

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.

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General comments

1) Hyun et al. have investigated pathways and rates of organic carbon mineralization at two sites in the Ulleung Basin, East Sea. They have used a combination of direct and indirect approaches to determine rates of the different electron acceptor processes

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and compare these to the depth distribution of the different oxidants in the upper 10 cm of sediments of a slope site (station M1) and a site in the central Ulleung Basin (station D3). The authors demonstrate that metal oxide reduction represents the dominant pathway of organic carbon oxidation in the surface sediments of the deep central basin and suggest that Mn and Fe reduction may be more important in driving biogeochemical processes in similar marine settings than previously thought. Furthermore, they point out that a significant increase in sea water (sea surface?) temperature is observed in the study area and that in this respect it is important to monitor the impact of this environmental change on biogeochemical cycles and element fluxes. The authors have generated an excellent and unique data set and the manuscript is definitely suitable for and should be published in Biogeosciences after some minor revision (cf specific comments below). (General response): 1. Thank you very much for your positive and critical comments that will improve the quality of this manuscript. I together with my co-authors will try to incorporate your comments as much as we can. 2. In this revised manuscript, as you suggested, 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.

2) One of my major points is that I would suggest to better focus the objectives and conclusions. Do the authors really think that the phenomenon of Mn reduction/metal oxide reduction dominating organic carbon mineralization in marine sediments is a phenomenon of continental margin sediments in general? My understanding is rather that manganese reduction seems to be of particular importance in basin settings where reactive (partly freshly precipitated) Mn oxide phases are supplied in higher relative abundance due to geochemical focusing. Therefore, I recommend that the authors more clearly point out on which kind of depositional marine environment/s they are focusing on – continental margins, deep sea, deep basin settings?! (: : : and also highlight this in the title). Moreover, I think that a deep basin setting is not a typical continental margin depositional environment.

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(Response): Thank you for this thoughtful comment. As you pointed out, if we consider the depth > 2000 m, the UB is a deep basin sediment, and the dominance of Mn reduction is of importance at the deep basin site. However, the East Sea including the Ulleung Basin is regarded a marginal sea since it is isolated from the open ocean (northwest Pacific), and is surrounded by Korean peninsula and Japan islands (Kang et al. 2010; Liu et al., 2010). On the other hand, as you pointed out, the dominance of Mn reduction is of importance in the basin site (D3), and is not significant for Corg oxidation processes at all in the slope site (M1). In this regard, I see that the title you suggested fits perfectly to resolve the two contradicting aspects.

Concerning the generalization of the results to other environments, the discussion (end of Section 4.2) is based mainly on the relationship of Mn reduction to sediment Mn oxide content (Fig. 7), which includes both continental margin sites and deep basins. Also the citations included as examples of locations with sufficiently high Mn oxide content for Mn reduction to make a substantial contribution to carbon oxidation include both continental margin and deep basin sites. While some of these sites are not clearly located in basins, we do agree that bottom topography is likely to play an important role in allowing geochemical focusing.

(Corrector): 1. We will change the title of the manuscript as you recommended in revised manuscript (please see the response on your specific comment #1).

2. We will add more description on the UB in the Study Site section in line 129 – 134 in the revised manuscript as follows “The East Sea is a marginal sea surrounded by the east Asian continent and Japanese Islands (Fig.1, Kang et al., 2010). The UB located in the southwestern part of the East Sea is a bowl-shaped deep basin (2000 – 3000 m depth) (Fig. 1) delimited by continental slopes of Korean Peninsula and the southwestern Japanese Archipelago on the west and south, respectively, and by the Korea Plateau and the Oki Bank on the north and east, respectively (Chough et al., 2000)”.

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3. We will also change the Discussion to clarify that Mn reduction is mainly expected to be important in basin settings in line 590-596 in the revised manuscript as follows: “Manganese enrichments of this magnitude have been reported for several locations on the continental margins and in deep basins (Murray et al., 1984; Gingele and Kasten, 1994; Gobeil et al., 1997; Haese et al., 2000; Mouret et al., 2009; Magen et al., 2011; Macdonald and Gobeil, 2012; Mewes et al., 2014) in addition to the relatively few places where dissimilatory Mn reduction was already indicated to be of importance, as discussed above. Thus, the process may be of more widespread significance, particularly in deep basin settings such as UB that allow geochemical focusing of manganese”. (Please see also the response to comment #43.)

