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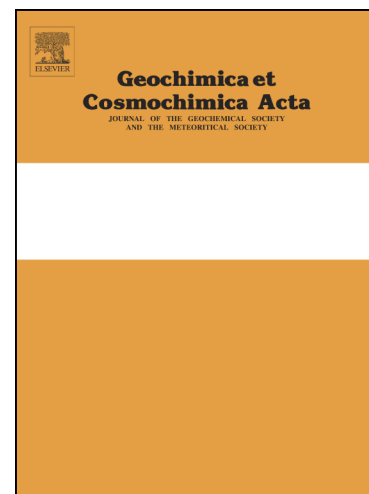
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**Significant role of organic sulfur in supporting sedimentary sulfate reduction
in low-sulfate environments**

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Significant role of organic sulfur in supporting sedimentary sulfate reduction in low-sulfate environments

Abstract

Dissimilatory sulfate reduction (DSR) is a major carbon mineralization pathway in aquatic sediments, soils, and groundwater, which regulates the production of hydrogen sulfide and the mobilization rates of biologically important elements such as phosphorus and mercury. It has been widely assumed that water-column sulfate is the main sulfur source to fuel this reaction in sediments. While this assumption may be justified in high-sulfate environments such as modern seawater, we argue that in low-sulfate environments mineralization of organic sulfur compounds can be an important source of sulfate. Using a reaction-transport model, we investigate the production of sulfate from sulfur-containing organic matter for a range of environments. The results show that in low sulfate environments ($<500 \mu\text{M}$) the in-sediment production of sulfate can support a substantial portion ($>50\%$) of sulfate reduction. In well-oxygenated systems, porewater sulfate profiles often exhibit sub-interface peaks so that sulfate fluxes are directed out of the sediment. Our measurements in Lake Superior, the world's largest lake, corroborate this conclusion: offshore sediments act as sources rather than sinks of sulfate for the water column, and sediment DSR is supported entirely by the in-sediment production of sulfate. Sulfate reduction rates are correlated to the depth of oxygen penetration and strongly regulated by the supply of reactive organic matter; rate co-regulation by sulfate availability becomes appreciable below $500 \mu\text{M}$ level. The results indicate the need to consider the mineralization of organic sulfur in the biogeochemical cycling in low-sulfate environments, including several of the world's largest freshwater bodies, deep subsurface, and possibly the sulfate-poor oceans of the Early Earth.

KEYWORDS: sulfate reduction, organic sulfur, freshwater sediments, Lake Superior, reactive transport modeling

1. Introduction

Biologically mediated reduction of sulfate is the dominant process in the sedimentary cycling of sulfur (Jørgensen, 1982; Holmer and Storkholm, 2001). It serves as an important mineralization pathway of organic carbon, regulates the production of hydrogen sulfide, mobilizes bioavailable phosphorus (Caraco et al., 1989; Katsev et al., 2006; 2016), mediates methylation of mercury (Gilmour et al., 1992), and affects the cycles of nitrogen and iron (Canfield et al., 1993; Hansel et al., 2015). On geological time scales, it affects the rates of organic matter preservation (Gaines et al., 2012) and shapes the isotopic signatures preserved in sedimentary sulfide rocks (Crowe et al., 2014). Whereas the process of sulfate reduction (SR) is relatively well understood, the source of sulfate, especially in environments with low concentrations of sulfur, may be overlooked. In marine environments, sulfate is delivered into sediments overwhelmingly from the abundant pool of bottom water sulfate. Sulfate, however, may also be generated from the pool of organic sulfur (S_{org}) that is delivered into the sediment with particulate organic matter (POM), during its diagenetic mineralization (King and Klug, 1982). Despite the ubiquitousness of this bioavailable S pool, bottom water sulfate has been assumed to be the main source of sulfate even in environments where sulfate concentrations are low, such as freshwater lakes (Gorham et al., 1974; Nriagu, 1984; Dornblaser et al. 1994). The contribution of the organic sulfur source in supporting sediment sulfate reduction has been characterized only under a limited range of conditions (King and Klug, 1982) and has been mostly neglected.

Sedimentary organic matter contains predominantly oxygen-bound S (R-O-SO₃H groups, such as ester-sulfates) characterized by high oxidation states of S_{org} (+4 to +6), and carbon-bound S (R-SH groups, such as amino acids and thiols), typically at low oxidation states (-2 to 0) (Sievert et al., 2007, Fitzgerald 1976). Carbon-bonded S is present in peptides and proteins, coenzymes, amino acids (methionine and cysteine), and heterocyclics. Some C-bound compounds, such as sulfonates (R-SO₃) and sulfones (R-SO₂-R), are characterized by higher oxidation states of S. Examples in soils and sediments include the sulfated polysaccharides produced by algae and bacteria, sulfated phenols and lipids, and

choline sulfate (Nriagu and Soon 1985). The sulfur-bearing organic matter, originating from either allochthonous terrestrial sources or autochthonous primary production (Zhao et al., 2006), enters the seston and becomes deposited at the sediment surface, where it often dominates the total S pool (Nriagu and Soon, 1985; Kokkonen and Tolonen, 1987; Couture et al., 2016). Oxidized fractions (S-esters) make up between 35% and 60% of the organic sulfur (S_{org}) pool, with more common values at the lower end of this range (David and Mitchell, 1985), e.g. in eutrophic Lake Wintergreen (35%; King and Klug, 1982). Carbon-bound S, mostly in the form of proteins, is estimated to make up another 20-40% (King and Klug, 1982). Other minor fractions include sulfolipids, coenzymes, and other compounds, with minimal contribution from elemental sulfur (King and Klug, 1982). In the dissolved fraction, soluble S_{org} (esters and C-bound) likely contributes less than 20% of total S (David and Mitchell, 1985).

Early work suggested that S_{org} could become a source of sulfate as the settled organic matter undergoes diagenetic mineralization (King and Klug, 1980; 1982; Lovley and Klug, 1986). Bacteria can access S_{org} using enzymes that cleave off the bonds in the respective chemical groups: R-O-SO₃H (e.g., aryl sulfatase) and R-SH (e.g., cysteine lyase). The produced SO₄²⁻ and HS⁻ then can be released into sediment porewater. In presence of oxygen, the reduced inorganic sulfur can be oxidized to sulfate, whereas in the anoxic sediment SO₄²⁻ can be used for dissimilatory reduction (Canfield et al., 2005). Based on the work in eutrophic lakes with sulfate concentrations in excess of 120 μ M (King and Klug, 1980; 1982), the in-sediment production of sulfate was suggested to be minor (<10%) relative to the fluxes of sulfate from overlying water. Surprisingly, little research was done on the fate of sedimentary S_{org} since the 1980s, and extrapolations to low-sulfate or carbon-poor systems have not been done. Studies of sedimentary organic sulfur mostly focused on the post-depositional sulfidization of organic matter (Couture et al., 2016; Werne et al., 2008; Goldhaber, 2003), which is the enrichment of organic matter with S as a result of hydrogen sulfide generation in anoxic sediment. Preservation of the resultant compounds is an important component of oil maturation process (Amrani, 2014). The geochemical transformations of the organic sulfur that was delivered into sediment by sedimentation, in contrast, have

been poorly quantified. Figure 1 illustrates the sediment S cycling that includes the degradation of S-bearing organic matter in both oxic and anoxic sediment zones, anaerobic microbial sulfate reduction, assimilatory reduction, oxidation of hydrogen sulfide by iron oxides, disproportionation of elemental sulfur, organic matter sulfurization, and precipitation of mineral sulfides. The sulfate generated from S_{org} within the sediment oxic layer can support sulfate reduction when it diffuses into the sediment anoxic zone. When S-bearing organic matter is buried below the penetration depth of water column sulfate, its mineralization may drive a cryptic cycle (Canfield et al., 2010; Holmkvist et al., 2011; Johnston et al., 2014) of sulfur reduction-oxidation. Cryptic cycling refers to a situation where a compound is produced and consumed quickly enough so that its concentration remains low despite high turnover rates. Cryptic production and oxidation of hydrogen sulfide, for example, was shown to mediate anammox and other N-cycling processes in marine oxygen minimum zones (Canfield et al., 2010), and cryptic formation of sulfate was shown to mediate the cycling of Fe in the sediment methane zone (Holmkvist et al., 2011). Such cycling could also affect the redox transformations of S and other elements in a zone where porewater sulfate concentrations are below detection and therefore where sulfate reduction could be otherwise thought of as negligible.

To quantify the contributions of organic S to sediment sulfate reduction and the resultant effects on S biogeochemical cycling, we set up a diagenetic diffusion-reaction model. The model is first applied to oligotrophic Lake Superior where sulfate levels are $<40 \mu\text{M}$, and then used to extrapolate the results to a broader range of aquatic environments. We show that the contributions from S_{org} may dominate sediment SR, in which case sediments may act as sources rather than sinks of sulfate to the overlying water columns. We then discuss the implications of our findings for the rates of sulfate reduction, total sulfur budgets, and sedimentary records of S cycling in low-sulfate ecosystems.

