



Isotopic evidence of the pivotal role of sulfite oxidation in shaping the oxygen isotope signature of sulfate



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ABSTRACT

The oxygen isotope composition of sulfate serves as an archive of oxidative sulfur cycling. Studies on the aerobic oxidation of reduced sulfur compounds showed discrepancies in the relative incorporation of oxygen from dissolved molecular oxygen (O₂) and water (H₂O) into newly formed sulfate, which likely result from slight differences in the production and consumption rate of sulfoxy intermediates that exchange oxygen isotopes with water. Sulfite is often considered the final sulfoxy intermediate in the oxidation of reduced sulfur compounds to sulfate and its residence time strongly affects the oxygen isotope signature of produced sulfate. However, data on the oxygen isotope signature of sulfate derived from sulfite oxidation are scarce.

We determined the oxygen isotope effects of abiotic oxidation of sulfite with O₂ or ferric iron (Fe³⁺) under different pH conditions (pH 1, 4.9 and 13.3). These parameters impact the relative contribution of oxygen from H₂O and O₂ to the produced sulfate, and control the competition between the rates of oxygen isotope exchange between sulfite and water and the sulfite oxidation. There is a striking overlap in the range of oxygen isotope offsets between sulfate and water from our experiments at different chemical conditions ($\Delta^{18}\text{O}_{\text{SO}_4 - \text{H}_2\text{O}}$ from 5.9‰ for anaerobic oxidation with Fe³⁺ up to 17.6‰ for oxidation at low pH with O₂ as sole oxidant, respectively) with the variations in the oxygen isotope composition of sulfate derived from oxidative processes in the environment. This implies that oxygen isotope effects during sulfite oxidation largely control the isotope signature of sulfate derived from the oxidation of sulfur compounds. However, our results also show that preexisting non-equilibrium isotope signatures of sulfite are likely partially preserved in the final sulfate product under most environmental conditions. Our study furthermore provides a mechanistic explanation for positive isotope offsets between the oxygen isotope composition of sulfate and water observed in anoxic pyrite oxidation experiments with Fe³⁺ as the sole oxidizing agent. This apparently inverse isotope effect is caused by the interplay between sulfite-water oxygen exchange and normal kinetic isotope fractionation effects during sulfite oxidation, the former driving the isotope composition towards the isotope equilibrium fractionation between sulfite and water, inducing a positive offset whereas the latter induces a negative offset.

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1. Introduction

1.1. Tracing of biogeochemical sulfur cycling by oxygen isotopes of sulfate

Sulfate is highly abundant in the ocean (~28 mM) and is an extremely important electron acceptor for microbial re-mineralization of organic matter during dissimilatory sulfate reduction in anoxic marine sediments where other electron acceptors such as O₂, nitrate or

metal oxides are rapidly depleted (Jørgensen, 1977; Canfield et al., 1993; Thamdrup et al., 1994; Holmkvist et al., 2011). Produced sulfide is mostly re-oxidized at the seabed (approximately 90%, Jørgensen, 1982; Ku et al., 1999; Pfeffer et al., 2012). Also solid reduced sulfur compounds such as elemental sulfur (S⁰) or sulfide minerals like pyrite (FeS₂), iron monosulfide (FeS), greigite (Fe₃S₄), galena (PbS), sphalerite (ZnS) can be oxidized back to sulfate if they become exposed to oxidized compounds (e.g. Pirlet et al., 2010; Ziegenbalg et al., 2010; Lindtke et al., 2011; Pirlet et al., 2012; Schwedt et al., 2012; Heidel et al., 2013). The oxygen isotope composition of sulfate serves as an archive for such processes, as sulfate does not spontaneously exchange oxygen with ambient water, with the exception of extreme environments at elevated temperatures and very low pH

