

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

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General Comments

I have read the paper by Algeo et al with great interest. The authors discuss ways to derive the concentration of sulfate in seawater from the stable isotope ratios observed in sulfides and sulfates. Attempts to do this date back decades, and it is commonly believed that the seawater sulfate concentration varied considerably through time. However, data (as opposed to interpretations) is restricted to a few Cenozoic samples.

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Some fluid inclusion data exists for the Mesozoic, but it is no longer primary data as their interpretation relies on un-testable assumptions about the chemical composition of Mesozoic seawater.

The authors present two different approaches to estimate the marine sulfate concentration. The first one is based on the rate of change of the observed S-isotope ratio, and basically states that if we assume that modern burial/weathering fluxes are representative, the rate of change is a measure of the reservoir size (aka sulfate concentration). As far as I understand it, this approach is only valid if the rate of change is equal to the residence time of the respective system. The authors allude to this somewhat obliquely on page 13192, line 8ff. However, what happens if the fluxes become so big that the rate of change is considerably faster than the residence time, and even affect the reservoir size itself?

This brings me to my main concern with this model. Equation 3 relates the rate of change to the marine sulfate concentration using a time invariant pyrite burial flux. However, the pyrite burial flux itself depends on the marine sulfate concentration. This dependency is weak above 12mM, but becomes significant for lower concentrations. While the exact relation is not known, and probably changes through time, Wortmann and Chernyavsky (2007) provide a useable parametrization in their supplemental data. This point requires attention before the MS can be published.

In their second approach, the authors provide an empirical relationship between sulfate concentration and the difference between the S-isotope ratios measured from sulfate and pyrite. This is intriguing but it remains unclear to me how reliable this proxy is, because we have not enough data to check their results against (Fig. 5 insinuates too much here, as the majority of the data shown there is not primary, but proxy data). I am particularly concerned about the mismatch between the authors data and the reconstructions by Wortmann and Paytan (2012). Granted, the latter paper is controversial, however the Cretaceous to Eocene interval is the one time in Earth history where we have large and fast S-isotope variations, a highly resolved marine S-isotope record,

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and fluid inclusion data which suggest sulfate concentration changes on the order of 20 mM. So this requires special attention.

If I understand the authors correctly, they argue: A) that the current $\delta^{34}\text{S}$ record could be a local record in the Tethys basin. However a significant part of the Cretaceous $\delta^{34}\text{S}$ data is from Site 305 (Shatsky Rise, W-Pacific) and fits nicely with the data from Site 766 (Indian Ocean, possibly restricted); B) that their model may not capture short term draw down events. If so, two questions come to mind: A) Even if the draw down may be short term, the recovery will take a very long time. Using modern fluxes, Wortmann and Paytan (2012) estimate that it takes 60 Million years for the sulfate concentration to recover. If the Algeo et al. model is indeed insensitive to "short term" draw down events, short term events will introduce considerable error in their reconstructions. B) More importantly however, why would be a sulfate-pyrite difference model like the one proposed here, be insensitive to short term draw down?

Specific Comments

1. p13188 l10, and p 13192 l10. The rate of change is not only determined by reducing the input/output flows to zero. You could also double or triple those flows, which would have a considerable effect on the rate of change. Or is this an oblique way to state that the model is only valid if the rate of change is equal to the residence time?
2. p13188 l20 ff and later in the manuscript. I always thought that the Early Triassic sulfate concentrations are low. The rapid changes observed during this time certainly require sulfate concentrations below 10 mM (e.g. Song et al., 2014)?
3. p13188 l23 What is the meaning of "varied only slightly since 250 Ma"? Some of our most reliable data on sulfate concentrations is of Jurassic and Cretaceous age, and even fluid inclusion data suggest pretty dramatic changes from 8mM

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during the Early Cretaceous to modern values around 28 mM (Lowenstein et al., 2001, 2003; Demicco et al., 2005)

4. p13188 l24 I'd add the Cretaceous here, see above.
5. p 13191 l15 there is a pretty rich literature on the subject, however the paper cited here only discusses data from a lake and lagoon.
6. p p 13192 eq 2 FPyr itself depends on the sulfate concentration (Wortmann and Chernyavsky, 2007). As stated, the equation will only work for concentrations above 12 mM.
7. p13192 l20. I seem to remember that the Paytan et al. (1998) data showed faster variations?
8. p13197 l17. Consider adding the work of Rudnicki et al. (2001).
9. p13197 l27, Canfield and Teske (1996), and their data indicates a spread up to 70 permil.
10. p13198 l25, the works of Rees (1973) and Brunner and Bernasconi (2005) are important here too.
11. p13199 1 para. Since this is a fairly exhaustive list of processes affecting S-fractionation, the author may want to consider to add Eckert et al. (2011) who show that cell external sulfide may affect S-fractionation (see also Brunner and Bernasconi, 2005).
12. p13201 l 2, add citation for the Lowess model.
13. p13202 l5ff, p13204, The Song et al. (2014) data suggests that the Permo-Triassic concentrations must have been low?

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14. p13207 I9, Canfield and Teske 1996, and the values reported there seem to go up to 70 permil?
15. p13207 I20ff If I understand this correctly, the rate based estimate really only works if the rate of change equals the residence time. If it is slower, or faster, this approach will fail. It might be useful to rephrase the discussion in the more general framework of residence time vs, rate of change.
16. p13209 I 5ff. I am not sure that I understand this argument. While I can see that the difference between CAS and Pyrite may be affected by the local hydrogeography, the sulfur data published by Paytan et al. (1998) are from coring locations in the Pacific, and as such not affected by local restriction. So the rate method should apply here.
17. Last but not least, it would be useful if the authors provide their p-values for their regression model, as the r^2 -value only describes how good the fit is, but says nothing about how probable the model is.

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