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Discussions

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 #1 Received and published: 10 July 2016

General comments

This paper proposes a method for quantifying the rates of organic C oxidation pathways in two deep continental margin sediment cores from the Ulleung Basin. It is one of the very few studies highlighting the role of Mn and Fe reduction as dominant organic C

oxidation process in marine sediments. The study presents an excellent geochemical dataset on the sediment and sediment pore-water and on anoxic incubations of sediments. I really appreciated many aspects of the modeling such as the effort made to evaluate distinctly the O2 consumption for the organic matter oxidation and for the reoxidation of reduced species, as well as to assess the adsorption of Mn+2 on Mn oxihydroxides. The manuscript is well written and judiciously refers the reader to previous works in the field. It assuredly deserves publication and will be of interest for a wide audience of aquatic geochemists. (General response): 1. Thank you very much for this highly positive comments on the manuscript. We will try to incorporate your comments as much as possible in the revisied version of the manuscript. 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 195: In addition to FeS and H2S, AVS also includes minute amounts of other metal sulfides. Isn't it? (Response) Yes. AVS includes several dissolved and solid-phase constituents such as H2S, FeS, iron sulfide nanoparticles and other metal sulfides (Rickard and Morse, 2005. Mar Chem 97: 141-197; Luther, 2005. Mar Chem 97: 198-205). Since FeS nanoparticles and FeSaq molecular clusters generally contribute only a small fraction of total AVS (Luther, 2005) and the content of other metals such as Zn and Cu is normally much lower than that of Fe, we assume that this is also the case here.

(Corretion): We will change the sentence to "For the determination of total reduced sulfur (TRS) that includes acid volatile sulfide (AVS = FeS + H2S and small amounts of other metal sulfides, see Rickard and Morse, 2005; Luther, 2005) and chromium-reducible sulfur (CRS = S0 + FeS2), ∼∼" in line 203 – 205 in the revised manuscript.

2) Line 209: I presume that the modeling of the O_2 micro-profiles with PROFILE was done assuming negligible bioirrigation and bioturbation but this is not specified. My deduction relies on the fact that a bioirrigation coefficient is not reported. However, these processes should not be insignificant since the authors state later in the MS that bioturbation realistically drives the Mn cycling in Ulleung sediments. I suggest clarifying this point.

Response: This is correct. Bioirrigation can contribute substantially to total oxygen uptake in some sediments, while sediment reworking through bioturbation is mainly of importance for the transport of solids. Thus, bioturbation coefficients are typically at least an order of magnitude lower than the molecular diffusion coefficient for oxygen (the biodiffusion coefficient estimated here (9.5 cm^2 y^{-1}) is ~50 times lower, but may yet be very important in the cycling of solids (e.g., Boudreau 1994, GCA 58:1243; see also response to comment #4). Bioirrigation has not been investigated in these 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).

(Correction): 1. Finally, we have corrected our quantative 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 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 (SO_4^{2-} > O_2 > 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."

3) Lines 246-249: It is not quite clear how the "abiotic Fe reduction coupled to H_2S oxidation" was estimated with reaction (5)? Some clarification should be provided. Do the authors assume that AVS mainly equals FeS? (Response): The procedure used was adopted from Gribsholt et al. (2003). The rationale is that in the presence of reactive Fe(III), H_2S produced from sulfate reduction reacts with Fe(III) and the Fe^{2+} produced from this reaction precipitates as FeS. The stoichiometry of abiotic reduction of 2Fe coupled to reaction of 3H_2S 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 (H_2S) can abiotically reduce Fe(III) oxyhydroxides: $2FeOOH + 3H_2S \rightarrow 2FeS + S^0 + 4H_2O$. H_2S reactions with Fe are especially important in marine environments, where high sulphate concentrations and microbial S reduction lead to pronounced H_2S production". So, the H_2S in the equation 5 represents the H_2S produced from the sulfate reduction that we directly measured using 35S injection incubation exeriment.

(Correction): We have changed the equation (5) to "$2FeOOH + 3H_2S$(produced by SR) = $2FeS + S^o + 4H_2O$, and add one more review paper as a reference (Melton et al., 2014) in line 256 – 259 in revised manuscript.

4) Line 606: The statement about the probable importance of bioturbation seems to be in contradiction with the well-defined utilization of the electron acceptors according to the order of decreasing energy yield for organic C oxidation that has been underscored

in lines 412-417? Again, I suggest clarifying this point. (Response): With bioturbation being a diffusive process, as assumed here and in other studies, we see no contradiction between the presence of bioturbation and the relatively distinct redox zonation. The estimated biodiffusion coefficient of (Db) of 9.5 cm2 yr-1 at Site D3 corresponds to ∼2% of the molecular diffusion coefficient of oxygen (388 cm2 yr-1). Judging from the absence of major fauna in the UB sediments, the mixing is brought about by small organisms with each individual affecting only a small area relative to the size of our cores, and the Db averaging many of these small but frequent events. Similarly, e.g., Hyacinthe et al (2001) found that well defined profiles can be observed in both sediments with low and high bioactivity in the Bay of Biscay. Therefore, we were able to see the well defined zonation of electron acceptors (Fig. 5F) in the UB where bioturbation is relatively weak.

Minor technical corrections

1) Line 218: Provide the value of Do with a reference. (Response): We will provide the value of Do with reference as follows “where Do (1.07 ïĆť 10-9 m2 s-1 at M1 and 1.03 ïĆť 10-9 m2 s-1 at D3) is the temperature-corrected molecular diffusion coefficient estimated from Schulz (2006)” in line 227 – 228 in the revised manuscript.

2) Line 221: Place in parentheses (see results section 3.2) after “. . .bimodal depth distribution”. (Response): We wil place it as follows “∼∼ bimodal depth distribution (see results section 3.2) ∼∼”. in line 231 - 232 in the revised manuscript

3) Line 262: Madison et al. (2013) does not appear in the list of references. (Response): Thank you. We will add the reference in the reference list in revised manuscript.

4) Line 276: I suspect that the units (ml/g) are erroneous? (Response): It is presented in Thamdrup et al (2000).

5) Lines 542-544: This sentence should be supported by references. (Response): Yes.

We have added references (i.e., Canfield et al., 1993b; Thamdrup et al., 2000) in the sentence (line 569-570).

Please also note the supplement to this comment: http://www.biogeosciences-discuss.net/bg-2016-222/bg-2016-222-RC1- supplement.pdf Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2016-222, 2016.

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