

**Dear Reviewer #1, 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.**

This manuscript presents a valuable dataset of dissolved and particulate Fe concentrations and their isotopic compositions in the Peruvian oxygen minimum zone during a post-El Niño period. Through comparison among multiple cruises conducted by the authors, together with comparisons with previously published cruises, the study highlights how the El Niño-Southern Oscillation influence sedimentary Fe release and the subsequent offshore Fe flux. These observations provide valuable constraints on the temporal variability of Fe cycling in oxygen-deficient marine environments and its sensitivity to climate-driven changes in ocean circulation and redox conditions. The manuscript is generally well organized and clearly written. However, several aspects of the interpretation and proposed mechanisms would benefit from further clarification and discussion.

Major concerns:

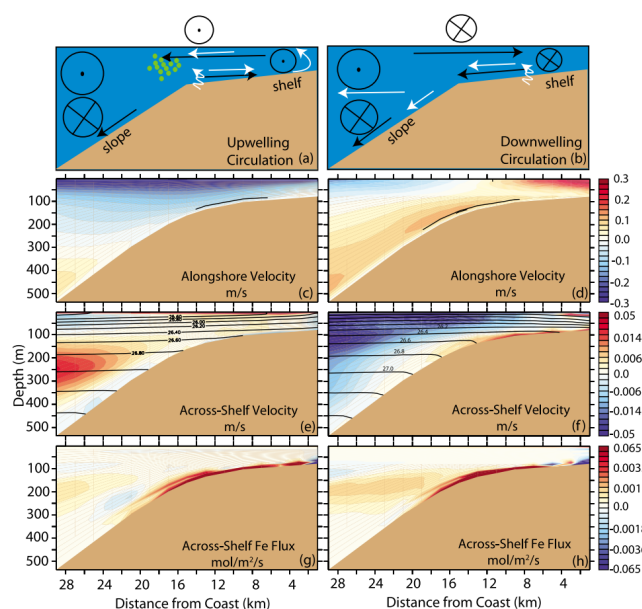
(1) In Discussion 4.1, the authors found that dFe and pFe were transported farther offshore in the Peruvian OMZ during their sampling period than during the GP16 cruise, and attributed this difference primarily to variations in upwelling intensity. However, it remains unclear whether the dFe efflux from shelf sediments differed between the two periods. In addition, variations in horizontal current velocity between the two periods could also influence the offshore transport of Fe. Could the authors provide evidence or further discuss whether these factors differed between the two periods?

**Response: The reviewer brought up a good point that temporal variation in sedimentary dFe efflux would impact offshore dFe transport. Benthic diffusive  $\text{Fe}^{2+}$  fluxes from sediments along the 12°S transect have been determined during both cruises of M136 and M137 in Plass et al. (2020, Biogeosciences), which ranged from 17.45 mmol m<sup>-2</sup> yr<sup>-1</sup> from the inner shelf (nitrogenous in bottom water) to 0.26 mmol m<sup>-2</sup> yr<sup>-1</sup> on the slope (suboxic in bottom water). Sedimentary  $\text{Fe}^{2+}$  effluxes have not been reported for the GP16 cruise, which was carried out during a neutral ENSO phase in austral spring 2013. Conversely, Scholz et al. (2016) have reported overall higher benthic  $\text{Fe}^{2+}$  fluxes (1.51 to 22.69 mmol m<sup>-2</sup> yr<sup>-1</sup>) from the 12°S inner shelf (bottom depths <250 m) during cruise M92 (austral summer 2013) than those during M136 and M137 (0.81 to 17.45 mmol m<sup>-2</sup> yr<sup>-1</sup>). Higher benthic  $\text{Fe}^{2+}$  fluxes during M92 have been linked to sulfidic conditions on shelf sediments in the neutral ENSO phase (Schlosser et al., 2018, Scientific Reports). Accordingly, we acknowledge that interannual variabilities in benthic diffusive  $\text{Fe}^{2+}$  fluxes exist, yet we cannot directly assess this difference between GP16 and M136/M137 due to lack of benthic  $\text{Fe}^{2+}$  flux from the former cruise.**

