

Dear Reviewer #2, we would like to sincerely thank you for reviewing our manuscript and your constructive comments. In this response letter, referee comments are listed, followed by our responses in bold.

The manuscript of Chen et al. investigates iron transfert across the slope offshore Peru during spring 2017. Six vertical profiles of dissolved and particulate iron concentrations with their associated isotopic signature δ^{56} are described and seem of good quality. Six propositions are done along the manuscript. They are presented by order of importance starting with 1) a plume of sediment-derived dFe originally from the inner shelf extends over more than 100 km offshore ; 2) this plume containt also significant amount of pFe produced in the inner shelf; 3) interannual variations compared to previous cruise (GP16) are due to El Nino event captured in 2017; 4) monthly variations between two legs of the cruise are due to Peru-Chile Undercurrent variations 5) in one station, the plume is not visible due to eddy transport 6) a previous proposition from John et al. 2018 to explain a deeper dFe plume over 1000 km is wrong because others studies have demonstrated that non reductive dissolution of sediment are important persistent sources of dFe.

Responses: Please note that in both our original and revised manuscript, we did not state that the reversible scavenging hypothesis by John et al. (2018) was wrong. Instead, we emphasized that our data do not show consistent, strong influence by margin plumes within the anoxic layer, and that these new data are more aligned with the ligand complexation hypothesis.

I have major reservations about the interpretations proposed. Propositions 3 and 4 are presented as hypothesis. Proposition 1 and 5 are not demonstrated which is a particular shame since the demonstration of proposition 1 should be the main goal of the manuscript. The demonstration of proposition 2 presents several contradictions or approximation (in particular with the figure 5). Finally the proposition 6 does not appear to be justified on the basis of the results presented in manuscript. I recomment the authors to reconsider all the discussion focusing on the propositions 1 and 2 but with a solid argumentation.

Response: While we appreciate the time the reviewer put into reviewing our manuscript, these comments are challenging to address in one text. Some of these propositions are relatively well established (e.g. there are several studies showing ‘1’), whereas others (such as propositions 3 and 4) are inevitably more difficult as they require the integration of multiple approaches and will always be subject to more uncertainties.

We would like to stress that we presented in the original manuscript strong evidence to support the temporal variations in benthic dFe supply. Repeat sampling of the same shelf stations at 12°S showed drastic decrease in bottom water dFe and pFe concentrations (Figure 2 in the original manuscript); these changes were accompanied by an intensification of the Peru-Chile Undercurrent (PCUC) driven by a downward displacement of the Coastal Trapped Waves (CTW), which in turn displaced the oxycline, nutricline and thermocline downward thus relaxing bottom water anoxic conditions (Figure S2 and S3 in the revised manuscript). In response, dissolved oxygen (DO)

concentrations in bottom waters over the shelf at 200 m depth increased from below detection limit during cruise M136 to over 5 $\mu\text{mol/kg}$ during cruise M137 (Lüdke et al., 2020). These temporal increases in bottom water DO concentrations allow DO diffusion from bottom water to sediment porewater, which would reduce upward Fe(II) flux from reducing sediments. Bottom water DO and H_2S levels have been shown to impact benthic Fe(II) fluxes (e.g., Schlosser et al., 2018; Rapp et al., 2020). This discussion is now included in the revised manuscript. Please also refer to our responses to reviewers #1 and #3.

The Fe(II) plume at 12°S (referred to as proposition 1 by the reviewer) are clearly shown in Figures 2 and 3 in the original manuscript, and in Zhu et al. (2021). Iron isotope ratios along this Fe(II) plume are light (-1.34‰ over the shelf and -0.27‰ at the slope) and that at shelf stations were close to the endmember value of sedimentary reductive dissolution. Similarly, the absence of such an Fe(II) plume influence has also been clearly shown in Figure 2 for the eddy station, which displayed much lower dFe and pFe, and heavier $\delta^{56}\text{dFe}$ values of $+0.05$ to $+0.73\text{‰}$.

Regarding the comment on proposition 6, we emphasized in the main text that our data do not show consistent, strong influence by margin plumes within the anoxic layer, and that these new data are more aligned with the ligand complexation hypothesis.

