



Non-steady state diagenesis of organic and inorganic sulfur in lake sediments

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Received 16 March 2016; accepted in revised form 23 August 2016; available online 31 August 2016

Abstract

Sulfur controls the fate of many geochemical elements in lake sediments, including iron, phosphorus and environmentally important trace elements. We measured the speciation of pore-water and sediment-bound sulfur (aqueous sulfate and sulfides, elemental sulfur, iron monosulfide, pyrite, organic sulfur) and supporting geochemical variables (carbon, oxygen, iron) in the sediments of a perennially oxygenated and a seasonally anoxic basin of an oligotrophic lake in Québec, using a combination of pore-water analyses, sequential extractions and X-ray absorption near edge structure. A non-steady state early diagenetic model was developed and calibrated against this extensive dataset to help unravel the pathways and quantify the rates of S transformations. Results suggest that the main source of S to the sediments is the settling of organic ester-sulfate (R-O-SO₃-H). Hydrolysis of these compounds provides an additional source of sulfate for anaerobic microbial oxidation of sedimentary organic matter, releasing sulfide to the pore-water. Reduced solid-bound S species accumulate as thiols (R-SH) and iron sulfides in the perennially oxygenated and seasonally anoxic basin, respectively. The model-estimated rate constant for R-SH formation is lower than previously estimated for this particular lacustrine site, but similar to that proposed for marine shelf sediments. The solid sediment S profiles, however, carry the imprint of the time-dependent sulfate input to the lake. Iron sulfide enrichments formed during past decades of elevated atmospheric SO₄ deposition are presently dissolving. In the sediments of the perennially oxygenated basin this reaction hampers the build-up of Fe(III) (oxy)hydroxide near the sediment–water interface.

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Keywords: Sulfur; Organosulfur compounds; Iron sulfides; Early diagenetic modeling; Seasonal anoxia; Oligotrophic lakes; X-ray absorption spectroscopy

1. INTRODUCTION

Sulfur (S) biogeochemistry is complex and of widespread interest due to its impact on many fundamental

environmental processes, ranging from terrestrial primary productivity (Scherer, 2009) and sediment microbial metabolism (Canfield et al., 2006), to organic matter (OM) preservation at long time-scales (Werne et al., 2004; Arndt et al., 2013). In lakes, the cycling of S in sediments is spatially and temporally dynamic, and tightly coupled to other biogeochemical species and processes (Holmer and Storkholm, 2001), as it partakes in an intricate network

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of geochemical reactions involving 8 valence states, ranging from +6 (e.g., sulfate, SO_4^{2-}), 0 (e.g., elemental sulfur, S^0), to -2 (e.g., sulfide, S^{-II} , and reduced organic sulfur) (Sievert et al., 2007).

The majority of S fluxes to lakes come from soils (Likens et al., 2002) and wetlands (Mandernack et al., 2000) within the catchment, generally as allochthonous organic matter containing oxygen-bound S (e.g., R-O-SO₃-H groups such as ester-SO₄ and other organo-sulfates) or carbon-bound S (e.g., R-SH groups such as amino-acids and other thiols). The latter two groups may constitute up to 98% of soil S pool (Vestergren et al., 2012). Aqueous fluxes of S to lakes originate from mineralization of such organics (Zhao et al., 2006), rocks weathering or direct atmospheric SO_4^{2-} deposition (Brimblecombe et al., 2003). Upon entering the water column, organic S (S_{org}) can be utilized by microorganisms via enzymes that cleave the R-O-SO₃-H (e.g., aryl sulfatase) and R-SH (e.g., cysteine liase) bonds, thus replenishing SO_4^{2-} and HS^- , respectively (Bunemann, 2008). Sources of S to the sediment surface comprises catchment-derived S, water-column SO_4^{2-} as well as S_{org} settling with seston (King and Klug, 1982; Likens et al., 2002). In the sediments, once dioxygen is depleted, SO_4^{2-} is mainly reduced to sulfide via dissimilatory reduction, from which the sulfate-reducing bacteria gain energy for growth and maintenance (Canfield et al., 2005).

