Widespread contamination of carbonate-associated sulfate by present-day secondary atmospheric sulfate: Evidence from triple oxygen isotopes

Yongbo Peng[1], Huiming Bao[2], Lisa M. Pratt[1], Alan J. Kaufman[3], Ganqing Jiang[4], Dustin Boyd[2], Qinxian Wang[2], Chuanming Zhou[5], Xunlai Yuan[5], Shuhai Xiao[6], and Sean Loyd[7]

[1]Department of Geological Sciences, Indiana University, Bloomington, Indiana 47405, USA
[2]Department of Geology & Geophysics, Louisiana State University, Baton Rouge, Louisiana 70803, USA
[3]Department of Geology and Earth System Science Interdisciplinary Center, University of Maryland, College Park, Maryland 20742, USA
[4]Department of Geoscience, University of Nevada, Las Vegas, Nevada 89154, USA
[5]LEPS and LPS, Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, Nanjing, JiangSu 210008, China
[6]Department of Geosciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA
[7]Department of Geological Sciences, California State University, Fullerton, California 92831, USA

ABSTRACT

The isotope composition of seawater sulfate is an important tracer of sulfur, carbon, and oxygen cycles in Earth's deep past. Carbonate-associated sulfate (CAS) extracted by acid digestion is widely used as a proxy for sulfate in paleo-seawater from which the carbonate minerals precipitated. Early and late diagenesis, weathering, and laboratory processing can in some cases compromise original seawater sulfate signals. Here, we report that extracted CAS can also be severely contaminated by recent atmospheric sulfate, especially when the sampled carbonates are from outcrops in arid to semi-arid climates or in heavily polluted regions. Our evidence comes from triple oxygen isotope compositions of sequentially extracted water-leachable sulfate and acid-leachable sulfate from carbonates of diverse ages from northwestern and north-central China and southwestern North America. Independent of the age of the rocks, almost all the water-leachable sulfates and half of the acid-leachable sulfates bear positive ^{17}O anomalies, clearly distinguishable from those of typical seawater sulfate. Because secondary atmospheric sulfate (SAS) is the only source of sulfate known to bear positive ^{17}O anomalies, we conclude that sulfate extracted from carbonate outcrops in these regions has a significant component of SAS. Because SAS generally has a much lower $\delta^{34}S$ value than paleo-seawater sulfate, it could shift the $\delta^{34}S$ of the extracted CAS to lower values and in some cases even lower than that of the co-occurring pyrite, i.e., the "super-heavy pyrite" enigma reported in geological records. Our findings call for a re-evaluation of many published, outcrop-based CAS data and conclusions.

INTRODUCTION

As a major anion in seawater, sulfate plays a central role in biogeochemical processes that impact Earth's surface chemistry and climate. Sulfur and oxygen isotopic compositions of marine sulfate are important geochemical proxies for reconstructing past Earth system processes. Although sulfate-bearing evaporite deposits are viable proxy reservoirs, these deposits are commonly discontinuous, subject to post-depositional alteration and/or fluid migration, and poorly constrained chronologically (Bottrell and Newton, 2006). Carbonate-associated sulfate (CAS), commonly referred as the structurally substituted sulfate in carbonate rocks (Pingitore et al., 1995; Takano, 1985), is readily available and widely used for retrieving the original sulfate in ancient water bodies at the time of carbonate precipitation. In the laboratory, CAS is extracted by acid digestion of carbonate rock powder after water leaching treatment. In light of growing interest and the wide use of CAS (Bottrell and Newton, 2006; Wotte et al., 2012, and references therein; over 130 journal papers as of December 2013), the community has made meticulous efforts in two major fronts to evaluate the nature of extracted sulfate from ancient carbonate rocks: laboratory procedures (Marenco et al., 2008) and diagenetic processes (Gill et al., 2008). Laboratory experiments show that new sulfate can be produced due to the release and subsequent oxidation of small pyrite grains within carbonate rocks (Marenco et al., 2008). Some suggest that sulfate generation from the oxidation of disseminated pyrite grains in the laboratory can be minimized if the procedures are conducted in an oxygen-free condition (Marenco et al., 2008; Wotte et al., 2012), but particulate oxidants contained within the rock may pose additional complications (Mazumdar et al., 2008). Early diagenetic bacterial sulfate reduction could have some effect on the original isotope composition of sulfate depending on pore-water sulfate concentration and sulfate reduction rate, yet site-specific studies suggest that primary signals may survive this subsequent diagenesis (Lyons et al., 2004). The issue of later diagenetic overprinting or alteration of sulfate isotope composition has been raised (Gill et al., 2008) but needs to be further investigated.