2. Methods

2.1 Sampling and analyses -- Sediment and water column samples were taken in Lake Superior on multiple cruises aboard the *R/V Blue Heron* (Table 1; Fig. 2). Temperature and dissolved oxygen distributions in the water column were measured using a Seabird 911plus conductivity, temperature, depth (CTD) probe with an Oxyguard flow-through oxygen sensor. Sediment cores of 94 mm inner diameter were recovered using an Ocean Instruments multi-corer. The landing sites were monitored using a Knudsen 320/R echo sounder with a 28 kHz transducer to select flat areas with laterally homogeneous sediment accumulation. The cores were subsequently stored at 4° C, which corresponds to the temperature (3 – 5° C) of Lake Superior bottom waters. Vertical distributions of dissolved oxygen in sediment porewaters were determined on-board as described in Li et al. (2012) and Li and Katsev (2014) using a Unisense (Clark-type) microelectrode (Revsbech, 1989). Separate sediment cores were sectioned on-board under a N₂ atmosphere at vertical intervals varying from 0.5 cm at the sediment surface to 5 cm below 20 cm. Pore waters were extracted immediately after sectioning under anaerobic conditions using Rhizon porous polymer micro samplers (0.1 µm membrane pore size) (Dickens et al., 2007). Porewater samples for sulfate analyses were frozen at -18°C until measurements. Sulfate concentrations were measured by ion chromatography (DIONEX ICS 1100) with the detection limit of 0.5 µmol L⁻¹. The organic carbon content was determined in freeze-dried sediment samples by coulometry on a CM150 total carbon (TC), total organic carbon (TOC), total inorganic carbon (TIC) analyzer. Sediment dating using ²¹⁰Pb was performed on cores from Sta. EM, CM, IR and FWM as reported in Li et al. (2012). Sediment porosity was calculated from water content as described and reported in Li et al. (2012) and Li and Katsev (2014).

2.2 Geochemical Model -- The biogeochemical cycling of sulfur was simulated with a diagenetic reaction-transport model (e.g., Katsev et al., 2006; Katsev and Dittrich, 2013). As bottom conditions in Lake Superior experience little seasonal variation (Li et al. 2012), vertical distributions of chemical species within the sediment were simulated with a diagenetic equation (Berner, 1980) at steady state:

$$0 = \frac{\partial}{\partial x} (\varphi D_i \frac{\partial C_i}{\partial x}) - \frac{\partial}{\partial x} (\varphi v C_i) + \varphi \sum_j R_{ij}$$

Here, x is depth below the sediment surface, C_i is the concentration of species i , D_i is the corresponding molecular diffusion coefficient corrected for sediment porosity φ using the Archie's law factor of $\varphi^{1.14}$ (Boudreau, 1997), and v is the burial velocity (neglected for solutes). R_{ij} are the rates of reactions that consume or produce species i . The diffusive fluxes within the sediment were calculated using the Fick's law of diffusion:

$$F_{C_i} = -\varphi D_i \frac{\partial C_i}{\partial x}$$

The intensities of bioturbation and bioirrigation in the sediments of Lake Superior were characterized previously (Li et al., 2012) and shown to be negligible below 2 cm depth. Based on the difference between the diffusive and total fluxes of oxygen, the contribution of bioirrigation to the total sediment-water exchanges of oxygen across the interface was estimated at 30-50%. While the bioirrigation contribution to the fluxes of sulfate is expected to be on the same order of magnitude, flux calculations in the present model include only the molecular diffusion fluxes, as they are better constrained from the vertical concentration profiles and the absolute values of sulfate fluxes are of secondary importance (in contrast to their direction). Importantly, the direction of bioirrigation fluxes is set by the concentration gradient (e.g. Katsev et al., 2007) and thus coincides with the direction of the diffusive flux.

The geochemical reactions included in the model and their rate formulations are listed in Tables 2 and 3. Model parameter values are listed in Table 4. In particular, the rate of sulfate reduction was simulated using the Michaelis-Menten kinetics:

$$R_{SR} = 0.5 \frac{V_m [SO_4^{2-}]}{K_m + [SO_4^{2-}]} \frac{K_i}{K_i + [O_2]}$$

Here, the Monod constant K_m describes the affinity of enzymes for substrate, K_i describes the inhibition effect of oxygen on sulfate reduction, and the stoichiometric factor 0.5 corresponds to two carbon atoms being oxidized for each sulfur atom reduced (Table 2). The organic carbon (OC) mineralization rate V_m was approximated as $V_m = k [\text{OC}]$ where the reactivity k was described by the Middelburg power law (Middelburg, 1989) as a function of carbon age t : $\log_{10} k = - (0.95) \log_{10} t - (0.81)$. This power law was recently shown to hold over a range of conditions including low-sulfate environments including Lake Superior (O’Beirne et al., 2017; Katsev and Crowe, 2015). Organic carbon concentrations at the sediment water interface were taken from measurements. Porosity profiles in the model were interpolated using the measured profiles for each station (Li, 2014). Sediment age (from Li et al., 2012) was linked to depth below the sediment surface using porosity ϕ and assumed solid sediment density $\rho = 2.65 \text{ g cm}^{-3}$, as described in Li et al. (2012); the initial carbon age at the sediment surface was chosen from best fit (O’Beirne et al., 2017; Katsev and Crowe, 2015).

In contrast to previous models (e.g. Katsev and Dittrich, 2013), the present model considered sulfur compounds of intermediate oxidation state, as they potentially can play a role in the sulfur cycle and the production of sulfate (Schulz and Zabel, 2006). In marine and lake sediments, these compounds are typically produced through the oxidation of hydrogen sulfide via several pathways (Table 5). We considered the oxidation of sulfide by iron oxides, which results in the formation of elemental sulfur. Production of S^0 through other pathways (Table 5) is thermodynamically unfavorable at the low sulfide levels considered in our model (Table 5), though some become favorable under higher levels of sulfide ($>100 \mu\text{M}$) (Canfield et al., 2005; Couture et al., 2016). The model did not consider thiosulfate and sulfite (Canfield and Andreas, 1996). While their concentrations have not been determined in Lake Superior, they are expected to be low and their contributions to sulfate production are expected to be minor: at low sulfide availability sulfide-oxidizing bacteria are expected to oxidize sulfide directly to sulfate without intermediate reactions (Pfennig, 1975; Canfield and Andreas, 1996). Although in marine sediments concentrations of thiosulfate may be of the same order of magnitude or even higher than sulfide

concentrations (Zopfi et al., 2004), in oligotrophic lakes with deep oxygen penetration, reoxidation of sulfide is suggested to be more complete, with fewer intermediate products (Urban et al., 1994). Similarly, post-depositional sulfidization of organic matter (Fig. 1) was not considered, as at the low sulfide level in oxygen- and iron-rich sediments of Lake Superior most of the produced sulfide is expected to be oxidized by oxygen to sulfate or stripped into iron sulfides, in contrast to more sulfidic and iron-poor sediments where the post-depositional formation of organosulfur can be significant (Ferdelman et al., 1991; Canfield et al., 1998).

The rate of organic sulfur mineralization, a multi-step process, was simulated as proportional to the rate of organic C mineralization with a fixed S:C ratio. In the absence of empirical information linking the rates of organic carbon mineralization and rates of organic sulfur mineralization, the release of oxidized and reduced S compounds from organic matter was assumed to occur stoichiometrically. While in soil literature enzymatic hydrolysis was hypothesized to be affected by SO_4^{2-} concentrations (Scherer 2009), such inhibition was not demonstrated in sediments and was not considered in the model for lack of any quantitative information on sulfate levels at which inhibition might occur. The R-O-SO₃H groups were assumed to constitute ~60% of the organic sulfur pool, based on results in oligotrophic lakes (Prietz et al., 2011). Their hydrolysis and mineralization was assumed to generate SO_4^{2-} . The rest of organic sulfur (R-SH groups, ~40%) such as in thiols and amino acids was expected to generate sulfide. The numerical significance of this partitioning between the oxidized vs reduced forms of organic sulfur is insignificant in well oxygenated systems like Lake Superior, as most of the reduced organic sulfur becomes aerobically oxidized and converted to sulfate within the sediment oxic zone. As the S:C ratios in lake sediments are not well established, the S:C ratio was varied in the model within a range of literature values for seston (Urban et al., 1999), which was assumed to be the major source of organic S to sediments (Urban, 1994). In contrast to marine ecosystems where S:C ratios are relatively consistent (0.008-0.014 wt/wt; Burdige, 2007), the S:C ratios in freshwater sediments vary within a wide range (0.03-0.40 wt/wt; King and Klug, 1982; Nriagu and Soon, 1985; Urban, 1994; Fagerbakke et al., 1996).

This variability in organic S is likely driven by a combination of organism physiology (specific sulfur requirements for biomass) and environmental conditions such as nutrient limitation. For example, in environments such as Lake Superior, P limitation in plankton results in a substitution of sulfolipids (and N-based lipids) for phospholipids (Bellinger et al., 2014), amplifying the sulfur deposition into sediments.

As the FeOOH profiles were not explicitly modeled, the distributions of FeOOH were imposed in the model (see Fig. 4), to mimic the measured profiles of 0.5 M HCl-extractable ferric iron (Roden and Wetzel, 2002) in Lake Superior sediments (Li, 2014). The boundary conditions for hydrogen sulfide, oxygen, sulfate, and dissolved iron were chosen as fixed-concentration at the sediment-water interface (SWI) (Table 4) and zero-gradient in the bottom of the integration domain. Equations (1) were iteratively solved in Matlab as a boundary-value problem using the "bvp4c" function.

