

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

**Matthias Egger et al.**

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We thank the anonymous referee for the positive remarks. We reply to the comments below and aim to revise the manuscript accordingly (i.e. we will include sensitivity analyses and will clarify our model formulation and corresponding results further).

Referee's comment: 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

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seems that partitioning of AOM must be sensitive to the parameterization of the pathways, which therefore needs to be discussed.

Author's reply: We acknowledge that the reason for the exclusion of organoclastic Fe reduction at depth in the sediment requires a more detailed explanation. The reason for this assumption was to test how important Fe-AOM could be for the CH<sub>4</sub> cycle, assuming that all the Fe reduction at depth would be exclusively due to Fe-AOM. We agree with the referee that organoclastic Fe reduction also provides a possible Fe reduction pathway and also state this in the manuscript (see, for example lines 31-33, 476-478 and 559-560). In the revised manuscript, we will clarify our model results and formulation, as well as include an appropriate sensitivity analysis.

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

Author's reply: We agree with the referee, and we will rephrase the text so that it is clear that we are not implying that this is a novel finding.

Referee's comment: 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.

Author's reply: We will elaborate on the CH<sub>4</sub> degassing and clarify our conclusions (lines 293-294) in the revised manuscript.

Referee's comment: 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 H<sub>2</sub>S profile seems straight or even concave in this region, and the same clearly goes for DIC, whereas the model profiles are

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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, so the fit here still influences the central conclusions.

Author's reply: We will work on improving the model fits for H<sub>2</sub>S and DIC in the marine deposits and re-evaluate the modeled rates.

Referee's comment: Fig. 6, further+ Fig. 3: There seems to be an error in the H<sub>2</sub>S production panel in Fig. 6 as H<sub>2</sub>S production from sulfate reduction is only a fraction of the sulfate reduction rate? Shouldn't these 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.

Author's reply: We thank the referee for pointing out these inconsistencies. The rate plots of Fig. 6 were not normalized to the same volume, meaning that the SO<sub>4</sub> reduction rate, CH<sub>4</sub> production and S<sub>0</sub> disproportionation should be multiplied by the solid volume fraction of the sediment, while rates of SO<sub>4</sub>-AOM and Fe-AOM should be multiplied by the sediment porosity. In addition, only 0.5 mole of CH<sub>4</sub> are produced per mole of organic matter during methanogenesis (see reaction R5 in Table 3). We will carefully check the unit conversion in the plotting, as well as the mass balance and revise Fig. 6 accordingly.

Referee's comment: 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

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decades ago (e.g., Jørgensen 1979, GCA 43:363).

Author's reply: We thank the referee for this critical remark. We agree that modeling of the methane isotopes would result in a more reliable estimation of the enrichment factors. However, isotopic fractionation was not the main aim of this study. In addition, considering that diffusion fractionation is likely minor compared to the fractionation associated with oxidation (e.g. Happell et al., 1995; Limnol. Oceanogr.; Chanton, 2005; Org. Geochem) and that diffusion might be slower than oxidation in our settings, it could be argued that we may be looking at a quasi close environment. We will clarify the limitation of our approach in the revised manuscript.

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

Author's reply: We agree with the referee and will clarify this in the revised version.

Referee's comment: 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 Fe<sub>2</sub>+?

Author's reply: We will elaborate on this in the revised manuscript.

Referee's comment: 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?

Author's reply: We acknowledge that lines 450-455 could be formulated better. The existing literature cited here indicates that Fe reduction could be coupled to CH<sub>4</sub> oxida-

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tion in aquatic sediments. The aim of this study was thus to evaluate whether the geochemical profiles could be reproduced assuming that all Fe reduction at depth would be coupled to Fe-AOM and to show the potential impact of Fe-AOM on the CH<sub>4</sub> cycle. We are not claiming that Fe-AOM is more likely than organoclastic Fe reduction, but rather show that Fe-AOM represents a plausible mechanism for the deep Fe reduction. We will clarify this in the revised manuscript. To our understanding, the underlying mechanisms of the reactivation of Fe oxides by methanogens as described by Sivan et al. (2016; *Geobiology*) remain enigmatic.

Referee's comment: 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?

Author's reply: The Fe-AOM reaction was implemented according to Beal et al. (2009; *Science*) and the rates were derived by fitting the modeled pore water and solid phase profiles with the observations as explained in the text (lines 229-231). In our view, it is not trivial to mention the difference in rates calculated here and observed in laboratory experiments in other settings. It illustrates that it may be difficult to perform laboratory incubations of Black Sea sediments to study Fe-AOM.

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

Author's reply: We will perform an appropriate model sensitivity analysis in the revised manuscript (see earlier comments).

Referee's comment: Table 3, R6+16: I understand that you need a sink for H<sub>2</sub>, but why is it only methanogenesis and not, at least sulfate reduction? This will lead to overestimation of methanogenesis in the sulfate zone.

Author's reply: H<sub>2</sub> is not included in our model.

Referee's comment: Table 4: R19+ R20 are biological processes and as such might

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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.

Author's reply: The bimolecular rate equation expression for AOM applied in this study is the most frequently used AOM parameterization in reactive transport models (e.g. Regnier et al., 2011; *Earth-Science Reviews*). We followed the bimolecular approach because of the high uncertainty in half-saturation constants, in particular for the putative Fe-AOM pathway. For a detailed discussion about AOM parameterization, the referee is kindly referred to the study by Regnier et al. (2011; *Earth-Science Reviews*).

Referee's comment: 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 CO<sub>2</sub> reduction rather than acetoclastic methanogenesis, i.e. that "Methanogenesis (OM)" is mainly CO<sub>2</sub>-based. "Methanogenesis (DIC)" is really a peculiarity of the model and completely and uniquely linked to pyrite formation, so "Methanogenesis (FeS<sub>2</sub>)" would be more appropriate (but see also comment to Table 3 above).

Author's reply: We agree with referee that reaction R6 in Table 3 and the labeling in Table 6 and Fig. 6 are difficult to understand and will improve it in the revised version.

Referee's comment: 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.

Author's reply: We will change Fig. 7 to a color version.

Sincerely, on behalf of all authors,

Matthias Egger