References:

Rapp, I., Schlosser, C., Browning, T. J., Wolf, F., Le Moigne, F. A., Gledhill, M., Achterberg, E. P., and Engel, A.: El Niño-Driven Oxygenation Impacts Peruvian Shelf Iron Supply to the South Pacific Ocean. *Geophys. Res. Lett.*, 47, e2019GL086631

Schlosser, C., Streu, P., Frank, M., Lavik, G., Croot, P. L., Dengler, M., and Achterberg, E. P.: H_2S events in the Peruvian oxygen minimum zone facilitate enhanced dissolved Fe concentrations. *Sci. Rep.*, 8, 12642

Zhu, K., Hopwood, M. J., Groenenberg, J. E., Engel, A., Achterberg, E. P., and Gledhill, M.: Influence of pH and dissolved organic matter on iron speciation and apparent iron solubility in the Peruvian shelf and slope region. *Environ. Sci. Technol.*, 55, 9372-9383, <https://doi.org/10.1021/acs.est.1c02477>, 2021.

I will further focus only on the main proposition, proposition 1, whose authors do not discuss its validity using expressions as « striking feature » l. 169 ; « were evidently transported » l.192, « was also evident » l.203 instead. However, an important discussion is required to state that 1a) the dFe of the plume is sediment-derived and 1b) it extend over « 100 km » (l.127) « to the open ocean » (l.192).

Responses: The “striking feature” referred to here highlights the concurrent shelf-slope plumes of both dissolved (with low $\delta^{56}\text{dFe}$) and particulate Fe (with low $\delta^{56}\text{pFe}$ but higher than $\delta^{56}\text{dFe}$), which we interpret to reflect processes that transport both phases of Fe off

shelf. In the same paragraph, we discussed that $\delta^{56}\text{dFe}$ in the elevated Fe(II) and dFe plumes and in proximity to shelf sediments have values as low as -1.34‰ that is consistent with reductive dissolution of Fe from Peruvian shelf sediments, thus clearly stating that the dFe in the plume is sediment-derived (lines 170 – 175 in the original manuscript). In the revised manuscript, we further discussed that “benthic diffusive Fe(II) fluxes along the 12°S transect during both cruises of M136 and M137 (Plass et al., 2020) have been reported to range from $17.45 \text{ mmol m}^{-2} \text{ yr}^{-1}$ from the inner shelf (nitrogenous in bottom water) to $0.26 \text{ mmol m}^{-2} \text{ yr}^{-1}$ on the slope (suboxic in bottom water)” (lines 180-183), thus citing direct evidence from an earlier study conducted during the same campaign to support our inference.

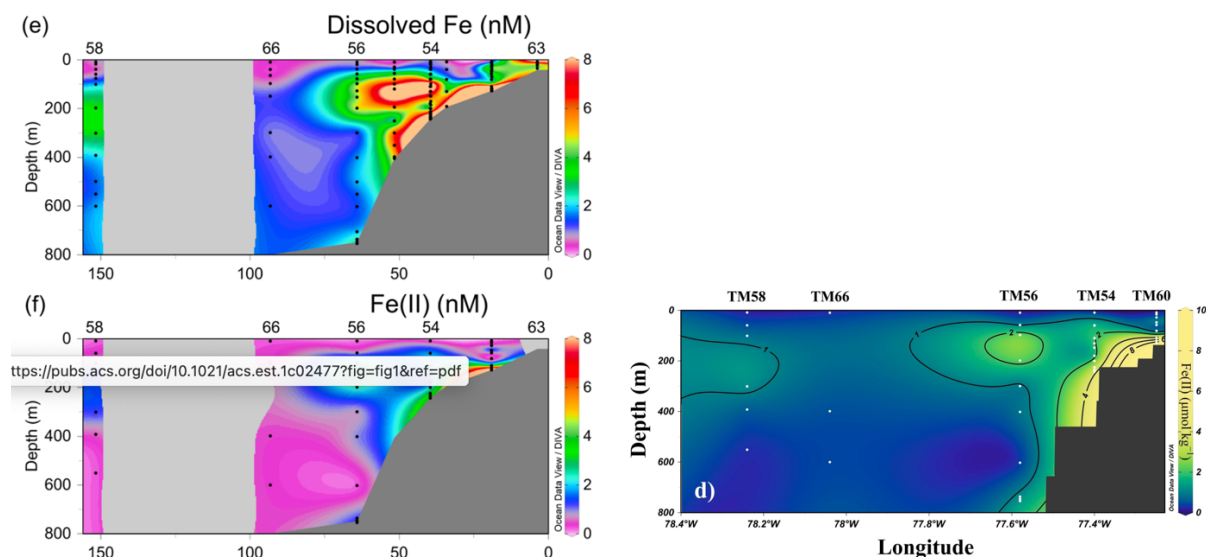
We showed in the original manuscript that such a sediment-derived Fe extended to over 100 km (lines 127-129 and Figure 2 in the original manuscript). Note that this long-distance transport of Fe(II) and dFe has been demonstrated in an earlier study (Zhu et al., 2021). Taking a step forward, we further showed that a strong plume of pFe, sourced from Peru sediments, has also been observed along the 12°S (lines 176-188 in the revised manuscript).

