The oxygen isotope equilibrium fractionation between sulfite species and water

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Abstract

Sulfite is an important sulfoxy intermediate in oxidative and reductive sulfur cycling in the marine and terrestrial environment. Different aqueous sulfite species exist, such as dissolved sulfur dioxide (SO_2), bisulfite (HSO_3^-), pyrosulfite ($S_2O_5^{2-}$) and sulfite *sensu stricto* (SO_3^{2-}), whereas their relative abundance in solution depends on the concentration and the pH. Conversion of one species into another is rapid and involves in many cases incorporation of oxygen from, or release of oxygen to, water (e.g. $SO_2 + H_2O \leftrightarrow HSO_3^- + H^+$), resulting in rapid oxygen isotope exchange between sulfite species and water. Consequently, the oxygen isotope composition of sulfite is strongly influenced by the oxygen isotope composition of water. Since sulfate does not exchange oxygen isotopes with water under most earth surface conditions, it can preserve the sulfite oxygen isotope signature that it inherits via oxidative and reductive sulfur cycling. Therefore, interpretation of $\delta^{18}O_{SO_4^{2-}}$ values strongly hinges on the oxygen isotope equilibrium fractionation between sulfite and water which is poorly constrained. This is in large part due to technical difficulties in extraction of sulfite from solution for oxygen isotope analysis.

To overcome these challenges, anoxic isotope equilibration experiments were performed with dissolved sodium sulfite in solutions with distinct oxygen isotope signatures. Sulfite was precipitated using two different agents, barium chloride and silver nitrate. The experiments were performed at 22 °C and varying pH of 1.5, 6.3, 6.6, and 9.7 to investigate how changes in sulfite speciation affect the oxygen isotope equilibrium fractionation between sulfite and water.

From the experiments at pH 1.5 where SO_2 is the dominant sulfite species, a rough estimate of 37.0‰ was determined for the oxygen isotope equilibrium fractionation factor between aqueous SO_2 and water ($\varepsilon_{SO_2 \leftrightarrow H_2O}^{EQ}$). The oxygen isotope equilibrium fractionation between the aqueous phases is much larger than the known oxygen isotope equilibrium fractionation between gaseous SO_2 and water vapor, probably because of a stronger association with water molecules. At pH values of 6.3–9.7 a more firm estimate for the oxygen isotope equilibrium fractionation between HSO_3^-, SO_3^{2-} and water ($\varepsilon_{SO_3^{2-} \leftrightarrow H_2O}^{EQ}$) of $15.2 \pm 0.7‰$ was obtained.

Our results provide new insights into the oxygen isotope fractionation during reductive and oxidative sulfur cycling. They demonstrate that isotope exchange between sulfite and water during dissimilatory sulfate reduction (DSR) alone is too small to be responsible for the apparent oxygen isotope equilibrium fractionation between sulfate and water mediated by DSR. Our

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estimates also provide a basis for tracing and quantifying the transformation of sulfoxy intermediates during the oxidation of reduced sulfur compounds to sulfate.
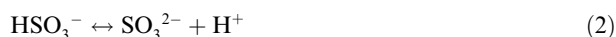
1. INTRODUCTION

1.1. The role of sulfite in shaping the oxygen isotope composition of sulfate

Due to its reactivity, sulfite is not abundant in the environment. It is released into the environment as SO_2 by magmatic processes such as the degassing of SO_2 from hydrothermal systems at the seafloor or from volcanically active terrestrial environments where it can undergo disproportionation to sulfate and sulfide or elemental sulfur (Kusakabe et al., 2000; Butterfield et al., 2011). An important anthropogenic source of SO_2 released into the atmosphere is the burning of fossil fuels (e.g. coal, oil, gas, wood and gasoline), which is one of the causes for acid rain (Holt et al., 1981; Zhao et al., 1988; Quinn, 1989; Pham et al., 1996).