**We agree with the reviewer that cross-shelf current velocities would impact offshore transport efficiency of Fe (and potentially other dissolved and particulate**

constituents). Such an effect has been shown in an earlier modeling study for the Peruvian shelf (see the Figure below, Siedlecki et al., 2012, GRL). In this modeling study, weakened upwelling (or downwelling) leads to enhanced surface shoreward currents (cooler colors in subplot b) and benthic offshore current velocities (warmer colors in subplot f), which in turn delivers more sediment-derived dFe offshore (subplot h). These modeling results agree with the upwelling scenarios for GP 16 and M136/M137. Xie et al. (2020) have demonstrated that upwelling rates for M136/M137 were an order of magnitude weaker than for GP16 (Kadko, 2017), potentially allowing more efficient offshore transportation of benthic  $\text{Fe}^{2+}$  from reducing sediments.

We have included the above discussion in Section 4.1 in the revised manuscript. Below shows a modeling result from Siedlecki et al. (2012) for the reviewer's reference.



This figure is from Siedlecki et al. (2012)

#### References:

- Plass, A., Schlosser, C., Sommer, S., Dale, A. W., Achterberg, E. P., & Scholz, F. (2020). The control of hydrogen sulfide on benthic iron and cadmium fluxes in the oxygen minimum zone off Peru. *Biogeosciences*, 17(13), 3685-3704.
- Scholz, F., Löscher, C. R., Fiskal, A., Sommer, S., Hensen, C., Lomnitz, U., ... & Canfield, D. E. (2016). Nitrate-dependent iron oxidation limits iron transport in anoxic ocean regions. *Earth and Planetary Science Letters*, 454, 272-281.
- Schlosser, C., Streu, P., Frank, M., Lavik, G., Croot, P. L., Dengler, M., & Achterberg, E. P. (2018). H<sub>2</sub>S events in the Peruvian oxygen minimum zone facilitate enhanced dissolved Fe concentrations. *Scientific Reports*, 8(1), 12642.
- Siedlecki, S. A., Mahadevan, A., & Archer, D. E. (2012). Mechanism for export of sediment-derived iron in an upwelling regime. *Geophysical Research Letters*, 39(3).

- Xie, R. C., Le Moigne, F. A. C., Rapp, I., Lüdke, J., Gasser, B., Dengler, M., Liebetrau, V., and Achterberg, E. P. (2020) Effects of  $^{238}\text{U}$  variability and physical transport on water column  $^{234}\text{Th}$  downward fluxes in the coastal upwelling system off Peru. *Biogeosciences*, 17, 4919-4936.
- Kadko, D. (2017) Upwelling and primary production during the U.S. GEOTRACES East Pacific Zonal Transect. *Global Biogeochem. Cycles*, 31, 218-232

In addition, the  $14^{\circ}\text{S}$  section differs from the  $12^{\circ}\text{S}$  section, particularly in terms of the pFe/pAl ratios. The authors attribute this difference mainly to variations in sedimentary reducing dFe efflux between  $12^{\circ}\text{S}$  and  $14^{\circ}\text{S}$ , potentially related to differences in the width of the continental shelf. However, the maximum dFe concentrations along the  $14^{\circ}\text{S}$  section do not appear to be much lower than those at  $12^{\circ}\text{S}$  (e.g., TM94 vs. TM56), which may suggest that the sedimentary dFe efflux at  $14^{\circ}\text{S}$  is not necessarily lower. Could differences in the transformation of dFe to pFe also contribute to the observed contrast in pFe/pAl ratios? In addition, TM94 at  $14^{\circ}\text{S}$  is much closer to the continent. Could an additional lithogenic particulate Fe input contribute to the relatively lower pFe/pAl ratios? Lithogenic proxies, such as particulate Al or Ti, may help constrain this possibility.

