Sulfide oxidation affects the preservation of sulfur isotope signals

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INTRODUCTION

Evidence for oxygen production in the oceans dates from 2.8 b.y. ago (Farquhar et al., 2004). This temporal offset raises questions about the importance of sulfate reduction and sulfide oxidation. These data demonstrate that small apparent sulfur isotope fractionations (\(\Delta^{34}S_{\text{Sulfate-AVS}} = 4.2‰ \pm 1.5‰; \text{AVS} = \text{acid volatile sulfides}\)) can be caused by dynamic sulfate cycling at millimolar sulfate concentrations. This is in contrast to current interpretations of the isotopic record and indicates that small fractionations do not necessarily indicate very low sulfate or oxygen.

METHODOLOGY

All samples were preserved using standard procedures (see references below, and further details in the GSA Data Repository†). The concentrations of sulfur species \([\Sigma S(-II), S^{2-}, S_{\text{O}_2}^{3-}, S_{\text{O}_3}^{2-}, SO_{3}^{2-}, SO_{4}^{2-}]\) were determined using established analytical procedures (see the Data Repository).

\[ \Delta^{34}S = \delta^{34}S_{\text{sulfate, surface water}} - \delta^{34}S_{\text{pyrite, sedimentary}} \]

ARCHAEOLOGICAL SEDIMENTARY ROCKS

Archean sedimentary rocks generally have lower \(\Delta^{34}S\) values than sedimentary rocks from later periods in Earth’s history (cf. Havig et al., 2017). One explanation for this observation is that seawater sulfate concentrations and atmospheric \(O_2\) during the Archean were low. At low sulfate concentrations, the magnitude of the apparent fractionation imparted during MSR may be suppressed due to physiological effects.

\[ \delta^{34}S = (\delta R_{\text{sample}}/\delta R_{\text{VCDT}} - 1) \times 1000, \]

where \(\delta R = \delta^{34}S/\delta^{34}S (x = 3 \text{ or } 4)\).

†GSA Data Repository item 2019266, methods and model description and equations, is available online at http://www.geosociety.org/datarepository/2019/, or on request from editing@geosociety.org.

CITATION: Findlay, A.J., et al., 2019, Sulfide oxidation affects the preservation of sulfur isotope signals: Geology, v. 47, p. 739–743, https://doi.org/10.1130/G46153.1
The minor isotope composition is presented using $\Delta^{33}S$ notation, which describes the deviation of $\delta^{33}S$ from a reference fractionation line (Farquhar et al., 2003):

$$\Delta^{33}S = \delta^{33}S - 1000 \times [1 + \delta^{33}S/1000 \times ^{33}S/^{32}S - 1].$$  \hspace{1cm} (3)

Detailed descriptions of the sampling, sample preservation, and analysis are provided in the Data Repository.

**BIOGEOCHEMICAL CYCLING IN AHA RESERVOIR**

Aha Reservoir is a seasonally stratified lake located in southern China (106°37'W, 26°34'N; Item DR1 in the Data Repository; Fig. 1). The 24-m-deep water column was stratified at the time of sampling (10–12 August 2016), with dissolved O$_2$ depleted by 6 m depth and sulfide undetectable to 22 m depth (Fig. 2A). Total Mn concentrations were as much as 22 µM, total Fe concentrations were <2 µM, and SO$_4^{2-}$ concentrations were as much as 22 µM, total organic carbon content higher than reduced Mn. MnS is rarely formed, thus Mn$^{2+}$ is a key factor in Fe and Mn toward sulfide. Both Mn and Fe oxides react with sulfide to form divalent metal ions and S$^2-$:

$$\text{MnO}_2 + \text{HS}^- + 3\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{S}^{0} + 2\text{H}_2\text{O},$$  \hspace{1cm} (4)

$$2\text{Fe(O)}\text{OH} + \text{HS}^- + 5\text{H}^+ \rightarrow 2\text{Fe}^{2+} + \text{S}^{0} + 4\text{H}_2\text{O},$$  \hspace{1cm} (5)