Here, we address another entirely overlooked issue with CAS proxy potential, the contamination of extracted CAS by recent atmospheric sulfate. We discovered this issue when analyzing the triple oxygen isotope compositions of CAS extracted from outcrop carbonate samples. The extracted CAS exhibits non–mass-dependent ^{17}O enrichments, i.e., its $\Delta^{17}O$ values are distinctly more positive than the –0.10‰ to –0.20‰ typical range of seawater sulfate values (Bao et al., 2008; Peng et al., 2011). The only known sulfate with a positive $\Delta^{17}O$ value is secondary atmospheric sulfate (SAS) generated through SO_2 oxidation in the atmosphere (Savarino et al., 2000). Thus, we hypothesize that carbonate outcrops that have been exposed for long periods of time or subjected to heavy anthropogenic SAS deposition may contain a substantial amount of SAS in their extracted CAS. If it is true, then SAS contamination would throw many reported CAS values into question. To test the hypothesis, we targeted carbonate outcrop rocks from diverse locations and of wide-ranging geological ages in northwestern and north-central China, southwestern United States, and northwestern Mexico. We measured the concentration of water-leachable and acid-leachable sulfates as well as the corresponding $\delta^{34}S$, $\delta^{18}O$, and $\Delta^{17}O$. Our data unambiguously demonstrate that extracted CAS is widely contaminated by present-day SAS, regardless of the age of rocks, particularly where the carbonate rocks crop out in arid to semi-arid or heavily polluted regions.

MATERIAL AND METHODS

Sixty (60) carbonate outcrop samples were collected by us from arid regions in northwestern China (AFT, AFQ, WS, and Delta series), the southwestern United States (WC and AH series), and northwestern Mexico (CRCP series). In addition, samples were also collected from north-central China (YB12 series) that were exposed in semi-arid, sub-humid regions and regions heavily polluted from combustion of sulfur-

rich coals. The geological ages of the samples range from Mesoproterozoic to Paleozoic (Table DR1 in the GSA Data Repository[1]). Sulfate in carbonate was first extracted by 10% NaCl solutions five times with different leaching durations, followed by a 3.5% HCl solution, which resulted in four water-leachable sulfate samples and one acid-leachable sulfate sample. Note that no sulfate was present in filtered solutions after the fifth leaching for all samples. The detailed method for the extraction and measurement of sulfate sulfur and oxygen isotope compositions is described in the Data Repository.

RESULTS

Concentrations of water-leachable sulfate ranged from 0 ppm to 837 ppm, and notably decreased with consecutive treatments (Fig. 1D; Table DR2). The $\Delta^{17}O$ values of water-leachable sulfate samples (n = 48) ranged from –0.11‰ to +1.41‰, with only four having slightly negative $\Delta^{17}O$ values (Table DR2). Water leachates from the first 24 h had consistently positive ^{17}O anomalies ($\Delta^{17}O$ value up to +1.41‰) (Fig. 1A). Concentrations of acid-leachable sulfate ranged from 0 ppm to 334 ppm (Table DR2). The $\Delta^{17}O$ values of acid-leachable sulfate samples (n = 50) ranged from –0.36‰ to +0.68‰; 28 of these samples exhibited positive $\Delta^{17}O$ values (Tables DR1 and DR2).

The $\delta^{34}S$ of water-leachable sulfates (n = 67) ranged from +5.0‰ to +33.8‰ (Table DR2). The $\delta^{34}S$ of acid-leachable sulfates (n = 52) and chromium reduction sulfur (CRS) (n = 30) ranged from +8.1‰ to +35.6‰ and –0.9 to +39.4‰, respectively; in 16 of the samples, $\delta^{34}S$ values were lower than those of the corresponding CRS (Fig. 1C; Tables DR1 and DR2). The concentrations of CRS ranged from 0 ppm to 56 ppm (Table DR2).

