Analysis of Molecular Biomarkers of cap carbonate from Amazonian Craton, Neoproterozoic, Brazil

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Introduction

The Neoproterozoic Era was characterized by global glaciations events so extreme that ocean surface was completely frozen. This theory is known as Snowball/slushball Earth (Hoffman et al., 1998). These events of extreme climatic changes were responsible by significant stress in the ocean life and triggered the deposition of organic matter after glaciation, mostly in the Neoproterozoic cap carbonate succession.

Figure 1. Geological, location map and general stratigraphy of study area.

In Brazil, the record of post-glacial cap carbonate related to the last event of Cryogenian was firstly reported by Nogueira et al. (2001, 2003, 2007) in outcrops nearby Mirassol d’Oeste city, State of Mato Grosso, Center-western Brazil. Afterwards, Soares and Nogueira (2008)described a new occurrence of cap carbonate in Tangará da Serra city, 135 km to the NE of Mirassol d’Oeste (Figure 1). The cap carbonate represent the basal portion of the Araras Group, that include the dolostones of Mirassol d’Oeste Formation and the limestone of the basal Guia Formation (Figure 1).

Experimental

The samples were submitted to acid treatment (HCl and HF). The remainder was extracted to Soxlet extractor by 72 h using CHCl₃. The organic extracts were fractioned using preparative TLC using hexane/ethyl acetate (95:5 v/v) and fractions were submitted to GC-MS e MRM GC-MS analysis. The chromatographic separations were achieved using HP-5MS capillary column and Helium as gas carrier at 1.0 mL/min flow. For GC-MS analysis a GC 7890A/5975C VL MSD Agilent instrument was used. The temperature program was 70 °C (1 min.) up to 300 °C (20 min.) at 4 °C/min. The injector was configured to split mode (1:1 split ratio) at 280 °C. For the full SCAN (50-600 Da) and SIM mode, the ions source was adjusted to EI (70 eV) at 210 °C. The transfer line was maintained at 310 °C. For the MRM GC-MS analysis was used a GC 7890A/7000 MS Triple Quad Agilent instrument with the same conditions for GC-MS analysis. The MRM transitions were chosen based on literature (Peters et al., 2005).

Results and Discussion

All samples exhibit a distribution of normal and branched alkanes, from C15 to C22, alkylcyclohexane and alkylcyclopentane from C15 to C30, and isoprenoids from C15 to C25. The Pr/(Pr+Ph) ratios ranged between 0.36 and 0.54.

The m/z 191 mass chromatogram of the samples from Mirassol d’Oeste locality is dominated for a distribution of tricyclic terpanes from C19 to, at least, C39. The mass chromatogram shows yet absence of the hopanoids compounds, including 17α-22,29,30-trisnorhopane (Tm), which prevents the use of the Ts/Ts+Tm ratio, as a more accurate evaluation of the thermal evolution. The m/z 191 mass chromatogram of Tangará da Serra samples exhibited not only tricyclic terpanes, but also a complete distribution of hopane-type compounds and gammacerane (Figure 2). The low values for Pr/(Pr+Ph) ratio and the presence of gammacerane, in case of the Tangará da Serra samples, indicate anoxic conditions associated with a saline paleoenvironment (Peters et al., 2005).

Both suite of samples (Mirassol d’Oeste and Tangará da Serra) showed a strong predominance of C27-pseudohomologues in the m/z 217 and m/z 218 mass chromatograms and M+ 358→m/z 217 and m/z 218→m/z 217 MRM chromatograms. The intensity of M+ 358→m/z 217 and M+ 358→m/z 217 MRM chromatograms correspond to elution positions expected for C28 and C29 components. The mass chromatogram of Tangará da Serra samples exhibited a strong predominance of C27-pseudohomologues in the m/z 191 mass chromatogram of the samples from Mirassol d’Oeste locality is dominated for a distribution of tricyclic terpanes from C19 to, at least, C39. The mass chromatogram shows yet absence of the hopanoids compounds, including 17α-22,29,30-trisnorhopane (Tm), which prevents the use of the Ts/Ts+Tm ratio, as a more accurate evaluation of the thermal evolution. The m/z 191 mass chromatogram of Tangará da Serra samples exhibited not only tricyclic terpanes, but also a complete distribution of hopane-type compounds and gammacerane (Figure 2). The low values for Pr/(Pr+Ph) ratio and the presence of gammacerane, in case of the Tangará da Serra samples, indicate anoxic conditions associated with a saline paleoenvironment (Peters et al., 2005).
Although cyanobacteria is the only microorganism known to biosynthesize monomethylalkanes, several origins have been suggested for these compounds, such as direct biological contributions of branched alkanes, or as diageneric products of carboxylic acids. Furthermore, monomethylalkanes can be generated by chemical process like equilibration of a limited range of isomers, or produced by thermal cracking of alkenes (Summons and Walter, 1990). Since the Amazonian Craton sedimentary rocks studied here showed an early mature thermal evolution level, catagenetic reactions as the origin for the monomethylalkanes is less likely and a contribution of cyanobacteria to the OM is more feasible.

Conclusions
A full suite of n-alkanes C15-C36 in all samples indicate a well preserved organic matter. Both sets of samples have homologous series of alkylcyclopentanes, alkylcyclohexanes and methylalkanes. All these compounds indicate a contribution of cyanobacteria to sediment and are considered characteristic biomarkers of Neoproterozoic organic matter. The RIC m/z 217 mass chromatogram exhibited the same sterane composition with predominance of C27 normal steranes for both location, but m/z 191 mass chromatogram revealed very low abundance (or absence) of hopanes and a large prevalence of tricyclic in Mirassol d’Oeste samples. Tangará da Serra samples showed a more usual profile of m/z 191 mass chromatogram with the presence of tricyclic, hopane biomarkers and gammacerane. The observed geochemical differences were probably due to local palaeoenvironmental variations that affected production and/or preservation of the primary organic matter.

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References