yet there are two key differences that led to the preferential retention of Fe in the sediment. First, the reaction between sulfide and MnO$_2$ is approximately four times faster than the reaction with Fe(O)OH (Yao and Millero, 1993, 1996). Second, Fe$^{3+}$ interacts differently with sulfide than reduced Mn. MnS is rarely formed, thus Mn$^{2+}$ diffuses from the sediment into the water column. In contrast, FeS forms readily at circum-neutral pH, thereby trapping Fe in the solid phase within the sediments and leading to the observed geochemical differences between the water column and sediments (Fig. 2; Fig. DR2). The effect of these different geochemical settings is that sulfur cycling and isotope dynamics in the water column and sediments are controlled by different processes.

**DECOUPLING BETWEEN SULFUR ISOTOPE COMPOSITION IN THE WATER COLUMN AND IN THE SEDIMENT**

The isotopic composition of sulfate above 7 m depth was similar to the isotopic composition of sulfate in rainwater (Fig. 2B; $\delta^{34}S_{\text{rainwater}} = -7\%e$; Song et al., 2011). The constant concentrations and $\delta^{33}S$ value of $-10.5\%e \pm 2.1\%e$ between 7 and 20 m water depth are consistent with coal-derived sulfate, the main source of sulfate to the lake ($\delta^{33}S_{\text{coal}} = -12\%e$; Song et al., 2011). An increase in $\delta^{34}S_{\text{sulfate}}$ and the presence of sulfate below 22 m depth indicates that microbial sulfate reduction was active within the water column. This activity results in $\delta^{34}S_{\text{sulfate}} - \delta^{34}S_{\text{sulfate-sediment}}$ from 17%e to 30%e and $\Delta^{34}S_{\text{sulfate-sediment}}$ of $-0.04\%e$ to $-0.09\%e$, within the range of fractionations produced by pure cultures of sulfate-reducing microorganisms.

Sulfate concentrations in the surface sediment pore water (0–4 cm, Fig. 2C) were higher than in the lake water column, despite constant chloride concentrations that are consistent with water column values (Fig. DR3). This indicates that sulfate oxidation in the upper sediment exceeds sulfate reduction and that non-steady-state conditions with high seasonal variability persist in the surface sediments. We suggest that Fe(III) (hydr)oxides are formed in the surface sediment during the winter, when the water column is mixed and oxygenated. In the early summer, these high concentrations of reactive iron (hydr)oxides result in reoxidation of sulfide produced by MSR. During the late summer and autumn, sulfate reduction likely prevails over sulfide oxidation. The decrease in sulfate concentrations below 6 cm combined with the high concentrations of reduced sulfur species (Fig. 2C) indicates that MSR is the net process at these depths. SO$_4^{2-}$ concentrations increased notably below 20 cm, concurrent with decreasing amounts of S$^0$, acid volatile sulfides (AVS), and chromium reducible sulfur (CRS), suggesting that extensio oxidative of sulfide also occurs deeper in the sediment.

