Constraining Sulfate Levels in Archean Oceans

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Sulfate-reducing organisms generally fractionate by between 20 to 45 permil during sulfate reduction with modern seawater sulfate levels of 28 mM. By contrast, the isotope record of sedimentary sulfides suggests small fractionations of < 10 permil between seawater sulfate and sedimentary sulfides before about 2.7 billion years ago (Ga) (Canfield, 2001). The most parsimonious explanation for these small fractionations is sulfide production during sulfate reduction with low concentrations of sulfate. We present new results on the ability of marine, freshwater, and hyperthermophilic, sulfate reducers to fractionated at low, sub-millimolar sulfate concentrations. We find that low fractionations, resembling those preserved in the Archean sulfur isotope record, are not found until < 200 μM sulfate. We therefore suggest that 200 μM is an upper limit to marine sulfate concentrations before 2.7 Ga.

Such low concentrations of sulfate were probably maintained by the volcanic outgassing of SO_2, followed by disproportionation to sulfate and sulfide, at rates much lower than modern riverine sulfate transport rates. We model the consequence of low sulfate concentrations on sediment diagenesis and find that 200 μM sulfate leads to a suppression of sulfate reduction by 4 to 5 times compared to rates at 28 mM sulfate. There is a concomitant rise in rates of sediment-hosted methanogenesis. Archean sediments, therefore, could have been a significant source of methane to the atmosphere, possibly adding to the greenhouse warming of the early Earth (Pavlov et al., 2000).

Canfield D.E. (2001), *Stable Isotope Geochemistry* (J.W. Valley and D.R. Cole eds.), pp. 607-636. *Reviews in Mineralogy and Geochemistry*, v. 43.

Pavlov A.A., Kasting, J.F., Brown, L.L., Rages, K.A. and Freedman, R., (2000), *J. Geophys. Res.* 105. 11,981-11,990.

Influence of redox oscillation on the reactivity of microalgal fatty acids in sediments

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In marine sediments, particle reworking and irrigation activities of benthic fauna influence the degradation of organic matter. Among the factors involved, repetitive redox oscillation may be one of the most important (Aller, 1994).

In this study, three series of sediment microcosms were incubated under oxic, strictly anoxic and oscillating (repetitive switches between oxic and anoxic) conditions in order to examine the influence of redox oscillation on the degradation of microalgal (*N. salina*) fatty acids.

Results show that the degradation rates of fatty acids subjected to oscillating conditions are comprised in between those obtained under stable conditions of oxygenation (Tab.1).

Tab. 1. Phytoplanktonic fatty acids degradation rate constants during the 35 days incubation.

k (d^{-1})	Oxic	Anoxic	Redox oscillation
FA16:1	0.031	0.011	0.019
FA16:0	0.030	0.011	0.018
FA18:1	0.026	0.012	0.020

The ratio of free fatty acids *versus* triglycerides (TG) was used to monitor the hydrolysis of TG. Results suggest that the hydrolysis of triglycerides is favoured in the presence of oxygen, whereas free fatty acids degradation predominates over hydrolysis under anoxic conditions (Fig.1).

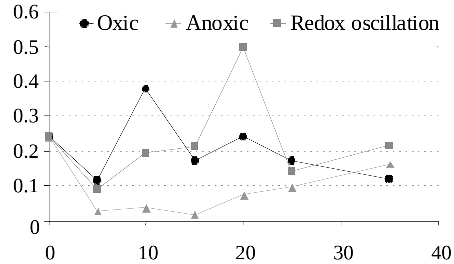

Fig. 1. Time-dependent ratio of free fatty acids *versus* triglycerides in phytoplankton enriched sediment microcosms.

We conclude that in marine sediments:

- exposure time to oxygen influences the degradation of lipid classes and individual components;
- redox oscillation influences lipid reactivity

Aller, R.C., (1994), *Chem. Geol.* **114**, 331-345.