**Response: Concentrations of dFe in coastal water could be comprised of Fe(II) derived from anoxic shelf sediments, and dFe from subsurface and upwelled water masses. It is Fe(II) concentration that can unmistakably infer sedimentary reducing dFe efflux, which is available only for the  $12^{\circ}\text{S}$  and not the  $14^{\circ}\text{S}$  transect. Upon diffusion from reducing sediments, part of the Fe(II) is transformed to Fe (oxyhydr)oxides, with the rest remaining in dissolved form. In the anoxic shelf waters, this transformation of dFe to pFe is dominated by authigenic pFe mineral formation, resulting in increases in pFe/pAl ratios in particles, e.g., particulate samples at  $12^{\circ}\text{S}$ . The relatively low pFe/pAl ratios at  $14^{\circ}\text{S}$  imply limited authigenic Fe formation. Accordingly, we interpret higher total concentrations of both dFe and authigenic pFe at  $12^{\circ}\text{S}$  to indicate larger Fe(II) fluxes from reducing sediments compared to that at  $14^{\circ}\text{S}$ , the latter of which lacks authigenic pFe signature (i.e., pFe/pAl in proximity to lithogenic endmember value).**

**Additional terrigenous input is another potential explanation for the low pFe/pAl ratios at  $14^{\circ}\text{S}$ . Indeed, pAl concentrations at  $14^{\circ}\text{S}$  were overall an order of magnitude higher than those at  $12^{\circ}\text{S}$ , which could potential mask authigenic pFe signatures. We have thus modified relevant discussion in the revised manuscript to include this possibility.**

Another possibility is that the relatively high pFe/pAl ratios along the  $12^{\circ}\text{S}$  section may partly reflect a biogenic Fe contribution. A pronounced secondary fluorescence maximum occurs near the oxic–anoxic interface, particularly at TM57 and TM56,

where relatively high pFe/pAl ratios are also observed. Ohnemus et al. (2016) reported elevated trace metal concentrations in the ODZ during the GP16 cruise and suggested the presence of low-light, autotrophic communities. Biogenic proxies, such as particulate P and C, may provide useful constraints on this possibility.

**Response:** We appreciate the reviewer's suggestion to evaluate the contribution of biogenic Fe to pFe/pAl at 12°S. We now estimated concentrations of biogenic Fe in the anoxic waters at TM56 and TM57, the stations that display the highest subsurface pFe/pAl values. At TM56 and TM57, particulate P concentrations at depths of 50-200 m where pFe/pAl ratios were elevated, averaged  $46 \pm 20$  nM (mean  $\pm$  one SD, n=6). Taking an average pFe/pP ratio of 52.5:1000 in prokaryotes (Cunningham and John, 2017, L&O), we estimated biogenic pFe concentrations at  $2.4 \pm 1.05$  nmol kg<sup>-1</sup>, accounting for ~4% pFe in particulate samples. This estimation demonstrates that biogenic Fe makes minor contribution to pFe in the Peruvian shelf anoxic waters, consistent with the conclusion in Ohnemus et al. (2017, L&O). We have included this related discussion in the revised manuscript.

**Reference:**

- Cunningham, B. R., & John, S. G. (2017). The effect of iron limitation on cyanobacteria major nutrient and trace element stoichiometry. *Limnology and Oceanography*, 62(2), 846-858.
- Ohnemus, D. C., Rauschenberg, S., Cutter, G. A., Fitzsimmons, J. N., Sherrell, R. M., & Twining, B. S. (2017). Elevated trace metal content of prokaryotic communities associated with marine oxygen deficient zones. *Limnology and Oceanography*, 62(1), 3-25.