2.3 Lake Superior sulfur budget – The geochemical budget of sulfur for the water column of Lake Superior was calculated using values from literature and sediment fluxes calculated from this work (Table 6). Sulfate inputs from watershed included discharges through St. Louis River, Pigeon River, White River, Kaministiquia River, Nipigon River, and Michipicoten River (Neff and Nicholas, 2005). Atmospheric deposition was calculated by extrapolating inputs (Minnesota Pollution Control Agency, 2002) to the area of Lake Superior. Outflow with St. Mary's River was calculated by multiplying the sulfate concentration in Lake Superior ($38 \mu\text{M}$) by the average outflow rate of $68 \text{ km}^3/\text{year}$. Lakewide fluxes in/out of sediment were estimated from fluxes calculated in this work by assuming 30 and 70% contribution from, respectively, high and low sedimentation areas. Sedimentation of organic sulfur was calculated by multiplying the S:C ratio (0.007) by the average organic carbon sedimentation flux (Li et al., 2012). As the terrestrial contribution to the bulk POM in Lake Superior was estimated at 5% (Zigah et al., 2012), the input of particulate organic sulfur to the lake from watershed was calculated as 5% of S_{org} sedimentation. The rate of sulfate buildup in the lake was calculated from the rate of historical increase in the water column sulfate concentration (Chapra et al., 2012).

3. Results

The distributions of porewater sulfate in the sediments of Lake Superior (Fig. 3) exhibit strong spatial heterogeneity, similarly to the previously described distributions of organic carbon, oxygen, and nitrogen species (Li and Katsev, 2014; Li et al., 2012). As in Lake Superior sediment composition and appearance often vary even within the same oceanographic station (~100 meter radius) (Li et al., 2012), differences among the profiles obtained from different cruises (Table 1) are more likely to reflect spatial rather than temporal variability, as sulfate concentrations in the overlying water remain largely unchanged (Fig. 3). In a striking departure from commonly observed diagenetic profiles where sulfate concentrations decrease monotonically downward from the sediment-water interface (e.g. Katsev and Dittrich 2013), porewater sulfate distributions (Fig. 3) in Lake Superior often exhibit peaks at or several mm below the interface. The sulfate concentrations below the peaks typically decrease into the anoxic sediments. A notable exception is Sta. NIP where sulfate concentrations continue to increase with depth. At this station, the sediment below about 5 cm depth consisted of dense cm-scale varves characteristic of organic-poor post-glacial sedimentation in Lake Superior (Johnson et al., 2012). Whereas in the offshore areas of Lake Superior oxygen typically penetrates into sediment by 3-12 cm (Fig. 4; Li et al., 2012), at this location the penetration depth was measured at 42 cm, creating an exceptionally deep oxidized zone. At locations where sulfate concentrations were higher in porewater than in overlying water (Fig. 3), the resultant diffusive effluxes of sulfate were calculated in a range from $0.007 \text{ mmol m}^{-2} \text{ d}^{-1}$ at Sta. EM to $0.047 \text{ mmol m}^{-2} \text{ d}^{-1}$ at Sta. TB. At several high-sedimentation sites (e.g., Sta. NB and several cores at Sta. IR), sulfate concentrations were higher in the overlying waters than in the sediments (Fig. 3). The corresponding sulfate fluxes into the sediment were $0.026 \text{ mmol m}^{-2} \text{ d}^{-1}$ at Sta. IR and $0.010 \text{ mmol m}^{-2} \text{ d}^{-1}$ at Sta. NB. Sulfate typically penetrated several cm below the penetration depths of O_2 and NO_3 (described in Li and Katsev, 2014). In sediments with deep oxygen penetration, sulfate penetrations were also deep (e.g., Sta. WM, CM, and several cores at Sta. FWM, ED, SW) (Fig. 3).

The model reproduced the measured distributions of sulfate, oxygen and organic carbon (OC) (Fig. 4). By considering the in-sediment generation of sulfate from organic S source, it also replicated the

peaks in dissolved sulfate observed within the oxic zone (e.g., Sta. ED, and EM). In fitting the data, parameters were selected as to provide a satisfactory fit against the whole dataset, rather than fit specific features of a single depth profile. The obtained profiles were used to calculate the rates of individual reactions: sulfate reduction, hydrogen sulfide reoxidation, iron sulfide precipitation, and elemental sulfur formation and disproportionation (Tables 2 and 3). Values of the depth integrated rates at each station are presented in Table 7. The depth integrated SR rates (Eq. 1) range from $0.004 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Sta. NIP) to $0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Sta. IR), with the average of $0.084 \text{ mmol m}^{-2} \text{ d}^{-1}$. Based on the previously determined rates of total sediment respiration (Li et al., 2012), sulfate reduction in Lake Superior sediments accounts for 0.6 – 5% of organic carbon mineralization. Sulfate reduction rates were higher at locations with high sedimentation rates (e.g. Sta. IR; average $0.18 \text{ mmol m}^{-2} \text{ d}^{-1}$) than at locations with low sedimentation rates (average $0.05 \text{ mmol m}^{-2} \text{ d}^{-1}$). The depth-integrated rates of sulfate production from organic source ranged between 0.07 and $0.008 \text{ mmol m}^{-2} \text{ d}^{-1}$ (average $0.034 \text{ mmol m}^{-2} \text{ d}^{-1}$). The depth distributions of these rates (Fig. 4) indicate that the production of inorganic sulfur from S_{org} is most significant in the upper layers of sediment where the rate of OC mineralization is high. In Lake Superior, this sediment zone (0-5 cm) is typically well oxygenated (Fig. 4). The depth integrated rates of sulfide oxidation ranged from $0.005 \text{ mmol m}^{-2} \text{ d}^{-1}$ (at Sta. NIP) to $0.09 \text{ mmol m}^{-2} \text{ d}^{-1}$ (at Sta. IR). The rates of elemental sulfur formation were significantly lower, ranging from $0.0001 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Sta. NIP) to $0.0009 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Sta. IR); the rates of FeS precipitation ranged from 0.009 (Sta. FWM) to $0.014 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Sta. IR). The rates of elemental S disproportionation were low ($0.00006 - 0.0006 \text{ mmol m}^{-2} \text{ d}^{-1}$).

4. Discussion

4.1 The in-sediment production of sulfate -- The presence of sub-interface peaks in the porewater sulfate profiles at many locations in Lake Superior indicates that the flux of sulfate there is directed from sediment into the overlying water column. As in that situation the water column cannot be a source of sulfate for the sediment, this suggests that the sulfate for sediment sulfate reduction must be generated entirely from an internal sedimentary source of sulfur. The clearest case of sulfate production

within the sediment is at Sta. NIP. The sediment at this location consists of glacial lacustrine varved clays underlying a thin layer of modern sediment (0-5cm). This old (>8000 yr; Johnson et al., 2012) sediment contains little organic matter (~0.2 wt%; Johnson et al., 2012) and has low O₂ uptake, which results in an exceptionally deep oxygen penetration (42 cm). The sulfate concentrations there increase into the sediment (Fig. 4), indicating that sulfate continues to be produced within the sediment during diagenesis. We hypothesize that in Lake Superior the internal sedimentary source of dissolved sulfate is predominantly the organic sulfur deposited to the sediment surface with settling organic matter.

Contribution of groundwater and dissolution of detrital sulfate minerals such as gypsum (the most abundant sulfate mineral) or other trace mineral sulfates, in principle, may also serve as internal sources of sulfate in some environments. In Lake Superior, however, the deep sediments are underlain by bedrock and the groundwater sources can be excluded (Grannemann et al., 2000). Freshwater systems with low levels of sulfate and calcium are undersaturated with respect to gypsum: based on the available water column concentrations (Chapra et al., 2012), the corresponding ratios of the ion activity products (IAP) to solubility products (K_{sp}) in Lakes Michigan, Baikal, and Superior are respectively 0.007, 0.003, and 0.0006; so potentially gypsum could become a source of sulfate if its particles survive dissolution in the water column. Sulfate also can be incorporated into authigenic minerals such as calcium carbonates and be subsequently released upon their dissolution in sediments. The available data on the dissolution kinetics of typical sulfur minerals (Katsev et al., 2004) suggest that these processes may supply sulfate to porewaters for up to several thousand years. In lakes with high abundances of sulfur-bearing minerals in the catchment, such as Lake Michigan (Black, 1997), their dissolution is thus likely to amplify the sub-interface peaks in porewater sulfate (e.g. Thomsen et al., 2004). However, as Lake Superior is surrounded by non-carbonate terrain with low gypsum and calcium levels (Dell, 1971), the contributions of mineral sulfur sources to sulfur sedimentation are expected to be insignificant. While data on trace mineral sulfur levels in Lake Superior sediments are absent, the fact that our model reproduces the observed sulfate peaks using realistic organic S:C ratios strongly argues for organic sulfur being the dominant source.

