A comprehensive sulfur and oxygen isotope study of sulfur cycling in a shallow, hyper-euxinic meromictic lake

William P. Gilhooly III [a,b,*], Christopher T. Reinhard [a,c], Timothy W. Lyons [a]

[a] Department of Earth Sciences, University of California, 900 University Avenue, Riverside, CA 92521, USA
[b] Department of Earth Sciences, Indiana University-Purdue University Indianapolis, SL118, 723 W. Michigan Street, Indianapolis, IN 46202, USA
[c] School of Earth & Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30332, USA

Abstract

Mahoney Lake is a permanently anoxic and sulfidic (euxinic) lake that has a dense plate of purple sulfur bacteria positioned at mid-water depth ($\sim$7 m) where free sulfide intercepts the photic zone. We analyzed the isotopic composition of sulfate ($\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$), sulfide ($\delta^{34}S_{H2S}$), and the water ($\delta^{18}O_{H2O}$) to track the potentially coupled processes of dissimilatory sulfate reduction and phototrophic sulfide oxidation within an aquatic environment with extremely high sulfide concentrations (>30 mM). Large isotopic offsets observed between sulfate and sulfide within the monimolimnion ($\delta^{34}S_{SO4-H2S} = 51\permil$) and within pore waters along the oxic margin ($\delta^{34}S_{SO4-H2S} > 50\permil$) are consistent with sulfate reduction in both the sediments and the anoxic water column. Given the high sulfide concentrations of the lake, sulfur disproportionation is likely inoperable or limited to a very narrow zone in the chemocline, and therefore the large instantaneous fractionations are best explained by the microbial process of sulfate reduction. Pyrite extracted from the sediments reflects the isotopic composition of water column sulfide, suggesting that pyrite buried in the euxinic depocenter of the lake formed in the water column. The offset between sulfate and dissolved sulfide decreases at the chemocline ($\delta^{34}S_{SO4-H2S} = 37\permil$), a trend possibly explained by elevated sulfate reduction rates and inconsistent with appreciable disproportionation within this interval. Water column sulfate exhibits a linear response in $\delta^{18}O_{SO4}$–$\delta^{34}S_{SO4}$ and the slope of this relationship suggests relatively high sulfate reduction rates that appear to respond to seasonal changes in the productivity of purple sulfur bacteria. Although photosynthetic activity within the microbial plate influences the $\delta^{18}O_{SO4}$–$\delta^{34}S_{SO4}$ relationship, the biosignature for photosynthetic sulfur bacteria is restricted to the oxic/anoxic transition zone and is apparently minor relative to the more prevalent process of sulfate reduction operative throughout the light-deprived deeper anoxic water column and sediment pore waters.
© 2016 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Sulfur isotope compilations of sedimentary pyrite and sulfates (gypsum, barite, carbonate-associated sulfate) have

provided proxy evidence for the increase in atmospheric oxygen from the Archean to the present. Three distinct stages have been recognized in the sulfur isotope record based on mass conservative ($^{34}S/^{32}S$) and mass-independent ($^{33}S/^{32}S$) fractionation effects. Small $\delta^{34}S$ fractionations (Canfield, 1998), associated with low oceanic sulfate levels (<2.5 μM) in the Archean (Habicht et al., 2002; Crowe et al., 2014), are congruent with $\Delta^{33}S$ photochemical isotope effects preserved under low atmospheric oxygen

* Corresponding author at: Department of Earth Sciences, Indiana University-Purdue University Indianapolis, SL118, 723 W. Michigan Street, Indianapolis, IN 46202, USA.
E-mail address: wgilhool@iupui.edu (W.P. Gilhooly).

levels (Farquhar et al., 2000). This stage ends with the Great Oxidation Event marked by an increase in $\delta^{34}S$ fractionations coincident with the loss of mass-independent signatures ~2.3–2.4 billion years ago (Bekker et al., 2004), indicating that oxygen accumulated to significant concentrations in the atmosphere. The third state, characterized by frequently large fractionations perhaps linked to strongly oxidative sulfur cycling and analogous to isotopic patterns seen today ($\Delta^{34}S_{sulfate-sulfide} > 50‰$), commenced during the Neoproterozoic (1050 to 640 million years ago) (Canfield and Teske, 1996; Canfield, 2001).

The isotopic offset ($\Delta^{34}S_{sulfate-sulfide} = \delta^{34}S_{sulfate} - \delta^{34}S_{sulfide}$) imparted during dissimilatory sulfate reduction can be large in magnitude, with $\Delta^{34}S_{sulfate-sulfide}$ exceeding 60‰ (Canfield et al., 2010; Sim et al., 2011), or muted (~0‰) at low sulfate concentrations (Harrison and Thode, 1958; Habicht et al., 2002). Similar offsets are produced by the oxidative sulfur cycle, ranging from the potentially large isotope effects (~20‰) that can occur during sulfur disproportionation (Canfield and Thamdrup, 1994; Habicht et al., 1998; Böttcher et al., 2001) to small isotope effects (±5‰) produced during chemolithotrophic sulfide oxidation (Fry et al., 1986) and anoxygenic photosynthesis (Fry et al., 1984; Fry, 1986; Zerkle et al., 2009; Brabec et al., 2012). An otherwise robust biosignature for sulfate reduction in modern sediments thus becomes non-diagnostic under sulfate-limited conditions as postulated for the Archean ocean or periods of rapid expansion of the oceanic sulfate pool such as the Neoproterozoic, when many reactions within the biologically mediated sulfur cycle may be operative. For example, the various explanations for an increase in the magnitude of sulfur isotope fractionations during the Neoproterozoic include an increased prominence of nonphotosynthetic oxidative sulfur metabolisms and associated disproportionation of the resulting intermediate sulfur species (Canfield and Teske, 1996; Johnston et al., 2005; Fike et al., 2006), reoxidation effects mediated by the onset of bioturbation (Canfield and Farquhar, 2009), and possibly reservoir effects linked with rising and falling sulfate concentrations within an evolving oceanic sulfur pool (Hurtgen et al., 2005).

