Controls on the abiotic exchange between aqueous sulfate and water under laboratory conditions

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Abstract

The oxygen atoms in sulfate are known to exchange with water at low pH and at high temperature; however, it is unclear what the timescale for exchange is for the pH and temperature conditions commonly experienced in the laboratory. We present a time series of sulfate-oxygen isotope data for solutions with two different sulfate concentrations (28 mM and 11 mM), at a range of low to intermediate pH values (1 to 5), using both hydrochloric and acetic acid. Using water enriched in 18O, we show that there is negligible exchange of oxygen atoms between sulfate and water over the course of 390 days. We use the external uncertainty in these results to calculate a lower bound estimate on the timescale for oxygen isotope exchange under these conditions. The lower bound of the timescale for oxygen isotope exchange between sulfate and water at laboratory pH is \(2 \times 10^5\) hours (~25 y), which is broadly in agreement with previous estimates. This result validates the use of \(\delta^{18}O_{SO_4}\) as geochemical tool for a variety of solutions that are subjected to low pH at room temperature.

Sulfur in various valence states between sulfate (+6) and sulfide (–2) plays a key role in microbially mediated subsurface redox reactions, including those involved in the oxidation of organic carbon (Kasten and Jørgensen 2000). Bacterial sulfate reduction (BSR) is estimated to account for ~50% of sedimentary organic carbon remineralization in modern marine sediments (Jorgensen 1982), as well as consuming a significant proportion of subsurface methane via anaerobic oxidation (Niewöhner et al. 1998; Reeburgh 2007). Sulfide oxidation, in turn, is a key anaerobic microbial metabolism, linked to iron, manganese, and nitrate reduction (Burdige and Nealson 1986; Schippers and Jørgensen 2002; Gervitz et al. 2000). In between sulfate and sulfide are intermediate valence state sulfur species that are also involved in a myriad of subsurface redox reactions, linking the subsurface biogeochemical sulfur cycle to other key redox cycles, such as iron and manganese (e.g., Thamdrup et al. 1993; Böttcher and Thamdrup 2001). Ultimately, the oxidation of organic carbon and/or the burial of reduced sulfur species (principally the mineral pyrite) impact the electron balance of Earth’s surface environment (Berner 1987; Canfield 2005). As a result of the wide importance of the sulfur cycle, the subsurface redox transformations of sulfur are of critical interest.

One of the primary tools for exploring the biogeochemical sedimentary sulfur cycle is through the measurement of the sulfur and oxygen isotopic compositions of sulfate (\(\delta^{34}S_{SO_4}\) and \(\delta^{18}O_{SO_4}\) respectively). Of these two isotope systems, sulfur isotopes have been far more widely applied (e.g., Rees 1973; Habicht and Canfield 1997; Brüchert et al. 2001; Habicht et al. 2002; Canfield et al. 2006). Each change in the valence state of sulfur—from the oxidized form of sulfate through to the reduced form of sulfide—partitions sulfur isotopes, such that the light 32S is continually concentrated in the reduced product (Canfield 2001).

In contrast, \(\delta^{18}O_{SO_4}\) is a relatively new geochemical tool applied to the subsurface sulfur cycle. Whereas \(\delta^{34}S_{SO_4}\) yields interesting insights on the overall throughput of sulfur through microbial communities, the \(\delta^{18}O_{SO_4}\) better illuminates the internal cell dynamics of sulfur cycling (Mizutani and Rafter 1973; Fritz et al. 1989; Brunner et al. 2005, 2012; Mangalo et al. 2007, 2008; Wortmann et al. 2007; Antler et al. 2013). Oxygen atoms in sulfate molecules equilibrate intracellularly when sulfur is in the intermediate valence state of sulfite (Kohl et al., 2012; Wortmann et al. 2007; Brunner et al. 2012; Kohl et al. 2012). \(\delta^{18}O_{SO_4}\) is useful for tracking the sulfur atom as it transitions among its various valence states during the subsurface sulfur cycle. Additionally, oxygen isotopes

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in sulfate provide valuable insight into different pathways of sulfide oxidation, both in the modern environment (Calmels et al. 2007), and possibly over geological time (Newton et al. 2004).

