Sulfur Isotope Fractionations During The Oxidation of Sulfur Compounds

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The multiple sulfur isotope fractionations accompanying the chemical oxidation of reduced (sulfide: H_2S, HS^-) and intermediate (sulfite: SO_3^{2-}, HSO_3^-) sulfur compounds via molecular oxygen have been investigated. Sulfide is produced during the anaerobic respiration of organic matter in marine sediments and euxinic basins. In the modern day, most (~80-95%) of this sulfide is eventually cycled back to sulfate via a variety of biological and chemical oxidative processes. The isotope effects associated with oxidation have received relatively little attention—in particular, little is known of how the relationships between the major ($^{34}S/^{32}S$) and minor ($^{33}S/^{32}S$, $^{36}S/^{32}S$) isotope ratios of sulfur are affected during oxidation. It remains unknown how these reactions affect the isotopic signals generated by other processes that produce more pronounced fractionations, e.g., DSR and disproportionating metabolisms. It is also unclear whether the biological and chemical processes of oxidation can be teased apart based on the fractionations they produce.

Preliminary chemical sulfide oxidation experiments at 25.0°C have revealed a relatively small 'normal' isotope fractionation with respect to the major isotope ratios ($1000\ln^{34}\alpha_{P\text{-}R} = -3.26 \pm 0.76$ ‰, 2 s.d., 2 expt.), consistent with previous studies [1], and a small shift in $\Delta^{33}S$ ($\Delta^{33}S_{P\text{-}R} = 0.040 \pm 0.006$ ‰, 2 s.d., 2 expt.). Subsequent ongoing experiments have been designed around reaction kinetics and the analysis of intermediates/products (i.e., sulfite, thiosulfate, and sulfate) to tie rates and product distributions to the observed isotope fractionations, with the aim of gaining insight into the origin of the relatively small but significant $\Delta^{33}S$ effect.

Sulfite is a major intermediate produced during sulfide oxidation and its oxidation is the primary pathway of sulfate production in chemical sulfide oxidation experiments [e.g., 2]. Separate experiments investigating its oxidation have also been carried out, revealing an apparent reversal in the direction of major isotope fractionation depending on pH/speciation. Linking rates and mechanisms to isotope fractionations during these reactions are also actively being investigated with the aim of determing the consequences of these fractionations on the overall chemical oxidation of sulfide.

[1] Fry, Ruf, Gest, and Hayes (1988) *Chem. Geol.* **V. 73**, 205-210 [2] Zhang & Millero (1993) *GCA* **V. 57**, 1705-1718