



# Theoretical estimates of equilibrium sulfur isotope effects in aqueous sulfur systems: Highlighting the role of isomers in the sulfite and sulfoxylate systems

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## Abstract

We present theoretical calculations for all three isotope ratios of sulfur ( $^{33}\text{S}/^{32}\text{S}$ ,  $^{34}\text{S}/^{32}\text{S}$ ,  $^{36}\text{S}/^{32}\text{S}$ ) at the B3LYP/6-31+G(d, p) level of theory for aqueous sulfur compounds modeled in 30–40H<sub>2</sub>O clusters spanning the range of sulfur oxidation state ( $S^n$ ,  $n = -2$  to  $+6$ ) for estimating equilibrium fractionation factors in aqueous systems. Computed  $^{34}\beta$  values based on major isotope ( $^{34}\text{S}/^{32}\text{S}$ ) reduced partition function ratios (RPFs) scale to a first order with sulfur oxidation state and coordination, where  $^{34}\beta$  generally increase with higher oxidation state and increasing coordination of the sulfur atom. Exponents defining mass dependent relationships based on  $\beta$  values ( $^{x/34}\kappa = \ln(^x\beta)/\ln(^{34}\beta)$ ,  $x = 33$  or  $36$ ) conform to tight ranges over a wide range of temperature for all aqueous compounds ( $^{33/34}\kappa \approx 0.5148$ – $0.5159$ ,  $^{36/34}\kappa \approx 1.89$ – $1.90$  from  $T \geq 0$  °C). The exponents converge near a singular value for all compounds at the high temperature limit ( $^{33/34}\kappa_{T \rightarrow \infty} = 0.51587 \pm 0.00003$  and  $^{36/34}\kappa_{T \rightarrow \infty} = 1.8905 \pm 0.0002$ ; 1 s.d. of all computed compounds), and typically follow trends based on oxidation state and coordination similar to those seen in  $^{34}\beta$  values at lower temperatures. Theoretical equilibrium fractionation factors computed from these  $\beta$ -values are compared to experimental constraints for  $\text{HSO}_3^- \text{T(aq)}/\text{SO}_2(\text{g, aq})$ ,  $\text{SO}_2(\text{aq})/\text{SO}_2(\text{g})$ ,  $\text{H}_2\text{S}(\text{aq})/\text{H}_2\text{S}(\text{g})$ ,  $\text{H}_2\text{S}(\text{aq})/\text{HS}(\text{aq})^-$ ,  $\text{SO}_4^{2-}(\text{aq})/\text{H}_2\text{S}(\text{aq})$ ,  $\text{S}_2\text{O}_3^{2-}(\text{aq})$  (intramolecular), and  $\text{S}_2\text{O}_3^{2-}(\text{aq})/\text{H}_2\text{S}(\text{aq})$ , and generally agree within a reasonable estimation of uncertainties. We make predictions of fractionation factors where other constraints are unavailable. Isotope partitioning of the isomers of protonated compounds in the sulfite and sulfoxylate systems depend strongly on whether protons are bound to either sulfur or oxygen atoms. The magnitude of the  $\text{HSO}_3^- \text{T}/\text{SO}_3^{2-}$  major isotope ( $^{34}\text{S}/^{32}\text{S}$ ) fractionation factor is predicted to increase with temperature from 0 to 70 °C due to the combined effects of the large magnitude  $(\text{HS})\text{O}_3^-/\text{SO}_3^{2-}$  fractionation factor ( $1000\ln^{34}\alpha_{(\text{HS})\text{bisulfite-sulfite}} = 19.9\text{‰}$ , 25 °C) relative to the  $(\text{HO})\text{SO}_2^-/\text{SO}_3^{2-}$  fractionation factor ( $1000\ln^{34}\alpha_{(\text{HO})\text{bisulfite-sulfite}} = -2.2\text{‰}$ , 25 °C), and the increased stability of the  $(\text{HS})\text{O}_3^-$  isomer with increasing temperature. We argue that isomerization phenomenon should be considered in models of the sulfur cycle, including models that describe the overall sulfur isotope fractionations associated with microbial metabolism (e.g., microbial sulfate reduction).

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## 1. INTRODUCTION

### 1.1. Overview

Quantum mechanical electronic structure calculations of aqueous clusters complement experimental investigations of

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isotope effects in aqueous systems (e.g., Rustad et al., 2008, 2010; Zeebe, 2009), and have been instrumental for predicting isotope effects when experimental determinations are unavailable (e.g., Li et al., 2009; Li and Liu, 2011). Theoretical approaches are especially useful for compounds like those of the sulfite and sulfoxylate systems that contain numerous compounds that are difficult to experimentally isolate and study directly. The aim of the present study is to: (1) provide an internally consistent set of constraints for equilibrium isotope fractionations among aqueous sulfur compounds relevant to low and high temperature conditions, emphasizing the poorly documented sulfite and sulfoxylate systems; (2) provide new constraints on the exponents of mass-dependence associated with equilibrium isotope fractionation in aqueous systems and their relationships to sulfur oxidation state and bonding environment; (3) compare our theoretical constraints to the available experimental datasets and make predictions where estimates are currently unavailable, and assess where future experimental work may be needed; and (4) illustrate the effects of isomerization on isotope partitioning in the sulfite system where isomerization leads to relatively large and apparently unusual effects in observable isotope fractionation behavior.