To estimate the plume extension, I visualized their dataset of dFe (from Zhu et al 2021) and compared it with GP16 dataset that supposedly missed the plume. The occurrence of a original « 100 km » long plume is not evident... station TM 58 and TM66 seems not related with the plume of dFe event during El nino 2017 while a plume above the slope was also detected in GP16. Station TM55 and TM56 does show a original feature, a more pronounced plume of dFe at about 150m depth not directly connected with the bottom sediment, but it does not extend over 100 km. The high interest of the presented dataset is the significant signal of ligh $\delta^{56}\text{dFe} < -1 \text{‰}$ (only visible on TM55 and TM56) that deserves to be discuss based on a solid argumentation (note that, surprisingly, no isotope data at high dFe concentration ($> 5\text{nM}$) is available from GP16). I recommand to the author to only focus on these stations to build a strong discussion about the extension and the origin of the plume.

Response: We cannot verify the dFe dataset the reviewer downloaded, nor the figure generated by the reviewer, as these are not available in the their report. Please note, the number of dFe profiles obtained over M135 to M138 (back to back cruises from 12°S to 17°S in the Peruvian upwelling zong) are much more extensive than the number of profiles with isotopic data, or Fe(II). The M135 data (17°S) extends furthest off shelf and does show dFe enrichment extending off shelf as stated (Hopwood et al. 2021). This is also evident in the specific stations which we refer to herein that contain additional Fe(II) and isotopic data at 12°S .

We would like to further clarify that in both our original and revised manuscripts, we never stated that GP16 missed the dFe plume. Instead, we stated that “Along the GEOTRACES GP16 section, which was sampled under close to neutral ENSO conditions in austral Spring, 2013, dFe and pFe were shown to be restricted to the Peruvian inner shelf” (lines 213-215). Fe(II) at 12°S off Peru was reported in Zhu et al. (2021) and the original data was documented in Pangaea under Hopwood et al. (2021) (the same data is

present in the latest GEOTRACES IDP). We plot below a cross-section plot from Zhu et al. (2021; left panel) and that regenerated in this study using the same dataset (right panel), both showing clear elevated dFe and Fe(II) extending from the Peruvian shelf westward for over 100 km. In contrast to the reviewer's comment that station TM58 was not influenced by the dFe plume, these figures below indicate that both dFe and Fe(II) at TM58 at ~100 to 350 m (plume depth) were significantly higher than samples shallower and deeper. Conversely, we've demonstrated in the original manuscript that eddy station TM66 did not align with the 12°S transect, and that biogeochemistry within this mesoscale eddy was distinctly different from those outside of the eddy.



Reference:

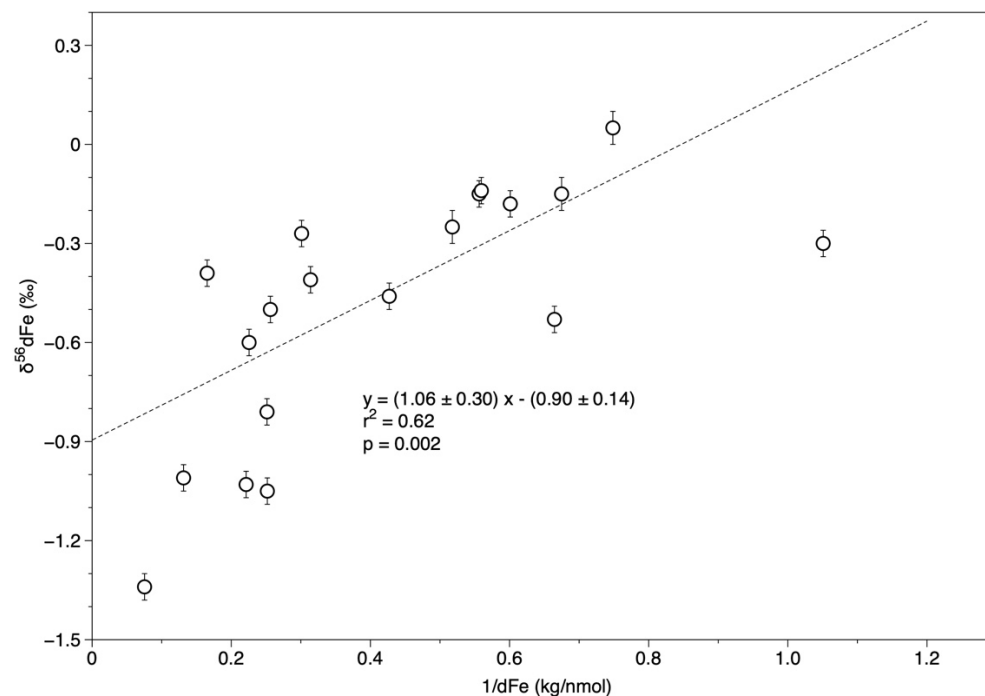
Hopwood, Mark James; Meyer, Judith; Achterberg, Eric Pieter; Gledhill, Martha; Mutzberg, André; Nehir, Münevver (2021): Trace metal data from water samples during METEOR cruise M136 [dataset]. PANGAEA, <https://doi.org/10.1594/PANGAEA.928118>

