

## ***Interactive comment on “Regulation of anaerobic methane oxidation in sediments of the Black Sea” by N. J. Knab et al.***

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Several studies have reported that in contrast to other marine deposits subject to anaerobic oxidation of methane (AOM) where generally a distinct sulfate/methane transition zone (SMTZ) is found, the profiles of sulfate and methane in Black Sea sediments mostly show considerable overlap (of sometimes a few meters) and often a significant upward tailing of the methane pore water profile. As a consequence there has been a debate for several years now which environmental and/or depositional conditions and factors - most likely unique to the sediments of the Black Sea - might be responsible for the obviously sluggish rates of AOM and the inefficient consumption of methane within the SMTZ.

The study of Knab et al. contributes to answering this question by presenting a cohe-

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sive and very valuable data set of pore water profiles, gross reaction rates derived on the base of radiotracer techniques, direct cell counts and stable carbon isotope values for three gravity cores retrieved from the north-western Black Sea. Based on their results the authors conclude that the inefficiency of AOM observed in the studied cores (at least in two of them) is linked to the limnic history of the sediment. Although this statement &#8211; as given in the Abstract - is still a bit vague and very general (in particular with respect to what the title suggests Regulation !!!) the study is certainly of great interest for microbiologists, biogeochemists and geochemists working on biogeochemical and early diagenetic processes in marine environments/deposits and definitely should be published in Biogeosciences. There are, however, several inconsistencies and uncertainties which need improvement and clarification before publication of this contribution/paper.

The major concern I have relates to the way (not to say the uncertainty with which) the depth position of the marine/limnic transition has been determined in the three investigated cores. (By the way, from a chronological point of view I would rather consistently call it the limnic/marine transition as has been done in the Abstract). Furthermore, the manuscript would also benefit from (1) a more careful discussion of the depositional factors and conditions that are most likely responsible for the observed different depth positions of the SMTZ with respect to the limnic/marine transition at the three sites (in particular: how might the assumed slumps have influenced the migration of biogeochemical reactions fronts over time and the current shapes of pore water profiles and rates of biogeochemical processes at site P824GC?), and (2) a more precise description and elaboration of the actual factors and conditions inherent in the limnic deposits and/or the limnic history of the sediments which are in fact responsible for the observed inefficient methane oxidation.

Specific and minor comments and corrections

It is not clear to the reader how the authors define their marine/limnic or better limnic/marine boundary or transition. Is it the first inflow of saline waters via the

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Bosporus OR the time of establishment of full marine conditions in the Black Sea? Please, explain this in detail. Generally, the Late Pleistocene/Holocene sediments of the Black Sea are subdivided into at least three major units. The authors should thus also explain to which unit boundary their marine/limnic transition corresponds.

The most important point is that it is also not clear at all on which parameters and/or sediment components the subdivision of the different units of the typical Black Sea stratigraphy and in particular the identification of the depth position of the limnic/marine transition is/are based on. From the description on page 2315 ff. I assume that the identification of this boundary was obviously done on the base of a core description. However, I doubt how precisely the boundary can be identified from a mere visual inspection - knowing that the large peak in TOC is generally not laminated and that the first inflow of saline waters cannot be identified at all by eye but only on the base of the elemental composition of the sediments.

As the interpretation and conclusions of the current manuscript heavily rely on an accurate and precise definition and identification of the limnic and marine (as well as brackish?!) sediments I strongly recommend to much more carefully establish the stratigraphy/lithology of the sediments and show TOC and CaCO<sub>3</sub> data for the three cores rather than simply giving the depth positions as done in Table 1. On page 2327 the authors mention that core P824GC has higher TOC contents than the other two examined sites. I therefore assume that these data must be available. Establishing an accurate stratigraphy is also of crucial importance for gravity core P824GC which is assumed to be disturbed by several slides and which - obviously for this reason - significantly differs from the two other investigated sites.

After elaborating the lithology/stratigraphy in detail I would also suggest to indicate the particular depths of the marine/limnic transition in the respective figures. That will make it much easier for the reader to follow the discussion (e.g., page 2323).

Furthermore, there are several inconsistencies concerning the pore water profiles of

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hydrogen sulfide and Fe<sup>2+</sup>. Astonishingly the H<sub>2</sub>S maximum at site P771GC is not found at the depth of the SO<sub>4</sub>/CH<sub>4</sub> overlap but well above. In that the H<sub>2</sub>S profile also significantly differs from the profiles for the nearby stations 6 and 7 presented by Jørgensen et al. (2004). In contrast, the H<sub>2</sub>S profile for core P824GC is found below the SMTZ. How do the authors explain these sulfide profiles?

