

Delineating Primary and Secondary Organic Carbon in Neoproterozoic Glacial Sediments

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Extractable biomarkers are often used to elucidate the environment and biota of ancient sediments, including those of the so-called Snowball Earth. However, recent research has shown that the method must be applied with care when analyzing these glacial sediments, as, like all glacial sediments, they have a potential for incorporation of older detrital carbon [1]. In Phanerozoic glacial sediments, the distinct elemental, molecular and isotopic compositions of the terrestrial and marine biomass allow discrimination between primary marine and redeposited terrestrial organic matter [2-4]. In contrast, the Proterozoic biosphere was largely microbial and marine, thus biomarker and isotopic analyses are insufficient for distinguishing primary organic matter from secondary reworked organic matter.

New High-Resolution Analytical Approaches

Although traditional bulk methods are not sufficient to discern separate sources of organic matter within Precambrian glacial sediments, the novel combination of Raman spectroscopy and biomarker analysis allows discrimination between mixed pools of organic carbon. Together, these methods reveal that sediments deposited in São Francisco craton in Brazil contain at least two generations of kerogen, one of low maturity and aliphatic character, and thus presumably syn-sedimentary, and the other more structurally ordered, of high maturity, and thus potentially older redeposited material. These conclusions are supported by the extractable biomarker data, as hopane and sterane abundance is highly correlated with rocks showing Raman spectra indicative of low maturity. This discovery has important ramifications for examining life during Snowball Earth, but also for the application of bulk analytical techniques to Precambrian glacial sediments. Finally, this combination of techniques provides a promising new high-resolution methodology not only for examining the preservation of microbes, but for separating them from their environment.

- [1] Olcott Marshall *et al.* (2009) *OG* **40**, 1115–1123.
[2] Fabianska *et al.* (2008) *Chem. Geol.* **253**, 151–161.
[3] Schouten *et al.* (2007) *OG* **38**, 1161–1168 [4] Villanueva, *et al.* (1997) *GCA* **61**, 4633–4646.

A predictive model for silicate mineral dissolution rates

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We are developing a predictive model that can approximate silicate mineral dissolution rates as a function of pH, rate of water exchange around a dissolved cation, ratio of metal cations to silicon in the mineral structure, and temperature. Our approach allows estimation of dissolution rates for minerals for which we do not have experimental data. Furthermore, our approaches highlights inconsistencies in published mineral dissolution kinetics data, and places constraints on possible reaction mechanisms. Numerous studies have examined the effect of pH and temperature on mineral dissolution kinetics. Casey and Westrich [1] showed that the rate of water exchange around an octahedral cation is correlated to the mineral dissolution rates in orthosilicates. It has also been suggested that minerals with a lower connectedness (the number of bridging oxygen atoms per silica tetrahedron) dissolve more quickly than minerals with a higher degree of polymerization.

Approximately 800 data from 39 studies have been compiled; using nonlinear multivariate regression, we produced the model

$$\log r = -9.41 + \frac{24200}{RT} + 0.25 pH + 1.0 \log k_{\text{solv}} + 3.0 \frac{X}{Si}$$

where R is the gas constant, T is temperature, k_{solv} is the rate of water exchange around a dissolved cation, and X/Si is the ratio of metal cations to silicon per tetrahedral unit in the mineral structure. This model reasonably predicts dissolution rates for all orthosilicates, as well as chrysotile, diopside, tremolite, wollastonite, augite, and hornblende. Conversely, it does not provide estimated rates that match experimental data for enstatite, anthophyllite, epidote, and talc. This model also estimates an activation energy of 57 kJ/mol, which is similar to the average E_a of 56 kJ/mol calculated by Wood and Walther [2].

- [1] Casey, W. & Westrich, H. (1992) *Nature* **355**, 157–159.
[2] Wood, B. J. & Walther, J. V. (1983) *Science* **222**, 413–415.