Evaluating SO_2 photolysis as the source of Archean sulfur MIF

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The most likely origin of sulfur mass-indepepndent fractionation (S-MIF) in Archean rocks is SO_2 photolysis in a low O_2 atmosphere. Laboratory SO_2 photolysis experiments, both narrowband (Farquhar *et al*. 2001) and broadband (Pen and Clayton 2008), have shown that elemental sulfur and undissociated SO_2 have S-MIF signatures. Pavlov and Kasting (2002) have demonstrated that the requisitie partitioning of sulfur into elemental (S_8) and sulfuric acid (H_2SO_4) occurs for $pO_2 < 10^{-6}$ atm, which provides the strongest geochemical constraint on O_2 abundance prior to the Great Oxidation Event. The underlying S-MIF mechanism is SO_2 self-shielding (Lyons 2007; 2008).

The hypthesis that SO_2 photolysis is the principal source of S-MIF has two potential difficulties. 1) Broadband experiments and theory show that a large mass-dependent fractionation (MDF) accompanies SO_2 photolysis, with $\delta^{34}S$ shifts ~ +100 ‰ for $\Delta^{33}S$ ~ +8 ‰ in S_8. This is in contrast to the narrow range of $\delta^{34}S$ values observed in Archean pyrites (-10 to +20 ‰). 2) Recently reported (Danielache *et al*. 2008) absorption cross sections for $^{32}SO_2$, $^{33}SO_2$, and $^{34}SO_2$ exhibit isotopolgue-dependent intensity variations that yield $\Delta^{33}S$ signatures of oppositie sign to the self-shielding theory (Lyons 2007), suggesting that perhaps a process other than self-shielding is important.

The large range of $\delta^{34}S$ values in photolytic S_8 and undissociated SO_2 may be reconciled with the pyrite record by mixing of $^{>}FeS_2$ (superscript '>' denotes $\Delta^{33}S>0$) formed from $^{>}S_8$ with $^{<}FeS_2$ derived from bacterial sulfate reduction (BSR; Shen *et al*. 2001) of $^{<}BaSO_4$ ($\Delta^{33}S<0$). Mixing calculations employing the formalism of Ono *et al*. (2006) suggest that a mixture of ~ 50-75% $^{>}FeS_2$ with the remainder $^{<}FeS_2$ derived from BSR can reproduce much of the observed range in $\delta^{34}S$ vs. $\Delta^{33}S$ and $\Delta^{33}S$ vs. $\Delta^{36}S$ in Archean pyrites (Lyons 2009, sub.).

The SO_2 isotopologue absorption spectra of Danielache *et al*. (2008), when used in a model of SO_2 photolysis (Lyons 2009, sub.), yield results inconsistent with broadband exepriments (Clayton and Pen 2008), i.e., undissociated SO_2 has $\Delta^{33}S$ with the wrong sign. New FTS absorption spectra measurements (resolution ~ 1 cm^{-1}) are will take place in Spring 2009, and will be reported at this meeting, and will hopefully resolve this significant discrepancy.

Euxinia in the Proterozoic ocean, trace metal abundances, and the potential impacts on life

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Previous models have hypothesized widespread anoxic and sulfidic (euxinic) conditions in the deep ocean beginning around 1.8 billion years ago, coincident with the disappearance of banded iron formations (BIFs) [1]. Diverse lines of evidence point to euxinia following this disappearance, including molybdenum isotope records, biomarker data, iron-sulfur systematics, trace metal distributions, and the first major occurrences of sedimentary exhalative (Sedex) massive sulfide deposits [2]. All are consistent with at least regional oxygen deficiency in the deep ocean and a fundamental shift from iron to sulfur dominance. However, the spatiotemporal coherence of Proterozoic euxinia remains fodder for debate, and new data point to the presence of at least transiently euxinic conditions in the latest Archean/earliest Paleoproterozoic ocean, ~700 millions years before the demise of BIFs.

This talk will explore the timing and extent of euxinia in the Proterozoic ocean, with a watchful eye for any associated metal limitations and possible biological impacts. Trace metals are essential cofactors in the enzymatic pathways of diverse metabolic processes, including those at multiple steps in the nitrogen cycle and during methanogenesis, and their inventories in seawater can be highly sensitive to global-scale redox. One can infer trace metal availability in the ocean generally through thermodynamic predictions constrained by estimates of prevailing redox conditions. Our approach is more direct, however, focusing on temporal trends in the enrichment of trace metals in euxinic, organic-rich shales distributed across the Proterozoic. An example is our earlier argument, based on muted enrichment, for drawdown of oceanic Mo in response to widespread sulfidic environments [3]. In contrast, our initial survey of Ni and Cu reveals concentrations roughly equivalent to those in modern euxinic sediments. Our remaining goals are balanced between refined estimates of early metal abundances and robust, quantitative predictions of corresponding biological sensitivity.

[1] Canfield (1998) *Nature* **396**, 450-453. [2] Lyons *et al*. (2006) *GSA Memoir* **198**, 169-184. [3] Scott *et al*. (2008) *Nature* **452**, 456-459.