Answer to referee comments

Dear editors, we would like to thank you and the reviewers for their comments, which we have taken into account. We believed this significantly improved our manuscript. We have added this sentence "*The three anonymous reviewers are thanked for their comments, which allowed significantly improving the manuscript.*" in the acknowledges section at lines 915-917.

Our replies point by point, in blue. The line numbers correspond to the lines in the revised version with hidden suppressions.

Referee comment 1

Summary

This study presents iron concentration and isotope data from the EUCFe cruise that extends along the equator from near Papua New Guinea to 140°W. Two earlier papers have resulted from this dataset, with this manuscript extending the dataset to some extra stations (Labatut et al., 2014; Radic et al., 2011). In their earlier papers, the authors reveal two distinct regimes: 1) a western margin zone dominated by lithogenic inputs from Papua New Guinea, including riverine, shelf and hydrothermal input, and 2) a central open ocean region where Fe is transported eastward via the Equatorial Undercurrent. Iron isotope signatures for particulate iron are close to the upper continental crust, and the offset between dissolved and particulate iron suggests equilibrium fractionation, perhaps via non-reductive dissolution. Measurements of iron isotopes in the deep chlorophyll maximum showed minimal isotopic fractionation with no clear preference for heavy or light isotopes.

Overall, the manuscript presents new iron isotope data; however, it appears that the main findings have been discussed previously in Labatut et al., 2014 and Radic et al., 2011. The new component of the manuscript presents a detailed examination of iron isotope fractionation in each water mass. I also wonder about the strength of the discussion relating to iron isotope fractionation by phytoplankton. The authors do not present any results relating to phytoplankton groups that are likely to take up iron and fractionate it. They just say that iron isotope fractionation "lies between -0.17 and +0.39 ‰ (+0.11 ± 0.28) at a 95% confidence level". There is little consideration that various phytoplankton species might have different iron acquisition strategies e.g. Sutak et al., 2020, which likely influences iron isotope fractionation. If possible, I think this needs to be explored a bit more in the manuscript.

Below are my comments on the manuscript, and below that, I address the guideline questions for peer review and interactive public discussion.

We thank the reviewer for this summary and for his recommendations.

Regarding the novelty of this article, the addition of 55 samples from 11 new stations (representing 72 % of the dataset) indeed strengthens the hypotheses and observations presented in Radic et al. (2011) and Labatut et al. (2014). We also believe that this addition does more than simply reinforce previous conclusions, and that novelty has been introduced for several reasons:

i) The observation of a particulate - dissolved exchange without redox reaction is extended from less than 100 kilometers off the coast to 1 200 kilometers, as already highlighted in our original submission in the sentence "The addition of data from five additional western stations reinforces the conclusions drawn from earlier studies and extends the geographic scope of these findings eastward beyond the

Bismarck Sea, to as far as 156°E.” in lines 455–457. This observation is significant, and it was not at all obvious that such a process would be observed so far from the coast and from sedimentary discharges. In order to take into account this recommendation, we have added in the conclusion at lines 833-834 “*New data from 11 additional stations demonstrate that this process extends up to 1 200 km from the Papua New Guinea coast.*” and in the abstract at lines 32-33 “*and extends up to 1 200 km from the coast*”.

ii) The preservation of an isotopic signature over such a distance (7 800 kilometers) had never been observed before. To emphasize the innovative aspect of this article, we have added the sentence “*Such a long distance of preservation of the* δ^{56}*DFe signature had never been observed before*.” at lines 702–703 and in the conclusion, we have added ‘*unprecedented*’ in the sentence “*The preservation of distinct Fe isotopic signatures over unprecedented long distances, 7 800 km, is a key observation of this study.*” at line 847.

iii) The addition of these new results changes the estimation of the fractionation associated to biological uptake between Radic et al. (2011) and this manuscript, due to new data and to the correction for lithogenic iron. We have added the sentence: “*Additional data and novel methodological approaches have refined these estimates.*” at lines 582-583.

iv) A second and previously unidentified source, originating from the oxygen minimum zones of the Eastern Pacific Ocean, has been identified. This was highlighted in our original submission in the conclusion, at lines 844-845, “an additional Fe source was identified bordering the lower EUC at 2°N and 2°S likely originating from the oxygen minimum zones (OMZ) of the eastern Pacific.”. We have added in the conclusion “*and introduces a novel suggestion about an iron source from the eastern Pacific OMZ.*” at lines 811-812.