Peaks in the porewater sulfate profiles are not unique to Lake Superior and have been reported in other systems (Och et al., 2012, 2016; Thomsen et al., 2004; Sass et al., 1997; Jørgensen, 1990). In particular, in Lakes Baikal (Och et al., 2012, 2016), and Michigan (Thomsen et al., 2004), where sulfate and oxygen levels are similar to those in Lake Superior, sediment porewaters exhibited similar peaks below the interface, indicating sulfate fluxes out of the sediment and suggesting an in-sediment source of sulfate. In Lake Baikal, sulfate peaks were also found within the deeper reduced sediment (25cm; Och et al., 2012, 2016), coincident with iron rich layers, and were hypothesized to have resulted from re-oxidation of sulfide by Fe(III) in a multi-step reaction. Given that the sediment at that location was a source of dissolved S to the water column, the ultimate source of S at that depth within the sediment must have been particulate sedimentation. In principle, peaks in dissolved sulfate may also reflect non-steady state conditions, for example in a situation where bottom water sulfate levels fluctuate seasonally. However, as sulfate levels in the bottom waters of large lakes, such as Lake Superior or Lake Baikal, are very stable over interannual time scales, and with little evidence for seasonal variability in porewater sulfate (Fig. 3), non-steady state effects are unlikely to explain these observations.

In Lake Superior, in addition to strongly affecting the sediment sulfur cycle, organic S also plays an important role in balancing the sulfur budget (Table 6). Mass balance budget calculation indicates that, contrary to the paradigm that sulfate behaves as a conservative hydrological tracer (Michel et al., 2002), sulfate incorporation into organic S and its subsequent sedimentation account for 32% of the total S outputs from the water column (Table 6).

4.2 Contribution of S_{org} to sulfate reduction -- To quantify the contribution of the internal sediment organic sulfur source to the production of sulfate, we define a parameter η as the ratio of the depth-integrated rates of sulfate generation and sulfate reduction. To account for the in-sediment recycling of sulfur, the latter is corrected (using the stoichiometry in Table 2) for the disproportionation of elemental sulfur and re-oxidation of hydrogen sulfide that is produced by sulfate reduction in the sediment anoxic zone. Sulfide produced from the mineralization of reduced organic sulfur is oxidized predominantly

within the sediment oxic zone and contributes to sulfate generation there. Using R^* as the notation for depth-integrated rates of the respective reactions (Table 2), the fraction of the sediment sulfate reduction that is supported by S_{org} is thus defined as

$$\eta = \frac{R_{PSO4}^* + R_{PH2S}^*}{(R_{SR}^* - (R_{SOX}^* - R_{PH2S}^*) - 0.25 * R_{Disp}^*)} \quad (4)$$

Values of η greater than one correspond to a situation where sediment acts as a source of sulfate to the water column, as all sulfate for SR is ultimately sourced from organic S. For $\eta < 1$, the flux of sulfate is directed into the sediment and sediment SR is supported by both water-column and sediment-produced sulfate. The fraction of sulfate originated from the external inorganic source is given by $1-\eta$. The values of η for individual locations in Lake Superior were calculated from the model-fitted profiles in Fig. 4. The contribution of organic source to sulfate reduction is highest at Sta. NIP: $\eta = 3.26$ (Table 7). At Sta. FWM and IR, the η values are respectively 0.87 and 0.73 (Table 7), i.e. 87% and 73% of SR are supported by organic-sourced S. At Sta. ED and EM, they are, respectively, 1.11 and 1.07 (Table 7), indicating that the in-sediment sulfate reduction is supported there entirely by organic-sourced S.

To estimate the potential contribution of organic S to sulfate reduction rates (SRR) in other environments, we extrapolated our results by varying in the model the water column concentrations of oxygen (20-350 μM) and sulfate (10-1000 μM), as well as the organic sulfur-to-carbon ratio (0.002-0.02). The sediment organic matter content and sedimentation rate were kept constant at values typical for Lake Superior (Table 4). Fig. 5 illustrates how the contribution of organic sulfur to SRR, η , varies with sulfate and oxygen concentrations, for a reasonable range of organic S:C ratios. Simulations reveal that the conditions in Lake Superior are near a threshold for the formation of porewater sulfate peaks, in agreement with the observed sulfate profiles (Fig. 4) and the η values around 1. In oligotrophic lakes characterized by low sulfate levels (<100 μM) and high levels of benthic oxygen ($\text{O}_2 > 300 \mu\text{M}$), production of sulfate from organic source is predicted to support more than 80% of sulfate reduction (Fig. 5). This finding is in strong contrast to the previously suggested (King and Klug, 1980, 1982; Marnette et

al., 1992) minor role (<10%) of S_{org} in supporting lacustrine microbial sulfate reduction. At higher sulfate levels, the contribution of external inorganic sulfur to SR increases, and the relative importance of the organic S source decreases. At >500 μM of sulfate, for oxygen levels <200 μM , S_{org} contributes <15% to sulfate reduction, though in well oxygenated systems ($\text{O}_2 > 300 \mu\text{M}$) its contribution could be still significant, up to 60% (Fig. 5).

4.3 Sulfate reduction rates -- While S_{org} can be a dominant source of sulfate, the provenance of sulfate from within sediment rather than from overlying water does not automatically mean a strong effect on sulfate reduction rates. Sulfate is generated from S_{org} predominantly in the sediment's upper 1-2 cm (Fig. 4) where the abundance of labile OC assures high mineralization rates. The in-sediment source of sulfate is thus spatially proximate to the water column, whereas the reduction takes place deeper in the sediment. In Lake Superior, for example, the sulfate reduction zone begins 4-8 cm below the interface, a few mm below the depth of oxygen penetration. Near that redox boundary, oxidation of sulfide by ferric iron constitutes an additional source of sulfate (Fig. 4). At several stations, this is manifested in kinks in the sulfate profiles (e.g. at 10 cm at Sta. ED (Fig. 3,4): the increased slope indicates that the downward fluxes of sulfate into the anoxic zone exceed the downward fluxes in the oxic layer. Sulfate is typically depleted to μM levels within several centimeters below the oxic zone.

The effect of the in-sediment production of sulfate on total (depth integrated) SR rates can be evaluated by comparing the model results that are obtained with vs. without the S_{org} contribution (Fig. 6). While sulfate production from S_{org} alleviates the limitation imposed by low sulfate availability, the effect is only significant at sulfate levels below about 500 μM . At 40 μM level characteristic of Lake Superior, the S_{org} increases SRR by about 20%. The effect on depth integrated SRR is thus relatively minor for most environmentally relevant sulfate levels. Simulations also reveal that, irrespective of the role of S_{org} , sulfate becomes a limiting factor for sulfate reduction only at concentrations below about 500 μM . At higher levels, the SR rates are limited by the amount and reactivity of organic carbon. This is reflected in the similarity of the sulfate reduction rates in Lake Superior and other freshwater lakes to those in marine

sediments (Fig. 7a): despite the three orders of magnitude difference in sulfate concentrations (5-500 μM in freshwater vs. 28,000 μM in marine environments), the SRR are similar among sediments of similar sedimentation rates. The higher concentrations of OC in freshwater sediments make up for the SRR limitation imposed by lower sulfate. Correspondingly, in Lake Superior sulfate reduction accounts for a much smaller fraction (0.6–5%) of the sedimentary organic carbon mineralization (Li, 2014; Li et al., 2012) than in marine environments (e.g. Katsev et al., 2007). The availability of OC affects the SR rates even at low sulfate levels (<500 μM), especially for low carbon concentrations (Fig. 6). The low-sedimentation areas (typically offshore) in Lake Superior have lower rates of sulfate reduction (average 0.012 $\text{mmol m}^{-2} \text{d}^{-1}$) than high-sedimentation nearshore areas (average 0.085 $\text{mmol m}^{-2} \text{d}^{-1}$).

As the organic carbon amount within the sulfate reduction zone, its reactivity, and the concentration gradients of sulfate are all affected by the position of the sulfate reduction zone below the interface, the SRR becomes correlated with the penetration depth of oxygen. As oxygen penetration deepens, both the amount and reactivity of organic matter that reaches the sulfate reduction zone decrease, while sulfate diffusion is slowed by a decreasing gradient. As a single parameter that reflects these changes, oxygen penetration depth (OPD) is expected to be a better predictor of SRR than organic sedimentation alone. Model simulations (Fig. 7b) illustrate that the relationship between the SRR and OPD holds for a number of systems that range from well oxygenated low-sulfate sediments in Lake Superior and other freshwater lakes, to marine sediments in a range of water depths. To obtain the model datapoints in Fig. 7b, model parameters that affect the SRR were varied within their corresponding wide ranges: sedimentation rate 0.01-0.2 $\text{g cm}^{-2} \text{yr}^{-1}$, organic carbon content 1-10 wt%, SWI oxygen concentration 0-350 μM , and SWI sulfate concentration 40-10000 μM . The produced correlations suggest that, irrespective of the contribution of S_{org} , the OPD can be used as a good predictor for sulfate reduction rates where oxygen penetration exceeds several mm (Fig. 7b).