Hopwood, Mark James; Meyer, Judith; Achterberg, Eric Pieter; Gledhill, Martha; Mutzberg, André; Nehir, Münevver (2021): Trace metal data from water samples during METEOR cruise M135 [dataset]. PANGAEA, <https://doi.org/10.1594/PANGAEA.928117>

How to build a solid argumentation concerning the plume origin ? First, the proposition have to be sustained clearly by the dataset. If dFe is transported from the sediment you should be able to draw a mixing line ($\delta^{56}\text{Fe} = f(1/\text{dFe})$) along the pycnocline of the water sediment interface releasing most of the dFe, in the inner shelf. The figure does not need to be perfect, but it will give the opportunity for the reader to get his/her own appreciation.

Response: The reviewer raises a good point and a testable hypothesis. We show in a figure below that, for samples within the Fe(II) plume, $\delta^{56}\text{Fe}$ displays a significant linear correlation with $1/\text{dFe}$ ($p < 0.05$, $R^2 = 0.62$). This good linear correlation supports our

inference that Fe(II) and dFe from shelf sediments are effectively transported offshore. We have included this new figure in the revised manuscript.



In the revised Figure 3, we further showed that this Fe(II) plume was transported offshore along isopycnals 26.0 to 26.5 kg/m³.

Second, the results not perfectly consistent with the proposition requires alternative explanations. Why no plume is visible before station TM54 (Figure R1) ? Why very light isotope signal often observed above the OMZ if it is only a signature of sediment effluxes ? If light isotope can origin from another source, why this alternative source not significant in TM55 and TM56 ?

Response: We do not follow this comment from the reviewer. From inner shelf to outer shelf, stations TM60, TM54, TM56 and TM58 all showed significantly elevated concentrations of Fe(II) within the core OMZ (please see Figures 2 and 3 in the original manuscript). Note the no Fe(II) measurement was conducted at station TM57.

Iron released from Peruvian reductive sediments have been shown to be isotopically light with $\delta^{56}dFe$ ranging from -0.5 to -1.2‰ (Chever et al., 2015; Scholz et al., 2014; John et al., 2018). The $\delta^{56}dFe$ measured within the Fe(II) plume in this study, with $\delta^{56}dFe$ increased from -1.34‰ over the shelf (TM57) to -0.27‰ offshore (TM58), are consistent with earlier findings. Additional potential Fe sources, including suspended sediments, aerosols and non-reductive dissolution of sediments, have $\delta^{56}dFe$ either higher (e.g., Scholz et al., 2014) or consistent with upper continental values (e.g., Little et al., 2025).

References:

Chever, F., Rouxel, O. J., Croot, P. L., Ponzevera, E., Wuttig, K., and Auro, M.: Total dissolvable and dissolved iron isotopes in the water column of the Peru upwelling regime. *Geochim. Cosmochim. Acta*, 162, 66-82, <https://doi.org/10.1016/j.gca.2015.04.031>, 2015.

John, S. G., Helgoe, J., Townsend, E., Weber, T., DeVries, T., Tagliabue, A., Moore, K., Lam, P., Marsay, C. M., and Till, C.: Biogeochemical cycling of Fe and Fe stable isotopes in the Eastern Tropical South Pacific. *Mar. Chem.*, 201, 66-76, <https://doi.org/10.1016/j.marchem.2017.06.003>, 2018.