We have modified Section 5.2.1, which addresses isotopic fractionation during biological uptake, in order to include more information on the phytoplanktonic composition of surface waters (see the responses to the questions below).

Comments

Line 218. The presentation of the blank contributions is percentage values relative to dissolved and particulate matter iron data. Is it possible to present the amount or concentration values as well?

Yes, we added the blank quantities (ng) for DFe and PFe analysis. In our original submission, we made an error by not recalculating the percentage that the blank represented for the complete dataset, rather than only for stations 24, 28, and 30 from Labatut et al. (2014). Consequently, the percentage values were slightly different and we have modified them at lines 219-222: “*The total procedural blanks were 0.74 ± 1.17 ng (2SD) for DFe and 7.47 ± 1.09 ng (2SD) for PFe. This amounts to 0.5 % and 0.6 % of the samples average Fe content for DFe and PFe, respectively and 2.8% and 9.7 % for the sample with the smallest Fe content for DFe and PFe, respectively*”.

Line 331. “Fe concentrations in the western equatorial Pacific were approximately seven times ...” It would be useful to explicitly state concentrations, perhaps in brackets, so the reader doesn’t have to search for the values. Fe enrichment in the western equatorial Pacific, e.g., “Fe concentrations were approximately twice as high for DFe and seven times higher for PFe compared to central Pacific stations.”

Yes, concentrations have been added at lines 348-351: “*Fe concentrations throughout the entire water column in the western equatorial Pacific were approximately twice as high for DFe (0.63 nmol.kg*$^{-1}$

compared to 0.30 nmol.kg^{-1}, on average) and approximately seven times higher for PFe (3.58 nmol.kg^{-1} compared to 0.49 nmol.kg^{-1}, on average) relative to the central equatorial Pacific stations.".

Lines 411 to 413. Have you considered that heavier δ^{56}DFe relative to δ^{56}PFe could be preferential complexation of dissolved iron to natural organic ligands present in seawater? Under equilibrium control, ligands should selectively bind heavier isotopes relative to lighter isotopes. If the majority of DFe is bound to strong organic ligands (Fe-L), then Fe-L should be heavier than inorganic Fe (Fe'). Persumability, Fe' is what exchanges with PFe. I guess this is what you are terming as non-reductive dissolution.

Indeed, we agree that the complexation of dissolved iron by natural organic ligands can be one possible explanation for non-reductive dissolution (our group proposed this as early as 2017 (Abadie et al. 2017)). However, desorption could also be involved. This is what we have explained in our original submission, at lines 469–471, "In all cases, at the sediment–seawater interface and within the water column, the exact processes involved remain unclear. Desorption and ligand-promoted dissolution have notably been suggested (Abadie et al., 2017; John et al., 2018; Homoky et al., 2021).". We therefore prefer to remain cautious regarding the specific process or processes involved. For clarity, we have added another sentence emphasizing this aspect at lines 470-471 in the conclusion "*Desorption and/or ligand-promoted dissolution are potential mechanisms, though the exact processes involved remain unclear (Abadie et al., 2017; Homoky et al., 2021).*".

Lines 456 to 459 – Figure 8. The colour scheme used in this Figure and subsequent ones makes it very hard to determine the difference between isotope values. I certainly found it difficult to see the subtle changes in blue between samples – this is highlighted in the lower panel with stations 13 and 14. Here are the values greater or less than 0‰? Perhaps change the colour palette away from Viridis to the ODV colour palette or Ferret_blue_orange.

We understand your point, but we would like to keep the "Viridis" color bar. As stated in Ocean Science's submission policy, "it is important that the color schemes used in your maps and charts allow readers with color vision deficiencies to correctly interpret your findings." The ODV color palette or Ferret_blue_orange are not suitable because they are not gradual and/or do not use colors that are distinguishable for all types of colorblindness. To make the maps more readable, we changed the color bar values in Figures 8, 9, 10, 11, and 12; the color scales are different for each figure, thus allowing better perception of the different colors. Consequently, we changed the sentence at lines 496-497 by removing "To facilitate comparison, the δ^{56}Fe color coding is the same for all density layers." and replacing it with "*To facilitate interpretation, the δ^{56}Fe color scales are different for each density layer.*". In Figure 8, we added the values in parentheses directly on the figure and included in the caption: "*Values are shown in parentheses due to the large range, which limits color scale readability. Their measurement uncertainties can be found in Section 5.2.1 and Table 2.*".