(2) In Discussion 4.3, the authors suggest that the relatively heavy  $\delta^{56}\text{dFe}$  and lighter  $\delta^{56}\text{pFe}$  observed in the anoxic waters at TM66 and TM75 are related to ligand effects. Is there any additional evidence that the ligands in this depth range have distinctive characteristics that could explain their apparent influence on Fe isotope fractionation?

**Response:** The reviewer raised a good point. Unfortunately, organic ligand samples were not collected during cruises M136, M137 and M138. Further south of our study site, along a transect at 30°S in the South Pacific Ocean extending from Chile to New Caledonia, equilibrium dFe and labile pFe (LpFe) partitioning has been demonstrated to be a critical pathway for dFe cycling, and that the heterogeneity of organic ligand binding site affinities strongly influence seawater dFe concentrations and potential authigenic particulate Fe formation (Gledhill et al., 2026). The distributions of  $\delta^{56}\text{dFe}$  and  $\delta^{56}\text{pFe}$  in the anoxic waters at the eddy stations in this study aligned well with those predicted based on field observations both in the Pacific and the North Atlantic (Conway and John et al., 2014; Gledhill et al., 2026; Tagliabue et al., 2023) and laboratory experiments (Morgan et al., 2010). We have modified section 4.3 accordingly to include this discussion.

## References:

- Gledhill, M., Gosnell, K., Humphreys, M. P., Delaigue, L., Helle, N., Zhu, K., ... & Achterberg, E. P. (2026). Chemical controls on iron distributions across the subsurface South Pacific Ocean. *Nature Communications*.
- Morgan, J. L., Wasylenki, L. E., Nuester, J., & Anbar, A. D. (2010). Fe isotope fractionation during equilibration of Fe– organic complexes. *Environmental Science & Technology*, 44(16), 6095-6101.
- Tagliabue, A., Buck, K. N., Sofen, L. E., Twining, B. S., Aumont, O., Boyd, P. W., ... & Sedwick, P. (2023). Authigenic mineral phases as a driver of the upper-ocean iron cycle. *Nature*, 620(7972), 104-109.
- Conway, T. M., & John, S. G. (2014). Quantification of dissolved iron sources to the North Atlantic Ocean. *Nature*, 511(7508), 212-215.

Furthermore, the authors discuss the potential influence of reductive and/or non-reductive dissolution of Peruvian slope sediments on deep water Fe. However, the dFe concentrations do not show an obvious increase in the deep waters, which raises questions about the extent to which Peruvian slope sediments influence the deep-water dFe pool. In addition, the authors state that “the  $\delta^{56}\text{dFe}$  of  $-0.5\text{‰}$  and  $0\text{‰}$  off Peru indicates both non-reductive and reductive release is important...” Could the authors clarify the sources of these two values? Is the  $-0.5\text{‰}$  value the minimum  $\delta^{56}\text{dFe}$  observed at TM75?

**Response:** The reviewer is correct that deep waters at offshore stations do not show an obvious increase in dFe compared to nearshore stations; instead, both offshore and nearshore stations have similar dFe concentrations and identical  $\delta^{56}\text{dFe}$  within errors (from nearshore to offshore,  $-0.18 \pm 0.52 \text{‰}$  at TM56,  $-0.25 \pm 0.11 \text{‰}$  at TM66,  $-0.30 \pm 0.40 \text{‰}$  at TM75, and  $-0.14 \pm 0.22 \text{‰}$  at TM58). These similar dFe concentrations and isotopic signatures indicate they are influenced by similar water masses. Deep water  $\delta^{56}\text{dFe}$  values in this study fall within the range between the characteristic  $\delta^{56}\text{dFe}$  values for reductive dissolution of  $-1.2\text{‰}$  (Chever et al., 2015) and non-reductive dissolution of  $0.1\text{‰}$  (Homoky et al., 2021). In addition, observations from the GP16 transect have shown evident deep dFe, pFe and lithogenic particle plumes extending from the Peruvian slope sediments to offshore waters. Based on this collective evidence, we infer contributions from both reductive and non-reductive dissolution of Fe to deep waters at our offshore stations. We have made corresponding modifications in the revised manuscript.

