Reply on RC1
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 NE Pacific" by Gerard J. M. Versteegh et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2021-112-AC1, 2021

We agreed with all comments and proposed changes. Below the comments and the responses to these are provided in detail.

This is a nice contribution that should be published. The interpretation is sound, but some of the wording that describes the interpretation should be changed to match the exact meaning. While I know what the authors are trying to convey, some of the wording isn’t exactly correct. There are some newer publications that should be examined especially those by D’Hondt and his collaborators. Even though there are a lot of suggested changes, most changes are related to word choice and if I didn't provide an accurate response, please change the sentence so that others will understand the point. I consider my suggestions to require minor modification and the manuscript should be published without the need to send it back to me. Geoff Wheat

21 This is especially the case where sediments are thin or in the proximity of faults. Also in the middle of gyres e.g. D’Hondt papers and IODP Exp. 329.

We added ‘such as in the middle of gyres’.

28 basement becomes a nitrate source. The basement is not a source of nitrate. The sediment is a source of nitrate to the basement but I understand that later in the paper you note that the nitrate in the basaltic formation fluid is higher than the concentration in pore waters. Nevertheless, this sentence needs to be fixed.

We fixed this by rephrasing into: ‘and nitrate diffuses from the basement fluid into the sediment’

Abstract in general - first describe completely the oxic situation, then describe the suboxic condition. Currently the text goes back and forth.

Has been fixed.

40 Most of the ocean floor has cooled over long periods and conversely, most ventilation
of the basaltic crust occurs at low temperatures. What are long periods? Crust that is 0.5 Ma is often very cool.

've long periods' has been changed into 'over time'

47 replace poor with low

done


has been added

58 is available it becomes - replace it with dissolved oxygen

done

69 benthic consumption deeper into the sediment - needs a reference – Steve Emerson and or Jim Murray did a lot of this work decades ago.

added Emerson and Hedges, 2003.

77 add Orcutt et al. 2013. Why single out these two locations where as the central gyres are DO depleted (IODP Exp. 329)?

has been added

83 In this zone of upward diffusing oxygen, oxygen exposure time of OM decreases upward from the sediment-basement interface to the point of DO depletion; however, in the case of a completely oxic sediment column, oxic conditions have persisted since deposition.

The statement after 'however' is only true if the sediment column or the bottom waters have always been oxic. However, during the past, bottom water DO levels have been temporarily considerably lower than today and carbon flux to the sediment may have been higher. As a result, the suboxic zones in the sediment may have expanded and sediment columns which are completely oxic today may not have been so in the past. With water entering the basement having significantly reduced DO levels and oxygen consumption in the basement, it remains to be seen if on their way through the porewater in the basaltic basement has become (regionally) anoxic and conversely, oxygen diffusion from the basement into the sediment (regionally) ceased. To take this into consideration we didn’t change the second part of our statement as suggested.

86 - Need to rethink the minimal aspects as there has been a lot of work related to 329 and a similar study led by D'Hondt in the Atlantic gyre (post 329)

We changed the statement by acknowledging the more recent developments and increase in understanding, adding also D'Hondt et al., 2015, 2019 and Morono et al., 2020.

94 - I don't think Ziebis hit basement and it was a piston/gravity coring expedition. Orcutt et al 2013 was drilling related in North Pond.
This statement is about ex. situ measurements and not about hitting the basement and Ziebis et al., 2021 did just that. We added Orcutt, 2013 as it is also a good example.

98 2018) thus ----- 2018), thus

changed

99 sedimentation and seawater circulation within the upper basaltic crust that delivered dissolved oxygen to the overlying sediment which penetrated the entire sediment column or at least to the deepest sediment recovered.

changed

101 long periods of oxidation

changed

102 phenomenon in abyssal ocean deposits - again Exp. 329 papers. Better to start here and go down the list. There are a lot of relevant papers related to the Pacific work and the more recent work in the Atlantic. https://scholar.google.com/citations?hl=en&user=n57iAiYAAAAJ&view_op=list_works&sortby=pubdate

This has been modified acknowledging the inferred widespread occurrence of completely oxic sediments in the oceanic gyres as based on oxygen measurements on sediments and modeled by D’Hondt et al., 2015 and updated by D’Hondt et al., 2019.

