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

Anonymous Referee #2

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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 sulfate 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.

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General Comments:

Rate method. The application of modern S fluxes and associated $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$ (through $\delta^{34}\text{Spyr}$, for example), it is quite difficult to accurately predict the source $\delta^{34}\text{S}$. 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 $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$.

MSR method. The linear relationship between $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$ from modern aqueous systems is striking and suggests that there is hope in reconstructing ancient seawater 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 ($> \sim 29 \text{ mM}$) would not exhibit higher fractionations?

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 demon-

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strated that these two records agree. Early work by Burdett et al. (1989) suggests 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 $\Delta^{34}\text{SCAS-pyr}$ accurately reflects cogenetic $\Delta^{34}\text{S}$ sulfate-sulfide?

Heterogenous 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 stratified-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?

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.

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 (Fike and Grotzinger, 2008).

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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.

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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.

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

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

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.

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?

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.

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

P 13202, In 21: The rate method-produced values may not be maxima, particularly if source $\delta^{34}\text{S}$ changes.

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.

P 13203, In 7: Diagenesis may also homogenize $\delta^{34}\text{SCAS}$ (and therefore reduce

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$\delta/\delta t(\text{max})$) depending on the nature of diagenetic fluids and the degree of recrystallization/alteration.

P 13207 and throughout: Although it is difficult to reconstruct ancient $[\text{Ca}^{2+}]$, very high values of $[\text{SO}_4^{2-}]$ are unlikely because of the tendency to saturate the oceans with respect to anhydrite and gypsum. With a modern $[\text{Ca}^{2+}]$ of $\sim 10 \text{ mM}$ and $[\text{SO}_4^{2-}]$ of $\sim 100 \text{ mM}$ fluids will be supersaturated (by 30X levels pertaining to saturation). Is there an upper limit to sulfate concentrations that can be calculated?

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 $[\text{SO}_4^{2-}]$ above seawater due to evaporation and restriction of MSR, respectively.

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