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Reply on RC2

Gerard J. M. Versteegh et al.

Author comment on "Geochemical consequences of oxygen diffusion from the oceanic crust into overlying sediments and its significance for biogeochemical cycles based on sediments of the northeast Pacific" by Gerard J. M. Versteegh et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2021-112-AC2, 2021

Also for this review we followed all suggestions for improvement. Below a detailed account of our response is provided:

General comments

This manuscript describes porewater and solid phase profiles of oxygen, nitrate, manganese, cobalt, and nickel in oligotrophic sediment within the German nodule exploration block of the Clarion Clipperton Zone in the northern Pacific Ocean. The authors document variable profiles of oxygen, with fully oxic sediment profiles in relatively thin sediment profiles near seamounts and thicker sediment packages overlying presumed subsurface faults. The profiles of oxygen indicate diffusion from the seawater-sediment and the sediment-basement interfaces, indicating oxic conditions in basement in this region, as had been documented before. By contrast, thicker sediment packages away from these features exhibit zones of suboxic conditions where dissolved manganese increases from solid phase Mn oxide dissolution, which also leads to mobilization of cobalt. It is presumed that oxygen also diffuses from basement into deeper layers of sediment, but the coring depths were too shallow to confirm this. The main points of the manuscript are that: 1) the depth of oxygen penetration from the seafloor is somewhat uniform, the depth of oxygen diffusion from basement is more variable and suggests highly variable basement oxygen concentrations, 3) nitrification in sediment can lead to a nitrate source to basement fluids in some instances, 4) cobalt and other redox sensitive elements are remobilized due to suboxic conditions and do not reflect initial burial conditions.

While this manuscript is well written and based on a very impressive dataset, I was disappointed that the authors did not put the results into a larger context of what is known about sediment-basement interactions at other locations. The results are described in exquisite detail, but the discussion section lacks comparison of these profiles and their patterns to recent comparable studies from the equatorial Pacific (Wheat et al. 2019, DOI: 10.1029/2018GC007933) or the south Pacific Gyre (D'Hondt et al. papers) or from the western North Atlantic (D'Hondt and colleagues) or from the flank of the Mid-Atlantic Ridge (Orcutt et al., 2013; Wankel et al. 2015, Ziebis et al. 2012, Kiel Reese et al. 2018). For example, how do the authors claims about sediment nitrate being a source or sink to basement compare to inferences from these other studies, besides just the earlier work from Fisher and Wheat 2008? (Disclaimer that this reviewer is a co-author on some of the work suggested for consideration and, thus, this suggestion may be viewed as a conflict of interest).

We expanded our discussion and better integrated our comparison with published literature:

Putting together the nitrate concentrations through marine sediments there seem to be three kinds of profiles. The first situation occurs in the more eutrophic ocean and coastal margins, where sediments get anoxic at depth and NO_3^- completely disappears from these anoxic sediments (e.g. Froelich et al., 1979). As NO_3^- is absent from the deeper sediment, a flux of NO_3^- will occur from the basaltic basement upwards, into the sediment where it gets consumed. Towards increasingly oligotrophic conditions, usually also with slower sedimentation, O_2 can diffuse deeper into the sediment. Denitrification rates NO_3^- decrease conversely, the depth at which NO_3^- is completely consumed increases as well e.g. just outside the South Pacific Gyre (SPG) core SPG-12 (D'Hondt et al., 2009), IODP 329 Site U1371 (D'hondt et al., 2015) and Western N. Atlantic KN223 Site 10 (Buchwald et al., 2018).

A second situation occurs where NO_3^- remains present throughout the sediment. It seems that this situation occurs with decreasing productivity/sedimentation rate and denitrification in the anoxic zone reduces such that it is insufficient to create a zone without NO_3^-. This occurs at e.g. at Dorado Outcrop on the East Pacific Rise (Wheat et al., 2019). Here, Mn reduction starts when NO_3^- gets below 10-20 µmol/kg. In such cases, the redox succession probably remains suboxic with Mn reduction, and doesn't enter the zone of Fe reduction. In the CCFZ cores we observe a linear negative relation and 1:1 relation between NO_3^- and Mn^{2+} concentrations (Fig 6). In the East pacific Rise (Wheat et al., 2019) dissolved Mn appears if NO_3^- gets below 25 µmol/kg and NO_3^- becomes depleted if Mn^{2+} concentrations are near 70µmol/kg so that a 1 µmol increase in NO_3^- results in a 2.8 µmol decrease in Mn^{2+}. As long as sedimentary NO_3^- remains lower than the NO_3^- in the basaltic basement, NO_3^- diffuses from the basalt upwards into the sediment. However, as maximum Mn^{2+} concentrations decrease, minimum NO_3^- concentrations increase and eventually, NO_3^- concentrations remain higher in the sediment than in the basaltic basement establishing a net NO_3^- flux from the sediment into the underlying basaltic basement. This is most probably the case at IODP 329 Site U1370 at the edge of the SPG (D'hondt et al., 2015).