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(Lloyd, 1968; Chiba and Sakai, 1985; Tichomirowa and Junghans, 2009). Nevertheless, the oxygen isotope composition of sulfate is dependent on the oxygen isotope composition of the surrounding water because abiotic and microbial reductive and oxidative sulfur cycling enables indirect oxygen isotope exchange between sulfate and water. Many biochemical processes are known to alter the oxygen isotope composition of sulfate, including dissimilatory sulfate reduction (Mizutani and Rafter, 1973; Fritz et al., 1989; Brunner et al., 2005; Brunner et al., 2012), oxidation of reduced sulfur compounds (Lloyd, 1967; Lloyd, 1968; Taylor et al., 1984a, 1984b; Van Stempvoort and Krouse, 1994; Balci et al., 2007; Brunner et al., 2008; Oba and Poulson, 2009a; Tichomirowa and Junghans, 2009; Heidel and Tichomirowa, 2010; Heidel and Tichomirowa, 2011; Kohl and Bao, 2011; Balci et al., 2012; Brabec et al., 2012; Heidel et al., 2013), and the disproportionation of elemental sulfur (Böttcher et al., 2001; Böttcher et al., 2005). Thus, the oxygen isotope composition of sulfate carries information about biochemical pathways and about the oxygen sources, typically H_2O or O_2 , but could also include oxygen bearing compounds involved in sulfur cycling such as other sulfoxy anions, nitrate or phosphate. Understanding and recognition of the oxygen isotope fingerprints caused by different biochemical processes is pivotal for a meaningful interpretation of the oxygen isotope signature of sulfate from environmental samples and laboratory experiments.

1.2. The role of sulfite as intermediate in oxidative S-cycling

Sulfite is a sulfoxy intermediate that exists in the form of different species, including sulfite *sensu stricto* (SO_3^{2-}), bisulfite (HSO_3^-), pyrosulfite/metabisulfite ($\text{S}_2\text{O}_5^{2-}$), and sulfur dioxide (SO_2); the relative abundance of these species is pH dependent (Betts and Voss, 1970; Horner and Connick, 2003; Müller et al., 2013). In the following, we use the expression sulfite as a general term for all sulfite species in solution.

In oxidative sulfur cycling a number of different sulfoxy intermediates are involved, such as thiosulfate ($\text{S}_2\text{O}_3^{2-}$), polythionates ($\text{S}_x\text{O}_6^{2-}$) or sulfite (SO_3^{2-}) (Lloyd, 1967; Sada et al., 1987; Xu and Schoonen, 1995; Schippers et al., 1996; Schippers and Jørgensen, 2001; Druschel et al., 2003; Rimstidt and Vaughan, 2003; Druschel and Borda, 2006; Hubbard et al., 2009; Kohl and Bao, 2011). The mechanisms during oxidation of reduced sulfur compounds are not understood in detail, however, it is evident that more than one

oxidation pathway exists (Rimstidt and Vaughan, 2003; Druschel and Borda, 2006). Still, sulfite is considered to be of special importance, because in many biochemical pathways the last step of the oxidation of sulfur compounds to sulfate proceeds via oxidation of sulfite to sulfate (Brunner et al., 2008 and references therein).

1.3. Potential pivotal role of sulfite for the oxygen isotope composition of sulfate derived from oxidation of reduced sulfur compounds

Unlike sulfate, sulfite is known to quickly exchange oxygen isotopes with ambient water (Betts and Voss, 1970). If the oxygen isotope signature of sulfite is reset by rapid isotope exchange with water only the oxidation of sulfite to sulfate is important for establishing the isotope composition of sulfate. Such a mode of function for sulfite has previously been postulated for the oxygen isotope effects during partially reversible dissimilatory sulfate reduction (Brunner et al., 2012). Also, for the oxidative part of sulfur cycling sulfite has been considered an intermediate that might affect the oxygen isotope composition of produced sulfate, however, differing oxygen isotope patterns were typically attributed to different oxidation pathways involving different sulfoxy intermediates, and not to different modes of sulfite oxidation (Hubbard et al., 2009; Kohl and Bao, 2011; Balci et al., 2012; Heidel et al., 2013).

