Mercury and C and Sr isotopes of two neoproterozoic cap carbonates in the Sergipano belt, northeastern Brazil

A.N. Sial[1], V.P. Ferreira[1], M.A. Silva Filho[2], C. Gaucher[3], D.R. Soares[1], M.M. Pimentel[4], L.D. Lacerda[5], E.V. Silva Filho[5] & G.B. Gantois[1]

1 NEG-LABISE, Dept. of Geol., UFPE, C.P. 7852, Recife, 50670-000, Brazil; e-mail: sial@ufpe.br
2 Companhia de Pesquisa de Recursos Minerais – CPRM, Recife, Brazil; e-mail: masf@re.cprm.gov.br
3 Dept. Geología, Facultad de Ciencias, Iguá 4225, 11400 Montevideo, Uruguay; e-mail: gaucher@chasque.apc.org
4 Institute of Geosciences, University of Brasilia, Brasilia, 70910-900, Brasília-DF, Brazil; e-mail: marcio@unb.br
5. Dept. of Geochemistry, Federal Fluminense University, Niteroi, R.J., 24020-007; e-mail: geoemma@vm.uff.br

Abstract Two cap carbonates have been identified in the Sergipano belt in northeastern Brazil. They are represented by the Acauã/Jacoca Formation (essentially carbonates) which rests on the Juetê/Ribeiropolis Formation (diamictites) and Olho D'Agua Formation (essentially carbonates) which overlies Palestina Formation diamictites. Metamorphism is of sub-greenschist facies. Values for $\delta^{13}C$ for the Acauã/Jacoca Formation group around -4 to -5‰ and all values for these carbonates are virtually negative. For the Olho D'Agua carbonates, however, negative values (around -5‰) are replaced up section by values close to zero and, abruptly, by positive values between + 8 and + 10‰. A preliminary attempt to demonstrate that CO_2 available for carbonate deposition was mainly mantle-derived (transferred to the atmosphere by volcanism and characterized by values around -5‰) using Hg concentrations as a proxy to volcanic emissions, showed that Hg contents in Jacoca Formation carbonates are much higher (280 $ng.g^{-1}$, locally) than in carbonates deposited elsewhere not concomitantly with volcanic activities (< 3 $ng.g^{-1}$) but are similar to those deposited during volcanic activities (e.g. Tertiary Punta Rocallosa carbonates in Chile), between 20 and 80 $ng.g^{-1}$.

Keywords: Cap carbonate, C isotopes, Sr isotopes, mercury, northeastern Brazil

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 Ribeiropolis 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'Agua Formation). The Jacoca/Acauã and Olho D'Agua Formations are probably cap carbonates.

The Acauã Formation overlies Juetê diamictites and unconformably the basement gneiss. It consists of basal dolostone, 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 Ribeiropolis 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 sub-greenschist facies.

CARBON AND OXYGEN ISOTOPES Sections of the Acauã Formation to the west of the Tucano basin, Bahia (at Serra da Borracha, near Patamuté and at São Gonçalo Farm near Euclides da Cunha), conform descriptions of 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 Ribeiropolis Formation) show hummocky and, locally, pseudo-tepee structures at its basal portion, passing into a thinning-upward carbonate succession up section. 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 Ferich claystone layer within this diamictite.

Analytical methods Only least altered portions of samples were microdrilled with 1 millimeter drill and analyzed at the stable isotope laboratory (LABISE), Federal University of Pernambuco, Brazil. CO_2 was extracted from these carbonate samples on a high vacuum line after reaction with phosphoric acid at 25°C, and cryogennically cleaned, according to the method described by Craig (1957). Released CO_2 gas was analyzed for O and C isotopes in a double inlet, triple collector mass spectrometer (VG Isotech SIRA II), using the BSC reference gas (Borborema skarn calcite) that was calibrated against NBS-18, NBS-19 and NBS-20, and has the $\delta^{18}O$ value of -11.3‰PDB and $\delta^{13}C$ = 8.6‰PDB. The external precision based on multiple standard measurements of NBS-19 was better than 0.1‰ for carbon and oxygen**.** Isotope analyses are expressed in the δ-notation in parts per thousand in relation to the international PDB scale. Selected samples were also analyzed for major and trace elements at the LABISE, by X-ray fluorescence, using fused beads and an automatic RIX-3000 (RIGAKU) unit. Fused beads were prepared using Li fluoride and Li tetraborate and uncertainties were better than 5% for Sr and Fe and 10% for Mn.

