

Carbon-isotope and Mercury Stratigraphies of the Frecheirinha Formation cap carbonate, Northeastern Brazil

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The Frecheirinha Formation is a carbonate unit of the Ubajara Group in the the Middle Coreaú Domain, state of Ceará, Brazil. This formation is composed of basal marls followed by limestone-dolostones rhythmites and by stromatolitic limestone in the top. It overlies red to purple slates and, locally, itabirites of the Caçaras Formation. The C-isotope pathway for the Frecheirinha Formation with negative $\delta^{13}\text{C} \sim -6\text{‰}$ values in the base and positive values up to 3.7‰ in the top of the formation is compatible with pathways for cap carbonates elsewhere. On the contrary to other studied cap carbonates in northeastern Brazil (e.g. Sergipano and Seridó Belts and Rio Pardo Basin), no $\delta^{13}\text{C}$ value $> +3.7\text{‰}$ has been recorded in the Frecheirinha Formation, and this raises the possibility of an Ediacaran age for this carbonate sequence. A preliminary Hg survey with carbonate samples from the Frecheirinha Formation was carried out, aiming to use Hg as a proxy of volcanism intensity and CO_2 buildup during a possible snowball event. Typically, Hg contents have been analyzed only from basal marls and that show negative $\delta^{13}\text{C}$ values $\sim -6\text{‰}$. In this way, only carbonates deposited at the earliest stages of the aftermath of glacial events were analyzed. The highest mercury contents were over 10 times higher than background values ($<1\text{ng}^{-1}$). This suggests that CO_2 in the basal portion of this carbonate formation is mostly mantle-derived, transferred to the atmosphere by volcanism. The only age available for the Frecheirinha Formation (0.61 Ga) is based on poor Rb-Sr isochron for clay fractions of the Caçara Formation [1]. The Mucambo pluton intruded these carbonates at 0.54 Ga [2]. These carbonates show $^{87}\text{Sr}/^{86}\text{Sr}$ values ~ 0.7075 which do not allow an unambiguous age assignment. Similar Sr-isotope values and associated itabirites without glacial features occur in the Ediacaran Arroyo del Soldado Group of Uruguay.

[1] Sial *et al.* (2003). IX Brazilian Geochemical Congress. Belém, Pará: 410-411. [2] Sial *et al.* (2000), *Annals of the Braz. Academy of Science*, **72**: 539-558.

Compound-specific stable isotope analysis of amino acids as a novel tool for ecological food web study

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Knowledge of the trophic position (TP) of organisms in food webs allows understanding of biomass flow and trophic linkages in complex networks of ecosystems. Compound-specific stable isotope analysis (CSIA) of amino acids is a novel method with that enables TP estimates of organisms in food webs [1-4]. This approach is based on contrasting isotopic fractionation during metabolic processes between two common amino acids: glutamic acid (Glu) shows significant ^{15}N -enrichment of $+8.0\text{‰}$ during reactions (transamination, deamination) that cleaves the carbon-nitrogen bond, whereas phenylalanine (Phe) shows little change in $\delta^{15}\text{N}$ values (by $+0.4\text{‰}$) during conversion to tyrosine that neither forms nor cleaves the carbon-nitrogen bond [3]. In the previous studies [3,4] we established based a number of natural and laboratory grown organisms a general equation for estimating the TP of organisms by CSIA of amino acids:

$$\text{TP} = [(\delta^{15}\text{N}_{\text{Glu}} - \delta^{15}\text{N}_{\text{Phe}} + \beta)/7.6] + 1$$

where β represents the isotopic difference between Glu and Phe in primary producers (-3.4‰ for aquatic cyanobacteria and algae, $+8.4\text{‰}$ for terrestrial C3, and -0.4‰ for terrestrial C4 plants). In the presentation, we briefly review this amino acid method and then show its application to various natural organisms in aquatic marine and freshwater as well as terrestrial food webs.

- [1] McClelland & Montoya (2002) *Ecology* **83**, 2173-2180.
 [2] Popp *et al.* (2007) In *Stable isotopes as indicators of ecological change*. Academic Press. pp 173-190.
 [3] Chikaraishi *et al.* (2009) *Limnol. Oceanogr.: Meth* **7**, 740-750. [4] Chikaraishi *et al.* (2010) *In Earth, Life, and Isotopes*. Kyoto University press. pp. 37-51.