The isotopic composition of oxygen bound in sulfate ($\delta^{18}O_{SO4}$) may provide an additional vector to better interpret the microbial processes responsible for sulfate synthesis and cycling over geologic timescales. Provided the associated isotope effects are constrained, $\delta^{18}O_{SO4}$ can be a powerful tool for tracing the ultimate source of sulfate to the ocean, given that the oxygen incorporated into the sulfate during sulfide oxidation can derive from either ambient water (H_2O) or the atmosphere (O_2). On a global basis, gypsum dissolution and oxidative pyrite weathering (the inputs) balance the outputs via evaporite precipitation and sulfate reduction with concomitant pyrite burial (Holser et al., 1979; Claypool et al., 1980). Tracking the sulfate–oxygen budget through these isotopically distinct reservoirs is complicated by oxygen isotope exchange at low pH (Hoering and Kennedy, 1957; Lloyd, 1968; Chiba and Sakai, 1985), post-diagenetic alteration (Turchyn et al., 2009), and numerous other processes that overprint the oxygen isotope composition of sulfate (Bottrell and Newton, 2006; Turchyn and Schrag, 2006).

Sulfur isotopes are relatively insensitive to inorganic sulfide oxidation effects, but sulfate formed from sulfide oxidation will carry different proportions of oxygen derived from water ($\delta^{18}O \leqslant 0‰$) and/or atmospheric oxygen ($\delta^{18}O = 23.5‰$) depending on the oxidation pathway (Taylor and Wheeler, 1984; van Everdingen and Krouse, 1985; Balci et al., 2007, 2012; Calmels et al., 2007). The oxidation of sulfide coupled to iron reduction derives oxygen entirely from water and results in $\delta^{18}O_{SO4}$ values lower than those produced by oxidation with molecular oxygen (Calmels et al., 2007). Hydrothermal sulfur inputs (~0‰) may be difficult to differentiate from biological cycling within a low sulfate reservoir; however, $\delta^{18}O_{SO4}$ produced by photosynthetic bacteria may reflect the isotopic composition of the parent water (Brabec et al., 2012).

Environmental conditions in the Paleo- and Mesoproterozoic, when atmospheric oxygen concentrations were still relatively low, and large portions of the oceans were anoxic and sulfidic (euxinic), were conducive to widespread carbon fixation by anoxygenic photosynthesis (Johnston et al., 2009). Phototrophic sulfur bacteria oxidize sulfide and fix carbon dioxide in the presence of sunlight without producing oxygen. Sulfide is oxidized to intracellular elemental sulfur, and the internal sulfur stores are ultimately oxidized to sulfate when sulfide becomes limiting (<1 mM) (Overmann and Pfennig, 1992). In the geologic record, this ecological niche is termed "photic zone euxinia," and organic biomarkers of sulfide-oxidizing phototrophs can provide proxy evidence for free sulfide at shallow depths in the water column (Brocks et al., 2005; Brocks and Schaeffer, 2008) provided the organisms were pelagic (Meyer et al., 2011). Biological oxidation of sulfide by anoxygenic photosynthesis may have contributed to the formation of sulfate in the Proterozoic water column (Johnston et al., 2009). With limited organic biomarker and geochemical evidence for widespread primary production by anoxygenic sulfur bacteria (Lyons et al., 2004), and the potential for metabolic overlap with cyanobacteria capable of sulfide oxidation but without a distinctive biomarker signature for this process (Johnston et al., 2009), additional proxies are needed to fingerprint the paleoecological and biogeochemical signals associated with euxinia in the photic zone. Paired $\delta^{34}S$ and $\delta^{18}O$ data from ancient sulfates (gypsum, barite, or carbonate-associated-sulfate) may offer an additional constraint on the history and ecological distribution of photosynthetic S-oxidation. Sulfate-oxygen can fractionate during sulfate reduction, but the extent of isotopic enrichment is controlled either by kinetic isotope effects imparted during intracellular enzymatic steps or equilibrium oxygen exchange with ambient water (Brunner et al., 2005, 2012; Antler et al., 2013). An improved understanding of these processes can be gained from modern natural environments.

The primary objective of this study was to track microbial sulfur oxidation and reduction in density stratified Mahoney Lake as a modern analog for biotic pathways that may have generated oxidants in Earth's early ocean. Free dissolved sulfide ([H_2S] = 30 mM) in the photic zone of the water column supports a perennial plate of purple sulfur bacteria (Northcote and Halsey, 1969; Northcote