Line 465. Any ideas on what phytoplankton species occupied the deep chlorophyll maximum (DCM)? This seems important when attributing isotope fractionation to biological production. Where nutrient and associated parameters were collected on the voyage to support the interpretation of how iron might be acquired by phytoplankton, new vs recycled iron etc? Cyanobacteria and diazotrophs vs eukaryotic species.

Yes, thank you for pointing out this omission. This addition greatly improves this section of the article. First, regarding terminology, we have added at lines 514-515 "*also called the deep chlorophyll maximum (DCM)*" in order to better include the scientific community specializing in these zones and in marine biology. Second, the phytoplankton community was investigated at one station at 10 m depth (Marchetti et al., 2010), at four stations in the DCM (Johnson et al., 2010), and at seven stations at different depths only for diazotroph species (Bonnet et al., 2009).

In the revised version, we added, at lines 516-526, the sentences: "*During the EUCFe cruise, the phytoplankton community was studied at station 2 at a depth of 10 meters (Marchetti et al., 2010), and in the chlorophyll maximum layer at station 2, station 25, and at two other stations lacking iron isotope measurements (0°, 165°E and 0°, 170°W) (Johnson et al., 2010). The cyanobacteria Prochlorococcus and Synechococcus dominate this community, followed by small pennate diatoms such as C. closterium and N. bicapitata (Johnson et al., 2010; Marchetti et al., 2010). This observation is consistent with previous studies in this equatorial upwelling region, which report a predominantly cyanobacteria-based community (Chavez et al., 1990; Landry et al., 1996). Unicellular diazotrophic cyanobacteria were also identified throughout the cruise, primarily picocyanobacteria, while the larger Trichodesmium was found only in coastal waters (Bonnet et al., 2009).*". Accordingly, we have added references for Bonnet et al., 2009; Chavez et al., 1990; Johnson et al., 1997; Landry et al., 1996; and Marchetti et al., 2010 to the References section.

Line 531. It might be worth considering the work of John et al. (2024), who tried to determine iron isotope fractionation in phytoplankton cultures.

Yes, thank you for this very useful recommendation. We added at lines 599-610 "Culture experiments examining isotopic fractionation by several diatom and a coccolithophore species (not the dominant species in our samples (Johnson et al., 2010; Marchetti et al., 2010)) revealed 'no clear relationship to species, growth rate, or Fe concentration' for biological uptake, possibly due to the sensitivity of kinetic isotope effects (John et al., 2024). During these experiments, biological uptake induced smaller fractionation (-1.3 ‰ to +0.60 ‰, mean +0.20 ± 0.38 ‰,1SD, n=62) compared to abiotic processes (approximately -4 ‰ to +5 ‰). These laboratory observations align with our in situ observations, although a comparison is not straightforward because iron acquisition processes are very different in cyanobacteria (Sutak et al., 2020). These authors suggested that seawater δ^{56}Fe may not be greatly impacted by biological uptake (John et al., 2024); a conclusion consistent with the findings of Lacan et al., 2008 and Radic et al., 2011."

We have also mentioned the work of John et al., 2024 at lines 626-627 by adding "*and culture experiments (John et al., 2024).*".

Consequently, we have added John et al., 2024 and Sutak et al., 2020 to the References section.

Lines 532 to 540. The discussion here is a little simplified and assumes that iron isotope fractionation by phytoplankton is likely to be similar across varying regions. At present, we have no real idea how cyanobacteria fractionate iron. The DCM is likely to be populated by Prochlorococcus and Synechococcus, as well as by unicellular diazotrophs, if nitrogen is limiting. Very little work has been done with these two bugs in fractionating iron under oxic conditions (Mulholland et al., 2015; Swanner et al., 2017). Perhaps this could be acknowledged. Again, it might also be worth referencing. John et al. (2024) here, who reported kinetic isotope effects during Fe(III) reduction in cultures. These findings could provide useful context for interpreting biological fractionation in this study.