Sulfide oxidation is reflected in the stable sulfur isotope composition in the sediment (Figs. 2D and 3). In the surface sediment, the observed fractionation between SO$_4^{2-}$ and reduced sulfur falls within the range for MSR; however, the relationship between $\delta^{34}S$ and $\delta^{33}S$ (i.e., the fractionation factor for $^{34}S$ and $^{33}S$ associated with a specific process) is inconsistent with MSR ($\delta^{34}S_{\text{sulfate-AVS}}$ [i.e., $\delta^{34}S_{\text{sulfate}} - \delta^{34}S_{\text{AVS}}$] = 1.5%e$-4.2\%e$, $\Delta^{34}S_{\text{sulfate-AVS}} = 0.03\%e-0.05\%e$), suggesting that the sulfur cycle is not driven solely by sulfate reduction. Furthermore, SO$_4^{2-}$ in the surface sediment ($\delta^{34}S_{\text{AVS}} = -13.7\%e$ to $-18.4\%e$) was isotopically lighter in $^{34}S$ than both bulk water column SO$_4^{2-}$ ($\delta^{34}S_{\text{sulfate}} = -10.5\%e$) and water column SO$_4^{2-}$ affected by MSR ($\delta^{34}S_{\text{AVS}} = 0.58\%e$). Even more intriguing are the positive $\Delta^{34}S_{\text{sulfate-AVS}}$ Values in the surface sediments ($\Delta^{34}S_{\text{sulfate-AVS}} = 0.03\%e-0.05\%e$; Fig. DR4), although models and observations corroborate a negative value for this parameter during MSR (Farquhar et al., 2007; Zerkle et al., 2010; Sim et al., 2011; Johnston et al., 2005b). We are only aware of two previous reports of positive $\Delta^{34}S_{\text{sulfate-AVS}}$ Values. First, positive $\Delta^{34}S_{\text{sulfate-AVS}}$ values were reported during sulfur isotope fractionation by disproportionating microorganisms at higher $\Delta^{34}S_{\text{sulfate-AVS}}$ than observed here (Johnston et al., 2005b). Second, the combination of positive $\Delta^{34}S_{\text{sulfate-AVS}}$ values and low posi-
tive $\delta^{34}$S$_{\text{sulfate-AVS}}$ values was attributed to fast, abiotic sulfur cycling in a hydrothermal pool (Cinder Pool, Yellowstone National Park, Wyoming, USA; Kamyshny et al., 2014).

To explore the possible combination of processes leading to the observed fractionations in the sediments of Aha Reservoir, we used a simple box model based on the metabolic model of Farquhar et al. (2007) that considers the theoretical isotopic fractionation (both $\delta^{34}$S and $\Delta^{33}$S) during different combinations of sulfate reduction (associated with high fractionation), intermediate disproportionation (associated with high fractionation), and sulfate oxidation (associated with low fractionation) in the upper 4 cm of the sediment. These processes connect three different sulfur pools: AVS (total labile sulfide), $\delta^{34}$S (an unspecified sulfur intermediate), and SO$_4^{2-}$. Oxidation of AVS forms $\delta^{34}$S and SO$_4^{2-}$. Sulfate reduction is modeled as a one-step reaction that results in formation of AVS (Fig. DR5).

We applied this model to three sets of biogeochemical processes: (1) AVS oxidation (without sulfate reduction or disproportionation), (2) AVS oxidation followed by disproportionation of $\delta^{34}$S and (3) sulfate reduction and AVS oxidation (Fig. 4). The first two scenarios do not agree with the observed isotopic values (Fig. 4; Item DR3); however, sulfate oxidation combined with sulfate reduction (>50%$\delta^{34}$S) without contribution from disproportionation fully encompass the observed values. $\delta^{34}$S$_{\text{sulfate-AVS}}$ and $\Delta^{33}$S$_{\text{sulfate-AVS}}$ in the surface sediment of Aha Reservoir are therefore consistent with a scenario in which sulfate oxidation plays an important role, along with sulfate reduction. The sulfur cycle in the sediment thus creates an isotopic signature distinct from that formed in the water column.

**IMPLICATIONS FOR THE INTERPRETATION OF STABLE SULFUR ISOTOPES**

In contrast to previous studies, we found that an oxidative sulfur cycle in the sediments of Aha Reservoir reduces the observed difference between the isotopic composition of reduced sulfur in the sediment and both pore water and surface water SO$_4^{2-}$. The prevailing paradigm regarding sulfide oxidation in sediment is that sulfide is chemically oxidized by Fe(III) (hydr)oxides to $\delta^{34}$S, which is then microbially disproportionated, resulting in a characteristically large isotopic difference between sulfide and sulfate (Canfield and Thamdrup, 1994; Böttcher et al., 2001). However, although $\delta^{34}$S disproportionation driven by Fe(III) (hydr)oxides can result in a large apparent isotopic fractionation between sulfide and sulfate, the degree of this apparent fractionation decreases if sulfide oxidation to SO$_4^{2-}$ occurs, for example driven microbially or by MnO$_4^-$ (Böttcher and Thamdrup, 2001). Our results clearly indicate that a broader view of potential sulfide oxidation processes and their isotopic signatures throughout geologic time is necessary.