When oxygen atoms are added to a sulfate molecule through sedimentary microbial redox processes, the resulting $\delta^{18}O_{SO_4}$ should remain “fixed” for the lifetime of that sulfate atom in the natural environment. This is because under open marine pH and temperature conditions, abiotic sulfate-oxygen exchange is understood to be very slow relative to the residence time of sulfate in the ocean (aqueous sulfate is estimated to fully exchange oxygen isotopes with water over $10^9$ years under marine pH and temperature conditions [Zak et al. 1980]; this is longer than the residence time of sulfate in the ocean, which is $\sim 10^7$ years). Using $\delta^{18}O_{SO_4}$ rests on the assumption that there is also minimal oxygen isotope exchange between sulfate and water during the variety of conditions imposed by sample storage and laboratory processing. After sampling, aqueous sulfate samples can be exposed to the addition of acid, a common practice with pore fluids, seawater samples, and culture media before analysis. Additionally, the extraction of sulfate from evaporites and carbonates by mineral dissolution in acid at low temperature, exposes sulfate to acidic conditions. The isotope fractionation factors for oxygen isotope exchange between water and sulfate ($SO_4^{2-}$), bisulfate ($HSO_4^-$), or sulfuric acid ($H_2SO_4$) are not well constrained, but are expected to be in the range of 18-40‰ (Zeebe 2010; Lloyd 1968; Mizutani and Rafter 1969). Thus, if even partial oxygen isotope exchange between sulfate-oxygen and water-oxygen does occur during sample storage or handling, it will overprint the original $\delta^{18}O_{SO_4}$.

Oxygen isotope exchange between sulfate-oxygen atoms and water-oxygen atoms has been shown to occur in exceptionally low pH ($<0$) solutions at $25^\circ C$ and $100^\circ C$ (with a half-life [time for half of sulfate-oxygen atoms to exchange—$\tau_{1/2}$] of $\sim 10^5-10^7$ h, Hoering and Kennedy 1957—see Fig. 1). A linear extrapolation of these experiments to a pH value of 1, yields half-life exchange times on the order of $10^7$ h ($\sim 1000$ y). At hydrothermal temperatures ($100-300^\circ C$), oxygen isotope exchange between sulfate and water has also been shown to occur between pH 4-8 ($\tau_{1/2} \sim 10^4-10^5$ h; Chiba and Sakai 1985). Extrapolating these results to laboratory temperatures and a pH of 1 yields $\tau_{1/2}$ estimates of $\sim 10^3$ h (using activity coefficients from Wirth 1971). The discrepancy in these two extrapolations for oxygen isotope exchange between sulfate and water at laboratory temperature and pH is likely to be due to the very different ionic strength of the two experimental setups, and because the Chiba and Sakai (1985) equations make assumptions about the chemical species undergoing isotope exchange that may not be valid at different pHs.

Another oxygen isotope exchange study was performed with samples across a large temperature range ($25-448^\circ C$),
which suggested that sulfate-oxygen exchange with water was still appreciably rapid at low temperature and circumneutral pH \( \tau_{1/2} \approx 10^8 \text{ h} \) at pH 7 and 25°C – Lloyd 1968, see Fig. 1). Unfortunately, the chemistry of the solutions in this experiment (and therefore the pH) were not well constrained, and may have been much lower than reported (Chiba and Sakai 1985). Thus far, the above studies have not made it possible to rule out oxygen isotope exchange between sulfate and water in the laboratory. It is, however, critical to establish whether sulfate-oxygen can be re-set by isotope exchange during laboratory processing, because this often involves increasing the temperature and decreasing the pH of the original solution (Chiba and Sakai 1985; Hall and Alexander 1940; Garus et al. 1967).