The third situation starts if Mn^{2+} approaches zero and the sediments become entirely oxic and denitrification ceases. This situation is reached in the CCFZ, NO_3^- concentrations reach 52 µmol/l. Mewes et al (2014) find a slightly higher threshold of 60 µmol/l (Fig. 6 green dots). In all these cases, sediments are a NO_3^- source to the basaltic basement. This is also observed at North Pond, Western Flank of the Mid Atlantic Ridge, at IODP 336 sites U1382B, U1383D, U1384A (Wankel et al., 2015) and in the latter study maximum NO_3^- concentrations increase with decreasing reaction rates.

We observe that from this situation of minimum O_2 concentrations just above zero, sediments exist with much higher minimum O_2 values. We infer that towards increasingly poor settings such as towards the centers of the oceanic gyres, minimum O_2 values increase and despite lacking denitrification, maximum sedimentary NO_3^- concentrations decrease. This situation is encountered in the SPG, cores SPG 1-11 (D'Hondt et al., 2009) and at IODP 329 sites U1365 to U1369 (D'hondt et al., 2015) where maximum NO_3^- concentrations decrease towards the SPG centre.

We observe that maximum NO_3^- concentrations remain close to those in the bottom waters and in the basaltic basement so that fluxes from the sediment to the basaltic are virtually absent and reduce towards the core centres.

Thus, on a global scale, the eutrophic regions and continental margins bear sediments with complete denitrification in the sediment and the basaltic basement is source of nitrate to the sediment. More mesotrophic conditions and at larger distance from land where sedimentation rates are lower, a zone occurs where denitrification is reduced such that NO_3^- remains available throughout the sediment. At the eutrophic side of this zone denitrification is sufficient to reduce sedimentary NO_3^- below basaltic basement values and a nitrate flux exists from the basaltic basement into the sediment. In the more oligotrophic side of this zone, denitrification is reduced such that NO_3^- values in the sediment remain higher than in the basaltic basement and the basaltic basement is a NO_3^- sink. Towards the oligotrophic oceanic gyres, the sediments become entirely oxic, and denitrification ceases. If the sediments are just oxic throughout, maximum NO_3^- concentrations approach those of sediments with a minimal suboxic zone. However, further to the oceanic gyres, increasing oligotrophy also increasingly limits the maximum NO_3^- concentration that can be reached will reduce again and approach (but still exceed) those in the bottom waters and basaltic basement and fluxes of NO_3^- from sediment to the basaltic basement (as well as to the bottom waters) reduce.

I am also a bit perplexed by the inference of the oxygen concentrations at the sediment-basement interface based on this study. In Table 2, the inferred basement oxygen concentration at one site is likely higher than bottom water oxygen concentration in this region (note: this isn't reported in the paper, but looking at the CTD profiles in the cruise report, along with WOCE datasets, indicates a regional bottom water concentration closer to 200 µM). Likewise, extrapolating the nearly linear profiles to the inferred basement depth in other profiles leads to similarly perplexingly high concentrations. The discussion section on porewater oxygen does not address this issue.

The data we report are based on gravity and piston cores. For both coring devices the uppermost sediment mostly gets lost upon recovery. Examining the World Ocean Atlas 2018 we arrive at 162 µmol/l for the region which is close to values reported by Mewes et al., 2015 and Mogollón et al., 2016 but these are higher than the value reported by Volz et al., 2018). Analyses of accompanying box cores shows that the values drop to those reported in the gravity- and piston-cores presented here within the top 5 cm. We added this information to the text.