Paleo-oceanographic interpretations rely upon $\Delta^{33}$S (Equation 1), which compares the isotopic composition of sedimentary sulfate with SO$_4^{2-}$ from surface waters. In modern low-sulfate systems, $\Delta^{34}$S is typically lower than the theoretical $\Delta^{34}$S values was attributed to fast, abiotic sulfur cycling in a hydrothermal pool (Cinder Pool, Yellowstone National Park, Wyoming, USA; Kamyshny et al., 2014).

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so that it is no longer diagnostic for the water cycling in the sediment affects the value of $\delta^{34}S$ in Aha Reservoir cannot be explained using not at steady state and the isotope fractionation ($\Delta^{34}S_{\text{SO}_4}$) is $\sim 1.5$ mM. This is because the system is thus appears to be dependent upon $SO_4^{2-}$ concentrations in Aha Reservoir using $\Delta^{34}S_{\text{SO}_4}$ and $\Delta^{34}S_{\text{AVS}}$ (AVS = acid volatile sulfides). $f_{\text{red}}$ and $f_{\text{ox}}$ are the fraction of sulfate reduced and sulfate oxidized, respectively. Listed values refer to $f_{\text{red}}$. Range of typical values measured in anoxic sediments is outlined by the dotted line (data from Johnston et al. [2008] and Pellerin et al. [2015]). Measured data points are shown in red.

Figure 4. Model results for (1) sulfide oxidation (black area), (2) sulfide oxidation and disproportionation (light gray area), and (3) concurrent sulfide oxidation and disproportionation without disproportionation (dark gray area). $\Delta^{34}S_{\text{SO}_4}$ represents $\delta^{34}S_{\text{SO}_4} - \delta^{34}S_{\text{AVS}}$ (AVS = acid volatile sulfides). $f_{\text{red}}$ and $f_{\text{ox}}$ are the fraction of sulfate reduced and sulfate oxidized, respectively.

**ACKNOWLEDGMENTS**

We acknowledge support from a joint Israeli Science Foundation (ISF)–National Natural Science Foundation of China (NSFC) grant to Kamysnyh (ISF 2214/115) and Guo (NSFC 415614005 and 41625006); a Fulbright Postdoctoral Fellowship, a Kreitman Fellowship, and a Marie Curie European Fellowship (SedSulphOx 746872) to Findlay; and funding from the Danish National Research Foundation (DNRF104) and the European Research Council (294200) (Pellerin). We thank Guangxu Zhu, Zhongyi Zhang, and Jingjing Zhao for help with fieldwork, Nir Ben Eliahu and Hadar Cohen for laboratory assistance, and James Faquhar, William Leavitt, and Bo Barker Jørgensen for comments on the manuscript. We thank the anonymous reviewers of this manuscript for their helpful comments.

**REFERENCES CITED**

Bekker, A., Holland, H.D., Wang, P.-L., Rumble, D., III, Stein, H.J., Hannah, J.L., Coetzee, L.L., and Beukes, N.J., 2004, Dating the rise of atmospheric oxygen: Nature, v. 427, p. 117–120, https://doi.org/10.1038/nature02260.

Bekker, A., Planavsky, N., Krapéž, B., Rasmussen, B., Hofmann, A., Slack, J.F., Rouxel, O.J., and Konhauser, K.O., 2014, Iron formations: Their origins and implications for ancient seawater chemistry, in Mackenzie, F.T., ed., Treatise on Geochemistry (second edition). Volume 9: Sediments, Diagenesis and Sedimentary Rocks: Waltham, Massachusetts, Elsevier Ltd., p. 561–628, https://doi.org/10.1016/B978-0-08-095975-7.00719-1.

Böttcher, M.E., and Thamdrup, B., 2001, Anaerobic sulfate reduction and stable isotope fractionation associated with bacterial sulfur disproportionation in the presence of MnO$_2$: Geochimica et Cosmochimica Acta, v. 65, p. 1573–1581, https://doi.org/10.1016/S0016-7037(00)00622-0.