109 has been ---was

changed

114 the current carbonate compensation

changed

118 the basaltic crust – the oceanic crust is made up of basalt and the overlying sediment

changed

128 Sediments have been - Sediment was

changed

129 cores consist generally of stiff and compact brown clays with color depending on the MnO2 contents. For example, less MnO2 (< concentration) resulted in a lighter brown color and more MnO2 (> concentration) resulted in a darker color

changed

142 pressure) and was calculate
154 have been - were – replace all and the have not been to were not

204 For most oceanic sediments oxygen is high at the sediment–water interface and steeply decreases to zero at depth (e.g., 205 Wenzhöfer and Gludd, 2002) due to mineralization of organic matter (OM - this reflects a portion of the ocean – the gyre are huge - you should re-think this statement. We rethought this statement and took into consideration D’Hondt et al., 2015 who estimated that that 9-37% of the sea floor has sediments that are completely oxygenated. This leaves 63-91% of the sea floor where oxygen concentrations decrease downwards to such an extent that oxygen becomes depleted in the sediment at depth. This can be shallow in the shallower and more productive sites or at tens of meters below the sediment surface in the oligotrophic gyres at large water depths. We modified the statement by removing 'steeply' and adding the estimate of D’Hondt et al. that 63-91% of the sea floor doesn’t have oxygen throughout the sediment.

209 consumption rates are low

221 with a suboxic zone with a second oxic zone

233 In the case where oxygen consumption exceeds supply

245-255 – too much emphasis is placed on the "measured" sediment thickness. The basaltic crust has hills and valleys at many different scales included at the scale that the sonar measurements were taken that interrogate a large footprint. Ship mounted sonars are insensitive to variations that one might consider for a basaltic mound or a depression. The information on sediment thickness is based on both parasound and seismic profiles (using a 100 m long streamer chain for signal detection and a GI airgun), and thus not only on ship mounted sonars. As such the measured sediment thicknesses are of sufficient accuracy to support the discussion. We added this extra information on the quality of the seismic profiles to the material and methods section, and had another critical look at the sediment thicknesses.

259 Especially in combination with extension, pore volumes may increase, so that it is conceivable that faults increase sediment permeability – there are no data to make this assertion or references. Even if the permeability is slightly increased this does not affect the diffusion of oxygen. Diffusion of DO is affected by porosity and tortuosity but you have no measurements and no data to suggest this permeability statement as fact. Odds are that the seafloor is not flat and the core was taken neat a topographic high that was not identified in the sonar data that encounters a wide swath and does poorly in rough terrain and against seamounts.
we took this in consideration

271 Over time, the reactivity of the basement decreases as does temperature – not necessarily so. Reactivity could likely increase with age because of cracking and temperature increases with age and because sediment thickness increases with age and acts like a blanket, warming the basaltic crust.

ah, yes, fully agree. The statement has been deleted.

275 As such it is conceivable that lateral oxygen diffusion, perpendicular to this venting, contributes to the upward oxygen profile for 69SL resulting in sediment columns in proximity of these venting systems that may be entirely oxic, possibly overruling the effect of sediment thickness. I don't see it. 69SL looks perfectly diffusional without any lateral interaction. While the data are not as monotonic as other profiles, the idea of invoking lateral flow means that you have lost. You have just introduced multiple degrees of freedom in a one-dimensional data set (barring figure 8). Also consider diffusion does not necessarily result in a linear concentration especially if there are changes in turtousity or porosity. In addition, lateral diffusion would not be point source; however, the slight deviations would require a point source if diffusion or advection was the driving force. Also there is no force that would drive lateral advection. Thus I don't see the need to invoke lateral forces unless you can physically/mathematically prove it.

We see the point. We included this since we may expect the diffusion to be perpendicular to the highest concentration difference. This means that for the sites where the basement fluid has a vertical component (e.g. where fluid enters or leaves the basaltic basement, diffusion will have a horizontal component. For a relatively homogeneous sediment and minimum oxygen levels in the upper 5 m, we may expect that this horizontal component could reach as far as the sediment thickness minus a few meters, which in case of 69SL would be about 65 m. Indeed it remains to be seen if 69SL was taken in such close proximity to the site of venting. We still need an explanation for the high oxygen levels in 69SL. These can’t be explained by a point source.

