

## CHEMOSTRATIGRAPHY OF TWO NEOPROTEROZOIC CAP CARBONATES FROM THE SERGIPANO BELT (NORTHEASTERN BRAZIL)

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### INTRODUCTION

Two cycles of sedimentation (both with a continental to shallow marine, basal siliciclastic megasequence, overlain by a carbonate sequence) are seen in the Neoproterozoic Sergipano belt, northeastern Brazil (D'el Rey da Silva, 1999). The lower siliciclastic megasequence (Juetê, Itabaiana and Ribeirópolis formations) and the lower carbonate megasequence (Acauã and Jacoca formations) form the Estância-Miaba Group. The upper siliciclastic megasequence is represented by Frei Paulo (phyllites and carbonates) and Capitão/Palestina formations (Vaza Barris Group) and the upper carbonate megasequence (Olho D'Água Formation). The Jacoca/Acauã and Olho D'Água formations are probably cap carbonates.

The Acauã Formation overlies the Juetê glacial diamictites and unconformably the basement gneiss. It consists of basal dolomite, limestone (with dolostone dropstones in proximal sections), and limestone/dolostones intercalations, and limestone/argillite rhythmites. This formation is observed in Bahia in an area to the west of the Tucano Basin. The Jacoca Formation overlies pebbly phyllites/diamictites of the Palestina/Ribeirópolis Formation and comprises metacarbonates and a mixed lithofacies of metasiliciclastics and metacarbonates, which is also observed in Sergipe. Jacoca and Acauã Formations are chrono-correlatable units. Rocks of the Jacoca Formation spread continuously across the São Francisco craton margin into the Sergipano belt where they occur around the Itabaiana and Simão Dias basement domes and are overlain by metadiamictite of the Palestina Formation and metacarbonate of the Olho D'Água Formation. Metasediments of the Vaza Barris Group (diamictites of the Palestina Formation and the upper carbonate megasequence) overlie the upper siliciclastic megasequence. These two megasequences underwent the same Neoproterozoic compressive deformation under subgreenschist facies.

### CARBON AND OXYGEN ISOTOPES

Sections of the Acauã Formation to the west of the Tucano basin, Bahia (at Serra da Borracha, near Patamutê and at São Gonçalo Farm near Euclides da Cunha), conform to descriptions of other Neoproterozoic cap carbonates worldwide, with dolostones at the base resting on diamictites. Dolostones of the Acauã Formation in sections at São Gonçalo and Serra da Borracha overlie diamictites of the Juetê Formation (equivalent to the Ribeirópolis Formation) show hummocky and, locally, pseudo-tepee structures at its basal portion, passing upwards into a thinning-upward carbonate succession. These carbonates rest directly on diamictite of the Juetê Formation, which shows boulders (granite, orthogneiss, phyllite, quartz) some of which cross the contact (dropstones) with a Fe-rich claystone layer within this diamictite.

Detailed C and O isotope chemostratigraphic sections made at São Gonçalo Farm, near Euclides da Cunha, Serra da Borracha hill and at Patamutê, reveal that  $\delta^{13}\text{C}$  values for the Acauã Formation carbonates tend to group mostly between -5 and -4‰, within the range for mantle values (Hoffman and Schrag, 2002) which could attest to the role of mantle-derived  $\text{CO}_2$  leading to greenhouse effect after a snowball phenomenon.

This is one of many possible explanations for the negative  $\delta^{13}\text{C}$  signatures of the cap carbonates. High proportional rates of carbonate deposition relative to organic C deposition would have the same effect, as would inputs from bacterial sulfate reduction, for example. Mercury contents of cap carbonates could, perhaps, help demonstrating the participation of volcanic  $\text{CO}_2$  in carbonate deposition.