4.4 Implications for other environments -- In addition to low-sulfate sediments of freshwater lakes, the organic sulfur may be an important source of substrates for the sulfate reducing microbial

communities in deep subsurface, below the depth of sulfate penetration. In recent studies it was repeatedly shown that sulfate reducers survive over long times of burial (D'Hondt et al., 2002; D'Hondt et al., 2004; Schippers et al., 2005). A conclusive explanation, however, is missing for how these organisms survive. While sulfate reducing organisms are known to be capable of surviving on fermenting metabolisms, an order-of-magnitude calculation suggests that the energy derived from the S_{org} -supported sulfate reduction may be sufficient to support communities of sulfate reducers in the deep subsurface even in the absence of external sources of sulfate. For example, a 100,000 year old sediment might contain 0.1 wt% of organic carbon, with mineralization rate characterized by the first-order reactivity constant on the order of 10^{-5} y^{-1} (Middelburg, 1989; Katsev and Crowe, 2015). For sediment porosity of 0.6, solid sediment density of 2.65 g cm^{-3} , and the orgS:orgC molar ratio of 0.005, such sediment is expected to support SRR on the order of $10 \text{ pmol cm}^{-3} \text{ y}^{-1}$. At the cell density of $10^3 \text{ cells cm}^{-3}$ (near detection limit for common methods), this translates into a cell-specific rate of $1 \text{ fmol y}^{-1} \text{ cell}^{-1}$, which is an order of magnitude greater than the minimum rates required for cell maintenance (D'Hondt et al., 2004). Under standard conditions, these rates of sulfate reduction would provide cells with $80 \text{ pJ y}^{-1} \text{ cell}^{-1}$ of energy.

The significant role of S_{org} in shaping the S cycling in low sulfate environments may also have important implications for the interpretations of the geological records from ancient oceans. Before the Great Oxygenation Event (GOE) about 2.35 Ga ago, oceanic sulfate levels were low, possibly below $10 \mu\text{M}$ (Crowe et al., 2014). Bottom waters were largely anoxic, with a possible exception of oxygenated “oases” in shallow environments (Olson et al., 2013). After the GOE and before 0.5 Ma, Proterozoic oceans were characterized by sulfate levels that were similar to those in modern lakes, below 1 mM (Canfield and Farquhar, 2009); oxygen levels could reach tens of μM (Lyons et al., 2014). Our knowledge about the sulfate levels in those early oceans comes from the analyses of the isotopic S signals preserved in sedimentary sulfides and their inferred isotopic differences from seawater sulfate (Crowe et al. 2014). The reconstructions of the sulfate levels under which those signatures have formed, however,

assumed that the sedimentary sulfate reduction was fueled by the sulfate from seawater (Cameron, 1982; Habicht et al., 2002; Canfield and Farquhar, 2009). The results above suggest that, for oxygen levels $<20 \mu\text{M}$ and sulfate $<100 \mu\text{M}$, production of sulfate from organic source (including reoxidation of organic-sourced sulfide) could have supported up to 40% of sediment sulfate reduction. This may necessitate a reinterpretation of the isotopic S records. Importantly, in addition to altering the diagenetic cycle of S by serving as an in-sediment source for biogeochemical cycling, organic sulfur may affect the isotopic composition of S directly, as the hydrolysis of organic S compounds is likely to generate isotopic fractionation (Saunders Jr, 1961). The magnitude of such fractionation is currently not constrained but thermodynamic estimates suggest that it may be significant, on the order of 15‰ (Saunders Jr, 1961). For comparison, isotopic fractionations occurring during microbial sulfate reduction at sulfate concentrations below $100 \mu\text{M}$ are thought to be on the order of 5-30‰ (Bradley et al., 2016).

5. Conclusions

Organic sulfur supplied into the sediment with organic sedimentation, upon its mineralization, supplies sediment porewaters with oxidized and reduced forms of inorganic sulfur. Modeling results demonstrate that in environments such as oligotrophic lakes the sulfate produced from this internal source may dominate sediment sulfate reduction, with excess sulfate fluxing into the water column. When the sediment serves as a sink for the water column sulfate, organic sulfur may support up to 60% of sediment sulfate reduction for the water column sulfate levels of $<500 \mu\text{M}$. Its contribution may also be potentially important in supporting microbial communities in the deep subsurface below the depth of sulfate penetration. In sulfate-poor environments, the sedimentation, mineralization, and burial of organic S compounds may strongly contribute to the geochemical cycling and overall geochemical budgets of sulfur. As the rate of the sedimentary sulfate reduction is strongly affected by the supply of reactive organic matter, organic sedimentation should be considered as an important factor for processes (e.g., methylation of mercury) that are controlled by the rates of sulfate reduction.

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ACCEPTED MANUSCRIPT

TABLES

Table 1. Sampling dates and locations.

Date	Station	Depth (m)	Latitude (N)	Longitude (W)
07 Jun 2010	FWM.1	166	47° 09.13'	91° 16.44'
20 Jul 2010	FWM.2	168	47° 02.14'	91° 16.38'
21 Sep 2010	FWM.3	166	47° 01.98'	91° 16.50'
21 Apr 2011	FWM.4	166	47° 02.15'	91° 16.31'
22 Aug 2011	FWM.5	166	47° 02.21'	91° 16.32'
10 Jun 2010	EM.1	229	47° 33.38'	86° 35.76'
22 Jul 2010	EM.2	228	47° 33.36'	86° 35.65'
22 Sep 2010	EM.3	226	47° 33.37'	86° 35.68'
26 Jul 2012	EM.4	232	47° 32.26'	86° 35.79'
11 Jun 2010	WM.1	169	47° 19.01'	89° 50.73'
22 Jul 2010	WM.2	174	47° 18.26'	89° 49.33'
25 Sep 2010	WM.3	169	47° 19.05'	89° 50.76'
23 Apr 2011	WM.4	171	47° 19.01'	89° 50.80'
08 Jun 2010	IR.1	234	47° 58.41'	88° 28.01'
21 Jul 2010	IR.2	237	47° 58.42'	88° 28.07'
22 Sep 2010	IR.3	235	47° 58.41'	88° 28.08'
21 Apr 2011	IR.4	235	47° 58.40'	88° 27.97'
25 Aug 2011	IR.5	235	47° 58.38'	88° 28.09'
27 Jul 2012	IR.6	235	47° 58.44'	88° 28.05'
08 Jun 2010	CM.1	252	48° 01.06'	87° 46.44'
21 Jul 2010	CM.2	236	48° 02.84'	87° 47.32'
22 Sep 2010	CM.3	235	48° 02.66'	87° 47.17'
22 Apr 2011	CM.4	239	48° 03.04'	87° 47.74'
21 Jul 2010	ED.1	316	47° 31.81'	87° 07.81'
22 Sep 2010	ED.2	318	47° 31.53'	87° 07.49'
22 Apr 2011	ED.3	312	47° 31.76'	87° 07.65'
22 Aug 2011	SW.1	117	46° 50.28'	90° 16.00'
24 Jul 2012	SW.2	120	46° 50.49'	90° 16.33'
25 Jul 2012	BB.1	26	48° 30.06'	88° 36.48'
25 Jul 2012	NB.1	29	48° 52.46'	88° 11.77'
26 Jul 2012	NIP.1	124	48° 36.62'	87° 20.52'
25 Jul 2012	TB.1	237	48° 11.29'	88° 53.04'

Table 2. Reactions included in the model

Reactions	Rate
$\text{CH}_2\text{O} + \text{O}_2 \Rightarrow \text{CO}_2 + \text{H}_2\text{O}$	R_{OX}
$\text{CH}_2\text{O} + 4 \text{FeOOH}_{(s)} + 7\text{CO}_2 + \text{H}_2\text{O} \Rightarrow 4\text{Fe}^{2+} + 8 \text{HCO}_3^-$	R_{FeOOH}
$\text{SO}_4^{2-} + 2\text{CH}_2\text{O} \Rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-$	R_{SR}
$\text{H}_2\text{S} + 2\text{O}_2 + 2\text{HCO}_3^- \Rightarrow \text{SO}_4^{2-} + 2\text{CO}_2 + 2\text{H}_2\text{O}$	R_{SOX}
$\text{R-O-SO}_3\text{H} + \text{H}_2\text{O} \Rightarrow \text{HSO}_4^{2-} + \text{R-OH}_2$	R_{PSO4}
$\text{R-SH} + \text{H}_2\text{O} \Rightarrow \text{H}_2\text{S} + \text{R-OH}$	R_{PH2S}
$\text{Fe}^{2+} + \text{HS}^- \Rightarrow \text{FeS}_{(s)} + \text{H}^+$	R_{FeS}
$2\text{FeOOH}_{(s)} + 3\text{H}_2\text{S}_{(aq)} \Rightarrow \text{S}^0_{(s)} + 2\text{FeS}_{(s)} + 4\text{H}_2\text{O}$	R_{S0}
$\text{SO}_4^{2-} \Rightarrow \text{R-SH}$	R_{Assim}
$4 \text{S}^0_{(s)} + 4\text{H}_2\text{O} \Rightarrow \text{SO}_4^{2-} + 3\text{HS}^- + 5\text{H}^+$	R_{Disp}
$\text{FeS} + \text{S}^0 \Rightarrow \text{FeS}_2$	R_{FeS+S}
$\text{FeS} + \text{H}_2\text{S} \Rightarrow \text{FeS}_2 + \text{H}_2$	R_{FeS+HS}

Table 3. Kinetics of the reactions included in the model. K_{FeS} , K_{H_2S} , and k_{Disp} are the equilibrium constants for FeS precipitation, acidity constant for H_2S , and rate constant of S^0 disproportionation, respectively.