The $\delta^{18}O$ values of water-leachable sulfates (n = 66) and acid-leachable sulfates (n = 51) ranged from +1.4‰ to +11.5‰ and +3.9 – +19.5‰, respectively (Table DR2). The $\delta^{18}O$ values of acid-leachable sulfates are always higher than those of the corresponding water-leachable sulfates (Fig. 1B).

The $\Delta^{17}O$ values of water-leachable sulfates and acid-leachable sulfates generally decrease, whereas the $\delta^{18}O$ and $\delta^{34}S$ values increase in succession with consecutive leaching steps, except for samples AFT-X-313, AFT-X-395, and WS-64 (Figs. 1A–1C). There are no significant correlations among $\Delta^{17}O$, $\delta^{34}S$, and $\delta^{18}O$ of sulfate samples (Fig. DR2 in the Data Repository). However, lower $\Delta^{17}O$ values are generally associated with higher $\delta^{34}S$ and $\delta^{18}O$ values (Figs. DR2A and DR2C).

DISCUSSION

Almost all water-leachable sulfates in this study exhibit positive ^{17}O anomalies (up to +1.40‰) regardless of the age of the rocks (Fig. 1A). This observation supports the view that SAS is a significant part of the water-leachable sulfate. It is known that only SAS has non–mass-dependent ^{17}O enrichment or positive $\Delta^{17}O$ values; sulfate from pyrite oxidation and seawater sulfate have $\Delta^{17}O$ values lower than –0.05‰ (Bao et al., 2008, 2009; Peng et al., 2011, 2013). Atmospheric O_3, in both the troposphere and the stratosphere, carries large positive $\Delta^{17}O$ signatures (Johnston and Thiemens, 1997). The $\Delta^{17}O$ signature of O_3 is transferred to SAS during the oxidation of sulfur gases such as biogenic sulfur gases, volcanic sulfur gases, and anthropogenic sulfur emission by O_3 and H_2O_2 in the atmosphere (Savarino et al., 2000). Recent sampling campaigns (Jenkins and Bao, 2006; Li et al., 2013) and modeling (Sofen et al., 2011) show that the average $\Delta^{17}O$ value for SAS in mid-latitudes of the Northern Hemisphere is ~+0.7‰. This suggests that up to 100% of the water-extracted sulfate
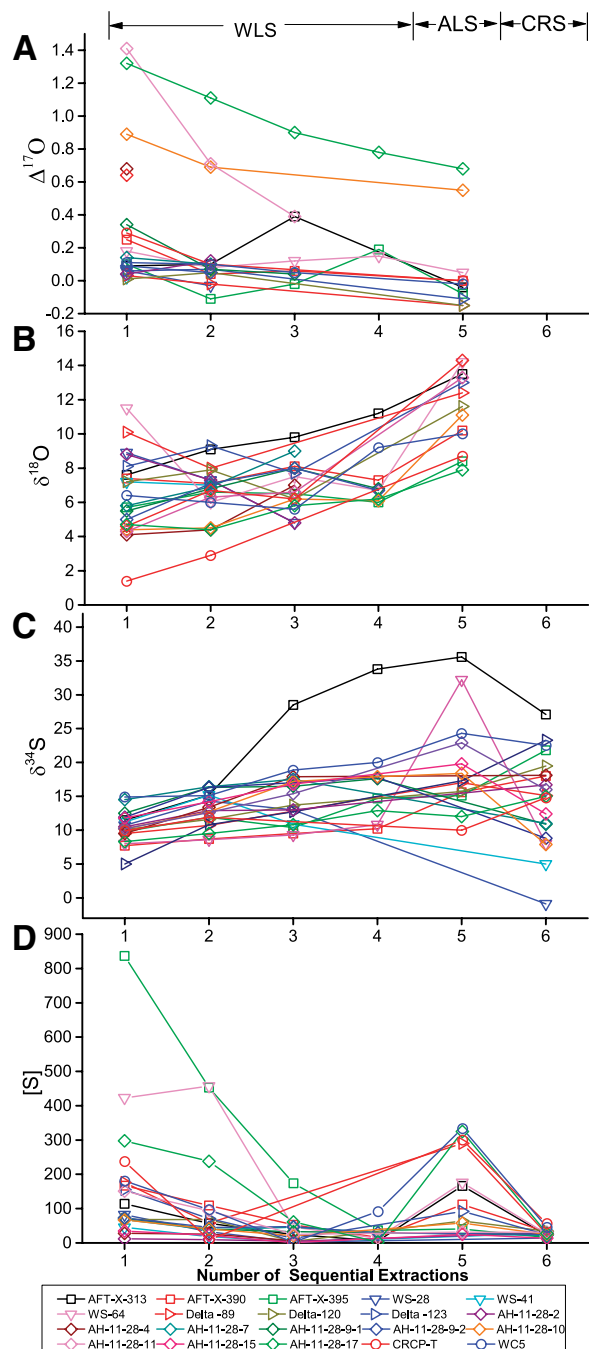
Figure 1. $\Delta^{17}O$, $\delta^{18}O$, $\delta^{34}S$, and sulfur (SO_4 or Ag_2S) concentration ([S], in ppm) values in a series of sequential extractions. On the horizontal axis, 1, 2, 3, and 4 are water-leachable sulfate (WLS) extracted using 10% NaCl; 5 is acid-leachable sulfate (ALS) extracted using 3.5% HCl following the water extractions; 6 is chromium reduction sulfur (CRS) extracted as Ag_2S from residues after acid leaching.