For the determination of total Hg concentrations, homogenized 0.5 to 1.0 g samples of sediments, dried at 60°C to constant weight, were digested with an acid mixture (50% *acqua regia* solution), and heated at 70°C during one hour, in a thermalkinetic reactor "cold finger". Glass and plastic ware were decontaminated by immersion during 2 days in 10% (v/v) Extran solution (MERCK), followed by immersion during 3 days in diluted HNO_3 (10 % v/v) and final rinsing with Milli-Q water. All chemical reagents used were of at least analytical grade. Cold Vapor Atomic Absorption Spectrophotometry, using a Bacharach Coleman (50D model) equipment, was used for Hg determination, after Hg^{2+} reduction with $SnCl_2$. All samples were analyzed in duplicates, showing reproducibility within 9.5%. A certified reference material (NRC PACS-2, Canada) was simultaneously analyzed to evaluate Hg determination accuracy. Such analysis showed a precision of 4%, as indicated by the relative standard deviation of three replicates, and presented a Hg recovery of 103±4%. The Hg detection limit varied between 1.26 $ng.g^{-1}$, as indicated by 3 times the standard deviation of reagent blanks. In all cases blank signals were lower than 0.5% of sample analysis. The concentration values obtained was not corrected for the recoveries found in the certified material.

C and O stratigraphy Detailed C and O isotope chemostratigraphic sections made at São Gonçalo Farm, near Euclides da Cunha, Serra da Borracha hill and at Patamuté, have revealed that $\delta^{13}C$ values for the Acauã Formation carbonates tend to group mostly between -5 and -4‰, within the range for mantle values (Hoffman & Schrag 2002) which attest to the role of mantle-derived CO_2 leading to greenhouse effect after a snowball phenomenon.

At Serra da Borracha hill, $\delta^{13}C$ values are kept very homogeneous upsection (around -5‰) for about 165m (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 $\delta^{18}O$ values for this interval of the section varies gradually up section from about -12 to about -5‰$_{V\text{-}PDB}$. Such enormous fractionation likely resulted from a gradual temperature decrease by the time dolostone dropstones were deposited.

The $\delta^{13}C$ 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‰$_{V\text{-}PDB}$ range while $\delta^{18}O$ values are mostly ~ -8‰$_{V\text{-}PDB}$. 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 seem to confirm that they have been simultaneously deposited.

At Serra da Canabrava hill, however, $\delta^{13}C$ values vary from -6 to -0.2‰ 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‰.

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

Marly and dolomitic carbonates of the Olho D'Agua Formation, near Simão Dias, Sergipe, by the contact with Palestina diamictites/pebbly metagrey-wackes display of $\delta^{13}C$ values as low as -4.7‰$_{PDB}$, increasing upsection to a plateau between 0 and 1‰$_{PDB}$ and finally to another plateau around +8 to 10‰$_{PDB}$. This behavior is observed in the sections at Serra do Capitão (Fig. 1b), at Rosário-Cocorobó, Bahia and to the north of Simão Dias, Sergipe.