## References:

- Chever, F., Rouxel, O. J., Croot, P. L., Ponzevera, E., Wuttig, K., & Auro, M. (2015). Total dissolvable and dissolved iron isotopes in the water column of the Peru upwelling regime. *Geochimica et Cosmochimica Acta*, 162, 66-82.
- Homoky, W. B., Conway, T. M., John, S. G., König, D., Deng, F., Tagliabue, A., & Mills, R. A. (2021). Iron colloids dominate sedimentary supply to the ocean

interior. *Proceedings of the National Academy of Sciences*, 118(13), e2016078118.

Minor comments:

**Line 84:** The original sentence does not explicitly indicate that M136, M137, and M138 are cruise names. We suggest adding this clarification, e.g., "...showing sampling stations from cruises M136, M137, and M138."

**Response: Agreed and fixed.**

**Line 103:** This sentence mentions "Class 5," but it is unclear which standard or classification system it refers to. I suggest briefly specifying the relevant standard in parentheses after "Class 5" to improve clarity.

**Response: Fixed.**

**Line 123:** Please clarify the source of the Fe(II) data and whether they were collected during the same period and at the same stations as those in this study.

**Response: We have added a sentence in the revised manuscript "These Fe(II) samples were collected and Fe(II) concentrations were measured on board cruise M136, and data covered stations TM56, TM58 and TM66 (Zhu et al., 2021)." (line 132 in the revised manuscript).**

**Line 131:** "..., while pFe varied from 1 to 17 nmol kg<sup>-1</sup> (Figs. 2c and 3)". The reported increase in pFe does not appear to be clearly supported by Figs. 2c and 3.

**Response: We realized this description was misleading, and have modified it as "..., while pFe varied from 1 to 9 nmol kg<sup>-1</sup> (near bottom samples not included, Figs. 2c and 3)" (line 139 in the revised manuscript).**

**Line 140:** Since the description of the particulate Fe data includes depth profiles at stations TM77, TM56, and TM75, as well as a few scattered data points at stations TM57, TM66, and TM58, the latter information should also be clarified in the first sentence.

**Response: Agreed. We have added a sentence in the revised manuscript "In addition, scatter  $\delta^{56}\text{pFe}$  samples for the surface and near-bottom waters were also collected at stations TM57, TM66 and TM58 (Fig. 2a, c and d)." (line 149 in the revised manuscript)**

**Line 142:** The full name of UCC should be provided when it first appears in the text.

**Response: Agreed and fixed.**

**Lines 150-155:** (1) In Fig.3, the location and extent of the continental shelf in the last panel appear inconsistent with those in the first three panels, but all four panels share the same latitude values on the x-axis. Although the authors state that the location of TM56 in panels (a)–(c) is offset for clarity, it would be preferable to use the same transect/location consistently across all four panels. This would avoid potential

confusion or misunderstanding when comparing the panels. (2) Please provide more explicit information. For example, the DO contours are shown with grey lines, this should be stated clearly in the figure caption. In addition, please clarify which cruise TM54 and TM60 belong to.

**Response: Agreed and fixed.**

**Line 175:** A period (".") should be used instead of a comma (",") at the end of this sentence.

**Response: Corrected.**

**Lines 182-184:** This sentence associates a  $\delta^{56}\text{pFe}$  value of approximately  $-0.2\text{‰}$  with the high pFe/pAl ratio at TM57. However, there seems no corresponding particulate Fe isotope data available for TM57. Could you please clarify the source of the  $-0.2\text{‰}$  value? If direct data from TM57 are unavailable, perhaps the particulate Fe isotope data from TM56 could be used as a reference, given their similar characteristics.

**Response: We thank the reviewer for pointing out this typo. Here 'TM57' should be 'TM56'.**