CARBON ISOTOPE FLUCTUATIONS IN PRECAMBRIAN MARBLES OF THE SERIDÓ BELT, BORBOREMA PROVINCE, NORTHEAST BRAZIL

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INTRODUCTION

Because the isotopic composition of seawater has changed through time and for this the isotopic composition of marine carbonates has been used for chemostratigraphic purposes. In particular, carbon, sulfur and Sr isotopes have proved to be very useful tools in this regard. The isotopic study of marine carbonates from several ages has allowed the reconstruction of the secular C/C-variation trend (Kaufman and Knoll 1995, Huffman et al. 1998). These variations are the response to global tectonic and climatic events. In carbon chemosтратigraphic it is fundamental to samples with primary values of δ13C and that have not been affected by diagenetic or metamorphic alterations. In this way, it will be possible to estimate the primary carbon isotope composition of the seawater from which carbonates have precipitated. In several Proterozoic and Paleoproterozoic sedimentary carbonate successions, dolomite is isotopically similar to the associated calcite, because dolomitization is syndepositional in the presence of fluids isotopically similar to the seawater (Tucker 1983, Darbonne et al. 1994). Metamorphism usually does not affect the primary carbon isotope composition of limestones. However, metamorphic events with express fluid circulation can promote isotopic modifications through decarbonation reactions usually in the presence of silicate minerals (Kaufman and Knoll 1995). This is usually a localized phenomenon, restrict to shear zones or metamorphic contact aureoles, easily recognizable. Therefore, the carbon isotope composition of a marble usually reflects the composition of its protolith. Hydrothermal alteration and weathering or metamorphism, however, can easily modify the primary carbon isotopes. One of the best selective criteria to detect post-depositional carbon isotope modifications consists in the exam of covariation between δ13C and δ18O. Hydrothermal alteration and weathering usually lower the δ18O values. δ13C of carbonate samples, in which δ18C and δ18O show no correlation between them, are regarded as primary ones.

In this study, we will discuss the δ13C chemostratigraphy of marbles from the Seridó Group, aiming at contributing to precise the age of deposition of the carbonate rocks in this belt.

THE SERIDÓ BELT AND ITS GEOLOGIC EVOLUTION

The Seridó belt encompasses a supracrustal sequence of high-temperature, low-pressure metamorphic rocks (gneissgrit to amphibolite facies) that have a NNE trend resulted from Neoproterozoic transcurrent shear zones. These rocks overlie a Paleoproterozoic gneissic-migmatitic substratum (2.15 to 2.23 Ga; Dantas 1991) that was intruded by anorogenic plutons, intruded synchronously to the deposition of the supracrustal rocks. Jardim de Sa and Salim (1995) indicate crystallization in the 1.9 to 2.0Ga interval. If these orthogneisses represent granitoids intrusive in the Seridó Group metasediments, this time interval would have recorded the oldest deformation that affected this belt and, therefore, would represent the minimum age for the Seridó Group metasediments. Achenjo and Salim (1986) proposed another stratigraphic subdivision for these supracrustal rocks. They subdivided these rocks into two units: the Paleoproterozoic Jucurutu Formation that includes a lower volcanosedimentary sub-unit (Jucurutu Formation), and an upper elastic sub-unit (Equador Formation). The Neoproterozoic Seridó Group metasediments (that includes a lower sub-unit composed of metacarbonate and Paragneisses and an upper sub-unit composed mainly of schists (Seridó Formation). Achenjo and Salim (1986) and Caby (1989) consider the G. granitoids as Paleoproterozoic anorogenic plutons, intruded synchronously to the deposition of the Jucurutu Formation sedimentary rocks. Nd isotopes yielded model age for the metasedimentary rocks of the Seridó Group ranging from 1.2 to 1.6 Ga. U-Pb in detrital zircons from paragneisses of the Jucurutu Formation indicate ages from 1.75 to 2.15 Ga for the source rocks (Van Schmus et al. 1995, 1996). On the other hand, zircons from felsic rocks, interpreted as volcanic intercalations, yielded ages of 0.74 Ga (Van Schmus 1986), and detrital zircons from the Seridó Formation, yielded an age of 0.69 Ga (Van Schmus et al. 1999). In summary, Van Schmus and co-workers maintain a Neoproterozoic age for the Seridó belt.

CARBON ISOTOPE CHEMOSTRATIGRAPHY

About 140 samples of carbonates have been collected perpendicularly to the strike at a centimeter to meter scale. This sampling includes marbles from the Jucurutu Formation collected nearby the Jucurutu town and southeast of the Caico town, state of Rio Grande do Norte, and marbles from the Seridó Formation, to the north of Santa Luzia town, state of Paraíba.

Carbon and oxygen isotope analyses have been carried out at the Stable Isotope Laboratory (LABISE) of the Federal University of Pernambuco. Recife, Brazil. Powdered samples have been reacted with orthophosphoric acid at 25°C overnight (dolomitic or calcitic + dolomitie samples were allowed to react for three days or more). An extended reaction period was preferred instead of increasing the reaction temperature. The released CO2 gas was cryogenically cleaned and after that analyzed in a fully automated V.G. ISOTECH SIRA II dual inlet, triple collector, mass spectrometer. The precision levels for carbon and oxygen isotopic ratios are about 0.1 %0. Results are expressed in the PDB (Peedee Belemnite) scale in %0.