In this study, we have tested for the likelihood of isotopic exchange between sulfate-oxygen and water-oxygen in aqueous samples at room temperature, over a range of pH values and over a timescale common to laboratory procedures. We use water enriched in \(^{18}\)O, so that, even with the smallest estimated fractionation factor from the literature, oxygen isotope exchange should be apparent. We estimate a lower bound on the timescale for exchange under these conditions, based on our results.

### Materials and procedures

**Experimental setup**

Two parallel experiments, using solutions of sulfate at two different concentrations and sulfate-oxygen isotopic compositions, were monitored for 390 days. Each experiment contained duplicate samples at ~ pH 1, 3, and 5 in hydrochloric acid and ~ pH 3 and 5 in acetic acid, as well as a nonacidified sample. The samples were maintained at laboratory (i.e., room) temperature (the temperature in the laboratory varies between 20 and 25°C), and sampled regularly for the oxygen isotope composition of sulfate. The oxygen isotope composition of the water used was enriched to \(20\%\) by evaporation (water was left to evaporate, and repeatedly sampled until it reached \(20\%\), before being used in this experiment) and thus any exchange over the course of the experiment should produce sulfate-oxygen isotope compositions increasing toward \(40\%\) or higher. The concentrations and initial isotope compositions of the experimental solutions are displayed in Table 1.

The oxygen isotope composition of the initial aqueous sulfate was measured by dissolving the starting sulfate minerals and precipitating insoluble BaSO\(_4\) via the addition of saturated barium chloride solution. The sulfate in the experimental solutions was similarly extracted; 0.5 mL experimental solution was removed and the sulfate precipitated as BaSO\(_4\).

**Oxygen isotope analyses**

The resultant barite precipitates were cleaned of possible BaCO\(_3\) contamination by addition of cold 6M HCl (removed rapidly to prevent possible exchange), followed by two rinses in 18.2 MQ water, before being dried. Approximately 180 µg dry precipitate was then weighed into silver capsules and baked overnight at 50°C to remove any adsorbed water. Capsules were crushed and introduced into a Thermo continuous flow Delta V Plus as CO, via a ThermoFinnigan thermal conversion elemental analyzer (TC/EA) at 1450°C. Samples were measured in duplicate, except for the solutions at pH 1 (HCl), which were measured in triplicate. Samples were bracketed in sets of twelve using triplicate measurements of two standards, NBS-127 (\(\delta^{18}\)O = 8.6‰) and an internal standard (\(\delta^{18}\)O = 12‰). Reproducibility, as measured using the standard deviation of the 6 bracketing NBS-127 samples was better than 0.4‰.

Results are presented in delta notation relative to Vienna Standard Mean Ocean Water (VSMOW):

\[
\delta = \left( \frac{R_{\text{sample}} - R_{\text{VSMOW}}}{R_{\text{VSMOW}}} \right) \times 1000
\]

and reported in units of permil (‰).

The oxygen isotope composition of the water was analyzed by cavity ringdown spectroscopy on a Picarro, calibrated with

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sulfate mineral</th>
<th>[SO(_4)](^{2-}) (mM)</th>
<th>(\delta^{18})O(_{SO_4}) (‰)</th>
<th>(\delta^{18})O(_{H_2O}) (‰)</th>
<th>Vial number</th>
<th>Acid</th>
<th>pH</th>
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<tbody>
<tr>
<td>1</td>
<td>MgSO(_4)(\cdot)7H(_2)O</td>
<td>28</td>
<td>14.6</td>
<td>20</td>
<td>1,2</td>
<td>None-control</td>
<td>4.5</td>
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<td>3,4</td>
<td>HCl</td>
<td>1.3</td>
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<td>5,6</td>
<td>HCl</td>
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<td>7,8</td>
<td>HCl</td>
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<td></td>
<td>9,10</td>
<td>CH(_3)COOH</td>
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<td></td>
<td>11,12</td>
<td>CH(_3)COOH</td>
<td>4.3</td>
</tr>
<tr>
<td>2</td>
<td>CaSO(_4).2H(_2)O</td>
<td>11</td>
<td>11.6</td>
<td>20</td>
<td>1,2</td>
<td>None-control</td>
<td>4.5</td>
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<td>11,12</td>
<td>CH(_3)COOH</td>
<td>4.3</td>
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3 international standards, GISP, SLAP and SMOW, and reported in delta notation versus standard mean ocean water (VSMOW). Each sample was measured a total of 9 times, with the first three measurements discarded and the remaining six averaged.