3) I also did not fully understand how this study may really contribute to monitoring the impact of environmental change (increase in surface water temperature) and how and why this future task is important in the framework of the present study. Do the authors assume that their investigation represents a kind of “baseline study” and will the detailed investigations performed here will be continued in the future? If yes, I would suggest to point this out more explicitly. On the other hand the authors have stated that the study area has (already) experienced the “fastest” (by the way: compared to what?) increase in sea water/sea surface temperatures. So, I assume that the study sites are already affected by this environmental change (because as you say – warming already started in 1982) and cannot really serve as a “pristine” (whatever that is) site or a location for a baseline study. So, if you mention the importance of assessing the impact of environmental changes on biogeochemical processes and cycles – please clearly explain how this precisely relates to the current study – or just delete.

(Response): We are sorry for this confusion. I have skipped too much in explaining the background of this last section, and I am glad to have a chance to refine the significance of monitoring the variations of the rate and pathways of Corg oxidation (i.e., monitoring relative significance of each TEAP) with the decreasing O₂ concentrations and temperature increase in the bottom layer of the UB (or East Sea) in predicting and

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understanding future biogeochemical processes in the East Sea. First, both the points raised here (i.e., baseline study and long-term monitoring) are correct. We see the measurements as a contribution to defining the current state as a baseline for monitoring potential future change, but we also acknowledge that some changes may have already taken place for last several decades.

(Correction): We will explain these aspects better in Discussion (line 663 – 688 in SECTION 4.4) in the revised manuscript as follows: “The East Sea is often called as “a miniature ocean” because of the independent thermohaline convection system that is driven by the high density surface water sinking (Kim et al., 2001) in a manner similar to that of the Great Ocean Conveyor Belt (Broecker, 1991). The turnover time (ca. 100 – 300 years) of the thermohaline circulation is shorter than that of the global conveyor belt of 1000 – 2000 years (Broecker and Peng, 1982). Because of the shorter time-scale, together with the relatively small volume, the East Sea is expected to be much more sensitive to global environmental changes (such as global warming) compared with the open oceans. In this regard, the East Sea has been considered as a natural laboratory that provides a useful field for large-scale oceanographic experiments to predict the response of oceans associated with long-term climatic/oceanographic changes (Kim et al., 2001). Over the last two decades (1982 – 2006), a rapid increase of sea surface temperature (SST) of 1.09 °C has been recorded in the East Sea, which is the fourth highest among the 18 large marine ecosystems in the world ocean (Belkin, 2009). Increased SST reduces the solubility of O₂ in the surface mixed layer and enhances stratification, which ultimately affects biological production in the water column and suppresses transport of O₂-rich surface water into the deep bottom. Indeed, recent oceanographic observations revealed that the gradual deoxygenation and warming of the bottom water of the East Sea over the last 30 years have resulted in an ~10% decrease in dissolved oxygen and ~0.04 °C increase in potential temperature, which suggested a weakening of the deep convection system (Kim et al., 2001; Gamo et al., 2011). Benthic metabolism and respiratory C_{org} oxidation coupled to various TEAP in the sediments are largely controlled by the combination of O₂ content, temperature

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and biological production overlying water column (Canfield et al., 2005). It is thus important to monitor any changes in the rates and partitioning of C_{org} oxidation to better understand and predict the variations of biogeochemical cycles of carbon, nutrients and metals potentially associated with long-term climatic changes in the UB, the biogeochemical hotspot of the East Sea.”

4) A further point is that references to more recent studies on organic carbon mineralization pathways and rates in deep-sea sediments are largely missing. Please, add the relevant more recent studies in the Introduction and Discussion chapters. (Response): Thank you for this comment, and providing those references. We will add the references in Introduction and Discussion. Please see the response on your specific comment # 6, 7, 31 and 35.

Specific comments

1) Title: the term “deep” suggests that you have worked in deep subsurface sediments – however, you have in fact studied surface sediments (i.e. the uppermost 10 cm). I would therefore suggest to rephrase the title to something like “Manganese and iron reduction dominate organic carbon oxidation in surface sediments of the deep Ulleung Basin” (Response): Thanks for the comment. We will change the title in revised manuscript as you suggested.

2) L. 38: : : : in “sediments of” the continental slope. (Response): Yes, we have changed this in line 38.

3) Ls. 50, 632 and 662: biogeochemical (Response): Thank you for the correction. We have corrected the mistyping in line 50, 661, and 710.