Studies on the oxygen isotope effects during oxidative sulfur cycling include reduced sulfur compounds such as H_2S , HS^- , FeS_2 , FeS , Fe_3S_4 , PbS , ZnS and S^0 (Lloyd, 1967; Lloyd, 1968; Taylor et al., 1984a, 1984b; Balci et al., 2007; Brunner et al., 2008; Oba and Poulson, 2009a; Tichomirowa and Junghans, 2009; Heidel and Tichomirowa, 2010; Heidel and Tichomirowa, 2011; Kohl and Bao, 2011; Balci et al., 2012; Brabec et al., 2012; Heidel et al., 2013). A considerable range of oxygen isotope fractionation effects has been reported as recently summarized by Brabec et al. (2012), as well as differences in the relative amount of oxygen derived from H_2O and O_2 in the produced sulfate. For example, the contribution of oxygen from H_2O to sulfate during pyrite oxidation varies widely (Lloyd, 1967: 68%; Taylor et al., 1984b: 23–100%; Balci et al., 2007: 87%; Tichomirowa and Junghans, 2009: 50–80%; Heidel and Tichomirowa, 2010: 91%; Kohl and Bao, 2011: 71–79%). The oxygen isotope fractionation effects between sulfate and H_2O ($\epsilon^{18}\text{O}_{\text{SO}_4-\text{H}_2\text{O}}$) reported in the aforementioned studies cover a wide range of inverse values (i.e. produced sulfate is enriched in ^{18}O relative to H_2O varying between 2.3‰ and 8.2‰) for oxidation experiments with Fe^{3+} as

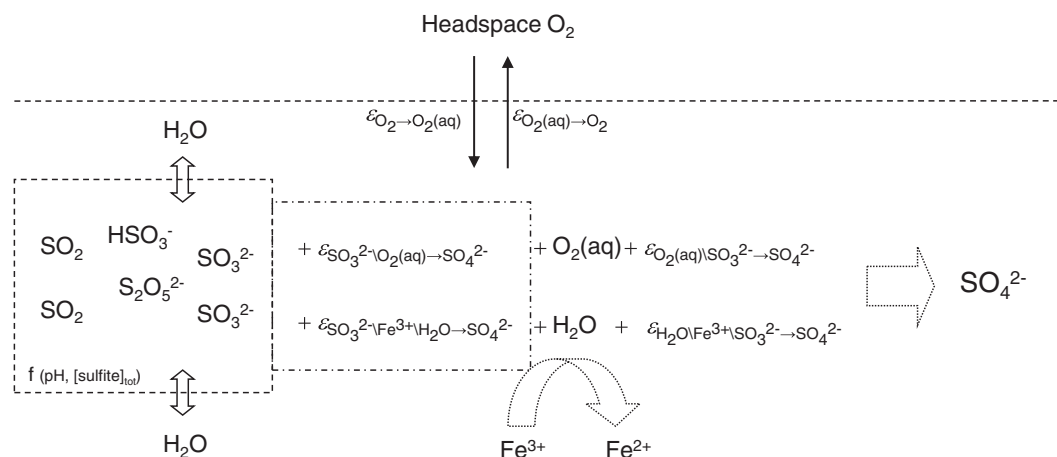


Fig. 1. Abiotic sulfite oxidation pathways and respective isotope effects. Sulfite speciation depends on pH and the total sulfite concentration (box on the left), whereas the rate of oxygen isotope exchange with water is mainly pH dependent. Sulfate is produced from the oxidation of sulfite that has partially or fully exchanged oxygen isotopes with water. Oxidants are either O_2 , or Fe^{3+} , the latter leading to incorporation of water oxygen. Both oxidation pathways compete with each other and have specific oxygen isotope effects.

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