Little, S.H., G.F. de Souza, and R.C. Xie, Metal stable isotopes in the marine realm, in *Treatise on Geochemistry* (Third edition), A. Anbar and D. Weis, Editors. 2025, Elsevier: Oxford. p. 285-332.

Scholz, F., Severmann, S., McManus, J., and Hensen, C.: Beyond the Black Sea paradigm: the sedimentary fingerprint of an open-marine iron shuttle. *Geochim. Cosmochim. Acta*, 127, 368-380, <https://doi.org/10.1016/j.gca.2013.11.041>, 2014.

Why no plume visible in station TM66 ? only the last question gets an answer in the current manuscript but without the required proves (proposition 5).

Response: Please note that station TM66 and TM75 were sampled within an anticyclonic mode eddy, where exchange of dissolved and particulate constituents across eddy peripheries is limited. We have explicitly discussed Fe and Fe isotope biogeochemistry at these eddy stations in section 4.3 of the main text, exploring three mechanisms that are in place, namely ligand complexation (highly likely, core OMZ depth), reversible scavenging (unlikely, core OMZ depth), and contributions from both reducing and non-reducing sedimentary release (possible, depth below the core OMZ).

Third, the proposition should also be defended face to alternative common explanations not even discussed in this version of the manuscript : as micronutrient, is the release of dFe during organic matter remineralisation significant in your system ? probably since you in a very productive area, can you estimate the dFe produced during remineralisation ?

Response: We agreed that contribution of dFe associated with organic matter remineralization should be considered in the discussion, yet its relative contribution to dFe is difficult to quantify without POC flux data in and out of the Fe(II) layer. Alternatively, in the revised manuscript, we stated that "... Sinking biogenic pFe formed in the productive surface waters may contribute to these elevated pFe/pAl signals. Assuming particulate phosphorus is overwhelmingly biogenic (Ohnemus et al., 2017) and using a mean Fe/P ratio of 52.5:1000 of prokaryotic cells (Cunningham and John, 2017), the biogenic pFe concentrations at Fe(II) plume depths at shelf stations closest to the margin (TM57 and TM56) are estimated to be $2.4 \pm 1.1 \text{ nmol kg}^{-1}$..." (lines 193-201). If all pFe within the Fe(II) plume at shelf stations gets remineralized, this would contribute to 18-

50% of dFe observed. These numbers are overly estimated, as sinking particulate organic matter are unlikely fully remineralized over the Peruvian shelf.

Due to lack of POC flux data, we did not include this discussion in the revised manuscript to avoid being speculative.

as a redox sensitive species, why the in situ reduction of Fe oxides (from atmospheric deposition, or offshore surface transport) negligible ?

Response: There is a misunderstanding here regarding Fe redox chemistry. Just because DO level in seawater is below detection limit does not mean it is ferruginous and favorable for Fe reduction. The redox sequence requires that DO, nitrate and dMn to be completely consumed before microbes would use dFe as an electron receiver. Hence, it is highly unlikely that the oxygen-depleted water over the Peru shelf sediments favors Fe reduction, given the high concentrations of nitrate. This is in contract to porewater geochemistry within Peruvian shelf sediments where DO, nitrate and dMn are depleted in sequence within several to tens of centimeter below the seafloor.

if reductive dissolution of Fe oxides occurs in the top of the OMZ, the isotopic signature should be as low as the one you measured ? Only such a reworking of the discussion will be able to convince the readers that the plume observed is originally from the sediment.

Response: Correct. Biotic dissimilatory Fe(III) reduction has been shown to induce large Fe isotope fractionation, so that porewater-sourced Fe(II) from reductive dissolution of sedimentary is isotopically light. Oxidation of this benthic Fe(II) diffused to overlying water would lead to even lower $\delta^{56}\text{dFe}$ values, reaching values as low as -1.25‰ reported over the Peruvian shelf or -3.5‰ in the global ocean (e.g., Chever et al., 2015; Severmann et al., 2010).

References:

Chever, F., Rouxel, O. J., Croot, P. L., Ponzevera, E., Wuttig, K., and Auro, M.: Total dissolvable and dissolved iron isotopes in the water column of the Peru upwelling regime. *Geochim. Cosmochim. Acta*, 162, 66-82, <https://doi.org/10.1016/j.gca.2015.04.031>, 2015.

Severmann S, McManus J, Berelson WM, and Hammond D.E.: The continental shelf benthic iron flux and its isotope composition. *Geochimica et Cosmochimica Acta* 74: 3984–4004. <https://doi.org/10.1016/j.gca.2010.04.022>, 2010