Böttcher, M.E., Thamdrup, B., and Vennemann, T.W., 2001, Oxygen and sulfur fractionation during anaerobic bacterial disproportionation of elemental sulfur: Geochimica et Cosmochimica Acta, v. 65, p. 1601–1609, https://doi.org/10.1016/S0016-7037(00)00628-1.

Bradley, A.S., Leavitt, W.D., Schmidt, M., Knoll, A.H., Gribits, P.R., and Johnston, D.T., 2016, Patterns of sulfur isotope fractionation during microbial sulfate reduction: Geobiology, v. 14, p. 91–101, https://doi.org/10.1111/gbi.12149.

Canfield, D.E., and Thamdrup, B., 1994, The production of $^{34}$S-depleted sulphide during bacterial disproportionation of elemental sulfur: Science, v. 266, p. 1973–1975, https://doi.org/10.1126/science.11540246.

Crowe, S.A., et al., 2014, Sulfate was a trace constituent of Archean seawater: Science, v. 346, p. 735–739, https://doi.org/10.1126/science.1258966.

Faquhar, J., and Wing, B.A., 2003, Multiple sulfur isotopes and the evolution of the atmosphere: Earth and Planetary Science Letters, v. 213, p. 1–13, https://doi.org/10.1016/S0012-821X(03)00296-6.

Farquhar, J., Johnston, D.T., Wing, B.A., Habicht, K.S., Canfield, D.E., Airieau, S., and Thiemens, M.H., 2003, Multiple sulfur isotopic interpretations of biogenetic pathways: Implications for biological signatures in the sulfur isotope record: Geobiology, v. 1, p. 27–36, https://doi.org/10.1046/j.1472-4669.2003.00077.x.

Farquhar, J., Johnston, D.T., and Wing, B.A., 2007, Implications of conservation of mass effects on mass-dependent isotope fractionations: Influence of network structure on sulfur isotope phase space of dissipative substitute reduction:

![Diagram](https://example.com/diagram.png)
Geochimica et Cosmochimica Acta, v. 71, p. 5862–5875, https://doi.org/10.1016/j.gca.2007.08.028.

Farquhar, J., Zerkle, A., and Bekker, A., 2011, Geologic constraints on the origin of oxygencic photosynthesis: Photosynthesis Research, v. 107, p. 11–36, https://doi.org/10.1007/s11120-010-9594-0.

Gomes, M.L., and Hurtgen, M.T., 2013, Sulfur isotope systematics of a euxinic, low-sulfate lake: Evaluating the importance of the reservoir effect in modern and ancient oceans: Geology, v. 41, p. 665–666, https://doi.org/10.1130/G34187.1.

Gomes, M.L., and Hurtgen, M.T., 2015, Sulfur isotope fractionation in modern euxinic systems: Implications for paleoenvironmental reconstructions of paired sulfate-sulfide isotope records: Geochimica et Cosmochimica Acta, v. 157, p. 39–55, https://doi.org/10.1016/j.gca.2015.02.031.

Habicht, K.S., Canfield, D.E., and Rethmeier, J., 1998, Sulfate isotope fractionation during bacterial reductive and disproportionation of thiosulfate and sulfite: Geochimica et Cosmochimica Acta, v. 62, p. 2585–2595, https://doi.org/10.1016/S0016-7037(98)00167-7.

Habicht, K.S., Gade, M., Thamdrup, B., Berg, P., and Canfield, D.E., 2002, Calibration of sulfate levels in the Archean ocean: Science, v. 298, p. 2372–2374, https://doi.org/10.1126/science.1078265.

Havig, J.R., Hamilton, T.L., Bachan, A., and Kump, L.R., 2017, Sulfur and carbon isotopic evidence for metabolic pathway evolution and a four-stepped Earth system progression across the Archean and Paleoproterozoic: Earth-Science Reviews, v. 174, p. 1–21, https://doi.org/10.1016/j.earscirev.2017.06.014.

