

Microbial iron cycling illuminates the biological contribution and potential climate drivers of deep-sea rare earth element enrichment

Corresponding Author: Professor Yinan Deng

This file contains all editorial decision letters in order by version, followed by all author rebuttals in order by version.

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Decision Letter:

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Dear Professor Deng,

Your manuscript titled "The overlooked role of microbial iron cycling for the enrichment of rare earth elements in deep-sea sediments" has now been seen by 3 reviewers, whose comments are appended below. You will see that they find your work of some potential interest. However, they have raised substantial concerns that must be addressed. In light of these comments, extensive revisions will be required before we can further consider the manuscript for publication. We would, however, be interested in considering a revised version that fully addresses these serious concerns.

In particular, the following criteria must be met before the manuscript can be considered for publication:

- 1) Clearly distinguish the results and conclusions of this study from those of the recently published paper "Impact of iron biogeochemical cycling in deep-sea environments on rare earth element enrichment" in Chemical Geology (<https://doi.org/10.1016/j.chemgeo.2025.122951>).
- 2) Provide more supporting information, including additional pore-water geochemical data, TOC%, additional SEM images of magnetite, and relevant proxy data for CG18.
- 3) Provide more substantial evidence, including source-sink constraints on Fe-P-REE, to exclude the abiotic hypothesis, and fully enhance the robustness of arguments regarding the microbial role in REE enrichment.

We hope you will find the reviewers' comments useful as you decide how to proceed. If additional work allows you to either incorporate or refute these criticisms, we will be happy to look at a substantially revised manuscript. If you choose to take up this option, please either highlight all changes in the manuscript text file, or provide a list of the changes to the manuscript with your responses to the reviewers.

When resubmitting, please provide a point-by-point response to the reviewers' comments. Please submit your responses as a separate file, distinct from your cover letter where you can add responses to the Editors' comments that you do not want to be made available to the reviewers. Word files are preferred. We recommend that any figures, tables or graphs that are included in the response to reviewers are also included in the main article or Supplementary Information.

Please bear in mind that we will be reluctant to approach the reviewers again in the absence of substantial revisions.

If the revision process takes significantly longer than three months, we will be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Earth & Environment or published elsewhere in the meantime.

We are committed to providing a fair and constructive peer-review process. Please do not hesitate to contact us if you wish

to discuss the revision in more detail.

Please use the following link to submit your revised manuscript, point-by-point response to the reviewers' comments with a list of your changes to the manuscript text (which should be in a separate document to any cover letter), a tracked-changes version of the manuscript (as a PDF file) and any completed checklist:

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Please do not hesitate to contact us if you have any questions or would like to discuss the required revisions further. Thank you for the opportunity to review your work.

Best regards,

Kai Deng
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REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

Peer-review for Communications Earth & Environment (COMMSENV-25-2787)

The overlooked role of microbial iron cycling for the enrichment of rare earth elements in deep-sea sediments

Summary

This manuscript addresses the potential role of dissimilatory iron reduction (DIR) in the migration and condensation of Rare Earth Elements (REE) from marine particulates into authigenic REE-enriched ores. Combining mineralogy of the magnetic fraction with pore water geochemistry, iron isotopes, and functional marker genes from a sediment core retrieved from 5700 m water depth in the Pigafetta Basin, western Pacific, the authors define an alternative diagenetic pathway potentially driven by microbial redox processes that can lead to an enrichment of REE in apatite concretions.

Based on the presence of multiple domain nano-magnetites, negative $\delta^{56}\text{Fe}$ values (-0.08‰), bulk sediment and pore water REE concentrations, the identification of specific taxa and functional marker genes involved in extracellular respiration, the authors claim that DIR exerts significant control on REE sorption processes, leading to in-situ formation of phosphate ores via dissolution/precipitation of transient iron oxides with adsorption in bottom waters and condensation in pore waters. Finally, global climate dynamics (i.e. productive upwelling conditions) are taken into account in the accumulation of biogenic phosphates.

(I) What are the major claims of the paper?

Microbial dissimilatory iron reduction could represent an alternative early diagenetic pathway explaining REE condensation and formation of authigenic ores through sorption processes driven by iron-reducing bacteria.

(II) Are these claims novel, and will they be of interest to others in the community?

Biotic/abiotic and pelagic/benthic processes have to be better distinguished as to clarify the diagenetic sequence and differential timing of in-situ formation of magnetite and apatite. The authors could provide constraints in terms of sources and sinks (Fe(II)-Fe(III), organic/mineral PO₄³⁻, REE in hydrothermal fluids and seawater).