Sulfide reacts with Fe to form amorphous monosulfide (mackinawite, $\text{FeS}_{\text{(m)s}}$) to crystalline pyrite ($\text{FeS}_{2\text{(s)}}$). The transformation of $\text{FeS}_{\text{(m)s}}$ to $\text{FeS}_{2\text{(s)}}$ is influenced by various factors, including the ratio of reactive Fe to available S^{-II} (Burton et al., 2011; Kraal et al., 2013), the inhibition by labile organic carbon (C_{org} ; (Morse and Wang, 1997; Morgan et al., 2012), the ability of $\text{S}_{\text{(aq)}^0}$ to promote pyritization via the polysulfide pathway (Sundby et al., 2004) and the effect of pH on $\text{FeS}_{\text{(m)s}}$ transformation kinetics (Morse and Luther, 1999). Overall, the interactions between S and Fe in anoxic waters, water-logged soils and sediments have been extensively studied (e.g., Carignan and Tessier, 1988; Holmer and Storkholm, 2001; Poulton et al., 2004; Rickard and Morse, 2005; Peiffer and Gade, 2007; Rickard and Luther, 2007; Burton et al., 2011; Morgan et al., 2012; Johnston et al., 2014; Hansel et al., 2015; ThomasArrigo et al., 2016).

Sulfide can also be sequestered as S_{org} (Francois, 1987), for instance as R-SH during OM sulfurization and assimilatory SO_4^{2-} reduction. Sulfide incorporation in OM has frequently been reported in marine sediments (Werne et al., 2008), but less so in lakes despite evidence of high thiols concentrations in freshwater sediments (Urban et al., 1999; Bostick et al., 2005; Sleighter et al., 2014). Sulfides can further be oxidized to form S^0 species, abundant both in solid (Burton et al., 2006b) and aqueous (Wang and Tessier, 2009) phases. S^0 reacts with Fe (Rickard and Luther, 2007) and metal(loid)s (Helz et al., 2002; Helz and Tossell, 2008; Wang and Tessier, 2009; Weber et al., 2009; Helz, 2014), and serves as a precursor for the formation of S_{org} compounds, including volatile species (Gun et al., 2000).

Here, we rely on two established approaches to gain a quantitative understanding of the biogeochemical cycling

of S in sediment: (1) detailed solid-phase speciation measurements (e.g., Urban et al., 1999; Bostick et al., 2005; Burton et al., 2011; Morgan et al., 2012; Kraal et al., 2013; Zeng et al., 2013; Johnston et al., 2014), and (2) reactive-transport diagenetic modeling (e.g., Katsev et al., 2006; Paraska et al., 2014). Table 1 lists 14 studies that have included the cycling of S in diagenetic models for freshwater sediments, nine of which present measured depth profiles of S species against which the model predictions are evaluated. In five cases SO_4^{2-} is the only species considered while in the four others data on aqueous reduced S species (i.e. S^{-II}) and on $\text{FeS}_{\text{(m)s}}$ and $\text{FeS}_{2\text{(s)}}$ are also considered. None of the models have reproduced the features of the depth-profiles of S_{TOT} in the solid-phase, or been tested against measurements of other dominant solid-phase species in lake sediments, such as S_{org} (Loshner and Kelts, 1989; Urban et al., 1999), or against measurements of S^0 , which is ubiquitous both in sediment and in pore-water (Wang and Tessier, 2009).

In recognizing the critical importance of S in controlling the fate of nutrients and of major and trace elements, our goal is to improve our quantitative understanding of the speciation and fate of S in freshwater sediments. Indeed, a more comprehensive integration of the S cycle in diagenetic models, is a stepping stone for the more accurate prediction of the biogeochemical cycles of other elements, such as C, O, Fe, and P (Meysman and Middelburg, 2005). We combine an extensive dataset on aqueous and solid-phase S speciation, gathered using aqueous analysis, sequential extraction and X-ray absorption near-edge structure (XANES) spectroscopy, with an updated reactive-transport model for S, C, O and Fe diagenesis. We estimate the rates of organic and inorganic S transformations in the sediment of two oligotrophic lacustrine basins experiencing different oxygenation conditions throughout the year, enabling us to quantify the pathways of S sequestration under both oxic and anoxic conditions.

2. METHODS

2.1. Sampling

Samples of settling particles in the water column, sediments, and sediment pore-water were collected in Lake Tantaré (47°04'15" N, 71°33'42" W), a Canadian Shield headwater oligotrophic lake located in an ecological reserve 38 km Northwest of Québec City, Central Canada. Atmospheric deposition is the only input of anthropogenic S to this 1.16 km² lake whose drainage basin has never been inhabited. This study was carried out in two adjacent basins of Lake Tantaré where depths reach 15 m (Basin A) and 21 m (Basin B). The shallow basin is perennially oxygenated, whereas the deep basin is occasionally anoxic. Sediment accumulation rates (σ ; mg cm⁻² yr⁻¹) and ages of the sediment layers in Basin A and B have been previously derived from unsupported ²¹⁰Pb data, obtained by low-background gamma spectrometry on freeze-dried sediment (Couture et al., 2008), and validated using ¹³⁷Cs stratigraphy. Sediment porosity (ϕ), determined from the dry sediment weight and water content after freeze-drying, as well

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