At Serra da Borracha hill,  $\delta^{13}\text{C}$  values remain homogeneous upsection (around -5‰) for about 165 m (Fig. 1a). Only about 1m of dolostone is present in the base of the section (part of the basal dolostones has been eroded away) being followed up by limestones for next 30m with some dolostones blocks (dropstones). The  $\delta^{18}\text{O}$  values for this interval of the section varies gradually up section from about -12 to about -5‰<sub>V-PDB</sub>. Such enormous fractionation likely resulted from a gradual

temperature decrease by the time dolostone dropstones were deposited. Although some other explanations could be invoked (diagenetic causes for example) the trend of variation and lack of covariance between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values seem to support that oxygen isotopes values are near-primary.

The  $\delta^{13}\text{C}$  values for the Jacoca Formation at the Capitão Farm, state of Sergipe, one of the best exposures of this Formation along the Vaza Barris River, are all negative, in their majority in the  $-5$  to  $-4\text{‰}_{\text{V-PDB}}$  range while  $\delta^{18}\text{O}$  values are mostly  $\sim -8\text{‰}_{\text{V-PDB}}$ . Usually the basal dolostone of this cap carbonate shows a relatively limited thickness (a couple of meters or less, especially in more distal sections). The behavior of C and O isotopes in the Acauã and Jacoca carbonates suggest (although do not prove) that they could have been simultaneously deposited (virtually all cap carbonates worldwide have similar carbon isotope variation, and therefore it is impossible to use the negative signatures alone as a correlation tool, even on a regional scale).

At Serra da Canabrava hill, however,  $\delta^{13}\text{C}$  values vary from  $-6$  to  $-0.2\text{‰}$  and a package of carbonates that seem to be stratigraphically above the Borracha hill (near Almeida locality) shows values varying from  $-0.5$  to  $+0.3\text{‰}$ .

Marls to marly carbonate lenses intercalated in phyllites of the Frei Paulo Formation, which underlies Palestina diamictites, in Sergipe, show  $\delta^{13}\text{C}$  values from  $+3$  to  $+8\text{‰}_{\text{PDB}}$  and  $\delta^{18}\text{O}$  from  $-9$  to  $-6\text{‰}_{\text{PDB}}$ .

Marly and dolomitic carbonates of the Olho D'Água Formation, near Simão Dias, Sergipe, by the contact with Palestina diamictites/pebbly metagreywackes display of  $\delta^{13}\text{C}$  values as low as  $-4.7\text{‰}_{\text{PDB}}$ , increasing upsection to a plateau between  $0$  and  $1\text{‰}_{\text{PDB}}$  and finally to another plateau around  $+8$  to  $10\text{‰}_{\text{PDB}}$ . This behavior is observed in the sections at Serra do Capitão (Fig. 1b), between Rosario and Cocorobó, Bahia and to the north of Simão Dias, Sergipe. The  $\delta^{18}\text{O}$  values in these sections vary from  $-7$  to  $-12$ . Low Mn/Sr and lack of co-variance between  $\delta^{13}\text{C}$  values and Mn/Sr values suggest that these isotopic values are primary.

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

Jacoca carbonates display average  $^{87}\text{Sr}/^{86}\text{Sr}$  of  $\sim 0.707974$ , Acauã carbonates vary from  $0.70717$  to  $0.70751$  and ratios for the Olho D'Água carbonates vary from  $0.70753$  to  $0.70828$ , all within the range typical for late Neoproterozoic seawater.

## MERCURY

Mercury accumulation rates were found to be larger by a factor of three in Quaternary sediments deposited in a layer in Lagoa da Pata Basin, Upper Rio Negro, Brazilian Amazon, after the last glacial maximum than in a layer deposited below (Santos et al., 2001). Thus, in regions where the geological background of mercury is negligible, mercury archived in sediments may be useful for interpretation of the paleoclimatology.

The Snowball Earth hypothesis assumes that mantle-derived  $\text{CO}_2$  is transferred by volcanism to the terrestrial atmosphere and its high concentration provokes melting of ice and deposition of cap-carbonates on top of glacial diamictites. Such volcanism may also allow for higher concentrations of mercury in cap carbonates after ice melting. To investigate this possibility, a preliminary survey with carbonate samples from the Acauã and Jacoca Formations (53 samples) was made.