in some of our samples (e.g., samples AH-11-28-4, AH-11-28-11, AH-11-28-15, AH-11-28-17) could have been derived from SAS. Half of the acid-leachable sulfate samples in this study possess distinctively positive $\Delta^{17}O$ values even after multiple water leaches (Tables DR1 and DR2) suggesting that acid-leachable sulfate still contains a fraction of SAS, some with more than 50% (e.g., samples YB12 and AH-11-28-17; Fig. DR1). The generally decreasing $\Delta^{17}O$ values of water-leachable sulfates with consecutive treatments suggest that water leaching indeed helped remove SAS, but some samples do not follow the pattern (Fig. 1A; e.g., samples AFT-X-

313, AFT-X-395, and WS-64). Apparently, SAS distribution in powdered host rock is not homogenous, and the pre-leaching procedure advocated by many laboratories does not necessarily eliminate the SAS component in acid-leachable sulfate.

It is known that SAS can accumulate and be incorporated into pedogenic carbonates in arid to semi-arid environments (Howell and Bao, 2006). In arid or semi-arid regions, SAS can accumulate on outer surfaces and micro-cracks of carbonate outcrops due to limited leaching by meteoric water or lack of recycling by sulfate-reducing microbes. To some extent, the original carbonate could be dissolved by meteoric water during rainy seasons and secondary carbonate formed through evaporation during dry seasons. Such processes would be accentuated in arid regions where evaporation exceeds precipitation. Meteoric water–carried SAS could be locked in secondary carbonate deposits along micro-cracks in outcrops or transferred to the subsurface via groundwater. In this case, it would be difficult to separate secondary carbonates from original carbonates by either physical or chemical methods. This explains the distinctively positive $\Delta^{17}O$ values in half of the acid-leachable sulfate samples even after multiple water leaches (Tables DR1 and DR2). Samples in series YB12 with $\Delta^{17}O$ values up to +0.36‰ (Table DR1) are from north-central China where the climate is semi-arid and sub-humid. These samples are less likely to have been impacted by atmospheric sulfate accumulation on outcrops due to relatively high precipitation. We suspect that the smoggy air resulting from the combustion of sulfur-rich coals in the region (Chan and Yao, 2008) is to blame. Since the industrial revolution, global sulfur emissions into the atmosphere have increased substantially, and today, on a global basis, anthropogenic sulfur emission is double that from natural sources (Smith et al., 2001). Therefore, the accumulation of SAS on continental rock and soil materials and potential contamination of extracted CAS by SAS are expected to be widespread.