4) L. 53: “fastest increase” compared to what exactly? Please explain. (Response): We have changed it to “ ~ where the gradual deoxygenation and warming of the bottom water have resulted in an ~10% decrease in dissolved oxygen and ~0.04 °C increase in potential temperature for the past three decades.” in line 53 – 55, and

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more explanation is presented in line 663 – 688 in discussion section of the revised manuscript (Please see the response and correction the we made for your general comment #3).

5) Ls. 78/80: In this context I would also refer to and cite papers which demonstrate the close coupling of phosphate to the redox recycling of iron (e.g. Slomp etc.) (Response): Thank you very much for this appropriate comments. We will add two more references in line 76 – 77 as you suggested.

Hensen et al., 2006 Benthic cycling of oxygen, nitrogen, and phosphorus (Marine geochemistry Ch.6). Slomp et al., 2013 Coupled dynamics of iron and phosphorus in sediments of an oligotrophic coastal basin and the impact of anaerobic oxidation of methane

6) Ls. 84 ff: Numerous papers on rates and pathways of organic matter mineralization in carbon-starved deep-sea sediments have been published in recent years and should be cited here as well. Amongst others, these comprise work in the South Pacific Gyre in the framework of the IODP (e.g. D'Hondt et al.) as well as in the Clarion–Clipperton fracture zone in the equatorial east Pacific Ocean (Mewes et al., 2014, Deep Sea Res., Part I, 91; Mewes et al., 2016, EPSL, 433; Mogollon et al., 2016, Geophys. Res. Lett., 43). (Response) We will cite those references (D'Hondt et al., 2015; Mewes et al. 2016) in the revised manuscript, and revised the sentence to “In general, aerobic metabolism dominates the organic matter mineralization in deep-sea sediments that are characterized by low organic matter content (Jahnke et al., 1982; Glud, 2008), especially in organic carbon-starved deep-sea sediments with low sedimentation rates (Mewes et al., 2014, 2016; D'Hondt et al. 2015; Mogollón et al., 2016).” in line 81 – 85.

7) Ls. 87 ff.: I would suggest to rephrase and to add the recent reference by Bowles et al. (2014, Science) on global rates of sulfate reduction: : : , sulfate reduction “can” account for up to 50% of total carbon oxidation : : . (: : ..; Bowles et al., 2014) (Response): Yes. We have added the reference in line 88.

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8) L. 95: : : such as “the” Panama Basin (Response): Thanks. We have corrected in line 95.

9) Ls. 101/102: “the” Japan Basin, “the” Yamato Basin and “the” Ulleung Basin : : : (Response): Thanks. We have corrected in line 101 – 102.

10) L. 102: Rephrase to: : : , the “surface waters” of the Ulleung Basin “are” characterized by higher : : : (Response): I have rephrased this in line 102 – 103.

11) L. 105: The enhanced biological production in the “euphotic zone of the Ulleung Basin” is responsible : : : (Response): We have rephrased it as you suggested in line 105 – 106.

12) L. 115: “surface waters” instead of water column (Response): Correction has been made in line 116 as you suggested.

13) L.118: : : : “at” the continental slope and rise : : : . (Response): Correction has been made in line 119

14) L. 132: delete “the” before two (Response): Yes. We did it in line 138.

15) L. 134: : : : continental “margin” sediments (Response): Yes. We have added the word in line 141.

16) L. 140: write: “in diameter”. I would suggest that you also give the length of the sediment cores that you have investigated in the framework of this study. (Response): Yes! I did it according to your suggestion in line 146 – 147.

17) L. 162: : : : in “a” N₂-filled glove bag : : : (Response): Correction has been done in line 168.

18) L. 164: “within” instead of in (4 weeks) (Response): Correction has been made in line 170.

19) L. 174: Mn²⁺ (Response): We changed it to Mn²⁺ in line 180

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20) Ls. 175 and 191: “inductively” coupled plasma-atomic emission spectrometry (Response): Thanks. Corrections have been made in line 181 and 199.

21) L. 187: : : “for the” (pore-water analysis) – instead of in (Response): Thanks. We have made a correction in line 195.

22) L. 192: What exactly do you mean with “free” Mn oxides? Please explain! (Response): Dithionite is used for extraction of all forms of iron and manganese oxides that are not protected (i.e., “free”) by an insoluble barrier such as a silica concretion surrounding oxide particles. Free oxides is a term used traditionally in studies of iron and manganese partitioning in soils and, later, sediments (see, e.g., Canfield 1989. GCA 53:619; Golden et al. 1994. Clay and Clay Minerals. 42: 53-62).

23) L. 194: What was the detection limit for Fe? (Response): We have added the detection limit of the Fe²⁺ (1 μM) in line 202.

