Seasonal changes in sulfur biogeochemistry of a dilute, dimictic Arctic lake: Implications for paired sulfur isotope records from ancient oceans

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ABSTRACT

Calibration of ancient marine sulfate levels has been done largely using experimental studies of the kinetic isotope effect associated with microbial sulfate reduction and work from modern ocean basins or high-sulfate lakes that are largely restricted and meromictic. The sulfur isotope record of sulfates and sulfides from sedimentary sequences have been used to reconstruct sulfate levels throughout the geologic record and indicate that sulfate concentrations were low relative to modern oceans (28 mM) for most of Earth's history. Despite the higher potential for modern low-sulfate systems to be a better analog for ancient oceans, there are few sulfur isotope studies that have been carried out in these environments. Here, we present $\delta^{34}S$ systematics of a modern low-sulfate ($\sim$330–600 μM) euxinic lake on the ice-free margin of southwestern Greenland. We find large isotope fractionations ($> 20‰$) between water column sulfate and sulfides, with this fractionation increasing from 23.9‰ during open-water conditions to 42.0‰ under annual ice-cover. While these large kinetic isotope effects associated with microbial sulfate reduction (ε_{SR}) are expressed in the water column of this lake, the underlying sedimentary sulfides preserve a notably smaller range of $\delta^{34}S$ values (13.0–26.6‰). Geochemical modeling of our data suggests that the $\delta^{34}S$ of water column sulfate and sulfides, along with sedimentary sulfides are primarily controlled by ε_{SR} and a reservoir effect established under strong thermal stratification during open-water conditions. Under ice-covered conditions ε_{SR} appears to be the dominant control on $\delta^{34}S$ values, and when combining both seasonal data sets ε_{SR} increases as a function of sulfate levels in the lake. Sulfur isotopic data presented here highlight the complexity of seasonal biogeochemical cycling of sulfur in low-sulfate systems, and how system openness affects $\delta^{34}S$ fractionations in modern euxinic depositional environments. Specifically, a reservoir effect is only documented in the water column $\delta^{34}S$ data under open-water conditions, however a reservoir effect is apparent from sedimentary sulfides under both ice-cover and open-water conditions due to time averaging pyrite $\delta^{34}S$ values. Our results add to the growing body of work on modern low-sulfate systems to help further constrain the use of ancient $\delta^{34}S$ records for paleoenvironmental reconstructions.

1. Introduction

Cycling of sulfur across physiochemical gradients is a critical adaptation that organisms have evolved to gain energy from a series of reduction-oxidation (redox) reactions as an alternative to aerobic respiration (Johnston, 2010). Microbes with sulfur-fueled metabolisms are important components of ecosystems within stratified water bodies and have been throughout much of Earth's history (e.g., Crowe et al., 2014a; Fike et al., 2006; Fry et al., 1991; Gomes and Hurtgen, 2013; Johnston, 2011; Leavitt et al., 2013; Lyons, 1997; Poulton et al., 2010).

Most of the sulfur within marine or freshwater systems on early Earth were derived from the oxidative weathering of sedimentary sulfides delivered via rivers as the anion sulfate (SO_4^{2-}) although weathering of evaporites played an important role increasingly through the Phanerozoic (Halevy et al., 2012; Wortmann and Paytan, 2012). The sulfate supplied to aquatic environments can be converted to hydrogen sulfide (H_2S) via microbial sulfate reduction (MSR) within anoxic portions of the water column and/or below the sediment-water interface. Conversely, anoxygenic phototrophic sulfur bacteria (i.e., green and purple sulfur bacteria) and chemotrophic microbes oxidize sulfide and fix

carbon dioxide when sulfidic conditions develop in the photic zone (Overmann and Tilzer, 1989; Overmann et al., 1991; Fike et al., 2015). The anoxic portion of the biogeochemical S cycle within stratified waters is driven by reduction and oxidation based metabolisms. The biogeochemical C and S cycles are intrinsically linked through MSR, which couples the oxidation of organic matter to the production of sulfide (e.g., Berner, 2004 and references therein). Over the last 40 million years MSR has likely been the dominant pathway for organic matter remineralization in anoxic marine settings, due to high-sulfate content (~28 mM) of the oceans (e.g., Jørgensen, 1982; Wortmann and Paytan, 2012). However, methanogenesis and methanotrophy can play a larger role in organic matter remineralization in low-sulfate environments and these processes could impact the concentrations of atmospheric greenhouse gases dramatically (Pavlov et al., 2003; Reeburgh, 2007; Weber et al., 2016).