How reliable are the Fe<sup>2+</sup> pore water data presented for core P824GC in figure 3, in particular above 430 cm sediment depth? I doubt that these values are correct because generally one would not expect a co-occurrence of hydrogen sulfide and Fe<sup>2+</sup> (c.f., H<sub>2</sub>S data for this core shown in Fig. 2). Do think that this miss-match could derive from the relatively large pore size (0.45 μm) used for pressure filtration which might have allowed some (fresh) colloidal iron sulfides or iron sulfide complexes to enter the pore water samples?

Abstract, line 3: where upward transport

Abstract, lines 6 ff.: If you mean core P771GC here (-> Danube paleo-delta), this core was certainly NOT recovered from the shelf (modern water depth: 683 m).

Page 2306, line 24: the wording diffusive sediments is not correct (either the sediments are cohesive or the transport processes taking place within the sediments are controlled by diffusion)

Page 2307, lines 24 ff.: The study by Niewöhner et al. (1998) was not performed in shelf sediments but at a water depth of about 1300 m. I would therefore say: In most marine shelf and slope sediments

Page 2308, line 8: please, specify what reactive iron means in this context. Reactive towards sulfide or reactive in the biological sense, i.e. bioavailability of iron minerals? (Please, also consider this for the methods chapter on page 2311 and the discussion on page 2317.)

Page 2309, line 15: Which kind of filter material (cellulose acetate, nylon, etc.) was

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used for the pressure filtration?

line 21: eluent

Page 2311, line 13: the reference Schulz and Zabel (2000) is not contained in the list of references; do you mean the paper by Schulz (2000) ? by the way: there is an updated edition of this textbook (Schulz and Zabel, 2006)

Page 2313, line 11: why do you call 32S the normal isotope?

Page 2317, line 23: Why is an increase in the amount of reactive iron consistent with the finding of the typical black bands consisting of FeS ?

Page 2319, line 16: A minor 13C enrichment

line 20: where instead of were

Page 2320, lines 2 ff., page 2322, lines 9 ff. and Fig. 6: A look at Fig. 6 demonstrates that maximum AOM rates in fact are found around 290 cm sediment depth, and not at 150 cm as stated by the authors. Furthermore, maximum rates at 290 cm amount to 18/19 nmol cm<sup>-3</sup> d<sup>-1</sup> - rather than to 13 as said by the authors in line 5.

Page 2320, lines 18 ff.: there is something missing in this sentence

Page 2321, line 5: limnic

line 26: it has to be sulfate - Please, use consistent spelling of sulfate/sulphate throughout the manuscript!

Page 2325, lines 16 ff.: If the hydrogen sulfide concentrations shown for core P771GC in Fig. 2 are correct (as stated above I had some doubts) there is no sulfide available below 300 cm which might potentially be oxidized and thus explain the presence (of low amounts) of sulfate below 330 cm - as discussed by the authors.

Page 2326, lines 1 ff.: The discussion about the processes consuming upward diffusing Fe<sup>2+</sup> and downward diffusing sulfide are imprecise. At the diffusional interface of

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Fe<sup>2+</sup> and sulfide it will certainly not be pyrite that precipitates but FeS which leads to the formation of the distinct black layers (and as has been described and shown by Jørgensen et al. (2004)).

line 5: Reduced iron ??? Do you mean Fe<sup>2+</sup> in pore water? If this is the case please say so - otherwise reduced Fe could also relate to Fe(II) contained in iron sulfide minerals

Page 2329, lines 6 and 7: I do not agree with this statement. To me it seems that it is really the other way round: While heavier stable carbon isotope values occur at the depth with highest rates of AOM below 200 cm (depends on whether you believe in your AOM rates in these deeper sediments or not) in core P824GC, significantly lighter values are found at the depths characterized by maximum AOM rates at sites PP771GC and P806GC. ???

References, page 2330, line 30: Pfeifer; Schulz, H.D.

References, page 2331, lines 11 and 33: Lüschen

Figure 1 is of a relatively poor quality and it would be helpful if at least the depth in meters could be indicated at the particular contour lines.

Figure 3: title of graph (b) has to be reactive

Figures 4-6: The way the d<sup>13</sup>C values of methane and DIC are plotted is a bit unusual generally isotopically lightest values are shown on the left side.

Figure 7: insert a and b into the figure

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