The SAS contamination can be further evaluated by the corresponding $\delta^{34}S$ and $\delta^{18}O$ values. The average $\delta^{34}S$ values of SAS are ~1.1‰ along the U.S. Gulf Coast at Baton Rouge, Louisiana (Jenkins and Bao, 2006), and 4.5‰ at Wuhan in central China (Li et al., 2013). These values are significantly lower than the $\delta^{34}S$ values (10‰ to 35‰) of seawater sulfate throughout the geologic time (Claypool et al., 1980). Therefore, SAS contamination can result in $\delta^{34}S$ values lower than those of the true paleo-seawater sulfate, thereby skewing the inferred seawater sulfate reservoir sizes. In extreme cases, the mixture of SAS with CAS could result in sulfate $\delta^{34}S$ values lower than those of the co-occurring pyrite in a carbonate rock. This phenomenon is well demonstrated in our data pairs (Fig. 1C; samples Delta-120 and Delta-123, AFT-X-390 and AFT-X-395, CRCP-T, and the AFQ series). The $\delta^{18}O$ value of modern SAS has a wide range from –0.7‰ to +29‰ (Jenkins and Bao, 2006), which is controlled by the oxygen isotope composition of local cloud water and oxidants such as OH radicals, O_3, and/or H_2O_2. The average $\delta^{18}O$ value of present SAS is ~+13‰ in most continental interiors, mid-latitude sites (Jenkins and Bao, 2006; Li et al., 2013). The $\delta^{18}O$ value of marine sulfate throughout the geological record ranges from +10‰ to +20‰ (Claypool et al., 1980). Although the difference in $\delta^{18}O$ between SAS and seawater CAS is smaller than the differences in $\delta^{34}S$ and $\Delta^{17}O$, it is expected that SAS-contaminated CAS would have lower $\delta^{18}O$ values. This is consistent with our data, in which $\delta^{18}O$ values increase with consecutive leaching steps and all acid-leachable sulfates have higher $\delta^{18}O$ values than the corresponding water-leachable sulfate (Fig. 1B). However, the $\delta^{18}O$ values of most samples are lower than +13‰, implying that other processes such as local meteoric water and/or burial diagenetic alteration may have systematically shifted $\delta^{18}O$ to lower values.

During microbial sulfate reduction, organisms preferentially utilize ^{32}S during the production of sulfide, generally leaving the residual sulfate reservoir enriched in ^{34}S ($\Delta^{34}S_{sulfate–sulfide} > 0$). $\Delta^{34}S_{sulfate–sulfide}$, therefore, should always be positive with its magnitude sensitive to sulfate concentration. This concept has been the cornerstone of a widely used approach in reconstructing sulfate concentrations and in inferring the redox conditions of the paleo-oceans (Canfield and Teske, 1996). One of the most puzzling phenomena reported by many researchers, however, is that the $\delta^{34}S$ of pyrite is often higher than that of the coeval CAS, yielding negative $\Delta^{34}S_{sulfate–sulfide}$ values, i.e., the "super-heavy pyrite" enigma (Habicht et al., 2002; Li et al., 2010; Loyd et al., 2012; McFadden et al., 2008; Reuschel et al., 2012; Ries et al., 2009; Shen et al., 2008, 2010, 2011). Shen et al. (2008) proposed that negative $\Delta^{34}S_{sulfate–sulfide}$ is the result of ocean stratification induced by deglaciation. In their model, pyrite was formed from sulfate reservoirs with enriched ^{34}S via closed-system Rayleigh distillation in anoxic bottom waters, while the CAS was formed in oxic surface waters with lower $\delta^{34}S$ due to post-glacial influx of sulfate from continental weathering. However, we found that half of the acid-leachable sulfates extracted from the Neoproterozoic Tereeken cap carbonates in the eastern Tianshan region, Xinjiang (northwestern China), where Shen et al. (2008) reported the negative $\Delta^{34}S_{sulfate–sulfide}$ values, possess positive $\Delta^{17}O$ values (sample series Delta and AFQ). More importantly, there is a strong negative correlation between $\Delta^{17}O$ and $\delta^{34}S$ of these acid-leachable sulfates, i.e., lower $\Delta^{17}O$ values are generally associated with higher $\delta^{34}S$ (Fig. DR2C). Thus, a reasonable reinterpretation is that the Xinjiang Neoproterozoic outcrops have undergone significant SAS contamination. The "super-heavy pyrite" problem has also been encountered in the Ediacaran Nama Group of southern Namibia (Ries et al., 2009). Ries et al. (2009) reported that disseminated pyrite was consistently enriched in ^{34}S (+20.5‰ to +80.2‰) relative to the coeval seawater sulfate preserved as CAS. They proposed a closed-system Rayleigh distillation model to explain the "super-heavy pyrite" phenomenon. Essentially, the ^{34}S enrichment in sulfides was achieved through aerobic reoxidation of sedimentary sulfides coupled with minimal sulfur isotope fractionation during anaerobic bacterial sulfate reduction under low seawater sulfate concentration. As Ferrini et al. (2010) pointed out, such a simplified, closed-system Rayleigh distillation model is not representative of the sedimentary sulfide reservoir and cannot explain the wide range of $\delta^{34}S_{pyrite}$ values, especially those exceeding +50‰. The samples of Ries et al. (2009) were collected from the Kalahari Desert in southern Namibia, and large quantities of rock powders (~300 g) were leached only once with pure water for 24 h before acid digestion for CAS extraction. Our data show that even after a 24 h water leaching by NaCl solution, extracted CAS still has a significant isotope signature overprinted by SAS. Therefore, we have good reason to speculate that the outcrops of the Nama Group are also contaminated by SAS, resulting in negative $\Delta^{34}S_{sulfate–sulfide}$ values. In many cases, SAS contamination may not have been enough to result in negative $\Delta^{34}S_{sulfate–sulfide}$ values or an apparent "super-heavy sulfide" phenomenon, but may have significantly lowered the $\delta^{34}S$ values of extracted CAS and the $\Delta^{34}S_{sulfate–sulfide}$ values. Our finding makes the $\Delta^{17}O$ measurement of extracted CAS essential in re-evaluating the nature of many of the published CAS data and in conducting future CAS-based studies.