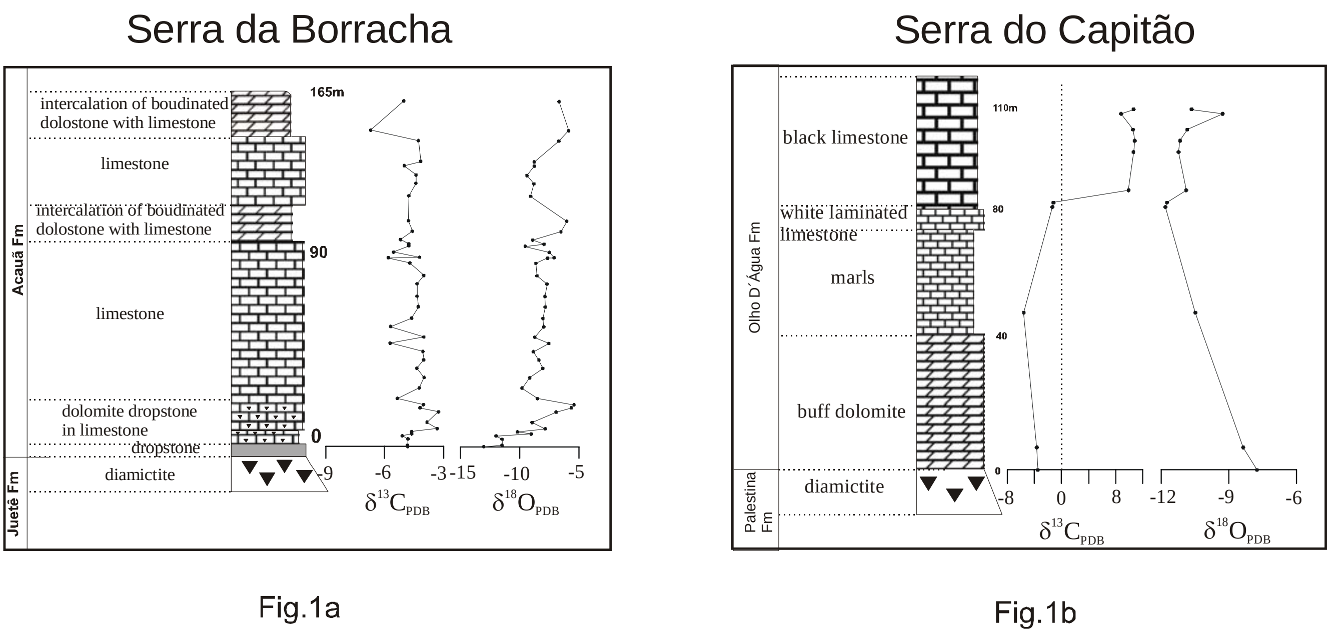


Figure 1. C and O isotope chemostratigraphic profiles for the Acauã/Jacoca (a) and Olho D'Agua (b) cap carbonates.

The δ^{18}O values in these sections vary from -7 to -11‰ and $\delta^{13}C_{PDB}$ from -5 to +9‰. Low Mn/Sr and lack of covariance between δ^{13}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 δ^{13}C values start with slightly negative values (~ -2‰) and about 10 m from the base, values change dramatically and form a well-defined plateau around +9, while the δ^{18}O values vary from -10 to -12‰$_{PDB}$.

Jacoca carbonates display average $^{87}Sr/^{86}Sr$ of 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 STRATIGRAPHY Mercury accumulation rate was 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 before that (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 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. Cataclysmic volcanoes have the potential to inject enough mercury to the atmosphere to change global and regional mercury cycles. For example, volcanic emissions of Hg to the atmosphere between 1980 and 2000 has totaled about 60t.yr^{-1}. Roos-Barraclough *et al.* (2002) found evidence of increasing Hg deposition in lake sediment cores from the Swiss Jura Mountains corresponding to known volcanic eruptions. Thus, volcanism may have allowed also for higher concentrations of mercury in cap-carbonates after ice melting.

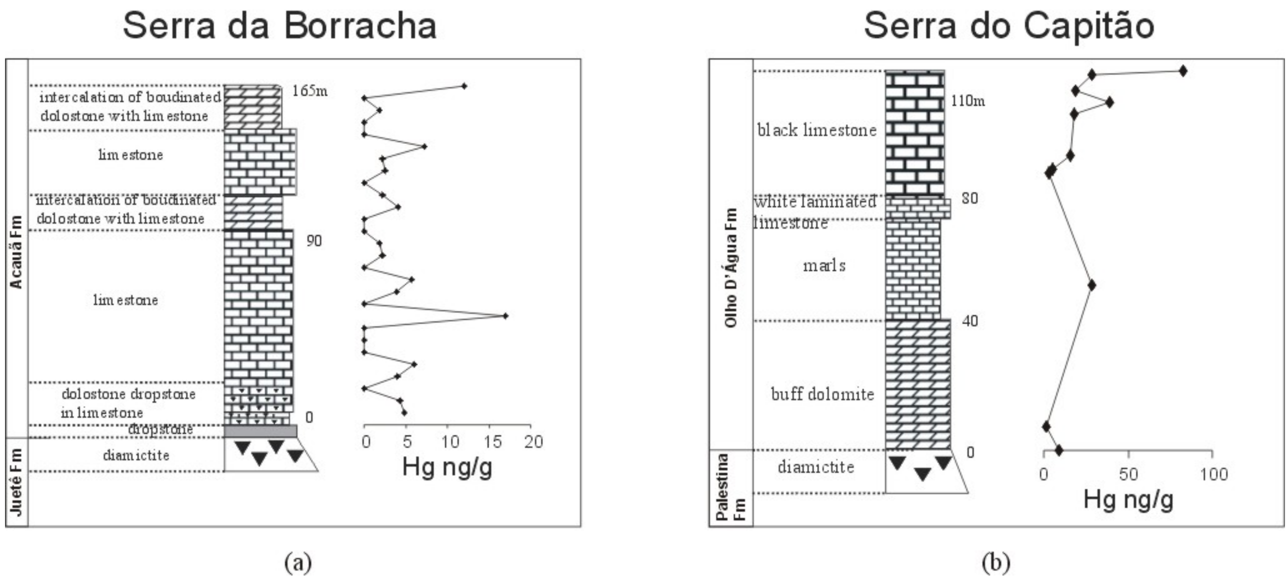
To our knowledge, no databank available for Hg in sedimentary carbonates is available. As a preliminary survey, 5 samples of Precambrian carbonates (Meso-Neoproterozoic transition, São Caetano complex, state of Pernambuco) from northeastern Brazil, Tertiary limestones from Topocalma (Chile) and Punta Rocallosa (Chilean Patagonia) and Yacoraite limestones (Argentina) were analyzed. There is no clear indication that these carbonates were concurrently deposited to volcanic activity, except at Punta Rocallosa. The precambrian and Yacoraite carbonates yielded values between 1.5 and 6 ng.g^{-1} of

Hg, while carbonates from Topocalma exhibited values of 8 and 10 ng.g^{-1}. However, two carbonate samples from Punta Rocallosa, yielded values of 23 and 73 ng.g^{-1}.

