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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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Hyan 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 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,

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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). 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.

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.

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.

Specific comments

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”

L. 38: . . . in “sediments of” the continental slope.

Ls. 50, 632 and 662: biogeochemical

L. 53: “fastest increase” compared to what exactly? Please explain.

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.)

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).

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)

L. 95: . . . such as “the” Panama Basin

Ls. 101/102: “the” Japan Basin, “the” Yamato Basin and “the” Ulleung Basin . . .

L. 102: Rephrase to: . . ., the “surface waters” of the Ulleung Basin “are” characterized by higher . . .

L. 105: The enhanced biological production in the “euphotic zone of the Ulleung Basin” is responsible . . .

L. 115: “surface waters” instead of water column

L.118: . . . “at” the continental slope and rise . . ..

L. 132: delete “the” before two

L. 134: . . . continental ”margin” sediments

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.

L. 162: . . . in “a” N2-filled glove bag . . .

L. 164: “within” instead of in (4 weeks)

L. 174: Mn2+

Ls. 175 and 191: “inductively” coupled plasma-atomic emission spectrometry

L. 187: . . . “for the” (pore-water analysis) – instead of in

L. 192: What exactly do you mean with “free” Mn oxides? Please explain!

L. 194: What was the detection limit for Fe?

L. 230: “dissolved” instead of soluble

L. 283: Canfield et al. (1993a) were certainly not the first to give this stoichiometry.

L. 309 and throughout the manuscript: Please, always speak of “site” or “station” M1/D3.

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

L. 339: “uptake” instead of utilization

L. 483: . . . of “the” respective electron acceptor —

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).

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.

L. 531: “fall” instead of falls

Ls. 560 ff.: I do not understand this sentence at all. Please rephrase.

Ls. 564: In this context we would like to bring to your attention further studies on solid-phase manganese contents - Gingele and Kasten (1994, Mar. Geol., 121) and Mewes et al. (2014, Deep Sea Res., Part I, 91).

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.

L. 611: Please delete “of” at the end of this line.

Ls. 617 and 623: . . . of “a” Chilean upwelling site

Ls. 619, 620 and 630: organic “carbon” flux/content

L. 637: . . . biogeochemical “cycles of” carbon . . .

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.

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.

L.650 ff: Is is 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 observed high Mn contents? Please, discuss.

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?

Ls. 664 ff: Fastest increase in sea water (I guess “surface water”) temperature compared to what exactly? Please explain.

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