CONCLUSIONS

Triple oxygen isotope analyses of sequentially extracted water-leachable sulfate and acid-leachable sulfate from carbonate outcrops of diverse ages show that extracted sulfates in arid to semi-arid or heavily polluted regions have a large component of recent SAS. The acid-leachable sulfate, the fraction that is widely regarded as the proxy for ancient water-body sulfate during carbonate precipitation, can be composed of more than 50% SAS. Depending on the SAS content and the isotopic difference between SAS and original CAS, SAS may significantly alter the isotopic composition of extracted CAS. The lower SAS $\delta^{34}S$ values will result in smaller $\Delta^{34}S_{sulfate–sulfide}$ and thus smaller inferred sulfate reservoir size than the actual one in the geological past. In some cases the $\delta^{34}S$ of SAS-contaminated CAS can be even lower than that of the co-occurring pyrite, thus offering an unfortunate but reasonable explanation to the "super-heavy sulfide" problem encountered in many previous CAS studies. Our finding

demonstrates that SAS contamination can be serious in arid or heavily polluted regions if the CAS is extracted from outcrop samples. We therefore suggest that some of the published CAS data and results that fall into these sampling conditions may require re-evaluation. The $\Delta^{17}O$ measurement should be a necessary step in examining the nature of extracted CAS. In addition, this study suggests that paleo-weathering crusts of carbonates may serve as a repository for ancient SAS compositions.

REFERENCES CITED

Bao, H., Lyons, J.R., and Zhou, C., 2008, Triple oxygen isotope evidence for elevated CO_2 levels after a Neoproterozoic glaciation: Nature, v. 453, p. 504–506, doi:10.1038/nature06959.

Bao, H., Fairchild, I.J., Wynn, P.M., and Spoetl, C., 2009, Stretching the envelope of past surface environments: Neoproterozoic glacial lakes from Svalbard: Science, v. 323, p. 119–122, doi:10.1126/science.1165373.

Bottrell, S.H., and Newton, R.J., 2006, Reconstruction of changes in global sulfur cycling from marine sulfate isotopes: Earth-Science Reviews, v. 75, p. 59–83, doi:10.1016/j.earscirev.2005.10.004.

Canfield, D.E., and Teske, A., 1996, Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies: Nature, v. 382, p. 127–132, doi:10.1038/382127a0.