Despite its scarceness in the environment, sulfite is assumed to be an important sulfoxy intermediate in reductive and oxidative sulfur cycling. It is an intermediate in dissimilatory sulfate reduction (DSR), where sulfate is used as electron acceptor in the oxidation of organic matter (Peck, 1962; Peck and Stulberg, 1962; Mizutani and Rafter, 1973; Fritz et al., 2002; Brunner and Bernasconi, 2005; Brunner et al., 2005, 2012; Turchyn et al., 2010). Sulfite is also thought to be an important intermediate during the oxidation of reduced sulfur compounds (e.g. H_2S, HS^-, FeS_2, and FeS) and elemental S which exist in high abundance under reducing conditions in marine sediments at the seafloor or in ore deposits (Schippers et al., 1996). These reduced sulfur compounds can be oxidized by microorganisms or abiotically where molecular oxygen (O_2) and/or ferric iron (Fe^{3+}) act as oxidants. Oxidative and reductive sulfur cycling leaves imprints in the oxygen isotope composition of sulfate, an ion that does not spontaneously exchange oxygen isotopes with water unless exposed to extremely high temperatures and/or extremely low pH (Lloyd, 1968; Chiba and Sakai, 1985). Therefore, the oxygen isotope composition of sulfate has been used to investigate sulfur oxidation (e.g. Lloyd, 1967, 1968; Böttcher et al., 2001, 2005; Balci et al., 2007; Brunner et al., 2008; Kohl and Bao, 2011; Balci et al., 2012; Brabec et al., 2012), DSR (Mizutani and Rafter, 1973; Fritz et al., 1989; Wortmann et al., 2007) as well as past and present reductive and oxidative sulfur cycling on Earth (Turchyn and Schrag, 2004; Bottrell and Newton, 2006; Bottrell et al., 2009; Pirlet et al., 2010; Riedinger et al., 2010). Unlike sulfate, sulfite easily exchanges its oxygen isotopes with ambient water, and due to its importance as intermediate in oxidative and reductive sulfur cycling, it is very likely that the isotope effects associated with this isotope exchange process are pivotal in shaping the isotope signature of sulfate. So far, the equilibrium isotope effect for oxygen isotope exchange between sulfite and water has not been determined accurately, only a preliminary estimate exists (~11.5‰ at 23 °C, Brunner et al., 2006).

1.2. Species-dependent oxygen isotope exchange between sulfite and water

In aqueous solutions, sulfite exists in the form of different sulfur species which have in common that the sulfur atom has an oxidation state of +IV. Simon and Waldmann (1955, 1956) investigated the characteristics of sulfite species in aqueous solutions (reaction 1, 2 and 3) and their dependence on the pH, as well as the total concentration of sulfite species. They observed that SO_2 in solution forms bisulfite ions (HSO_3^-, reaction 1) with sulfurous acid (H_2SO_3) as a hypothetical intermediate. However, H_2SO_3 as species so far has not been detected in aqueous solutions (Sülzle et al., 1988). Simon and Waldmann (1955, 1956) observed that bisulfite forms sulfite *sensu stricto* (SO_3^{2-}) and another proton via reaction 2 and described a reaction where two HSO_3^- ions react to form pyrosulfite ($S_2O_5^{2-}$) and water (Eq. 3). All abbreviations in the text are listed in Table 1 with a short explanation.

$$SO_2 + H_2O \leftrightarrow (H_2SO_3) \leftrightarrow HSO_3^- + H^+ \tag{1}$$

$$HSO_3^- \leftrightarrow SO_3^{2-} + H^+ \tag{2}$$

and

$$2HSO_3^- \leftrightarrow S_2O_5^{2-} + H_2O \tag{3}$$

By now, the reactions between sulfite species have been studied in more detail, and the kinetics of oxygen exchange between water and sulfite species are fairly well constrained (Eigen et al., 1961; Betts and Libich, 1970; Betts and Voss, 1970; Connick et al., 1982; Horner and Connick, 1986, 2003). Betts and Voss (1970) determined the kinetics of the sulfite water exchange (Eq. 1) with ^{18}O as stable isotope tracer and by mass spectrometry. Horner and Connick (1986, 2003) evaluated the equilibrium constants for the isomerization of the bisulfite ion (Eq. 4) as well as the kinetics between the isomers of bisulfite, of pyrosulfite ($S_2O_5^{2-}$) and water (Eq. 3) by studying the characteristics of these sulfite species in solution with ^{17}O nuclear magnetic resonance spectroscopy.

$$HSO_3^- \leftrightarrow SO_3H^- \tag{4}$$

The relative distribution of the bisulfite isomers as a function of pH range is currently not well constrained. Horner and Connick (2003) observed that the SO_3H^- reacts more rapid with H^+ via Eq. (1) with decreasing pH, whereas exchange between the two isomers via Eq. (4) increases with pH, which is possibly related to the presence of SO_3^{2-} as an intermediate at higher pH. Given the equilibrium constants (e.g. from Horner and Connick, 2003) and total sulfite concentration it is possible to quantitatively predict the sulfite species distribution in an aqueous solution as a function of pH. Fig. 1 depicts such a distribution for a total sulfite concentration of 0.02 M – the concentration chosen for the