**Assessment**

The oxygen isotope composition of sulfate in both experiments was monitored over the course of 390 days. No sulfate mineral precipitation was observed in the experimental vials over the course of the experiment. Results are presented in Fig. 2, grouped by experiment and acid composition. The δ¹⁸O SO₄ of all samples analyzed are within 2σ of the original sulfate-oxygen isotope composition (denoted by the gray bars). The sulfate-oxygen isotope composition of the lowest pH samples in both experiments (Fig. 2b&c) does show an apparent ~ 1‰ increase in δ¹⁸O SO₄ compared with the samples in solutions at higher pH over the course of the experiment, however these results are still within 2σ analytical error of the original δ¹⁸O SO₄. This potential increase in the oxygen isotopic composition of sulfate in low pH samples is in the correct direction for oxygen isotope exchange, given the δ¹⁸O of the water at 20‰; sulfate that had equilibrated its oxygen atoms with this water should have a δ¹⁸O SO₄ approaching 44‰. However, our signal is not distinguishable from the noise within the data.

**Analytical noise**

The δ¹⁸O SO₄ measurements for the duration of the experiments span the full range of ±2σ analytical error, which is calculated from repeated measurements of standards. Highly variable δ¹⁸O SO₄ may be the result of contamination of the experimental solutions over time, contamination during processing, water bound within the barite lattice, or mass spectrometer-related instability. If the experiment vials have become contaminated, then it would be expected that the experiment with lower sulfate concentrations (experiment 2)

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**Fig. 2.** δ¹⁸O SO₄ over time for 28mM (a-c) and 11mM (d-f) solutions of sulfate at pH values 1-5. The grey bars indicate the original isotopic composition of the sulfate ±2σ. (0.8‰, n=10). Sample error bars are 2σ of the variation in the bracketing standards on the mass spectrometer (always taking the 2σ from the most variable of the two groups of bracketing standards), except for pH1 and control solutions, where the error is 2σ from 3 sample replicates. Solutions were made up from water with a δ¹⁸O composition of 20‰ and sulfate with starting δ¹⁸O SO₄ values of 14.6‰ (a-c) and 11.6‰ (d-f), so that exchange would become immediately apparent (fractionation factors range from 18‰ – 40‰; Zeebe, 2010; Lloyd, 1968; Mizutani and Rafter, 1969). The solutions were sampled regularly for 390 days.
would show higher variability. Moreover, it is possible that this variability would increase over the timescale of the experiment, especially if we were introducing the contaminant during sampling. In our experiments, $\delta^{18}O_{SO_4}$ results are not more variable in experiment 2 than experiment 1, and do not get significantly more variable with time, but instead remain within $\pm 2\alpha$ of the original $\delta^{18}O_{SO_4}$. This suggests that the observed variability is not the result of increasing contamination of the sample vial over time, but is rather due to variable performance in the TC/EA (although it is not possible to rule out the contribution from lattice bound water).

TC/EA measurements have reported relatively poor external precision for nitrates, sulfates, and phosphates, and can vary from 0.1‰ (1σ) to 0.6‰ (1σ) within the same laboratory (Vennemann et al. 2002; Boschetti and Iacumin 2005). The 1σ analytical error reported here (0.4‰) is consistent with this range, especially as we report the standard deviation of $\delta^{18}O_{SO_4}$ on duplicate or triplicate (rather than quadruple) measurements. There are several hypotheses for the variable performance of the TC/EA-CFIRMS (continuous flow isotope ratio mass spectrometry), including memory effects resulting from oxygen isotope exchange between newly generated CO and residual BaO from previous samples during subsequent sample analyses (Boschetti and Iacumin 2005). The buildup of memory effects was mitigated in our analytical setup by running a blank sample every ~12 samples. However, this may not be sufficient to eliminate all memory effects, which may have contributed to some of the variability we observe.