Sulfur isotopic compositions of dissolved ions in the water column, along with minerals and organic matter in the sediments are sensitive indicators of sulfur utilization by microbes in natural environments. Sulfide produced by MSR can be isotopically depleted in ^{34}S by up to 70‰ relative to starting sulfate in laboratory experiments (Harrison and Thode, 1958; Habicht and Canfield, 1996; Canfield et al., 2010; Sim et al., 2011a, 2011b). Within an environment, expression of the MSR kinetic isotope effect ($\varepsilon_{SR} = \delta^{34}S_{SO4} - \delta^{34}S_{H2S}$) can vary widely in magnitude and is dependent upon cellular physiology/biochemistry and environmental conditions that affect the rates of microbial sulfate reduction (Leavitt et al., 2013 and reference therein). Although organic matter (electron donor) is often a limiting reactant in MSR, dissolved oxygen content, sulfate concentrations (electron acceptor), temperature, and nutrients can also strongly affect the rates of MSR and the magnitude of S isotopic fractionations between reactants and products (Canfield, 2001; Habicht et al., 2002; Johnston, 2010, 2011; Leavitt et al., 2013). Sulfide produced in marine sediments today is predominantly cycled back to sulfate via a series of oxidation reactions, although if iron is available it can be buried as pyrite (Canfield et al., 1992; Bottrell and Newton, 2006). The oxidative portions of the sulfur cycle impart modest isotope effects from sulfur disproportionation (~20‰; Canfield and Thamdrup, 1994; Habicht et al., 1998) to small fractionations from sulfide oxidizing bacterium (≤5‰; Kaplan and Rittenberg, 1964; Fry et al., 1988; Zerkle et al., 2009). Rates of pyrite burial in sedimentary environments are largely dependent upon sulfate concentrations, extent of organic matter burial, water-column redox state, and Fe^{2+} availability (Berner, 1985). Ultimately the sedimentary sulfur isotope records are largely reflective of the balance between sulfur oxidation reactions and pyrite burial, and these records have been used to assess marine sulfate concentrations throughout Earth's history.

The isotopic difference between sulfur in sulfate and sulfides in sedimentary rocks ($\Delta^{34}S$ or $^{34}\varepsilon_{GEO} = \delta^{34}S_{sulfate} - \delta^{34}S_{pyr}$) has been used to reconstruct marine sulfate concentrations of ancient oceans, with dramatic implications for the evolution of biogeochemical cycling, climate, and redox throughout Earth history (Canfield, 1998; Habicht et al., 2002; Leavitt et al., 2013). While fluid inclusions provide estimates of sulfate concentrations in Neoproterozoic and Phanerozoic oceans, the sedimentary records of them are scant (Horita et al., 2002; Lowenstein et al., 2003, 2005; Brennan et al., 2013; Spear et al., 2014). Paired $\delta^{34}S$ analyses of sulfate evaporites and carbonate-associated sulfate (CAS) with sedimentary pyrite provide high temporal resolution records that are more easily dated and correlated than fluid inclusions. Small $\Delta^{34}S$ values in sedimentary rocks (Canfield, 1998) in association with large $\Delta^{33}S$ anomalies ($\Delta^{33}S > 0 \pm 0.2$‰; whereas $\Delta^{33}S_{sample} = \delta^{33}S_{sample} - 0.515 \times \delta^{34}S_{sample}$) due to photolytic reactions of sulfur aerosols in an anoxic early Earth atmosphere (Farquhar et al., 2000, 2001) are consistent with sulfate being in trace quantities (< 2.5 μM) in Archean oceans (Habicht et al., 2002; Crowe et al., 2014b). Marine sulfate likely rose as high as low millimolar concentrations (1–2% of modern values, 28 mM) approximately