24) L. 230: “dissolved” instead of soluble (Response): We changed it to “dissolved” in line 240.

25) L. 283: Canfield et al. (1993a) were certainly not the first to give this stoichiometry. (Response): Honestly, I do not know the original paper that presented the equations first. Basically, those equations assuming an oxidation state of zero for the organic carbon can be found easily in several books and papers (e.g., Froelich et al. 1979). I chose the Canfield et al. (1993a), and hope that is fine with you.

26) L. 309 and throughout the manuscript: Please, always speak of “site” or “station” M1/D3. (Response): To make the manuscript more concise, We renamed the “Station M1” to “M1” and “Station D3” to “D3” in the Study area section in revised manuscript (line 139-140). Otherwise, there are too many places to express St. D3 or St. M1, which seems to be too redundant. I hope it is okay for you.

27) L. 332 and throughout the manuscript: I would suggest to always speak of “contents” (instead of concentrations) when you refer to solid-phase values. (Response):

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Thank you for the comment. We will change the solid-phase values to “contents” in revised manuscript.

28) L. 339: “uptake” instead of utilization (Response): Yes. We will change it to “uptake” in line 348

29) L. 483: : : of “the” respective electron acceptor \hat{A} (Response): Yes. We have added “the” in line 502.

30) L. 507: What exactly do you mean with “anoxia” here? Anoxic conditions in the surface sediments or anoxia in the water column (I assume you mean former). (Response): You are right. I changed the phrase to “Despite the anoxic condition and nitrate depletion during the sediment incubation,” ~. in line 528 in the revised manuscript.

31) L. 507 ff.: You describe here that there is a discrepancy between Mn²⁺ accumulation in the pore water and rates inferred from DIC accumulation and contribute this discrepancy to adsorption on Mn²⁺ to fresh Mn oxide surfaces. In this context we would like to bring to your attention our recently published paper on the coupling of manganese and nitrogen cycling in deep-sea sediments of the Clarion-Clipperton fracture zone in the equatorial Pacific Ocean (Mogollon et al., 2016, Geophys. Res. Lett., 43). In this paper we suggest that Mn²⁺ may act as a reducing agent for oxidized nitrogen species. Do you think that this process might potentially also play a role in the surface sediments of the Ulleung Basin? – in particular because the sample/depth interval where this discrepancy occurs is characterized by the presence of nitrate. Please discuss. (Response): Thank you for the suggestion and the references associated with the Mn²⁺ oxidation coupled to NO_x reduction. The process would not explain the absence of Mn²⁺ accumulation in the anoxic incubations, because nitrate was rapidly depleted, but it could play a role in situ. We will add to the discussion as follows “Low Mn²⁺ together with the rapid decrease of nitrate at 0-2 cm depth at D3 (Fig. 2F, 2G) also suggested that dissolved reduced manganese might act as a reduc-

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ing agent for nitrate as it was suggested by Aller et al. (1998) in the Panama Basin and Mogollón et al. (2016) in the deep-sea sediment of the Clarion-Clerton fracture zone in the northeast equatorial Pacific.” in line 533 – 537 in the revised manuscript.

32) L. 531: “fall” instead of falls (Response): Thanks. We did it in line 557.

33) Ls. 560 ff.: I do not understand this sentence at all. Please rephrase. (Response): The sentence says that there is a good relationship between MnO₂ content and the contribution of Mn reduction, and that the contribution of Mn reduction is important even at low MnO₂ content. And additional discussion is presented after the sentence. As it seems to be confusing, as you pointed out, we have changed it to “The plot indicates a close correlation between Mn oxide content and the importance of Mn reduction. Curve-fitting yields a concentration of MnO₂ at 50 % of contribution of manganese reduction to total Corg oxidation (K_s) of 8.6 μmol cm⁻³ similar to the approx. 10 μmol cm⁻³ suggested before (Thamdrup et al., 2000). This indicates that Mn reduction can be a dominant Corg oxidation process even at low concentrations of Mn oxides compared to those found at UB” in line 584 – 589 of the revised manuscript.

34) Ls. 564: In this context we would like to bring to your attention further studies on solidphase manganese contents - Gingele and Kasten (1994, Mar. Geol., 121) and Mewes et al. (2014, Deep Sea Res., Part I, 91). (Response): Thanks for providing the references on the solid phase Mn. We have included them in line 591 – 593.

