

## ***Interactive comment on “Reconstruction of secular variation in seawater sulfate concentrations” by T. J. Algeo et al.***

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NOTE: SEE SUPPLEMENTARY DOCUMENT FOR FULLY FORMATTED REVIEW-AND-RESPONSE

Comments by Anonymous Reviewer

Overview

Algeo et al. reconstruct ancient seawater sulfate concentrations using two simplistic yet elegant approaches applied to available data sets spanning back to the late Precambrian. These two approaches include 1) a “rate” method that takes advantage of the rate of sulfate sulfur isotope variability through time and 2) a microbial sulfate reduction (MSR) fractionation method that relates the degree of fractionation to absolute sul-

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fate concentrations. Both stem from previously developed approaches, however here the authors take the next step and apply modified empirical/theoretical relationships to geochemical data preserved in the rock record. I commend the authors’ efforts and broadly agree with the potential utility of their approaches, however important issues deserve detailed discussion.

Response: We thank the reviewer for these positive comments.

General Comments

Rate method. The application of modern S fluxes and associated  $d_{34}S$  values to ancient systems is likely an over-extension and probably produces some of the uncertainty (and some of the unrealistic values) in reconstructed sulfate concentrations. Whereas there are ways to get at output  $d_{34}S$  (through  $d_{34}S_{pyr}$ , for example), it is quite difficult to accurately predict the source  $d_{34}S$ . Indeed, previous authors infer that the sulfur isotope composition of the source flux has differed from modern values quite significantly (e.g., Fike and Grotzinger, 2008). To a first order, it is hard to envision the source  $d_{34}S$  value as invariant over long timescales. Changes in the fractional burial of S as pyrite and sulfate minerals through time (thought to drive much of the marine sulfate  $d_{34}S$  variability) almost requires a change in the source as rocks of differing ages are later weathered on land in different proportions. Ultimately, it would be useful if the authors included model sensitivity analyses to changing source  $d_{34}S$ .

Response: We agree that source flux  $d_{34}S$  has probably varied through time, and that such variation may have influenced the  $d_{34}S$  of seawater sulfate. We also agree that sensitivity analysis might be applied to test the potential influence of the source flux on seawater sulfate  $d_{34}S$ . However, this is beyond the scope of the present study. Our rate method (Equations 2-4) does not depend on source flux  $d_{34}S$ , so there is no need to engage in this exercise.

MSR method. The linear relationship between  $D_{34}S_{sulfate-sulfide}$  from modern aqueous systems is striking and suggests that there is hope in reconstructing ancient sea-

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water sulfate concentrations with this approach. It would be useful if the authors distinguished which data points in Fig. 2 are derived from water column S phases, pore water S phases, solid S phase, etc. It seems somewhat coincidental that aqueous sulfate concentrations near the modern seawater sulfate concentration happen to yield the maximum  $\delta^{34}\text{S}$ , above which fractionations are essentially constant. Might the hypersaline environments explored be unrepresentative due to high ionic strength or some other dissolved constituent that limits isotopic discrimination? In other words, can we be certain based on the current data set that seawater with higher sulfate contents (>29 mM) would not exhibit higher fractionations?

Response: In Figure 2, all sulfate  $\delta^{34}\text{S}$  values used in calculation of  $\text{D}_{34}\text{S}_{\text{sulfate-sulfide}}$  are based on measurements of aqueous sulfate, as stated in the text. For sulfide  $\delta^{34}\text{S}$ , we used four different sulfur phases: pyrite, sediment acid-volatile sulfur (AVS), sediment total reduced sulfur (TRS), and aqueous  $\text{H}_2\text{S}$  (note: this information has been added to the sulfide  $\delta^{34}\text{S}$  column of Table A1). At the reviewer's request, we have constructed a version of Figure 2 that shows the different sulfide phases, and we calculated separate regressions for each phase (Fig. B3—see Supplementary document). The following points should be noted about this figure. First, each of the four phases yields a statistically significant regression ( $r = 0.81\text{--}0.92$ ;  $p(a) < 0.05$ ; see Table B1 below). Second, the four phases have similar regression slopes although slightly variable y-intercepts. For this reason, TRS and AVS yield  $\text{D}_{34}\text{S}_{\text{CAS-PY}}$  values that are, on average, slightly larger for a given  $[\text{SO}_4^{2-}]_{\text{SW}}$  value than pyrite and aqueous  $\text{H}_2\text{S}$ . Third, the four regression lines generally converge at higher  $[\text{SO}_4^{2-}]_{\text{SW}}$ , and the largest differences occur at low  $[\text{SO}_4^{2-}]_{\text{SW}}$ , where data is sparser. Whether there are real differences in the regression relationships among these four sulfide phases is an issue that will require further inquiry—the regression lines in Figure B3 are not statistically different. One could argue in favor of using the pyrite  $\delta^{34}\text{S}$  data alone, which would result in a small change in the regression relationship used to calculate paleoseawater  $[\text{SO}_4^{2-}]_{\text{SW}}$  values. We opted to use a larger sulfide  $\delta^{34}\text{S}$  dataset, especially one containing more data at low  $[\text{SO}_4^{2-}]_{\text{SW}}$ , in order to generate a stable