Reaction	Rate expression
Sulfide Oxidation	$R_{SOX} = k_{SOX}[O_2][H_2S]$
Sulfate production from R-O-SO ₃ H	$R_{PSO_4} = 0.6 * \frac{S}{C} V_m$; Where S/C is the sulfur to carbon molar ratio
Sulfide production from R-SH	$R_{PH_2S} = 0.4 * \frac{S}{C} V_m$; Where S/C is the sulfur to carbon molar ratio
Aerobic Respiration	$R_{OX} = \frac{V_m[O_2]}{K_i + [O_2]}$
Iron Reduction	$R_{FeOOH} = \frac{V_m[FeOOH]}{K_{FeOOH} + [FeOOH]} \frac{K_i}{K_i + [O_2]}$
Sulfide Precipitation	$R_{FeS} = k_{FeS} \left(\frac{\Omega}{K_{FeS}} - 1 \right)$ $\Omega = \frac{[Fe^{2+}][HS^-]}{[H^+]}$ $[HS^-] = \frac{[H_2S]}{1 + [H^+]K_{H_2S}}$
FeS ₂ precipitation with S ⁰	$R_{FeS+S} = k_{FeS+S}[FeS][S^0]$
FeS ₂ precipitation with H ₂ S	$R_{FeS+HS} = k_{FeS+HS}[FeS][H_2S]$
Sulfate Reduction	$R_{SR} = \frac{V_m[SO_4^{2-}]}{K_m + [SO_4^{2-}]} \frac{K_i}{K_i + [O_2]}$
Assimilatory Sulfate Reduction	$R_{Assim} = k_{Assim}(R_{FeOOH} + R_{OX} + R_{SR})$
Elemental Sulfur Formation	$R_{S_0} = k_{S_0}[FeOOH][H_2S]$
Elemental Sulfur Disproportionation	$R_{Disp} = k_{Disp}[S^0] \left(1 - \frac{[H_2S]}{[H_2S]_{stop}} \right) \quad \text{For } [H_2S] < [H_2S]_{stop}$ $0 \quad \text{For } [H_2S] \geq [H_2S]_{stop}$

Table 4. Parameters for reactive transport modeling

Parameter	Symbol	Value	Unit	Typical Range	Ref.
Diffusion coefficient of sulfate	D_{SO_4}	300	$cm^2/year$	200-400	Canfield 2006
Diffusion coefficient of sulfide	D_{H_2S}	500	$cm^2/year$	400-600	Burdige 2006
Diffusion coefficient of oxygen	D_{O_2}	500	$cm^2/year$	300-500	Burdige 2006
Sulfide oxidation rate constant	k_{OXD}	160	$\mu M^{-1} year^{-1}$	16-1600	Katsev et al. 2004
FeS precipitation rate constant	k_{FeS}	10^{-5}	$mol\ g^{-1}\ yr^{-1}$	$10^{-7}-10^{-5}$	Katsev et al. 2004
FeS equilibrium constant	K_{FeS}	10^{-4}	M	-	Dyrssen and Kremling 1990
Rate constant for FeS_2 precipitation with S^0	k_{FeS+S}	10^4	$mol^{-1}g\ yr^{-1}$	-	Dyrssen and Kremling 1990
Rate constant for FeS_2 precipitation with H_2S	k_{FeS+HS}	0.003	$\mu M^{-1} year^{-1}$	-	Dyrssen and Kremling 1990
Sulfur-to-carbon ratio in organic matter	S:C	0.007	mol/mol	0.002-0.015	Urban et al., 1999
Acid-base equilibrium constant for H_2S	K_{H_2S}	2.48×10^{-7}	-	-	Dyrssen and Kremling 1990
S^0 formation rate constant	k_{S^0}	8×10^{-3}	$\mu M^{-1} year^{-1}$	$10^{-5}-10^{-1}$	Van Cappellen and Wang 1996
Assimilatory reduction of sulfate rate constant	k_{Assim}	10^{-4}	-	-	-
S^0 disproportionation rate constant	k_{Disp}	0.01	$year^{-1}$	0.001-0.1	Jourabchi 2007
Threshold H_2S concentration for disproportionation	$[H_2S]_{stop}$	10	mM	-	Jourabchi 2007
Monod constant for SO_4^{2-} reduction	K_m	20	μM	5-25	Katsev et al. 2004
Monod constant for O_2 (inhibition constant)	K_i	1	μM	0.5 – 2	Katsev et al. 2004
Monod constant for $FeOOH$ reduction	K_{FeOOH}	20	$\mu mol/g$	15-30	Katsev et al. 2004
Sulfate at SWI (sediment water interface)	$[SO_4^{2-}]$	40	μM	-	-
Sulfide at SWI	$[H_2S]$	0	μM	-	-
Oxygen at SWI	$[O_2]$	350	μM	-	-
Iron at SWI	$[Fe^{2+}]$	0	μM	-	-
$Fe(OH)_3$ concentration scale	$[Fe(OH)_3]_1$	10	mg/g	-	-
Density of dry sediment	ρ_s	2.65	g/cm^3	-	-
Grid size	dz	6.67×10^{-3}	cm	-	-
pH	pH	6	-	-	Li 2014
Organic Matter content	OM	3.5	wt%	3-5	Li 2014
Burial Velocity at the bottom	V_{burial}	0.05	$cm.yr^{-1}$	0.04-0.08	Li 2014
Initial Carbon age	C_{age}	15	year	-	Katsev and Crowe 2015

Table 5 Thermodynamic favorability of reactions for elemental sulfur formation. Gibbs free energy at in situ conditions, ΔG_r , was calculated as $\Delta G_r = \Delta G^0 + RT \ln Q$, where ΔG^0 is the standard-state free energy, Q is the reaction quotient, T is temperature (277.15 K), and R is the ideal gas constant (8.314 J/mol-K)

Reaction	ΔG^0 (kJ/mol)	ΔG_r (kJ/ mol)	Concentration Ranges					
			[H ₂ S] or [HS ⁻] (μM)	[H ⁺] (μM)	[Fe ²⁺] (μM)	[Mn ²⁺] (μM)	[CO ₂] (μM)	[HCO ₃ ⁻] (μM)
2FeOOH _(s) + 3H ₂ S _(aq) => S ⁰ _(s) + 2FeS _(s) + 4H ₂ O	-79	-57	10	-	-	-	-	-
MnO _{2(s)} + HS ⁻ _(aq) + 3H ⁺ _(aq) => Mn ²⁺ _(aq) + S ⁰ _(s) + 2H ₂ O	-52	34	10	1	-	40	-	-
H ₂ S _(aq) + 4CO ₂ + 2Fe(OH) _{3(s)} => 2Fe ²⁺ _(aq) + S ⁰ _(s) + 2H ₂ O + 4HCO ₃ ⁻	98	104	10	-	40	-	10	1000
Fe ₃ O _{4(s)} + HS ⁻ _(aq) + 7H ⁺ _(aq) => 3Fe ²⁺ _(aq) + S ⁰ _(s) + 4H ₂ O	171	182	10	1	40	-	-	-
HS ⁻ _(aq) + 2Fe(OH) _{3(s)} + 5H ⁺ _(aq) => 2Fe ²⁺ _(aq) + S ⁰ _(aq) + 6H ₂ O	78	31	10	1	40	-	-	-

Table 6 Estimated sulfur budget in Lake Superior water column (mol s^{-1}). Positive=inputs, negative=outputs.

Sulfate input from watershed	375
S input from atmosphere	5
Organic S input from watershed	3
Outflow	-100
Sediment exchange fluxes	
Organic S sedimentation	-54
Sulfate flux in	-30
Sulfate flux out	4
Total	203
<i>Buildup</i>	192

Table 7 Depth integrated rates of sulfate reduction, hydrogen sulfide reoxidation, production of sulfate and sulfide via S_{org} hydrolysis, elemental sulfur disproportionation and formation, and iron sulfide precipitation, and the contribution of S_{org} to sulfate reduction (η), for individual stations in Lake Superior.

Stations	Rates ($\text{mmol m}^{-2} \text{d}^{-1}$)							η
	R_{SR}	R_{SOX}	R_{PSO4}	R_{PH2S}	R_{Disp}	R_{S0}	R_{FeS}	
IR	0.2	0.09	0.07	0.04	0.0006	0.0009	0.014	0.734067
FWM	0.05	0.035	0.012	0.008	0.0002	0.0005	0.009	0.87146
EM	0.095	0.05	0.05	0.03	0.0005	0.0008	0.012	1.068447
ED	0.07	0.045	0.03	0.02	0.0003	0.0007	0.01	1.112966
NIP	0.004	0.005	0.008	0.005	0.00006	0.0001	-	3.262233
Average	0.0838	0.045	0.034	0.0206	0.000332	0.0006	0.01125	-

FIGURE CAPTIONS

Fig 1 Sediment sulfur cycle with contributions from organic sulfur sedimentation

Fig 2. Sampling locations in Lake Superior.