To investigate if the CO_2 of the two cap carbonates under consideration was mantle-derived through volcanism that followed snowball events, a mercury survey with carbonate samples from the Acauã and Jacoca Formations (53 samples) and Olho D'Agua Formation (11 samples) was carried out.

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 ng.g^{-1}. The mercury curve varies upsection from 11 to 26 ng.g^{-1} (average 19 ± 5). At Serra da Borracha (Fig. 2a), a rhythmic variation of mercury content was observed (total variation from <3 to 20 ng.g^{-1}), while at Patamuté, values are ~ 11 ng.g^{-1} with an increase to 41 ng.g^{-1} at about 8m from the base where gray marls grades 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 ng.g^{-1}, higher by a factor of 10, if compared to the rest of this profile (average 20 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 higher mercury atmospheric deposition, originated from volcanism, resulted in higher leaching from land surface accumulating along argillaceous carbonates, similarly to the processes described in the Swiss Jura Mountains for quaternary sediments (Roos-Barraclough *et al.* 2002).

At Capitão hill (Fig. 2b), Olho D´Agua Formation carbonates show a total variation from <3 to 83 ng.g-1 with a slight increase towards the top (dark carbonates show the higher values).



Fgure 2. Mercury chemostratigraphic profiles for the Jacoca (a) and Olho D'Agua (b) cap carbonates.

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

The younger 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 (Hoffman *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 $\delta^{13}C$ 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 & W. R. Van Schmus, written communication) in the Ribeiropolis diamictite below the Jacoca Formation, suggests 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.

Acknowledgements We want to express our gratitude to Mr. Teodomiro Mendes Filho for logistic support during our field work at the Borracha and Canabrava Hills, in northern Bahia. We are also grateful to CNPq for the financial support through the PROSUL/CNPq project n. 490349/2004-8 and CNPq/472506/2003-0.

References

CALVER R.C., BLACK L.P., EVERARD J.L. & SEYMOUR D.B., 2004. U-Pb zircon age constraints on late Neopro-terozoic glaciation in Tasmania. *Geology*, **32**(10):893-896.

D'EL REY SILVA L.J.H. 1999. Basin in-filling in the southern-central part of the Sergipano Belt (NE Brazil) and implications for the evolution of Pan-African/ Bra-siliano cratons and Neoproterozoic sedimentary cover. *Journal of South American Earth Sciences*, **4-5** (2):1-18.

FANNING C.M. & LINK P.K. 2004. U-Pb SRIMP ages of Neoproterozoic (Sturtian) glaciogenic Pocatello For-mation, southeastern Idaho. *Geology*, **32**(10):881-884.

HOFFMAN P.F. & SCHRAG D.P. 2002. The snowball Earth hypothesis: testing the limits of global change. *Terra Nova*, **14**:129-155.

HOFFMANN K.H., CONDON D.J., BOWRING S.A. & CROWLEY J.L. 2004. U-Pb zircon date from the Neopro-terozoic Ghaub Formation, Namibia: constraints on Ma-rinoan glaciation. *Geology*, **32**(9):817-820.

ROOS-BARRACLOUGH F., MARTINEZ-CORTIZAS A., GARCIA-RODEJA E. & SHOTYK W. 2002. A 14500 year record of the accumulation of atmospheric mercury in peat: volcanic signals, anthropogenic influences and a correlation to bromine accumulation. *Earth and Planetary Science Letters*, **202**:435-451.

SANTOS G.M., CORDEIRO R.C., SILVA FILHO E.V., TURCQ B., LACERDA L.D., FIFIELD L.K., GOMES P.R.S., HAUSÇADEN P.A., SIFEDDINE A., ALBUQUERQUE A.L.S. 2001. Chronology of the atmospheric mercury in Lagoa da Pata Basin, Upper Rio Negro of Brazilian Amazon. *Radiocarbon*, **43**:801-808.

ZHOU C., TUCKER R., XIAO PENG Z., YUAN X. & CHEN Z. 2004. New constraints on the ages of Neoproterozoic glaciations in south China. *Geology*, **32**(5):437-440.