Another likely cause of the poor reproducibility of repeated $\delta^{18}O_{SO_4}$ analyses is asymmetrical peaks, which are often observed in the determination of $\delta^{18}O$ via TC/EA-CFIRMS. Asymmetrical peaks result in the poor calculation of the sample’s isotope composition, and can occur due to sluggish pyrolysis or poor flushing of the sample CO through the TC/EA and to the mass spectrometer (LaPorte et al. 2009). In this experiment, sample peaks did occasionally show more tailing near the end of a run—samples were analyzed as they were generated over the course of the experiment, and so in any given reactor, samples could fall at the beginning, middle, or end of the life of the crucible. Due to the increased helium flow restrictions that develop over the life of a crucible, this is likely to contribute to the variation in the analytical uncertainty over the course of the experiment.

Sluggish or incomplete pyrolysis can also be the result of poor placement of the graphite crucible, such that it does not lie in the hottest part of the furnace. Variations in the height of the crucible result in a greatly decreased CO yield (to a ~75% yield—Boschetti and Iacumin 2005), which is unlikely to be problematic in the TC/EA setup used in this study, where the packing depth has been optimized over years of analyses.

**Discussion**

**Timescales for exchange over low temperature**

Using the lack of change in the $\delta^{18}O_{SO_4}$ over the course of the experiment, we can calculate an upper limit for the rate of oxygen isotope exchange between water and sulfate-oxygen suggested by our data. We perform this calculation using the “analytical error envelope” of our isotopic measurement as the bounding conditions for maximum possible isotope exchange between sulfate and water that could have occurred over the 390 days. We calculate the error envelope using the starting value for $\delta^{18}O_{SO_4}$ (14.6‰ and 11.6‰ for experiments 1 and 2, respectively), and assuming that the final $\delta^{18}O_{SO_4}$ is within 0.8‰ of the starting composition after 390 days as shown in Fig. 3.

We calculate the timescale for oxygen isotope exchange (or lack thereof) between sulfate and water using the following equation, derived initially by Chiba and Sakai (1985):

$$\ln\left(\frac{\alpha_f - \alpha_i}{\alpha_f - \alpha_e}\right) = -R\frac{(4X+Y)}{4XY}t$$

where $\alpha_i$, $\alpha_f$, and $\alpha_e$ are the oxygen isotope fractionation factors at equilibrium, the end and the start of the experiment, respectively. R is the overall rate of isotope exchange, and X

![Fig. 3. An estimate of the maximum possible oxygen isotope exchange between sulfate-oxygen and water over the duration of the experiment. No isotopic exchange that was distinguishable from the starting isotope composition by $2\alpha$ was observed, thus the maximum possible isotopic excursion must be $\pm 2\alpha$ of the original oxygen isotope composition. We therefore take the maximum to be $\delta^{18}O_{original\ SO_4} + 2\alpha$.](image-url)
and Y are the total number of sulfate and water molecules in the solution, and \( y_1 \) is the mole fraction of those water atoms that have a \(^{16}\text{O}\) atom. (It can be assumed that \( y_1 \approx 1 \)). When half of the sulfate atoms have exchanged oxygen atoms with water, Eq. 2 becomes

\[
\ln(0.5) = -R\left(\frac{4X+Y}{4XY}\right)t_1
\]

(3)

Our experimental set-up is clearly far from isotopic equilibrium for the sulfate-water system. However, the half-life of the oxygen isotope exchange can still be calculated, and a plot of \( \ln (\alpha_e - \alpha_i)/(\alpha_e - \alpha_f) \) against run time, \( t \), should produce a straight line with a slope of \( - R(4X + Y)/4XY \). This derivation is valid irrespective of the order of the reaction (Chiba and Sakai 1985) and further assumes that only one sulfate species is undergoing exchange, neglecting exchange from co-occurring sulfate species (e.g., both sulfate and bisulfate undergoing exchange simultaneously). At a pH 1 and 25°C, the majority of the sulfate in solution is in the form of \( \text{HSO}_4^- \) (see Fig. 4), and so this derivation is likely to hold.