Fig 3. Vertical distributions of porewater sulfate in Lake Superior sediments. Horizontal and vertical dashed lines correspond to sediment water interface (SWI), and sulfate level at SWI.

Fig 4. Sediment profiles of oxygen, organic carbon (OC), HCl (0.5 N)- extractable iron, sulfate, sulfide, and rates of organic sulfur hydrolysis ($R_{\text{PSO}_4} + R_{\text{PH}_2\text{S}}$), sulfate reduction (R_{SR}), and sulfide re-oxidation (R_{SOX}) for five stations in Lake Superior. Symbols correspond to measured values and lines are results from the model.

Fig 5. Simulated contribution of S_{org} to sulfate reduction in Lake Superior-type sediments. Vertical axis is the ratio of the depth-integrated rates of sulfate production from S_{org} and sulfate reduction (corrected for sulfide re-oxidation and S^0 disproportionation). Ratios above 1 correspond to a situation where the excess sulfate effluxes into the water column. (a) Lines correspond to S:C molar ratios in settled material, for oxygen level of $350 \mu\text{M}$. (b) Lines correspond to different oxygen concentrations at sediment water interface, for the S:C ratio of 0.007. Vertical line (LS) marks the sulfate level in Lake Superior.

Fig 6. Simulated effect of sulfate concentration, organic matter content (OC), and S_{org} mineralization on the depth-integrated rates of sulfate reduction. Oxygen level at the sediment water interface is $350 \mu\text{M}$ (black; typical in Lake Superior), and $200 \mu\text{M}$ (gray; near saturation value in seawater).

Fig 7. The depth-integrated rates of sediment sulfate reduction vs. sedimentation rate (a) and oxygen penetration depth (b). Data are from Lake Superior (this study), marine sediments (Jørgensen, 1982; Vaynshteyn et al., 1984; Christensen et al., 1984; Canfield, 1989; Sagemann et al., 1998; Ferdelman et al., 1997 and 1999), Lake Michigan (Thomsen et al., 2004), Lake Washington (Kuivila et al., 1988 and 1989), Lake Stechlin (Sass et al., 1997), Lake Loosdrecht (Sinke et al., 1992), and Lake Vechten (Steenbergen et al., 1993). Model datapoints are obtained by varying the sedimentation rate, organic carbon content, and sulfate and oxygen levels within ranges specified in the text.