## 1.2. Sulfite and sulfoxylate in the sulfur cycle

The sulfite (denoted  $\text{SO}_3^{2-}$ ) and sulfoxylate systems (denoted  $\text{SO}_2^{2-}$ ) are the series of inorganic compounds and oxyanions that contain sulfur in the +4 and +2 oxidation states, respectively. These oxidation states are intermediate between the most common end member sulfur oxidation states of  $-2$  as the most reduced (e.g.,  $\text{H}_2\text{S}/\text{HS}^-/\text{S}^{2-}$ ) and  $+6$  as the most oxidized (e.g.,  $\text{SO}_4^{2-}$ ). Sulfite is a well-documented intermediate in a variety of settings where sulfur is cycled, and sulfoxylate species, while very rarely observed, are inferred to be a ‘missing-link’ oxidation state in sulfur redox processes between zero-valent sulfur compounds (e.g., generically as  $\text{S}^0$ ) and those of the sulfite system.

### 1.2.1. Sulfite In the sulfur cycle

Sulfite *sensu lato* in natural environments is typically transient and does not comprise a significant fraction of the bulk sulfur in Earth’s surface environment but nevertheless plays essential roles in the environmental cycling of sulfur and related elemental cycles. The hydrolysis and subsequent oxidation of sulfur dioxide in atmospheric water droplets is a major pathway of acid-rain formation (e.g., Brandt and van Eldik, 1995). Sulfite is a major intermediate in both the oxidative and reductive portions of the sulfur cycle, including the microbial production and subsequent oxidation of sulfide ( $\text{HS}^-/\text{H}_2\text{S}$ ; Zhang and Millero, 1993; Zopfi et al., 2004). In marine sediments containing relatively high amounts of organic matter, sulfide is generated as a byproduct of anaerobic respiration (microbial sulfate reduction; MSR) and ca. 80–95% of the sulfide produced is eventually re-oxidized through intermediates like sulfite back to sulfate (Jørgensen, 1977, 1982; Jørgensen et al., 1990; Canfield and Teske, 1996;

Jørgensen and Nelson, 2004). Depending on the conditions and biota present, the sulfite thus produced can support or supplement a variety of metabolisms carried out by microorganisms that oxidize, reduce, and disproportionate sulfite and other intermediate sulfur compounds for overall energy conservation and metabolic function.

At the intracellular level, sulfite (*sensu lato*) is a pivotal intermediate during microbial sulfate reduction (MSR), which in general is responsible for the oxidation of much of the organic matter contained in modern marine sediments (e.g., Bowles et al., 2014). Intracellular sulfite within a sulfate reducing microorganism sits between two reversible transformations: (1) its production via the reduction of activated sulfate (adenosine-5'-phosphosulfate; cleaving an S–O bond) and (2) its reaction with the heme active site of dissimilatory sulfite reductase where it is reduced to eventually form the end waste product sulfide via other enzymatically-bound intermediates like sulfoxylate ( $\text{S}^{2+}$ ) and zero-valent sulfur ( $\text{S}^0$ ) (Parey et al., 2010). The sulfide thus produced and its subsequent cycling in the environment places primary controls on the isotopic composition of authigenic pyrite, which in sedimentary rocks serves as a major archive of the sulfur cycle through geologic time. Isotope network models that attempt to constrain the overall sulfur isotope fractionations that occur during the stepwise reduction of sulfate have relied on estimations of fractionation factors involving sulfite compounds (e.g., Wing and Halevy, 2014), but these fractionations have yet to be determined in detail. In particular, present network models simplify the intracellular inorganic speciation of sulfite (assuming sulfite *sensu stricto* only,  $\text{SO}_3^{2-}$ ) and have yet to take into consideration the influence of bisulfite compounds (generically:  $\text{HSO}_3^-$ ).

### 1.2.2. Sulfur isotope partitioning in the sulfite system

Despite the recognized importance of sulfite in the overall cycling of sulfur, the determination of the equilibrium isotope fractionations among various sulfite species has received very little attention. To our knowledge, only one set of experimental constraints has been reported (Eriksen, 1972a,b,c), suggesting a fractionation factor between bulk bisulfite in solution and gaseous  $\text{SO}_2$  ( $1000\ln^{34}\alpha_{\text{bisulfite-SO}_2(\text{g})}$ ) of  $10.9 \pm 1.4\text{‰}$  (1 s.d., 10 experiments) at 25 °C (Eriksen, 1972a). No resolvable change in this fractionation factor was observed over the investigated temperature range of 25–45 °C. Fractionations among aqueous sulfite species (e.g., the bisulfite compounds and sulfite) are completely unconstrained. Given that these are the dominant species under most natural conditions as well as within sulfate reducing organisms, these fractionations are key to a detailed understanding of sulfite isotope systematics in natural systems.

### 1.2.3. Sulfoxylate in the sulfur cycle

Sulfoxylate species are difficult to detect and analyze and their role in the (bio)geochemical cycling of sulfur is not well understood. Hoffmann and Lim (1979) were among the first to suggest sulfoxylate as a reaction intermediate of the sulfide oxidation mechanism in a scheme of hypothetical reactions known as the polar mechanism

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