2.3–2.4 billion years ago concurrent with the Great Oxidation Event (GOE). The GOE was marked by disappearance of large anomalous fractionations of $\Delta^{33}S$ from the sedimentary record (Bekker et al., 2004; Guo et al., 2009) and expanded range of $\delta^{34}S$ fractionations (Canfield, 2005) among other sedimentary indicators (i.e., Holland, 2006). Sulfate concentrations in the global oceans probably remained low, a few millimolar, until the Neoproterozoic (1050 to 540 million years ago), when sulfate levels may have cycled from ~10 mM to 1 mM during the course of multiple 'Snowball Earth' glaciations (Hurtgen et al., 2002, 2006; Kah et al., 2004). Although a recent study of Paleoproterozoic evaporites suggest that sulfate concentrations could have been as high as 10 mM at ~2.0 Ga, just after the GOE (Blattler et al., 2018). Frequent large $\delta^{34}S$ fractionations ($\Delta^{34}S > 50$‰) have been documented throughout the late Neoproterozoic and Phanerozoic sedimentary records and have been linked to increased sulfate concentrations and corresponding O_2 levels (Fike et al., 2006; Gill et al., 2007, 2011; Wortmann and Paytan, 2012). Sulfur isotope proxy records generally indicate that sulfate levels were variable and low relative to modern oceans (28 mM) throughout most of Earth history, with a general increase in concentration with each geologic era (Habicht et al., 2002; Kah et al., 2004; Holland, 2006; Gill et al., 2007).

The geologic record of marine sulfate inventory has been aligned largely using work from modern ocean basins or high-sulfate lakes that are mostly restricted and meromictic (e.g., Fry et al., 1991; Lyons, 1997; Lyons et al., 2003; Gilhooly et al., 2016). Although numerous sulfur isotope systematic studies of modern oceanic settings have been done (e.g., Chanton et al., 1987, 1991, 1993), there are few sulfur isotopic studies of modern low-sulfate systems, despite a greater potential to being more suitable analogs to Earth's ancient oceans (e.g., Crowe et al., 2014b; Gomes and Hurtgen, 2015). Recent work in low-sulfate lacustrine environments have shown that $\Delta^{34}S$ is controlled by both the fraction of the sulfate reservoir consumed during sulfate reduction and location of pyrite formation (reservoir effect), thus strongly influencing the $\delta^{34}S_{pyr}$ preserved in sediments (Hartmann and Nielsen, 1969, 2012). This study aims to add to the recent growing body of work in low sulfate systems that not only demonstrate the importance of the kinetic isotope effects associated with microbial sulfate reduction (ε_{SR}) but also the reservoir effect on $\delta^{34}S$ variations within these environments. Here, we report $\delta^{34}S$ values of water column profiles of sulfate, hydrogen sulfide, and sedimentary sulfide minerals near the sediment-water interface to assess seasonal variability in microbial sulfur cycling within a small Arctic lake in western Greenland. Our data show how the reservoir effect strongly influences $\delta^{34}S_{SO4}$ and $\delta^{34}S_{H2S}$ values that are recorded within open-water conditions while kinetic isotope effects become the dominate control on water-column microbial sulfur cycling under ice-covered conditions. To the best of our knowledge this study provides the first sulfur isotope systematics under both ice-covered and open-water conditions in a low-sulfate periglacial lacustrine system which significantly adds to our understanding of seasonal cycling of sulfur within low-sulfate aqueous environments. When our results are combined with other recent studies of low-sulfate systems they provide key constraints on paleoenvironmental interpretations of $\Delta^{34}S$ records from ancient marine sediments and evaluating the evolution of the marine reservoir of sulfate.

2. Background

The ice-free margin of Greenland exposes several deeply eroded Paleoproterozoic tectonic terranes separated by strongly deformed orogenic belts such as the bedrock in the Kangerlussuaq region (Fig. 1A) which is part of the Nagssugtoqidian Orogeny (Henriksen et al., 2009). The Nagssugtoqidian folded belt is inferred to extend beneath the ice sheet to the Ammassalik region in South-East Greenland. Folding resulted from a collision between the North Atlantic Craton of southern Greenland and the Rinkian metamorphic terrane to the north. The Nagssugtoqidian belt is divided into three tectonic segments (van Gool