

Interactive comment on “Manganese and iron reduction dominate organic carbon oxidation in deep continental margin sediments of the Ulleung Basin, East Sea” by Jung-Ho Hyun et al.

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Response on the interactive comment on “Manganese and iron reduction dominate organic carbon oxidation in deep continental margin sediments of the Ulleung Basin, East Sea” by Jung-Ho Hyun et al.

Anonymous Referee #3 Received and published: 13 July 2016 The zonation of terminal electron accepting processes (TEAPs) in marine sediments and the importance of anaerobic TEAPs to the overall degradation of deposited organic carbon are concepts that all students of biogeochemistry learn very early in their careers. Nevertheless, as the authors point out, there are very few studies that attempt to quantitatively estimate the contributions of the various anaerobic dissimilatory processes to overall organic

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carbon decomposition. Employing a carefully calibrated set of biogeochemical rate measurements Hyun et al. tease apart the contribution of Mn, Fe and sulfate reduction to organic carbon degradation in the Ulleung Basin of the East Sea bordered by Korea, Russia and Japan. This builds on a research approach pioneered in the nineties by Thamdrup, Canfield and co-workers. Here, Hyun et al. show that Mn reduction can be a powerful and important TEAP in during sedimentary organic matter degradation. While there are a number of assumptions built into the experiments used to estimate dissimilatory Fe and Mn reduction rates, this is still state of the art approach in sedimentary biogeochemistry. Moreover, from such experiments, they conclude that Mn reduction may be underestimated as a process in marine sediments as the techniques for studying Fe and Mn reduction require thorough and careful experimentation, as demonstrated in this study. Hyun et al.'s study is a further, solid step in the right direction and stands in stark contrast to recent efforts that only examine pore water concentration profiles (e.g. Bowles et al., Science 2014), which underestimate or miss the contribution of Fe, Mn and sulfate reduction towards organic carbon decomposition in near-surface sediments. I especially appreciated the attempt to link the relative contribution to total carbon oxidation as a function of the Mn content of the sediment. In general, this is a solid contribution to marine sediment biogeochemistry and I look forward to using these results as an excellent example of anaerobic TEAP processes in classes for the next generation of biogeochemistry students. (General response): 1. Thank you very much for this highly positive comments. We will incorporate your comment in revised manuscript as much as we can. 2. In this revised manuscript, we have modified the title of the manuscript to: "Manganese and iron reduction dominate organic carbon oxidation in surface sediments of the deep Ulleung Basin, East Sea" to clarify that the dominance of Mn and Fe reduction occurs in the surface sediments of the deep basin.

Specific comments:

1) Line 91: The authors might want to consider estimates from D'Hondt et al.

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Science 2004, where areal rates of Mn and Fe reduction in the Peru Basin have been estimated. Although derived from deep sub-surface pore water profiles, it would be interesting to see how the Peru Basin site maps onto Figure 7. (Response): Thank you for this suggestion. I agree that it will be nice if it fits onto Figure 7. The contribution of Mn reduction in total anaerobic Corg oxidation in the Peru Basin was 60% (see Table 1 in D'Hondt et al. 2004). The MnO content in the same site was 0.21 wt.% (see, http://www-odp.tamu.edu/publications/201_IR/chap_12/c12_t2.htm#1005989, Initial report of ODP Leg 201), that is equivalent to 46 $\mu\text{mol cm}^{-3}$. So, if we incorporate the value of the Peru Basin (PB) into the Fig. 7, it comes out as below;

It looks good at first glance. Please note, however, that the other data in the Fig. 7 is derived from the contribution of Mn reduction in a given depth interval in the sediment compared to the DCA-extractable Mn content in the same interval, with both parameters changing with depth in the sediment. The Panama Basin value, however, represents a depth-integrated value. Thus, the numbers are not really directly comparable, and we may have to decide not to add the point to the graph in the manuscript. Thank you again for adding an idea, and it was exciting to execute your idea. You may use the plot that we produced above. 2) Line 169: Pore water analysis....can approximate detection limits be provided? (Response): We have provided the detection limit or reproducibility of each constituent as you recommended in line 185 - 187 in the revised manuscript as follows "The detection limit of H₂S, Ca²⁺, Mn²⁺ and Fe²⁺ was 3 μM , 1.8 μM , 3 μM and 1 μM , respectively. Reproducibility of DIC and NH₄⁺ was better than 10%. Precision of NO₃⁻ was 1 – 2%."

