

## ***Interactive comment on “Pleistocene sediment offloading and the global sulfur cycle” by S. Markovic et al.***

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Please see supplement for formatted response.

Comments by P. Meister

General comments The main result consists of a  $\delta^{34}\text{S}$  record of sedimentary barite from the Eastern Equatorial Pacific. The barite was extracted from sediment cores of the Ocean Drilling Program. Furthermore, a mass balance model is presented to simulate the  $\delta^{34}\text{S}$  of marine sulphate based on the main sources and sinks. A decrease in  $\delta^{34}\text{S}$  of marine sulphate over the last 1.5 Ma is interpreted as result of pyrite oxidation due to offloading of shelf sediments during glacial sealevel lowstands. The study is interesting to read and certainly an important contribution to the understanding of the

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sulphur cycle. The text is well written and figures are useful and clear. The interpretation seems well supported by the data and model results, respectively. Nevertheless, I mention a few thoughts that could be discussed in more detail and which may improve at the same time the clarity of the manuscript for the reader.

We thank Dr Meister for a constructive review and for his support of the study.

1) During sealevel lowstand the zones of coastal upwelling would migrate further offshore and hence still be active in burial of pyrite but at greater water depth. As a result the deep water compartment would in fact counteract the effect of sediment offloading on the shelf. Therefore, it would be important to include the effect of changes in pyrite burial in the deep ocean compartment in the sensitivity study.

This is an important point. The burial of pyrite in the deep sea is likely higher during lowstands. However, we note that the upwelling zones, although highly productive have a small areal extent, and thus a modest impact on the overall organic carbon burial (<10% Berner 1982, Hedges and Keil, 1995; Hu and Cai, 2011). Furthermore, pyrite burial is often limited in the upwelling zones by the lack of reactive iron (e.g., Morse and Emeis, 1990; Mossmann et al., 1991; Schenau et al., 2002; Brückert et al., 2003; Suits and Arthur, 2000), and the majority of pyrite is actually buried in the continental shelf and estuaries (e.g., Berner 1982, Hu and Cai, 2011).

We added a note highlighting these relationships in the model discussion.

2) If a higher flux of sulphide from the shelf occurs during glacial lowstand without compensation by another sink, the sulphate concentration in the ocean would increase. This would then not represent a real steady state. The authors should also discuss how a new steady state would look like if the increased influx of sulphate is compensated somewhere else. Possible sinks could be an upwelling zone that is shifted offshore, or a higher flux into evaporites due to higher sulphate concentration of seawater.

Our model is not based on steady state assumptions, and fluxes react dynamically to

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sea level change. The sulfate concentrations increase by 1 to 3mM (depending on the size of pyrite reservoir in the shelf).

Pyrite burial and  $\delta^{34}\text{S}_{\text{pyr}}$  are sensitive to changes of sulfate concentrations but only at low sulfate levels (Habicht et al., 2002; Wortmann and Chernyavsky, 2007). The changes suggested by our results are small compared to the already high sulfate concentrations before Quaternary (~25-29mM, Horita et al., 2002; Brennan et al., 2014; note that starting sulfate concentration in our model is 27mM). Therefore the impact of increased sulfate concentration on pyrite burial is likely negligible.

On the other hand, evaporite burial is not controlled by sulfate concentrations (Halevy et al., 2012); instead it is affected by occurrence of suitable sedimentary environments with high evaporation (Halevy et al., 2012). Thus we think that small increase of sulfate concentrations likely had no impact on the evaporite burial rates during Quaternary.

3) Another sensitivity test would be to change only the  $\delta^{34}\text{S}_{\text{pyr}}$  without the effect of sediment offloading. Likewise, the effect of changes in deep ocean pyrite burial should be visualized alone.

This is an excellent idea and a point that we incorporated upon reading the comment. The new plot A1 shows the effect of  $\delta^{34}\text{S}_{\text{pyr}}$  alone. Fig. 1 shows the impact of  $\delta^{34}\text{S}_{\text{pyr}}$  change. During glaciations  $\delta^{34}\text{S}_{\text{pyr}}$  increases which produces the positive shift of sulfate  $\delta^{34}\text{S}$  values. This change is the most pronounced in the past 1Myr. We added this plot and a brief discussion in the revised text.

Holding all other parameters constant, we run sensitivity tests with pyrite burial alone. Model outputs lag behind isotope record and undershoot  $\delta^{34}\text{S}$  regardless of the volume of initial fluxes. This suggests that changes of pyrite burial alone cannot account for the Quaternary seawater sulfate  $\delta^{34}\text{S}$  record. We added this plot in the Appendix and a brief discussion in the revised text.

4) Generally, the Methods chapter includes a lot of discussion. This chapter could be

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significantly reduced in length if these discussions are moved to Results and Discussion.

We agree that the methods section is indeed long. We believe that it should be as thorough as possible for anyone who would appreciate the added details concerning model development (or might want to replicate it). However, most of these details are only tangential to the main message of this study. Therefore, we think that moving substantial part of Methods to Discussion section would only distract from it and disrupt the flow of ideas.