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relationship over a wider range of  $[\text{SO}_4^{2-}]_{\text{SW}}$  values.

Table B1. Regression statistics for reduced sulfur phases used in calculation of  $\text{D}_{34}\text{S}_{\text{sulfate-sulfide}}$

Sulfur phase	n	r	m	b	p(a)
Pyrite	48	0.92	0.46	-0.35	<0.01
Sediment AVS	6	0.81	0.42	-0.06	<0.05
Sediment TRS	11	0.89	0.33	0.20	<0.01
Aqueous $\text{H}_2\text{S}$	16	0.84	0.44	-0.20	<0.01

The second part of the reviewer's comment concerns the reasons why the hypersaline environments in our dataset (Table A1) do not conform to the 'MSR trend', i.e., the regression relationship for environments with salinities of <40 psu (= practical salinity units) (Fig. 2). Whether MSR fractionations reach a maximum at the salinity of modern seawater (35 psu) and then remain essentially unchanged at higher salinities is uncertain. Our dataset certainly suggests that this might be the case, but the number of examples of hypersaline environments ( $n = 6$ ) is too small to reach firm conclusions. Because we are not even certain that the MSR fractionation trend changes above 35 psu, it would not be useful to speculate on what factors might make this small set of hypersaline environments "unrepresentative". We simply raise the possibility of a change in the MSR fractionation trend at salinities >40 psu with the intention of encouraging further research into this issue.

Action: We have added a brief mention of these issues to the text of the manuscript and an extended discussion as Appendix B of the revised manuscript. We did not insert this material into the text as it is of tangential importance to the development of the main theme of our paper.

Reliability of CAS and pyrite  $\delta^{34}\text{S}$  as accurate, whole-ocean proxies. The modern global open ocean  $\delta^{34}\text{S}$  value is derived from barite records (Paytan et al., 1998; 2004). However much of the ancient sulfate record, particularly the early Paleozoic and Neoproterozoic, is derived from carbonate platform CAS. It has yet to be demonstrated that these two records agree. Early work by Burdett et al. (1989) suggests

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that foraminifera CAS records agree with the Neogene barite record, but they analyzed pelagic planktonic foraminifera more closely associated with open ocean environments and not margin platforms. Lyons et al. (2004) show that very recent carbonate platform muds conform to the modern marine  $\delta^{34}\text{S}$  sulfate record, but these do not extend very far back in time. The authors do a good job critically choosing specific sulfur phases (e.g., shallow pyrite) to construct the MSR method equations. Whereas, modern environments provide the opportunity to be picky, ancient environments can only be probed through rock-bound proxies. Pyrite records are particularly sensitive in this regard, how can we be confident that the rock-bound pyrite is in fact shallow and therefore that  $\delta^{34}\text{S}$ (CAS-pyr) accurately reflects cogenetic  $\delta^{34}\text{S}$ sulfate-sulfide?

Response: First, fractionation of S isotopes during precipitation of sulfate evaporites and incorporation of CAS in carbonates has been shown to be small ( $<1\%$ ) (Schidlowski et al., 1977; Burdett et al., 1989; Kampschulte et al., 2001). The Phanerozoic records of CAS  $\delta^{34}\text{S}$  and evaporite  $\delta^{34}\text{S}$  were compared by Kampschulte and Strauss (2004), who found considerable overlap and no systematic bias toward higher values in one or the other dataset.

Second, we agree that the type of pyrite present in ancient sediments needs to be evaluated in order to assess whether it is syngenetic/early diagenetic and, thus, useful for calculating paleoseawater sulfate concentrations. There are well-established petrographic and geochemical techniques for this type of evaluation (e.g., Wilkin et al., 1996; Lyons and Severmann, 2006). This is an issue that each researcher making use of the methods developed in this study for estimation of paleoseawater sulfate concentrations will need to consider in regard to his/her specific study units.