Marbles of the Jucurutu Formation are fine to coarse-grained, predominantly calcite, sometimes displaying a banding with alternate gray and white layers. Near the Jucurutu town, marble lenses show a N45°E foliation and are in contact with the Jucurutu paragneisses. These marbles display δ13C within a narrow range (+8.3 to +10.5 %0o) and an average value of +10 %0o, and an average value of +10 %0o (Fig. 2a). There is no
substantial difference between the white and gray marble bands. Oxygen isotopes exhibit a broader variation with values ranging from -12.2 to -5.5 ‰. As shown in Figure 2b, there is no correlation between $\delta^{13}$C and $d^{18}$O, indicating that the carbon isotope ratios should be, in principle, identical to those in the protolith.

The Seridó marbles appear to be more deformed than those of the Jucurutu Formation. They are usually tightly folded and found as lenses. Near the contact with micaschists, marbles exhibit xenomorphic garnet grains and sillimanite crystals usually disposed parallel to axial planes of the folds. In marbles of this Formation, $\delta^{13}$C values are found in a broader range (+4.4 to +10.6 ‰; Fig. 3a) while $\delta^{18}$O values vary from -6.9 to -12.6 ‰. Samples cluster into two groups (Fig. 3b) when $\delta^{13}$C is plotted against $\delta^{18}$O, with a gap between them. There is a weak positive correlation between $\delta^{13}$C and $\delta^{18}$O for samples collected near the contact with biotite-schists (group a in Fig. 3b). This suggests that the carbon isotope signatures for this cluster of samples are not primary. They were probably affected by decarbonation reactions that led to the formation of Ca-rich garnet and lowered the C isotope values. If these values are discarded, $\delta^{13}$C for the Seridó marbles will be restricted to the +6 to +10.7 ‰ interval.

DISCUSSION There are several $d^{13}$C variation curves available in the literature. In this study we will adopt the $d^{13}$C-variation curve proposed by Hoffman et al. (1998) with minor modifications introduced by Kha et al. (1999). For the Proterozoic, this curve shows strong positive anomaly for the Paleoproterozoic in the 2.33 to 2.06 Ga interval (Lomagundi or Jatulian event; Schidlowski et al. 1976, Melezhik et al. 1997) ascribed to the stromatolite explosion. The Neoproterozoic is characterized in the 0.8 to 0.54 Ga interval by a series of successive strong oscillations, that become stronger towards the Precambrian-Cambrian boundary. The positive oscillations have been related to the increase of the organic carbon reservoir relative to the inorganic carbon reservoir, while the negative ones were caused by glacial events (Knoll et al. 1986).

The carbon isotope patterns obtained in this study have been compared to the $d^{13}$C secular variation curve for the Proterozoic. The interval of $d^{13}$C variation for the Jucurutu and Seridó Formations have been plotted in Fig. 4 and are represented by interval variation bands that intercept the carbon secular variation curve in three Proterozoic age intervals (a, b and c in this Figure). Based on this Figure, three age intervals can be proposed:

(a) Paleoproterozoic (2.25-2.28 Ga). This age interval can be discarded because it would ascribe the Jucurutu and Seridó Formations an age older than their basement, the Caico Complex (2.23-2.15 Ga).
Figure 2. (a) $\delta^{13}C$ profile for the Jucurutu Formation metasedimentary carbonates. Most values lie between +9.5 and +10%oPDB- (b) $\delta^{13}C$ versus $\delta^{18}O$ plot for the samples shown in Figure 2a. Apparently no correlation is evident in this plot.

Figure 3. (a) $\delta^{13}C$ profile for the Seridó Formation metasedimentary carbonates, (b) $\delta^{13}C$ versus $\delta^{18}O$ plot for the samples shown in Figure 3a. Samples cluster in two groups. Group "a" that corresponds to samples collected near the contact between the metasedimentary carbonates with biotite-schists shows a correlation. Samples in group "b" show no correlation.

Figure 4. Secular variation in $\delta^{13}C$ (PDB) values of marine carbonates from 2.5Ga to the present (modified from Hoffman et al. 1998). The interval of variation of $\delta^{13}C$ of the Jucurutu and Seridó Formations has been indicated by horizontal gray bands, a, b and c indicate the probable age intervals for each of these two Formations. See text for discussion.

(b) Paleoproterozoic (2 to 2.15Ga). This age interval coincides with the age interval found for orthogneisses (G2) regarded as intrusive in the Jucurutu and Seridó Formations. 

(c) Neoproterozoic (600 to 650 Ma). A Neoproterozoic age of 740 Ma for the Seridó Group has been proposed by Van Schmus et al. (1996) and, more recently, an age of 600 Ma has been determined (Van Schmus et al. 1999). The hypothesis of an age of 740 Ma would imply in $\delta^{13}C$ values $<8$%PDB (Fig. 4), and this conflicts with the observed C-isotope variation for the Seridó metacarbonates.

If elected the 600Ma-age hypothesis, one would expect that some geological events, globally recorded, and had been registered in the Seridó Group metasediments. For example, it is known that around 600 Ma, an important glacial event (Varanger) was globally observed. This event has been recorded by diamictites above which sedimentary carbonate displays well pronounced negative $\delta^{13}C$ values. Such features have not been yet observed in our field and isotopic data.

CONCLUSIONS From this carbon isotope investigation, it seems reasonable to assume that the Jucurutu and Seridó carbonate rocks were deposited during the same sedimentation cycle. Although the age inferences based on carbon isotope patterns, here discussed, are not conclusive, the current data associated to the available information on the regional geology seem to favor a Paleoproterozoic age for the Seridó Group. Further Sr and Nd isotope chemostratigraphic studies of
these carbonate sequences would allow to definitely discard the Neoproterozoic-age hypothesis.

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