Chan, C.K., and Yao, X., 2008, Air pollution in mega cities in China: Atmospheric Environment, v. 42, p. 1–42, doi:10.1016/j.atmosenv.2007.09.003.

Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., and Zak, I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation: Chemical Geology, v. 28, p. 199–260, doi:10.1016/0009-2541(80)90047-9.

Ferrini, V., Fayek, M., De Vito, C., Mignardi, S., and Pignatti, J., 2010, Extreme sulphur isotope fractionation in the deep Cretaceous biosphere: Journal of the Geological Society, v. 167, p. 1009–1018, doi:10.1144/0016-76492009-161.

Gill, B.C., Lyons, T.W., and Frank, T.D., 2008, Behavior of carbonate-associated sulfate during meteoric diagenesis and implications for the sulfur isotope paleoproxy: Geochimica et Cosmochimica Acta, v. 72, p. 4699–4711, doi:10.1016/j.gca.2008.07.001.

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, doi:10.1126/science.1078265.

Howell, K.J., and Bao, H., 2006, Caliche as a geological repository for atmospheric sulfate: Geophysical Research Letters, v. 33, L13816, doi:10.1029/2006GL026518.

Jenkins, K.A., and Bao, H., 2006, Multiple oxygen and sulfur isotope compositions of atmospheric sulfate in Baton Rouge, LA, USA: Atmospheric Environment, v. 40, p. 4528–4537, doi:10.1016/j.atmosenv.2006.04.010.

Johnston, J.C., and Thiemens, M.H., 1997, The isotopic composition of tropospheric ozone in three environments: Journal of Geophysical Research, v. 102, p. 25,395–25,404, doi:10.1029/97JD02075.

Li, C., Love, G.D., Lyons, T.W., Fike, D.A., Sessions, A.L., and Chu, X.L., 2010, A stratified redox model for the Ediacaran ocean: Science, v. 328, p. 80–83, doi:10.1126/science.1182369.

Li, X., Bao, H., Gan, Y., Zhou, A., and Liu, Y., 2013, Multiple oxygen and sulfur isotope compositions of secondary atmospheric sulfate in a mega-city in central China: Atmospheric Environment, v. 81, p. 591–599, doi:10.1016/j.atmosenv.2013.09.051.

Loyd, S.J., Marenco, P.J., Hagadorn, J.W., Lyons, T.W., Kaufman, A.J., Sour-Tovar, F., and Corsetti, F.A., 2012, Sustained low marine sulfate concentrations from the Neoproterozoic to the Cambrian: Insights from carbonates of northwestern Mexico and eastern California: Earth and Planetary Science Letters, v. 339, p. 79–94, doi:10.1016/j.epsl.2012.05.032.

Lyons, T.W., Walter, L.M., Gellatly, A.M., and Blake, R.E., 2004, Sites of anomalous organic remineralization in the carbonate sediments of South Florida, USA: The sulfur cycle and carbonate-associated sulfate, in Amend, J. P., et al., eds., Sulfur Biogeochemistry: Past and Present: Geological Society of America Special Paper 379, p. 161–176, doi:10.1130/0-8137-2379-5.161.

Marenco, P.J., Corsetti, F.A., Hammond, D.E., Kaufman, A.J., and Bottjer, D.J., 2008, Oxidation of pyrite during extraction of carbonate associated sulfate: Chemical Geology, v. 247, p. 124–132, doi:10.1016/j.chemgeo.2007.10.006.

Mazumdar, A., Goldberg, T., and Strauss, H., 2008, Abiotic oxidation of pyrite by Fe(III) in acidic media and its implications for sulfur isotope measurements of lattice-bound sulfate in sediments: Chemical Geology, v. 253, p. 30–37, doi:10.1016/j.chemgeo.2008.03.014.

McFadden, K.A., Huang, J., Chu, X., Jiang, G., Kaufman, A.J., Zhou, C., Yuan, X., and Xiao, S., 2008, Pulsed oxidation and biological evolution in the Ediacaran Doushantuo Formation: Proceedings of the National Academy of Sciences of the United States of America, v. 105, p. 3197–3202, doi:10.1073/pnas.0708336105.