Figure 1

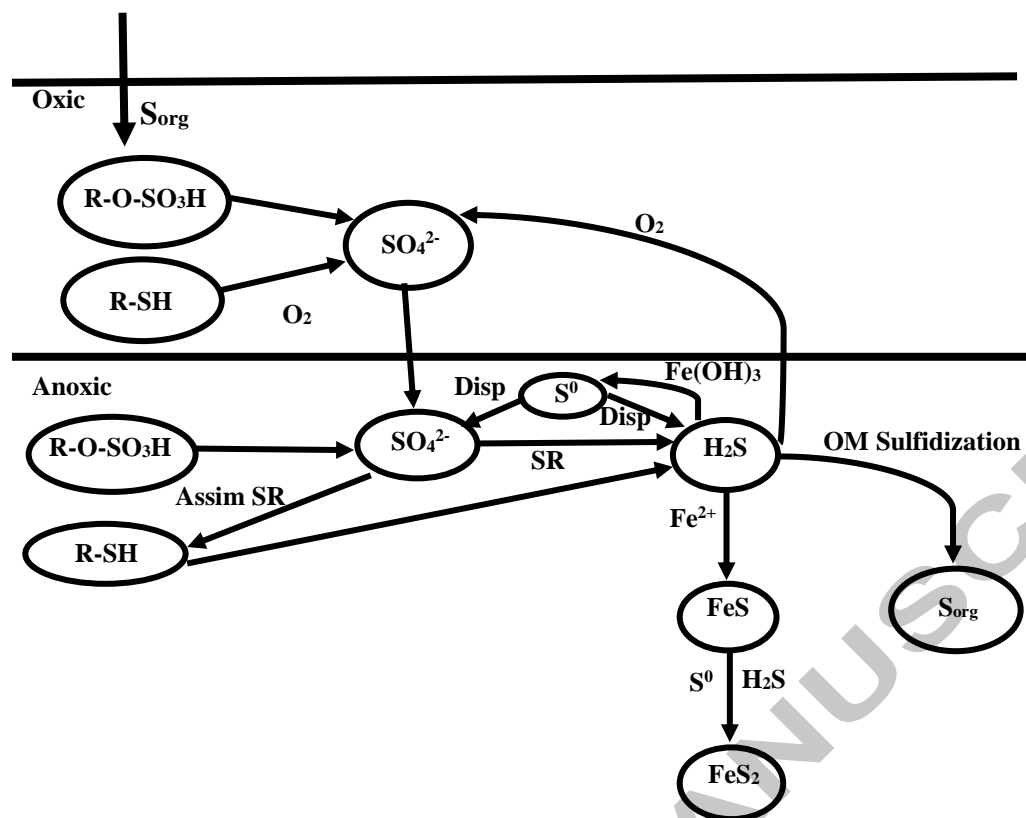


Figure 2

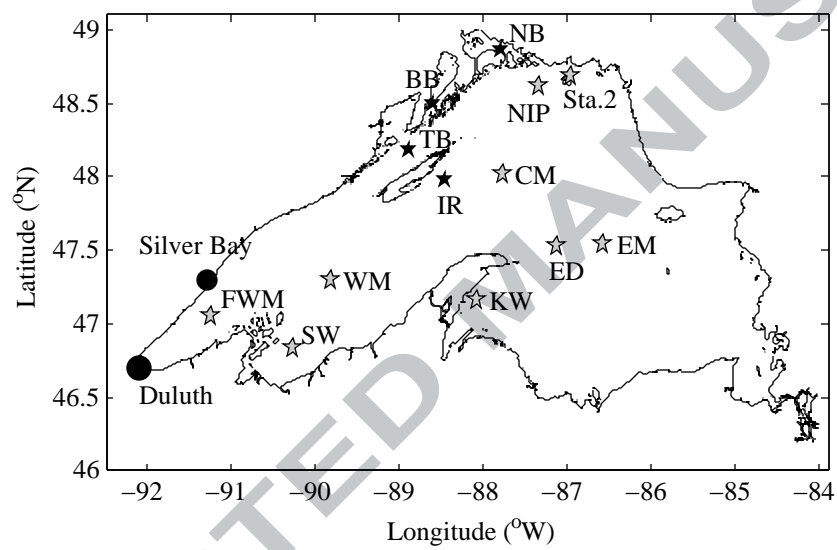


Figure 3

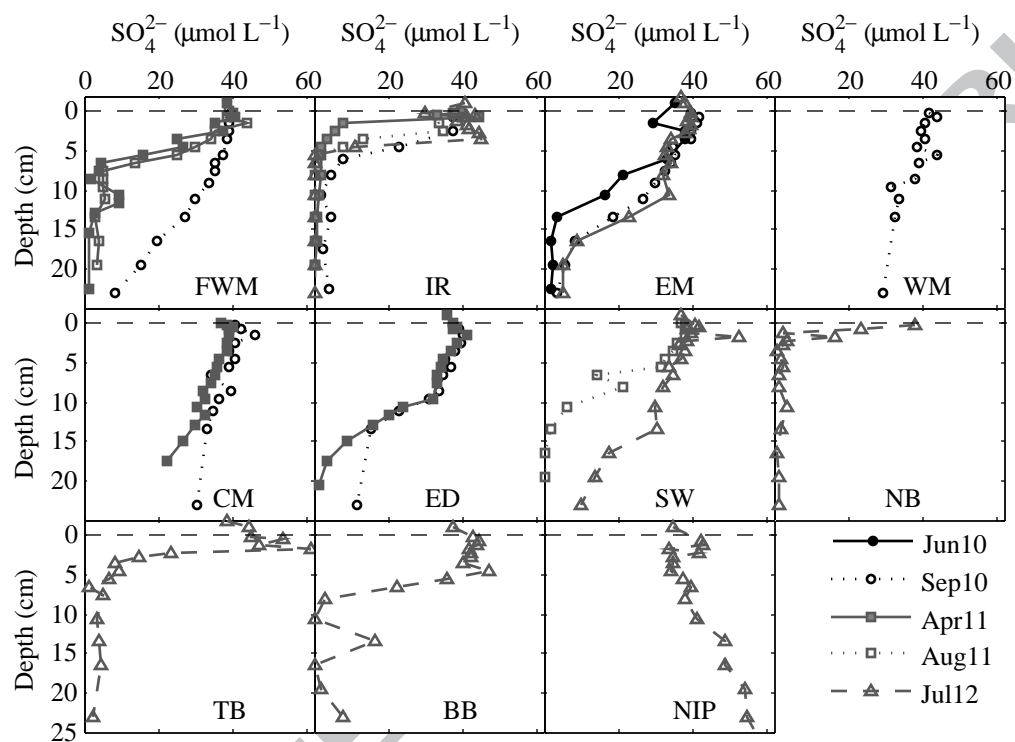


Figure 4

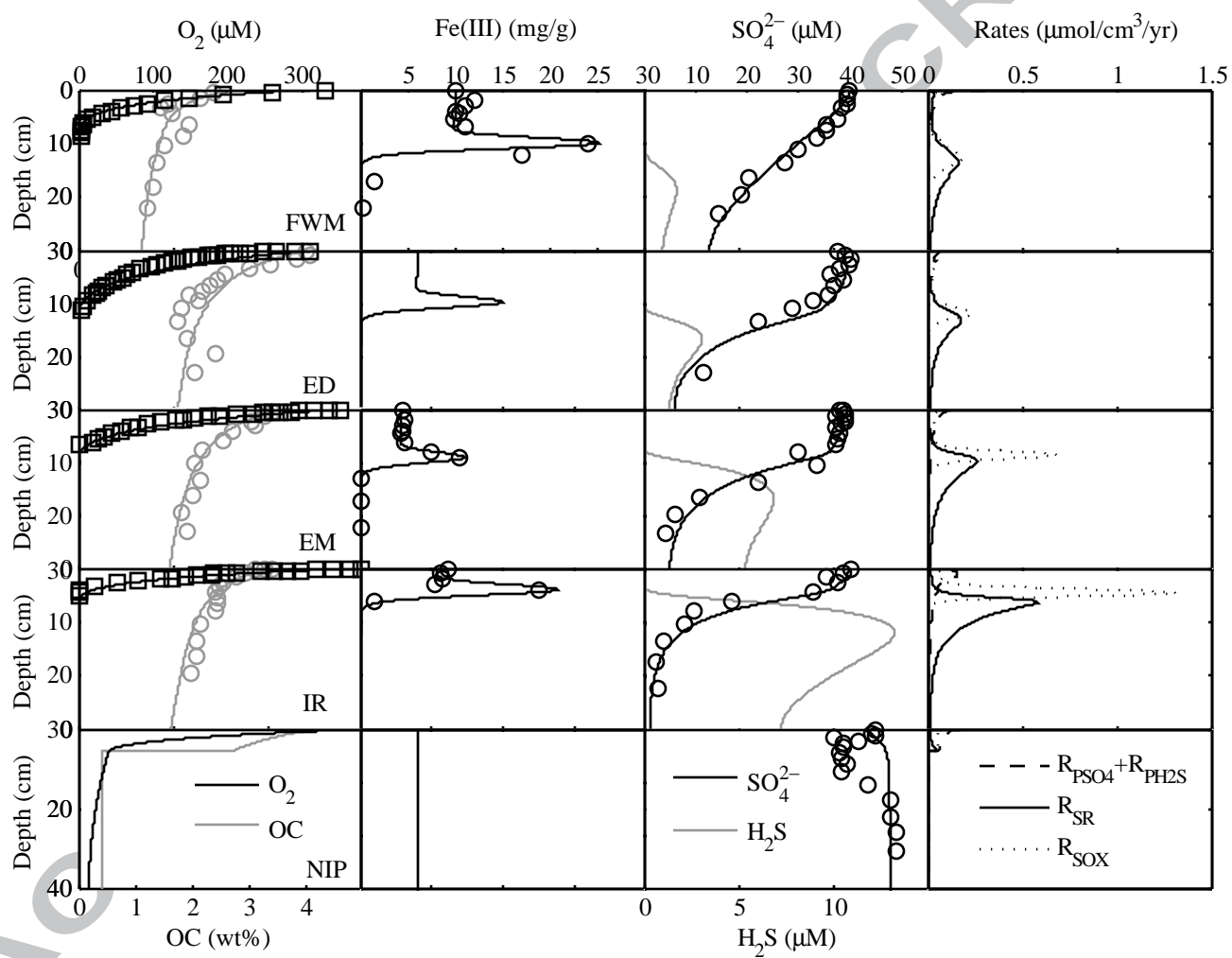


Figure 5

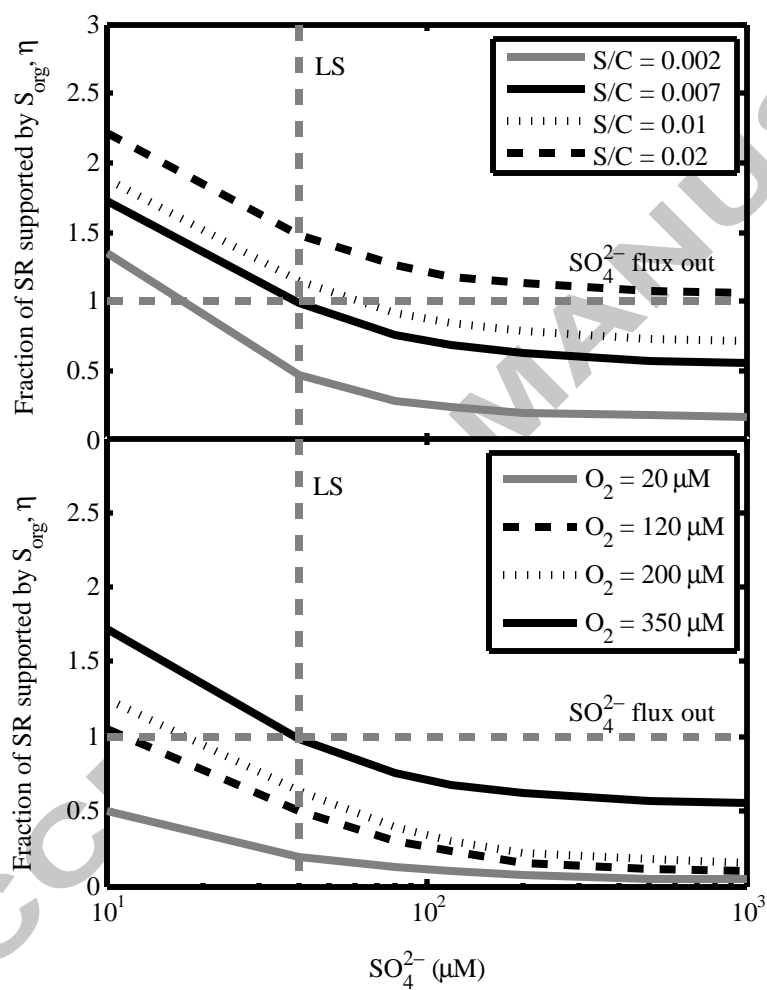


Figure 6

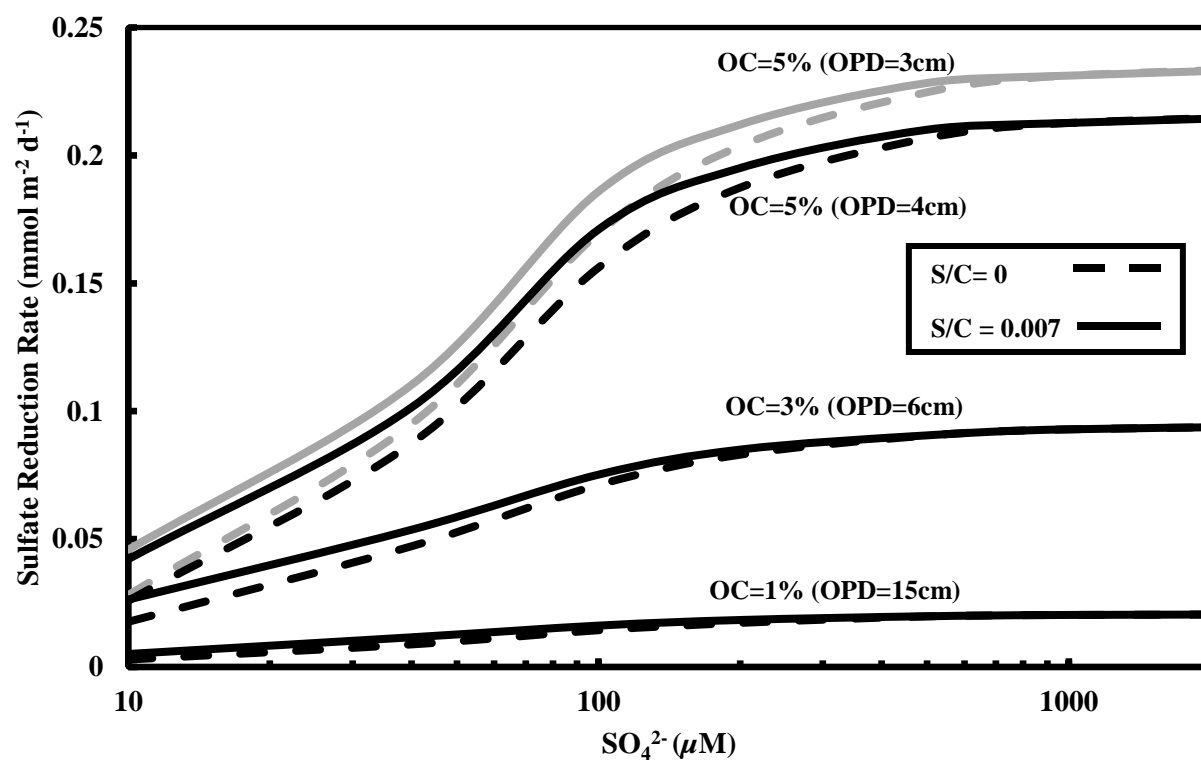


Figure 7