At São Gonçalo Farm section, where a sharp contact between diamictite and cap dolostone is seen, a dolostone sample few centimeters from the contact yielded a value of  $30 \text{ ng Hg g}^{-1}$ . The mercury curve varies upsection from  $11$  to  $26 \text{ ng g}^{-1}$  (average  $19 \pm 5$ ). At Serra da Borracha, a slight increase of mercury was observed towards the top (total variation from  $10$  to  $28 \text{ ng g}^{-1}$ , average  $15 \pm 5$ ), while at Patamuté, values are  $\sim 11 \text{ ng g}^{-1}$  with an increase to  $41 \text{ ng g}^{-1}$  at about  $8\text{m}$  from the base where gray marls change to carbonatic phyllite. At Capitão Farm, near the Vaza Barris River, two samples from near the bottom of the section showed mercury contents of  $281$  and  $194 \text{ ng g}^{-1}$ , higher by a factor of  $10$ , if compared to the rest of this profile (average  $20 \text{ ng g}^{-1}$ ). These samples are from limestones interlayered with phyllites. The association of higher contents of mercury to carbonates finely interlayered with more terrigenous sediments suggests that mercury, originated from volcanism, has been leached from land surface and deposited along argillaceous carbonates.

## CONCLUSIONS

In the light of the current C isotope data, values for the older of the two cap carbonates under consideration are all negative (around  $-5\text{‰}$ ) even in the most thicker sections ( $165\text{m}$  at the Borracha hill). This behavior differs from what is observed in most inferred "Sturtian" cap carbonates worldwide, where in general  $\delta^{13}\text{C}$  values shift from negative into positive after  $2\text{-}20\text{m}$  above the contact with the basal diamictite.

[I have always held out that the Maieberg with its long stratigraphic throw of negative  $\delta^{13}\text{C}$  values is a Sturtian event. My colleagues at Harvard have reinterpreted this as Marinoan, but there are no real age constraints on this. Even the Hoffmann et al. (2004) age is problematic as those authors did not make a convincing case that the Swakop diamictite is actually equivalent to the Ghaub. It could just as easily be equivalent to the Blazkranz on the Kalahari Craton, which is beneath Nama Group beds that are clearly Ediacaran in age.

The Jacoca/Acauã cap carbonate also shows this unusual behavior and negative values have been observed for about 100m sometimes, shifting to positive values up section (+ 8 to + 10‰).

Despite of the large effort recently made to date Neoproterozoic glaciations (Hoffmann et al., 2004; Fanning, et al., 2004; Zhou et al., 2004; Calver et al., 2004) this subject is still a matter of strong debate. Therefore, any compiled temporal  $\delta^{13}\text{C}$  secular variation curve becomes a mobile target and its use perhaps leads to erroneous assumptions. A zircon age of 720Ma in acidic volcanics (B.B. Brito Neves and W. R. Van Schmus, written communication) in the Ribeirópolis diamictite below the Jacoca Formation, suggest these carbonates have been deposited right after the Sturtian glaciation. The age of a gabbro that intruded Palestina pebbly metagreywacke near Bendegó, Bahia, right below Olho D'Água will constrain the age of the younger cap carbonate. As to the use of mercury as a paleoclimatic tracer, high contents in carbonates to carbonatic phyllites of the Jacoca Formation may result from volcanism that followed a snowball event. However, much detailed study is necessary before one can assume mercury as a tracer for glacial events.

