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Interactive comment on "Anaerobic oxidation of methane alters sediment records of sulfur, iron and phosphorus in the Black Sea" *by* Matthias Egger et al.

Anonymous Referee #2

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This study addresses the diagenetic implications of anaerobic methane oxidation in Black Sea sediments where marine deposits overlie a freshwater facies into which a sulfate front is advancing. High-resolution geochemical profiles of dissolved and solid species are presented from two adjacent sites, and the profiles are simulated in a complex non-steady-state diagenetic model that derives rates of the relevant processes.

The subject is interesting, obviously relevant to Biogeosciences, and the results and conclusions presented here are novel and add substantially to our understanding of sediment biogeochemistry and diagenesis. The text is well written, clear, and concise, the data is of good quality, and the conclusions are generally justified by the data and modelling. The authors particularly deserve credit for clearly distinguishing model

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results from reality.

My main concern with the paper is that I miss a deeper analysis and discussion of the extent to which the modelling results are forced by the formulation and parameterization of the model. This could involve a sensitivity analysis or testing of alternative scenarios. Additionally, some aspects of the model results and formulation require clarification.

It is particularly the conclusions concerning sulfate- and iron-coupled AOM that require attention. The occurrence of Fe-AOM appears to be forced by the exclusion of organoclastic Fe reduction from the model, although there is plenty of evidence that organotrophic microbes can reduce crystalline Fe oxides, and there is no evidence that organotrophic Fe reduction cannot co-occur with methanogenesis if Fe reduction is limited by the availability/reactivity of iron oxides. Furthermore, is seems that partitioning of AOM must be sensitive to the parameterization of the pathways, which therefore needs to be discussed.

Specific issues: 22-23+89-90: The finding that sulfate-AOM enhances the sulfide flux is not novel according to lines 72-75.

289-96: Just a comment: The difference in the two methane profiles is strange and it is difficult to understand how degassing would have caused a proportional decrease in methane in the zone above the zone of saturation. Nonetheless, I agree that it is the most likely explanation given the similarity of all other profiles, including the methane isotopes. I suggest rephrasing 293-294 to clarify which methane data this applies to.

339-41+Fig 6: I don't understand the very high rates of sulfate reduction and methanogenesis in the sapropel, and the model doesn't seem to fit the data well here. Albeit noisy, the measured H2S profile seems straight or even concave in this region, and the same clearly goes for DIC, whereas the model profiles are convex, which suggests that the model overestimates the rates substantially. Although this zone is not of primary interest in this study, an overestimation of rates and product concentrations results in a shallower gradient from unit II to the SMTZ and therefore in lower sulfate-AOM rates,

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so the fit here still influences the central conclusions.

Fig. 6, further+ Fig. 3: There seems to be an error in the H2S production panel in Fig. 6 as H2S production from sulfate reduction is only a fraction of the sulfate reduction rate? Shouldn't hese be 1:1 as is the case for sulfate-AOM and sulfide production from sulfate AOM? Also, what happens to methane produced in unit II? The methane profile appears flat, yet only a fraction of the production is consumed by AOM. Please provide blow-ups of modelled methane in the upper 2 m and of sulfate below the SMTZ in Fig. 3.

391-5: This is the only real flaw in the paper. The Rayleigh function applies to closed systems and should never be used in open systems such as this one, where diffusion affects the relative distribution of the isotopes. Accurate enrichment factors can only be derived through modelling (e.g., Alperin et al. 1988). The closed-system approach will underestimate enrichment factors substantially in most cases, and likely explains the low value derived here. This problem was described decades ago (e.g., Jørgensen 1979, GCA 43:363).

401: I think some of these studies observed sulfate reduction and did not only postulate it?

442-3: Under which conditions, if any, within a realistic parameter space or with an alternative set of reactions, would a cryptic sulfur cycle be able to explain the accumulation of Fe2+?

450-5: The references listed here suggest that AOM may be coupled to Fe reduction, but here you really use them to support the assumption that Fe reduction can be coupled to AOM rather than to organoclastic Fe reduction – Is there any support for that in any of those references? As stated in l. 463, organoclastic Fe reduction is clearly limited at these depths, but that doesn't mean that it is absent. Furthermore l. 474-6 seems to suggest organoclastic Fe reduction anyway, even if it is by archaea? But what special skills do these organisms have that would enable them to reactivate Fe oxides?

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489-93: It seems trivial that in situ rates under the given conditions are low compared to lab-based rates. What is the observational basis for the parameterization of the reaction?

494-5: How sensitive is the sulfate/Fe-AOM partitioning to the parameterization?

Table 3, R6+16: I understand that you need a sink for H2, but why is it only methanogenesis and not, at least sulfate reduction? This will lead to overestimation of methanogenesis in the sulfate zone.

Table 4: R19+ R20 are biological processes and as such might obey biological (saturation) kinetics? These are key reactions in the paper and the observational basis for the kinetic expressions, and their impact on the conclusions should be discussed. Table 6 + Fig 6: The labelling of the two kinds of methanogenesis is misleading. The light isotopic composition of methane implies that it is formed mainly through CO2 reduction rather than acetoclastic methanogenesis, i.e. that "Methanogenesis (OM)" is mainly CO2-based. "Methanogenesis (DIC)" is really a peculiarity of the model and completely and uniquely linked to pyrite formation, so "Methanogenesis (FeS2)" would be more appropriate (but see also comment to Table 3 above).

Fig. 7: Consider a colour version here. The darkest shading on the scale bars always appears darker than the darkest part of the figures. Because the shading varies so little from min. to max. it is very difficult to extract quantitative information.

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