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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 B. Mayer

The authors have composed a well-written manuscript describing and interpreting a high-resolution sulfur isotope record of marine sulfate determined on authigenic marine barite crystals from an Eastern Equatorial Pacific ODP site spanning the last 3 million years. The manuscript is written in a logical sequence, is well organized, easy to read and understand. Previous literature is appropriately considered and figures and tables are of good quality. Most conclusions appear well supported by the provided data and by the utilized sulfur cycling model. The analytical approaches are very sophisticated giving confidence in the presented data. The authors describe a >1.0‰ decrease in ïĄď34S of marine sulfate from circa 22.0 ‰ to <21.0 ‰ with the majority of the change occurring between 1.5 and 1.0 Ma. The authors use a sulfur cycle model to conclude that erosion during sea level low-stands was only partly compensated by increased sedimentation during times of sea level high-stands, an interpretation that appears well justified based on the presented data and model runs.

We thank Dr Mayer for his support of the study.

1) The authors suggest that the observed decrease in ïĄď34S is related to the Milankovic cycle driven change from 41 kyr (and 23 kyr) interglacial-glacial periodicity earlier in the Pleistocene to 100 kyr by 700,000 years ago. While the end of the reported d34S decrease described in this manuscript is consistent with this interpretation, the question arises why the decrease in d34S values of marine sulfate started as early as 1.5 Ma ago if it is linked to 100 kya cycles? To my best knowledge, oxygen isotope records of benthic foraminifera place this transition somewhere between 1.0 and 0.7 Ma ago (e.g. Ruddiman, W. F. (2008): Earth's Climate, Freeman & Co, New York), but your Figure 2 indicates that a 0.7 ‰ shift in d34S of marine sulfate had already occurred between 1.5 and 1.2 Ma ago, which appears inconsistent with the larger 100,000 yrs interglacial-glacial periodicity capable of removing much larger sediment loads from the shelf. The authors should add some explanation on the timing of this early onset of the decrease in d34S of marine sulfate reported in their paper, and possibly compare it to the d18O record of benthic foraminifera, which has reportedly been used for age-dating the samples (page 1209, line 3).

This is a very perceptive catch and something that we have overlooked. While the "true" 100kyr cycles did not appear until ∼900ka (e.g., Elderfield et al., 2012; Pena and Goldstein, 2014) the early signs of change in amplitude and duration of glaciations probably took place ∼1250ka (e.g., Clark et al., 2006; Lisiecki, 2014). The LR04 stack of globally distributed benthic foraminifera d18O records indicates increased severity of glaciations as early as 1.5Ma (Lisiecki and Raymo, 2005; Clark et al. 2006). More pronounced sea level low stands from 1.5Ma to 0.7Ma are reflection of this change (see Figure 1 in discussion paper, data from Miller et al. 2011). It is this lower sea level during glaciations that resulted in increased weathering of shelf pyrite. However, the language we used obscured this main point and suggested that d34S shift is a result of longer glaciations, when in fact it is due to progressively lower sea level and associated aerial exposure of previously inundated continental shelf (Figure 1 in discussion paper). We thank the reviewer for pointing out this ambiguity and we changed the language throughout the text to make it clearer what is the main driver of shift in seawater sulfate d34S value.

2) I am also curious why organic sulfur compounds receive so little attention in the sulfur cycling models, but assume that they play only a very minor role in the reported S fluxes. Nevertheless it should be acknowledged (e.g. on page 1217, line 10) that some sulfur is also buried in organic form.

This is indeed something that we have overlooked. We thank the reviewer for this suggestion and we added the following: “Also note that the burial of organic sulfur is poorly constrained (Werne et al., 2004). Although it is generally considered to be minor compared to pyrite burial (e.g., Goldhaber, 2003; Werne et al., 2004), in some environments (e.g. Peru shelf, the Miocene Monterey Formation, marine sapropels) it is the dominant form of reduced solid sulfur compounds (e.g., Mossmann et al., 1991; Canfield et al., 1998; Suits and Arthur, 2000).”

3) And finally, in section 4.2 the authors comment on the link between pyrite oxidation, acidification-enhanced carbonate dissolution/precipitation and associated CO2 release into the atmosphere. While I agree with the principle geochemical arguments, I am a bit puzzled about the link of the here presented data showing a d34S decrease in marine sulfate starting 1.5 mio years ago and ending 700,000 years ago, and the claim that this is partly related to CO2 increases 600kyr and 400kyr ago. The authors should provide further arguments on the temporal connections of their S isotope record with the ice core CO2 record in order to substantiate their argument of a causal relationship.

We thank you for this comment, which identified the area where we probably promised more than we can deliver at this point. The language we used in discussion might have erroneously suggested that there is a direct link between sulfide oxidation and atmospheric CO2. However, this link is indirect and complex.

While sulfide weathering increases the dissolved inorganic carbon (DIC) amount in the ocean (Hu and Cai, 2011; Torres et al., 2014,) CO2 is released only after precipitation of calcium carbonate. Characteristic time scales for this process are in the 100-200 kyr range (Sundquist and Visser, 2003; Zeebe and Wolf-Gladrow, 2009) and therefore, DIC addition and CO2 release are not synchronized. It is possible that competing effects of biological pump and carbonate precipitation resulted in the increase of atmospheric CO2 some time after the pulse of DIC produced during sulfide oxidation. However, the temporal changes of these processes are well beyond the scope of this paper. We therefore changed the language in the last section of discussion and dropped the suggestion that there is a direct link between CO2 concentrations and increased pyrite weathering.

On a technical note, d34S should be followed by “values” (d34S values) rather than compositions” and certainly not “ratios”.

Thank you for the comment. We changed the language throughout the text.

Table A1: add units (‰ after d34S and use same number of significant digits behind the comma for reporting the results;

Done.

Figure 4, y-axis label, unit missing (‰.

Corrected.

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Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/12/C938/2015/bgd-12-C938-2015-supplement.pdf

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