Johnston, D.T., Wing, B.A., Farquhar, J., Kaufman, A.J., Strauss, H., Lyons, T.W., Kah, L.C., and Canfield, D.E., 2005a, Active microbial sulfur disproportionation in the Mesoproterozoic: Science, v. 310, p. 1477–1479, https://doi.org/10.1126/science.1117824.

Johnston, D.T., Farquhar, J., Wing, B.A., Kaufman, A.J., Canfield, D.E., and Habicht, K.S., 2005b, Multiple sulfur isotope fractionations in biological systems: A case study with sulfate reducers and sulfur disproportionators: American Journal of Science, v. 305, p. 645–660, https://doi.org/10.2475/ajs.305.6-8.645.

Johnston, D.T., Farquhar, J., Habicht, K.S., and Canfield, D.E., 2008, Sulfur isotopes and the search for life: Strategies for identifying sulfur metabolisms in the rock record and beyond: Geobiology, v. 6, p. 425–435, https://doi.org/10.1111/j.1472-4669.2008.00171.x.

Kamyshny, A., Jr., Druschel, G., Mansaray, Z.F., and Farquhar, J., 2014, Multiple sulfur isotope fractionations associated with abiotic sulfur transformations in Yellowstone National Park geothermal springs: Geochemical Transactions, v. 15, 7, https://doi.org/10.1186/1467-4866-15-7.

Ono, S., Wing, B., Rumble, D., and Farquhar, J., 2006, High precision analysis of all four stable isotopes of sulfur ($\delta^{34}$S, $\delta^{33}$S, $\delta^{32}$S and $\delta^{36}$S) at nanomole level using a laser fluorination isotope-ratio-monitoring gas chromatography–mass spectrometry: Chemical Geology, v. 225, p. 30–39, https://doi.org/10.1016/j.chemgeo.2005.08.005.

Pellerin, A., Bui, T.H., Rough, M., Mucci, A., Canfield, D.E., and Wing, B.A., 2015, Mass-dependent sulfur isotope fractionation during reoxidative sulfur cycling: A case study from Mangrove Lake, Bermuda: Geochimica et Cosmochimica Acta, v. 149, p. 152–164, https://doi.org/10.1016/j.gca.2014.11.007.

Shen, Y., Knoll, A.H., and Walter, M.R., 2003, Evidence for low sulphate and anoxia in a mid-Proterozoic marine basin: Nature, v. 423, p. 632–635, https://doi.org/10.1038/nature01651.

Sim, M.S., Bosak, T., and Ono, S., 2011, Large sulfur isotope fractionation does not require fractionation: Science, v. 333, p. 74–77, https://doi.org/10.1126/science.1205103.

Song, L., Liu, C., Wang, Z., Teng, Y., Wang, J., Liang, L., and Bai, L., 2011, Seasonal variations in sulfur isotopic composition of dissolved SO$_4^{2-}$ in the Aha Lake, Guiyang and their implications: Chinese Journal of Geochemistry, v. 30, p. 444–452, https://doi.org/10.1007/s11631-011-0530-6.

Yao, W., and Miller, F.J., 1993, The rate of sulfide oxidation by $\delta$MnO$_2$ in seawater: Geochimica et Cosmochimica Acta, v. 57, p. 3359–3365, https://doi.org/10.1016/0016-7037(93)90544-7.

Yao, W., and Miller, F.J., 1996, Oxidation of hydrogen sulfide by hydrous Fe(III) oxides in seawater: Marine Chemistry, v. 52, p. 1–16, https://doi.org/10.1016/0304-4203(95)00072-0.

Zerkle, A.L., Kamyshny, A., Jr., Kump, L.R., Farquhar, J., Oduro, H., and Arthur, M.A., 2010, Sulfur cycling in a stratified euxinic lake with moderately high sulfate: Constraints from quadruple S isotopes: Geochimica et Cosmochimica Acta, v. 74, p. 4953–4970, https://doi.org/10.1016/j.gca.2010.06.015.

Printed in USA