3) Line 249 and following : It would be helpful to have a formula that includes the effect of SR the estimate of dissimilatory Fe (III) reduction (Equation 4) that includes the stoichiometry from Equation 5. (Response): The procedure used was adopted from Gribsholt et al. (2003). The rationale is that in the presence of reactive Fe(III), H₂S produced from sulfate reduction reacts with Fe(III) and the Fe²⁺ produced from this

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reaction precipitates as FeS. The stoichiometry of abiotic reduction of 2Fe coupled to reaction of 3H₂S in marine sediments is presented in several studies. For example, Melton et al. (2014, Nature Reviews. Microbiol.12: 797 – 808) stated that “At neutral pH, hydrogen sulphide (H₂S) can abiotically reduce Fe(III) oxyhydroxides: 2FeOOH + 3H₂S → 2FeS + S₀ + 4H₂O. H₂S reactions with Fe are especially important in marine environments, where high sulphate concentrations and microbial S reduction lead to pronounced H₂S production”. So, the H₂S in the equation 5 represents the H₂S produced from the sulfate reduction that we directly measured using ³⁵S injection incubation experiment.

(Correction): We have changed the equation (5) to “2FeOOH + 3H₂S(produced by SR) = 2FeS + S₀ + 4H₂O, and add one more review paper as a reference (Melton et al., 2014) in line 256 – 259 in revised manuscript.

4) Line 376...."that" does not take a comma. (Response): I removed the comma (line 385).

5) Line 388 and 414: Are "evidenced" and "zonated" proper verbs? (Response): We will change the 'evidenced that ~~' to “presented evidence that ~~” (line 397). We will also change the “systematically zoned with discrete sequential depletion according to the order of decreasing energy yield for Corg oxidation” to “systematically distributed with discrete zonation (line 422) according to the order of decreasing energy yield for Corg oxidation”

6) Line 440 "Consequently" not necessary (Response): I will remove the “Consequently” in revised manuscript (line 448).

7) Line 489 Replace "this" with "these" (Response): Yes. I will replace it in revised manuscript (line 510).

8) Paragraph at line 498: I find this argument to be a bit of a stretch. Basically the authors are saying because Canfield et al. had a negative result with a complexed Fe

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experiment that they also have no effect of ferrous iron on MnO₄ reduction. This is a bit weak. (Response): Thank you for this comment. In addition to the experimental results by Canfield et al., we also discussed that the MnO₂ reduction is a favorable Corg oxidation pathway that produces Mn²⁺ in line 526-527).

9) Paragraph starting at Line 548: I found this part very interesting. What happens when one moves out into total oxic sedimentary environments where oxygen penetration is deep and there are plenty of Mn oxide crusts (deep ocean sediment)? Should perhaps the Figure 7 refer to relative contribution of Mn reduction to "anaerobic" carbon oxidation? (Response): Thank you for this comment. Yes! It is a contribution of Mn reduction to anaerobic C oxidation. To avoid the confusion, I changed the figure caption of the Figure 7 as follows "The relative contribution of Mn reduction to anaerobic carbon oxidation as a function of the concentration of Mn(DCA) at 3 different sites. BS, Black Sea (Thamdrup et al. 2000); UB, Ulleung Basin (This study); Sk, Skagerrak (Canfield et al. 1993b)" We also replaced "total" with "anaerobic" in line 583.

10) Line 594: The authors might point out that they are probably underestimating total oxygen uptake. Bioirrigation might very likely play a major role in these sediments. (Response): It is correct that bioirrigation can contribute substantially to total oxygen uptake in some sediments. Bioirrigation has not been investigated in the UB sediments. We have discussed the potential underestimation of oxygen uptake and the consequences for the conclusions based on the large dataset reviewed by Glud (2008; Mar Biol Res 4: 243-289).

1. Finally, we have corrected our quantitative estimation on the partitioning of Corg oxidation pathways at each station in line 476 – 488: "Additionally, our partitioning of carbon oxidation pathways could be biased towards the anaerobic electron acceptors due to the use of the diffusive oxygen uptake (DOU) rather than total oxygen uptake (TOU), which will exceed DOU if bioirrigation is active (Glud 2008). Bioirrigation was not determined at our sites, but the pore water profiles show no indication of strong irrigation (Fig. 2). An average DOU/TOU ratio of ~0.6 has been reported for sediments

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at 1.5 – 2.5 km depth (Glud 2008). Using this ratio, and assuming that TOU is partitioned similarly as DOU between aerobic carbon oxidation and reoxidation, aerobic carbon oxidation would account for 25%, while Fe and sulfate reduction would account for 11% and 46% of of carbon oxidation, respectively. This, the potential bias from using DOU is not expected to affect the ranking of electron acceptors by quantitative importance (SO₄²⁻ > O₂ > Fe(III)), and, as discussed further below, the partitioning of Corg oxidation at M1 falls within the range previously reported for continental margin sediments.”

2. We also discussed the significance of aerobic respiration at basin site (D3) in line 505 - 507 in revised manuscript: “Correction for a potential underestimation of TOU, as discussed for M1, would reduce the contributions of Mn and Fe reduction slightly to 41% and 18%, respectively.”

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Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/bg-2016-222/bg-2016-222-AC3-supplement.pdf>

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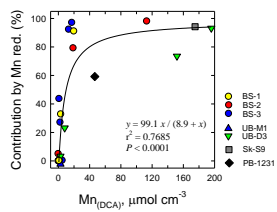


Fig. 1.