283 to see this – to observe this changed

286 We find this back in the .. This result was observed in the multi core data changed

289 OM mineralization slows down with changed

297 have a relatively constant nitrate concentration – constant to what??

constant concentration is used in absolute sense (in μmol/L), otherwise it would be a ‘constant relative nitrate concentration’

298 It also implies that the seismic–based estimates of sediment thicknesses must be relatively accurate.
It is not clear to us what has to be changed here.

This stability of nitrate concentrations at the sediment–basement interface contrasts with the variability of inferred oxygen concentrations at this interface suggesting very different dynamics such as a much stronger influence of processes in the basement on oxygen concentrations. This could be true or it could be a result of the gradients and the higher diffusion coefficient for DO than nitrate. You will have to calculate the flux. This is comment not clear to us. 1. gradients of what, 2. calculate fluxes of what? We neither know porosity nor tortuosity of the sediment.

317 edit
changed

335 the Wheat and Fisher paper is a little out of date given a better analysis in the Wheat et al EPSL paper in 2017. Cool seafloor hydrothermal springs reveal global geochemical fluxes that shows that the nitrate is the same as bottom seawater. However, this paper suggests that the nitrate concentration is the same as bottom seawater. Note that the Wheat et al 2020 paper in G-cubed (North Pond) shows a higher nitrate concentration in basaltic formation fluids than bottom seawater. This one is more appropriate to your statement.

We added the Wheat er al 2020 paper


Has been added

341 – this is the same as the pore waters drilled on IODP Exp 336, in which there is one profile with measurement Mn and none with Fe.

This is the profile for U1382B. As far as we know these data are only available from the Janus Database (http://www-odp.tamu.edu/database/). We added a remark to this observation.

362 water oxygen content – not correct in the sense that the crustal fluid is bottom seawater that is slightly aged (thousands of years) and deep-water DO changes on much longer time scales than a few thousand years.

However, there is a close link between marine production at the sea surface and oxygen consumption at the sea floor and conversely in it as well. This can change already from year to year but also may follow longer oscillations. These annual to decadal variations are likely to appear less pronounced in the crustal fluid due to the much larger time path involved in the transport of oxygen through the basalt, its diffusion through the sediment and ultimately its arrival at the site of consumption. We modified removed this statement to avoid further discussion.

372 movement -- diffusion
changed
374 – would help to incorporate thoughts from D’Hondts work in the comparison.

*Yes, that would be interesting indeed. However, we consider a discussion on the degradation rates of the organic matter out of the scope of this paper. We have not investigated why oxygen profiles are quasilinear in the lower oxygen profiles, we only observe this in some cases – if this is due to the nature of the OM in these sediments, accessibility to degradation or to limitation by diffusion (as discussed by D’Hondt et al., 2019 doi: 10.1038/s41467-019-11450-z).*

*We changed the text to avoid the idea that we only consider the persistence to degradation of the OM as a variable.*

376 reaction time is long and may equal sediment age - need to reword
*changed to better illustrate the long duration of oxic conditions*

376 Here, not oxygen exposure time is limiting the … Here, oxygen exposure time is not limiting the
*changed*

384 Considering the large amount of time available, --while I agree the rest of the sentence, I don't follow the time statement. New DO is constantly be fluxed into basal sediment. The OC in basal sediment is refractory resulting in slow rates of reaction. I know what you are saying, but there must be a better way to say it.
*changed*

Line 395 equal flux - No flux????
*changed into no flux*

Section 4.6 - Introduce figure 8 in this section.
*done*

411 organic carbon mineralization is exhaustive – OM is not exhausted. There is some there. Only the more refractory compounds remain.
*changed into very low*

412 Nitrate production is larger than nitrate removal via denitrification – With ample DO why would there be denitrification?
*changed*

419 (see conclusion 4). -- add .... in the sampled region.
*added*

Conclusions – Much of the conclusions are a re-hash of the paper. The first 7 items should
be shortened to get to the main point but with a broader brush as to how this work will be applicable to other areas and with how we think of global systems. The last two items #8 and #9 are good in that these statements go beyond the immediate data and area of study. Think big.

*The conclusions 1-6 have been shortened.*

*The following consideration has been added.*

*The widespread interaction between basement fluid and the overlying sediment through diffusion of dissolved substances adds an important dynamic component to the geochemical interaction of sediment, basement and deep ocean (as compared to direct exchange between the surface sediment and the ocean bottom waters).*

*Fig 2 and 3 - It would be nice to list the estimated sediment thickness for each core added and captions have been adapted accordingly.*