5) Minor comments: p. 1208, line 14: "... Shipboard Scientific Party"

Thank you. Corrected.

p. 1208, line 24: The statement that sulphate reduction is not prevalent at the Eastern Equatorial Pacific sites because the sulphate concentration is not depleted is not necessarily true. Blake et al. (2006; Proc. ODP, Sci. Results, v. 201) showed based on  $\delta^{18}\text{O}$  data that sulphate is being cycled.

This is indeed a very valid point. We thank you for pointing this out. We changed mentioned sentence: "These conditions suggest that the barite samples in sediments at these sites are not affected by barite dissolution and/or reprecipitation, and thus originate from sinking particles in the water column (e.g. marine barite)."

p. 1209, lines 6 – 12: This section should be part of the introduction.

Thank you for suggestion. We moved this part to introduction p.1207, line 27 to p.1208, line 4.

Figures: The time axis should be plotted from past to present from left to right.

A number of recent publications presented stable isotope results and model data from present to past from left to right (e.g., Turchyn and Schrag, 2004, 2006; Hoogakker et al., 2006; Elderfield et al., 2012; Lisiecki, 2014; Pena and Goldstein, 2014). On the

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other hand, there are also publications using different layout (e.g., Köhler and Bintanja, 2008; Clark et al., 2006). Since it appears that this is a matter of preference rather than convention we would prefer to retain the current layout, as to us, it makes more sense that the numbers (age before present) increase towards the right, rather than decrease.

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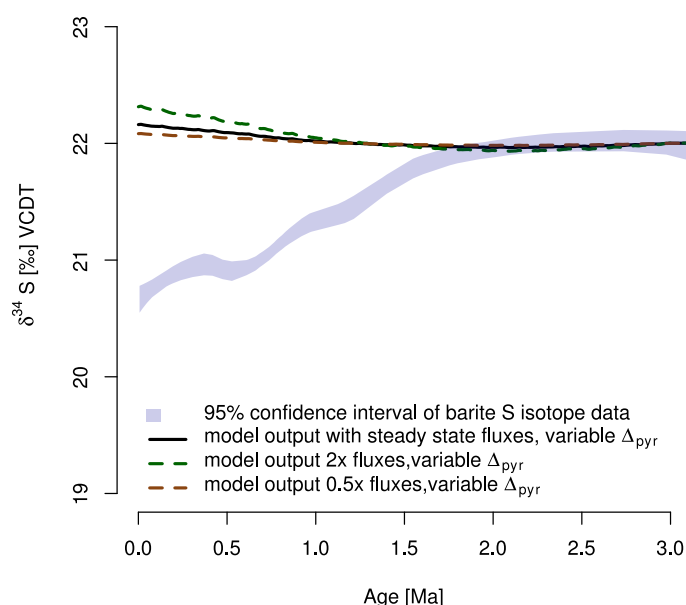
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Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/12/C923/2015/bgd-12-C923-2015-supplement.pdf>

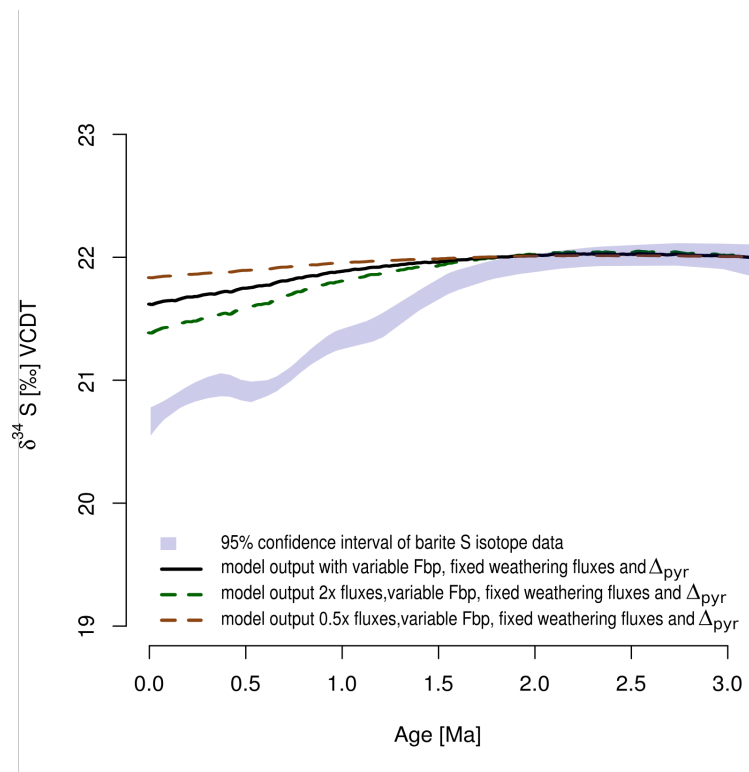
Interactive comment on *Biogeosciences Discuss.*, 12, 1205, 2015.

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**Fig. 1.** Figure 1. Model output using variable  $\Delta_{pyr}$ . Black solid line – model output produced assuming constant steady state fluxes and variable  $\Delta_{pyr}$ . Green dashed line – model output produced assuming constant

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**Fig. 2.** Figure 2. Model output with variable pyrite burial and fixed weathering fluxes and  $\Delta_{pyr}$ . Black solid line – model output produced assuming initial fluxes at steady state values, variable pyrite burial