35) Ls. 578: With respect to the geochemical focusing of Mn in deep central parts of basin settings, I would also like to bring your attention to the work of Schaller et al. who have worked on lake sediments and describe very similar accumulation mechanisms. (Response): Yes. I have added the “Schaller and Wehrli (1997)” that fits well in the sentence in line 609 in the revised manuscript.

36) L. 611: Please delete “of” at the end of this line. (Response): Yes. We have deleted “of” in line 640.

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37) Ls. 617 and 623: : : : of “a” Chilean upwelling site (Response): Yes. We have added the “a” in line 646 and 652.

38) Ls. 619, 620 and 630: organic “carbon” flux/content (Response): Yes. I have added “carbon” in line 649 and 659 in the revised manuscript

39) L. 637: : : : biogeochemical “cycles of” carbon : : : (Response): Yes. I have changed it in line 686 in the revised manuscript.

40) L. 638: I still do not understand why the Ulleung Basin is a “biogeochemical hotspot”? Is it because organic matter mineralization is dominated by metal reduction? This is not clear at all and I would therefore suggest to better explain or to delete this. (Response): It is not because organic carbon mineralization is dominated by metal reduction. The reason that we stated the UB as a biogeochemical hot spot is that the overall organic carbon oxidation in the UB is higher than those measured in major upwelling system such as Benguela upwelling system and is even comparable to those reported at the continental slope of the Chilean upwelling system at a similar depth range of 1000 – 2500 m. Please see the line 640 – 662 in the revised manuscript.

41) I also do not like very much the statements you give with respect to the uniqueness of the study and the study site (eastern Asian marginal seas) in lines 547/548 and 646 ff. I think that you have performed a unique and excellent study and there is no need to justify this in terms of being the first study of this kind for this particular region. (Response): As you wished, we will delete the sentence in line 646 in original version (i.e., For the first time in the Asian marginal seas, and in one of only few experimental studies of the partitioning of Corg oxidation pathways in deep-sea sediments in general, we~). We feel that the statement in line 570-573 in the revised manuscript makes the sentence stronger and more determinant and fluent. I hope this is fine with you.

42) L.650 ff: Is it possible that all Mn initially contained in the settling particles has been reductively mobilized from the deeper/buried sediments and has successively been concentrated in the uppermost sediments of the deep basin – leading to the ob-

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served high Mn contents? Please, discuss. (Response): Yes, our interpretation is that essentially all Mn is stripped from the settling particles during burial, and the surface enrichment further requires that the Mn oxides that form from reoxidation of Mn²⁺ in the surface sediment are also reduced and recycled over and over. Nonetheless, at steady state, the net sedimentation and burial fluxes should be the same. We added some text to clarify this in line 612 – 619 in the revised manuscript as follows: “Adopting the sediment accumulation rate of 0.07 cm y⁻¹ in the UB determined at a station 50 km from D3 (Cha et al., 2005), the average Mn(DCA) concentration of 1.1 μmol cm⁻³ at 10 – 20 cm depth (Fig. 2G) corresponds to a flux for permanent burial of 0.002 mmol m⁻² d⁻¹ or just 0.03 % of the Mn reduction rate (Table 3), i.e., an Mn atom is recycled 3800 times before it finally gets buried – first by stripping from the particles that settle to the seafloor and subsequently, over and over, by reductive dissolution of the Mn oxides that form by reoxidation in the oxic surface layer (or, potentially, in the nitrate zone; Aller et al. 1998, Mogollón et al. 2016)”.

43) L. 656: Is Mn reduction really generally important in “deep-sea sediments”? Isn't it rather that Mn reduction/metal reduction is important in deep basin settings? (Response): Yes – we have changed this to deep basin sediments. As mentioned in the response to comment #2, Mn enrichments also appear widespread in continental margin sediments. However, the present study mainly focuses on the deep basin setting, and we have therefore chosen to emphasize this type of environment in the conclusion. (Correction): We will change the sentence to “ ~ thereby that the process might be more important in continental margin and deep basin sediments than previously thought” in line 702 – 704 in the revised manuscript.

44) Ls. 664 ff: Fastest increase in sea water (I guess “surface water”) temperature compared to what exactly? Please explain. (Response): We will replace this sentence with “Over the last 30 years, the gradual deoxygenation and warming of the bottom water of the East Sea have resulted in an ~10% decrease in dissolved oxygen and ~0.04°C increase in potential temperature” in line 711 – 713 in the revised

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manuscript. (For more explanation, please see the response and correction made to your general comment #3.)

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Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/bg-2016-222/bg-2016-222-AC2-supplement.pdf>

Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2016-222, 2016.

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