Indeed, the inferred O_2 concentration at the sediment/basalt interface for core 69 is close to that of the bottom water concentrations. This is easy to explain if we accept that the site of inlet is close to the core site so that there has been virtually no drop in porewater oxygen concentrations on its way from the site of inlet to the core site. We took a closer look at the inferred sediment depths and the obtained regression lines, for all cores and took into account better estimates of sediment thicknesses. We added estimates of O_2 concentrations at the sediment/basalt interface for the other cores in Table 2, where possible and discuss this in the text. Site 69 provided the highest O_2 concentration (156 µM) inferred for the sediment/basalt interface. This equal to just below the concentration in the bottom waters. Core 69SL is taken close to a seamount which is a potential site for basement fluid intake. As such the waters circulating through the basement below 69SL must have entered the basement relatively recently and the site of inlet may be relatively active so that it may be expected that at the sediment/basement interface the O_2 concentration is close to that of the bottom waters.

Continuing the oxygen theme, the variable depths of the suboxic fronts are really intriguing to me. The authors state that the variability in the shallower front being related to variability in bottom water oxygen conditions. I am curious why the authors do not consider variable bioturbation impacts, a non-steady state phenomenon, also as a possible cause. The highly variable depth of the deeper suboxic front is also fascinating, and I'd like to see more discussion about that.

Bioturbation appears to by highly variable in the German license area of the CCFZ but reaches mostly to only 7 cm and occasionally to 13 cm (Volz et al., 2018) and as such are not an explanatory variable to understand why in our cores the suboxic front varies between 10 cm and 350 cm below the sea floor. Even if we underestimate bioturbation depth by a factor 2 this would make no difference. For this reason, bioturbation was not taken into consideration in the paper. We included a statement on this now.

The highly variable depth of the deeper suboxic front is a direct consequence of the highly variable oxygen fluxes from the basaltic basement into the sediment. These in turn depend on the degree to which the basement fluid penetrates through the basement (flow rate), the length of way from the inlet to the site of diffusion into the sediment and the reactivity of basement and sediment on the route from the inlet to the lower suboxic front. There are too many uncertainties in these parameters to predict what will be observed in reality. We only can observe the positions of the lower oxidation fronts, infer from this oxygen concentrations at the basement/sediment interface and deduce from this that the oxygen flux must be very variable.

So, overall, I find this to be an interesting study, but I would like to encourage the authors to spend a bit more time putting the results in a larger context of what is known. Below I also highlight a few specific areas that need attention to improve clarity:

Specific comments

Line 95: I am not sure that the Fischer et al. 2009 and Ziebis et al. 2012 citations are appropriate references here for a comment about measuring oxygen in ocean drilling program cores, as these studies were on gravity core samples. More appropriate references would be D'Hondt et al. 2015 for the South Pacific Gyre and/or Orcutt et al. 2013 for North Pond, which are the only two drilling expeditions with porewater oxygen data.

Has been corrected

Line 171: I think "nearly linear" might be the more appropriate phrase here, since some of the deeper oxygen profiles show some curvature in their profile below the minimum oxygen depths.

Changed

In the methods and/or acknowledgement section of the paper, the authors should state that the working areas are within the area contracted by the International Seabed Authority to the German Federal Institute for Geosciences and Natural Resources for exploration of polymetallic nodules.

Done

Table and Figure comments:

- overall, there are several inconsistencies in the labeling of sites between tables and figures. please carefully check.

Done

Table

- consider adding an additional column, or to modify the core name column, to indicate the "SM" and "F" categories of the cores used in the figure.

We added these designations to the core names

Figure 1.

- there seems to be a mismatch in the shapes used to indicate the various working areas in panel B compared to the zoomed-in panels. For example, panel B indicates WA-1 is a vertical rectangle shape, whereas the zoomed in panel indicates a horizontal rectangle shape. Also the seamounts shown in the zoomed in panels do not match the features indicated for WA-1 and 2 in panel B. Please clarify.

The lower four panels are cut-outs of the working areas, taken such to best illustrate the bathymetry in approximate distance, and of relevance to the core locations (so far available). A reference to the original publication has been added).

- consider using different colors and/or shapes to indicate the core locations being either "SM" or "F", to aid in understanding.

The symbols have been modified

- Please indicate in the figure caption what software and datasets were used to create the bathymetric maps, or if the maps are already published. Also indicate what the contour spacing is, as it is hard to discern the small text in the figures.

Done

Figures 2-4: consider using different symbol shapes, in addition to color, to distinguish between variables in plots. This can aid with interpretation for those with color sensitivities or when viewing printed in black and white.

Done, we now use open and closed circles and triangles.

Figure 4:

- panel a: should the label be "9KL" instead of “9SL"?

corrected

- panel c: should the label be "42SL" instead of “42KL”?

corrected