Action: We have added a brief synthesis of these points to the manuscript.

Heterogeneous marine  $\delta^{34}\text{S}$  records. Unfortunately,  $\delta^{34}\text{S}$  records of most time intervals have only been developed from one or two locations. The multiple records from the Neoproterozoic indicate both lateral (horizontal; Loyd et al., 2012; 2013) and strat-

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ified type (vertical; Li et al., 2010) variability probably stemming from overall low, but likewise variable, marine sulfate concentrations (as the authors mention, P13209-10; Ins 34-30, 1-7). Similar heterogeneity may occur during other time intervals as well. In the face of potentially large heterogeneity, how reflective is a single succession of the global ocean? Furthermore, how can we be confident that intervals with data from only one or two successions can be used to accurately constrain a global signal?

Response: We agree that spatial heterogeneity in seawater sulfate concentrations may become pronounced at low average concentrations, as during the Neoproterozoic. This does not invalidate an estimate of seawater sulfate concentrations for a particular time and locale. It does mean that a single estimate will not suffice to characterize seawater globally, and that a number of estimates from widely separated locales would be desirable to characterize the range of variation in seawater sulfate concentrations at a given time. These considerations in no way invalidate our methodology for estimating seawater sulfate concentrations.

Action: We have added a brief synthesis of these points to the manuscript.

Specific Comments

P 13191, Ins 5-7: It seems difficult to rationalize such a broad statement. Local source  $\delta^{34}\text{S}$  values and fluxes will be particularly influential, especially if low oceanic  $[\text{SO}_4^{2-}]$  lends to short residence times.

Response: Whether such a statement is overly broad or not depends on one's outlook—there is no inherently correct view on such a matter. We agree with the reviewer that local variations in sulfate concentration and isotopic composition will become more pronounced at low average concentrations. The significance of this point was considered in the preceding response.

P 13191, Ins 16-20: Perhaps, at least this is generally assumed but not adequately substantiated. Some authors interpret variable source  $\delta^{34}\text{S}$  during specific time intervals

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(Fike and Grotzinger, 2008).

Response: We agree that this inference has not been fully substantiated. However, in terms of controls on seawater sulfate  $\delta^{34}\text{S}$ , there is a lot more evidence to support variable sulfur burial fluxes rather than variable source  $\delta^{34}\text{S}$  as the dominant source (e.g., Kampschulte and Strauss, 2004; Bottrell and Newton, 2006; Halevy et al., 2012; Song et al., 2014).

P 13191, In 22: "Cogenetic" formation is difficult to prove, however the authors do attempt to get as close to cogenetic as possible through targeted data mining.

Response: We agree on both points.

P 13192, Ins 8-10: The direction of isotopic change indicates which term goes to zero. A negative change indicates pyrite burial going to zero, a positive change indicates the sulfate source going to zero. This deserves an explicit mention.

Response: We are discussing the source flux specifically. We have changed the wording to reflect that the source flux is specifically meant here.

General Note: What about stratified water columns? Since the proxy records are based on pyrite are they more strongly influenced by bottom water conditions?

Response: In marine systems, stratified water columns will have no effect on dissolved sulfate because its residence time is sufficiently long that sulfate will be uniformly distributed vertically. With regard to pyrite, syngenetic pyrite can form in the anoxic deep-waters of stratified watermasses. However, fractionation of syngenetic pyrite and that of early-formed diagenetic pyrite (when formed in an open system) should be similar—the effect of sediment on porewater chemistry is limited until permeability is reduced significantly.

P 13192, Ins 24-25: Nor has the pyrite flux gone to zero.

Response: This comment is cryptic—we cannot reply.

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P 13194, Ins 19-21: But what's important is that shallow pyrite hasn't experienced overgrowth of more isotopically enriched pyrite formed in deeper, closed-system sediments. Also, it seems like shallow AVS would be the best target based on this argument. Ultimately, pyrite must be used because that's what is preserved in the geologic record.

Response: We agree with all of these comments. However, these issues are already adequately addressed in the manuscript.

P 13195, In 7: This mathematical relationship is only valid if the original fluid is sourced from seawater. What about mixing with saline, non-seawater fluids?