In our original submission, with the sentence "The above differences in biological fractionation probably reflect regional variabilities, including differences in phytoplankton community, as well as differences in methodology such as the direct measurement of particles and the consideration of their phases" we intended to highlight the limitations of this study and the potential variability of these results depending on location, phytoplankton community, and other factors. In the revised submission, we have taken your recommendations into account. We have clarified this point by adding and modifying some sentences at lines 611-621: "*The differences in biological fractionation probably reflect variations in phytoplankton community composition, ligand types (John et al., 2024), regional variability, and methodological approaches such as the direct measurement of particles and the consideration of their phases. Potential iron fractionation during biological uptake, if it occurs, may depend on numerous parameters, including species-specific iron acquisition processes (Sutak et al., 2020), as well as pH, ligand, and reductant types, which strongly influence kinetic isotope effects (John et al., 2024). Our study region is particularly challenging in this regard, as it is a cyanobacteria-dominated system where isotopic fractionation processes remain poorly understood (Mulholland et al., 2015; Swanner et al., 2017). Iron isotope fractionation by diazotrophic cyanobacteria has not been investigated, despite these organisms contributing disproportionately to Fe uptake relative to their numerical abundance (Lory et al., 2022).*"

To further emphasize this point, we have added the sentence "*Estimates of fractionation due to biological uptake must include consideration of phytoplankton composition, dominated here by cyanobacteria.*" to the conclusion, at lines 838-839.

Consequently, we have added Lorry et al., 2022; Mulholland et al., 2015 and Swanner et al., 2017 to the References section.

Lined 701 to 702. A supporting reference for AAIW circulation in this region and the South Pacific is Bostock et al. (2013). It may be worth noting that this study region lies near the northern extent of AAIW influence, as discussed by Bostock et al. (2013), who reviewed AAIW circulation and mixing using geochemical tracers and Argo float data.

We have already cited several sources on AAIW circulation in Section 2, including Bostock et al., 2010. Therefore, we have not added Bostock et al., 2013 but have re-cited Tomczak and Godfrey, 2003 and Bostock et al., 2010 at line 790.

Review guidelines

1. Does the paper address relevant scientific questions within the scope of OS?

Yes

1. Does the paper present novel concepts, ideas, tools, or data?

Somewhat – as mentioned, the manuscript presents some new iron isotope data; however, it appears that the main findings have been discussed previously in (Labatut et al., 2014; Radic et al., 2011)

1. Are substantial conclusions reached?

More work is needed on how phytoplankton fractionate iron isotopes./

1. Are the scientific methods and assumptions valid and clearly outlined?

Yes the scientific method and measurements are sound.

1. Are the results sufficient to support the interpretations and conclusions?

Generally, see comments about iron isotope fractionation by phytoplankton

1. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?

This is fine

1. Do the authors give proper credit to related work and clearly indicate their own new/original contribution?

Yes they credit previous work

1. Does the title clearly reflect the contents of the paper?

I think a better title would be “Iron isotopes provide insights into the biogeochemical cycling of iron in the equatorial Pacific”

1. Does the abstract provide a concise and complete summary? Yes

1. Is the overall presentation well structured and clear?

Generally, figure colours could be improved to allow the reader to distinguish between iron isotope values.

1. Is the language fluent and precise? yes

1. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? yes

1. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? no

1. Are the number and quality of references appropriate? yes

1. Is the amount and quality of supplementary material appropriate? yes

references

Bostock, H.C., Sutton, P.J., Williams, M.J.M., Opdyke, B.N., 2013. Reviewing the circulation and mixing of Antarctic Intermediate Water in the South Pacific using evidence from geochemical tracers and Argo float trajectories. Deep-Sea Research Part I: Oceanographic Research Papers, 73: 84-98.

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Labatut, M. et al., 2014. Iron sources and dissolved-particulate interactions in the seawater of the Western Equatorial Pacific, iron isotope perspectives. Global Biogeochemical Cycles, 28(10): 1044-1065.

Mulholland, D.S. et al., 2015. Iron isotope fractionation during Fe(II) and Fe(III) adsorption on cyanobacteria. Chemical Geology, 400: 24-33.

Radic, A., Lacan, F., Murray, J.W., 2011. Iron isotopes in the seawater of the equatorial Pacific Ocean: New constraints for the oceanic iron cycle. Earth and Planetary Science Letters, 306(1-2): 1-10.

Sutak, R., Camadro, J.-M., Lesuisse, E., 2020. Iron Uptake Mechanisms in Marine Phytoplankton. Frontiers in Microbiology, 11(2831).

Swanner, E.D. et al., 2017. Iron Isotope Fractionation during Fe(II) Oxidation Mediated by the Oxygen-Producing Marine Cyanobacterium Synechococcus PCC 7002. Environmental Science & Technology, 51(9): 4897-4906.

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