We assume that the final experimental \( \delta^{18}\text{O}_{\text{SO}_4} \) is elevated by 0.8‰ (+2σ analytical error) after 390 days. We further assume a range of possible oxygen isotope equilibrium fractionation factors for sulfate and bisulfate, respectively, of 18–23‰ and 28‰ (Zeebe 2010; Lloyd 1967; Mizutani and Rafter 1969) to estimate the fastest possible half-life. Using this we estimate the half-life for isotopic exchange for the two experiments at pH 1, as illustrated graphically in Fig. 5. Our calculation suggests a half-life for oxygen isotope exchange between sulfate and water of \( 2.2 \times 10^3 - 2.9 \times 10^3 \) h, for a range of oxygen isotope fractionation values between sulfate and water at room temperature. These calculations suggest that it would take at least 25 years for aqueous sulfate at low-to-intermediate pH at room temperature to isotopically exchange half its oxygen atoms with water. Our lowest calculated timescale for oxygen isotopic exchange between sulfate and water is two orders of magnitude faster than the timescale of isotope exchange first calculated by Hoering and Kennedy (1957). However, our calculation only provides a lower limit on the timescale for exchange. This is because our extrapolation of the oxygen isotope ratio of the experimental solution assumes the maximum possible oxygen isotope exchange between sulfate and water within the duration of the experiment (>1 y), when, in fact, there is little to no variation in \( \delta^{18}\text{O}_{\text{SO}_4} \) of the solutions.

The calculated half-life for experiment 1 is lower than that of experiment 2, for each value of the oxygen isotope fractionation between sulfate and water that is assumed. Given the uncertainties involved in this extrapolation, it is not possible to determine whether this difference is significant, however it is possible that the reaction rates for experiment 1 and 2 should differ slightly, because in each experiment sulfate is complexed by a different cation (magnesium and calcium, respectively).

**Fig. 4.** Bjerrum plot of the relative proportion of sulfate as \( \text{H}_2\text{SO}_4 \) (solid line), \( \text{HSO}_4^- \) (dashed line) and \( \text{SO}_4^{2-} \) (dot/dash line) for 25°C (black lines) and 200°C (grey lines). Dissociation constants at 200°C are taken from Ohmoto and Lasaga, (1982). The shaded grey region is the pH range investigated in this study.
This result confirms that oxygen isotope analyses of sulfate are not re-set by exchange with water at room temperature when being processed in the laboratory over short to intermediate timescales, even at a pH of 1. This lends additional confidence to the robust nature of reported $\delta^{18}O_{\text{SO}_4}$ for a variety of natural systems.

**Comments and recommendations**

The oxygen isotope composition of aqueous sulfate in medium to low pH (1-5) solutions at room temperature does not show isotope exchange with water on short to medium timescales. This rules out abiotic sulfate-oxygen exchange as a significant contribution to observed sulfate-oxygen isotope trends measured, when working at ambient temperatures and moderate pH values.

This is consistent with timescales for exchange extrapolated from rates calculated at hydrothermal temperatures. The lower bound of sulfate-oxygen isotope exchange at pH 1.3 at 25°C is $\sim 2 \times 10^4$ hours. This lower bound estimate on the $r_{1/2}$ is likely to be much smaller than the true half-life for sulfate-oxygen exchange, because of the relatively short timescale of this experiment. This result engenders confidence in low temperature laboratory procedures when analyzing $\delta^{18}O_{\text{SO}_4}$ in low pH solutions.

**References**


![Fig. 5. Extrapolation of our lower bound on the magnitude of oxygen isotope exchange after 390 days, in order to estimate the half-life of exchange at pH 1 for both the 28mM and the 11mM experiments, using Equation (2) from Chiba and Sakai, (1985).](image)


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