Response: This relationship is valid for mixed fluids that contain a seawater component >5% (where the second fluid is low-sulfate freshwater). It would not be valid for a purely terrestrially sourced fluid. Sulfate concentrations for all freshwater systems in our dataset (Table A1, records 1-18) were measured, not calculated from salinity. Of the 36 brackish systems in our dataset (Table A1, records 19-54), we estimated sulfate concentrations for 9 of them from salinity data. By definition, our brackish systems had total salinities of 10 to 30 psu and thus consisted of 28-86% seawater. The calculated sulfate concentrations are therefore reliable—there are no problems with the sulfate concentrations in our dataset (Table A1).

P 13196, Ins 3-5: The Habicht et al. (2002) data show a clear step function, not a linear relationship as seen in the natural samples.

Response: The statement in question is: "Our results are similar to, although more linear and more statistically robust than, those reported by Habicht et al. (2002) on the basis of culture experiments." Our results are similar to those of Habicht et al. in terms of the broad relationship between MSR fractionation and aqueous sulfate concentration, although more linear (as noted by the reviewer). We stand by our statement.

General Note: It would be nice to see how water column sulfide compares to shallow pyrite in modern systems where both are measureable or have been measured. This

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would provide confidence in the use of pyrite as a “cogenetic” proxy.

Response: This is related to the request by this reviewer for a figure showing the different sulfide phases used in calculating D34S<sub>sulfate-sulfide</sub> (see above). This figure (Figure B3—see Supplementary document) shows that the D34S<sub>sulfate-sulfide</sub>-[SO<sub>4</sub><sup>2-</sup>]<sub>SW</sub> relationships are similar for pyrite and aqueous H<sub>2</sub>S. Although further detailed study might document a systematic offset between these sulfide phases, we cannot identify one in our dataset (Table B1).

P 13202, In 21: The rate method-produced values may not be maxima, particularly if source d34S changes.

Response: The rate-method estimates are based on D34S(CAS-pyrite) and  $\max(\partial\text{SO}_4^{2-}/\partial t)$  (see Equations 2-4). They are not dependent on source d34S. Variation in source d34S would matter only if average seawater sulfate concentrations were so low that seawater sulfate was no longer well-mixed globally.

P 13203, Ins 1-4: I disagree. The further back in time, the less confidence we have in S flux magnitudes and isotopic compositions, accurate determination of which are required for a valid rate model.

Response: Sulfur isotopic fractionations (D34S(CAS-pyrite)) are quite well-determined for >2.3-Ga samples, being uniformly small (<4‰). The difficulty with rate estimates for samples this old is not the sulfur isotopic compositions but limited age control. With adequate age control, the rate method may be quite useful for very old samples. This is largely a matter of opinion—we respect the reviewer’s but stand by our own.

P 13203, In 7: Diagenesis may also homogenize d34SCAS (and therefore reduce d34S(CAS)/dt(max)) depending on the nature of diagenetic fluids and the degree of recrystallization/alteration.

Response: We agree. Diagenesis was mentioned as an example of a process that might increase variance in d34SCAS, but it might also reduce variance. We have

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inserted a brief mention of this possibility.

P 13207 and throughout: Although it is difficult to reconstruct ancient [Ca<sup>2+</sup>], very high values of [SO<sub>4</sub><sup>2-</sup>] are unlikely because of the tendency to saturate the oceans with respect to anhydrite and gypsum. With a modern [Ca<sup>2+</sup>] of ~10 mM and [SO<sub>4</sub><sup>2-</sup>] of ~100 mM fluids will be supersaturated (by 30X levels pertaining to saturation). Is there an upper limit to sulfate concentrations that can be calculated?

Response: This is an interesting idea, and one that has been considered previously. Variation in seawater [Ca<sup>2+</sup>] and [SO<sub>4</sub><sup>2-</sup>] has been estimated for the Phanerozoic in at least three studies (Hardie, 1996; Horita et al., 2002; Lowenstein et al., 2003). We included some of the results of these studies in Figure 5 of our paper (Algeo et al., 2014).

P 13208, Ins 22-24. A restricted basin may exhibit elevated or reduced sulfate concentrations. Restricted evaporative basins or those with limited reactive organic carbon may exhibit [SO<sub>4</sub><sup>2-</sup>] above seawater due to evaporation and restriction of MSR, respectively.

Response: We agree. Such basinal watermass effects may underlie the unusual behavior exhibited by some of the Mesozoic units in our paper (Fig. 8; see discussion in Section 4.3).

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Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/11/C8304/2015/bgd-11-C8304-2015-supplement.pdf>

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Interactive comment on *Biogeosciences Discuss.*, 11, 13187, 2014.