Peng, Y., Bao, H., Zhou, C., and Yuan, X., 2011, ^{17}O-depleted barite from two Marinoan cap dolostone sections, South China: Earth and Planetary Science Letters, v. 305, p. 21–31, doi:10.1016/j.epsl.2011.02.014.

Peng, Y., Bao, H., Zhou, C., Yuan, X., and Luo, T., 2013, Oxygen isotope composition of meltwater from a Neoproterozoic glaciation in South China: Geology, v. 41, p. 367–370, doi:10.1130/G33830.1.

Pingitore, N.E., Meitzner, G., and Love, K.M., 1995, Identification of sulfate in natural carbonates by x-ray-absorption spectroscopy: Geochimica et Cosmochimica Acta, v. 59, p. 2477–2483, doi:10.1016/0016-7037(95)00142-5.

Reuschel, M., Melezhik, V.A., Whitehouse, M.J., Lepland, A., Fallick, A.E., and Strauss, H., 2012, Isotopic evidence for a sizeable seawater sulfate reservoir at 2.1 Ga: Precambrian Research, v. 192–195, p. 78–88, doi:10.1016/j.precamres.2011.10.013.

Ries, J.B., Fike, D.A., Pratt, L.M., Lyons, T.W., and Grotzinger, J.P., 2009, Superheavy pyrite ($\delta^{34}S_{pyr} > \delta^{34}S_{CAS}$) in the terminal Proterozoic Nama Group, southern Namibia: A consequence of low seawater sulfate at the dawn of animal life: Geology, v. 37, p. 743–746, doi:10.1130/G25775A.1.

Savarino, J., Lee, C.C.W., and Thiemens, M.H., 2000, Laboratory oxygen isotopic study of sulfur (IV) oxidation: Origin of the mass-independent oxygen isotopic anomaly in atmospheric sulfates and sulfate mineral deposits on Earth: Journal of Geophysical Research, v. 105, p. 29,079–29,088, doi:10.1029/2000JD900456.

Shen, B., Xiao, S., Kaufman, A.J., Bao, H., Zhou, C., and Wang, H., 2008, Stratification and mixing of a post-glacial Neoproterozoic ocean: Evidence from carbon and sulfur isotopes in a cap dolostone from northwest China: Earth and Planetary Science Letters, v. 265, p. 209–228, doi:10.1016/j.epsl.2007.10.005.

Shen, B., Xiao, S., Zhou, C., Kaufman, A.J., and Yuan, X., 2010, Carbon and sulfur isotope chemostratigraphy of the Neoproterozoic Quanji Group of the Chaidam Basin, NW China: Basin stratification in the aftermath of an Ediacaran glaciation postdating the Shuram event?: Precambrian Research, v. 177, p. 241–252, doi:10.1016/j.precamres.2009.12.006.

Shen, B., Xiao, S., Bao, H., Kaufman, A.J., Zhou, C., and Yuan, X., 2011, Carbon, sulfur, and oxygen isotope evidence for a strong depth gradient and oceanic oxidation after the Ediacaran Hankalchough glaciation: Geochimica et Cosmochimica Acta, v. 75, p. 1357–1373, doi:10.1016/j.gca.2010.12.015.

Smith, S.J., Pitcher, H., and Wigley, T.M.L., 2001, Global and regional anthropogenic sulfur dioxide emissions: Global and Planetary Change, v. 29, p. 99–119, doi:10.1016/S0921-8181(00)00057-6.

Sofen, E.D., Alexander, B., and Kunasek, S.A., 2011, The impact of anthropogenic emissions on atmospheric sulfate production pathways, oxidants, and ice core $\Delta^{17}O$ (SO_4^{2-}): Atmospheric Chemistry and Physics, v. 11, p. 3565–3578, doi:10.5194/acp-11-3565-2011.

Takano, B., 1985, Geochemical implications of sulfate in sedimentary carbonates: Chemical Geology, v. 49, p. 393–403, doi:10.1016/0009-2541(85)90001-4.

Wotte, T., Shields-Zhou, G.A., and Strauss, H., 2012, Carbonate-associated sulfate: Experimental comparisons of common extraction methods and recommendations toward a standard analytical protocol: Chemical Geology, v. 326, p. 132–144, doi:10.1016/j.chemgeo.2012.07.020.