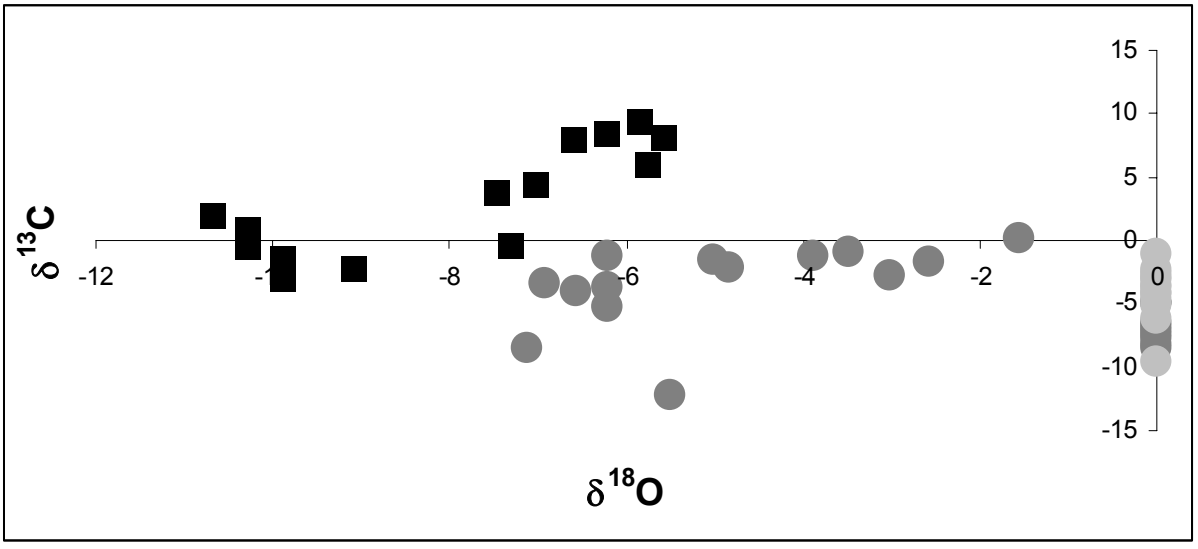

Figure 3 – $\delta^{13}C$ versus $\delta^{18}O$ variation in phosphates and associated carbonates from the studied areas. No $\delta^{18}O$ determinations were made in phosphates from Rocinha and Lagamar.

■ Early cc+dol: Irece and Rocinha ● Phosphate: Irece ● Phosphate: Rocinha and Lagamar