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#### RESUMO

Há dois ciclos de sedimentação (sequência siliciclástica basal, continental a marinha rasa, coberta por sequência carbonática) na Faixa Sergipana, nordeste do Brasil. A sequência siliciclástica inferior (Formações Juetê, Itabaina e Ribeirópolis) e a sequência carbonática inferior (Formação Jacoca) formam o Grupo Estância-Miaba. A megasequência superior siliciclástica é representada pelas Formações Frei Paulo (filitos e carbonatos) e Capitão/Palestina (Grupo Vaza Barris) e a megasequência carbonática superior (Formação Olho D'Água). A Formação Acauã recobre diamictitos Juetê e consiste de dolomito basal, calcário (com "dropstones" de dolomitos em seções proximais), intercalações calcários/dolomitos e ritmitos de calcá-rios/argilitos. A Formação Jacoca (metacarbonatos, litofacies mixta de metasiliciclásticos/metacarbonatos) recobre filitos seixosos/diamictitos da Formação Ribeirópolis é estratigraficamente equivalente a Formação Acauã. As Formações Jacoca/Acauã e Olho D'Água são provavelmente carbonatos de capa.

Valores de  $\delta^{13}\text{C}$  sempre  $\sim -5\%$  para a Formação Jacoca/Acauã (165 m na Serra da Borracha) contrastam com a maioria das capas carbonáticas onde valores negativos são substituídos por positivos 2 a 20m acima do diamictito basal. A capa carbonática mais jovem mostra valores negativos até cerca de 100m do contato basal, mudando abruptamente para valores positivos ( $\sim +9\%$ ).

Na Fazenda Capitão, calcários intercalados com filitos mostram valores de mercúrio de 281 e 194ng g<sup>-1</sup>, mais altos 10 vezes se comparados com a média (20 ng g<sup>-1</sup>). Teores mais altos associados a carbonatos intercalados com sedimentos terrígenos sugere que mercúrio (origem vulcânica) foi lixiviado do continente e depositado com carbonatos argilosos.

Uma idade de 720 Ma (zircão, SHRIMP) para vulcânicas ácidas na Formação Ribeirópolis (B.B. Brito Neves comunicação escrita) sugere que a Formação Jacoca depositou-se após a glaciação Sturtiana. A idade de um gabro que intruiu metagrauvaca seixosa da Formação Palestina próximo a Bendegó, limitará a idade da capa carbonática mais jovem. Teores altos de mercúrio em filitos carbonáticos/filitos podem ter resultado do vulcanismo que se seguiu a evento "snowball".

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### Serra da Borracha

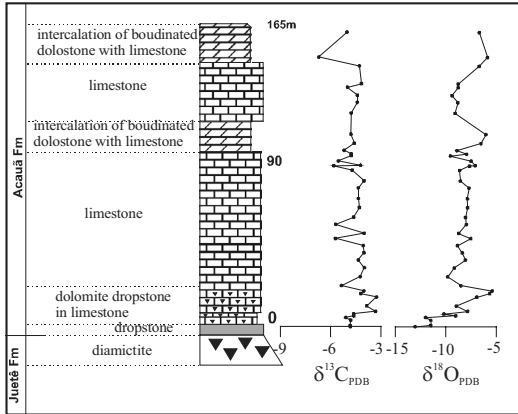


Fig.1a

### Serra do Capitão

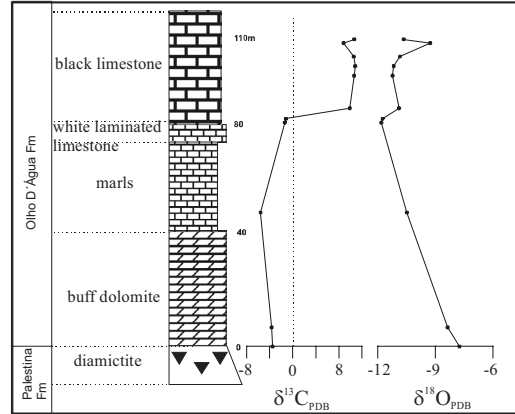


Fig.1b

Fig. 1. C and O chemostratigraphic profiles for the Acauã/Jacoá and Olho D'Água cap carbonates.