Furthermore, abiotic fractionation of Fe isotopes due to partial oxidation of ferrous to ferric Fe could produce poorly crystalline (pelagic) magnetites exhibiting slightly negative $\delta^{56}\text{Fe}$ values during mixing of hydrothermal fluids with seawater. This has not been considered (or occulted as common knowledge?) although it is an essential part of the discussion. Although apatitic phosphate concretions are known to form as diagenetic products in marine sediments, phosphate sources, their scavenging by iron oxides prior to deposition and transformation from organic to authigenic during time of burial are not introduced either. Environmental conditions at the time of deposition (e.g. upwelling, productivity, intraplate tholeiitic iron-rich volcanism, hydrothermal activity) have to be introduced and discussed in parallel, not limited to the final part of the discussion. Otherwise, the manuscript gives the impression of being deliberately biased in favor of the research hypothesis.

(III) Is the work convincing, what further evidence would be required to strengthen the conclusions?

The abiotic hypothesis seems to have been dismissed a little too quickly, and the line of argumentation chosen by the authors remain highly speculative:

- Crystallographic analysis of microdomain and single-domain magnetites (assumed to reflect microbially-mediated magnetite and magnetosome, respectively) complemented by $\delta^{56}\text{Fe}$ values around -0.08‰ do not constitute sufficient evidence that enable the distinction between microbial iron reduction and mixing of hydrothermal fluids with seawater. Abiotic (oxidative) processes and sources of iron and REY are not addressed in sufficient detail.

- The only pore water geochemical data documented in this manuscript are REY concentrations. Rare Earth Elements being mostly redox-conservative, they may possibly reflect bottom water conditions at the time of deposition (e.g. negative anomaly of Ce^{3+/4+}), or release after microbial reduction of Fe(III) oxides. To infer metal reduction processes after deposition, additional pore water geochemical data are needed (e.g. Fe²⁺, Mn²⁺, As²⁺, trace metals).

- There is no characterization of the sediment organic fraction (e.g. TOC) and some contradictory statements are scattered throughout the manuscript (minimal organic content, sediment anoxic conditions due to organic mineralization). Interpretations in terms of microbial reduction of iron and organic matter mineralization have to be supported by additional downcore profiles (i.e. the authors' own data, not literature).

- The metagenomic data (only available for download on Zenodo) are succinct and do not clearly establish metabolic potential for dissimilatory iron reduction (DIR), or magnetosome formation. The taxa reported in this supplement are mostly aerobes, likely originating from environments that would argue against post-depositional microbial processes, i.e. oceanic bottom waters (e.g. *Limnobacter*, *Muricauda*) and hydrothermal vents (*Thermoaerobaculum*). The sequence data has to be submitted to a public repository and an accession number provided to the reader.

- In the absence of clear functional marker genes for DIR, metagenomic data was tested using the FeGenie pipeline but not consistently reported, e.g. siderophores, magnetosomes, and Fe(II/III) redox processes, Fe regulation. The few functional genes selected to identify metabolic potential for DIR were identified at very low read counts. These predicted genes relate to the multiple heme cytochrome C reductase (not specific to metal reduction) and extracellular respiration electron transfer (nanowires are not common in sediments).

- In the final part of the discussion, the authors mention that past upwelling conditions (ca. 12 Ma ago) could explain phosphate accumulation at the seafloor. More background information on sedimentary conditions that led to phosphate concretions are necessary. Indeed, iron oxides expelled during hydrothermal activity could trap both REY and orthophosphates. The authors have to distinguish between pelagic and benthic processes, as well as disentangle biotic-abiotic processes, in order to provide time constraints on magnetite and apatite in -situ formation.

(IV) do you feel that the paper will influence conceptual understanding or technological capability?

At this stage, evidence for microbial processes of metal reduction is not compelling. Additional SEM/TEM images of magnetite could be produced as a single grain is documented (Fig. 4). Please provide additional SEM/TEM images in the supplement.

Specific comments

Introduction: Some basic background information on REE is missing (e.g. redox states, hydrothermal release, distribution

and type of ores)

- I. 24: Add "Understanding the mechanisms... is vital"
- I. 27: migration rather "dissolution and subsequent incorporation"; organic matters --> organic matter
- I. 30: the authors do not document or report biological data per se
- I. 31: datasets --> data
- I. 33-37: this mechanism is known and referred to as "diagenetic redistribution of iron".
- I. 45: REY deposits, be more specific, what type? Polymetallic nodules, massive sulfide deposits, phosphatic concretions, else?
- I. 51: what about the initial sources and mechanisms releasing REY in marine waters? Detrital sources, basalt alteration and hydrothermal vents, global versus local processes? What are the common REY concentrations in seawater? There is no mention of their very low initial concentrations and necessity to condense them to obtain minable ores, what these ores are and where they are usually found...
- I. 53: re-released --> solubilized, released and thereby concentrated in the pore water / how can REE³⁺ substitute for Ca²⁺ in the crystal lattice of apatite? How is the charge imbalance equilibrated?
- I. 54: provide the normal formula of apatite; what about anapaite which commonly forms concretions in marine environment?
- I. 56: crystallization-dissolution, rather dissolution-precipitation cycles. Do this imply Oswald ripening and transient phases?
- I. 63: are these values corresponding to cell densities in seawater or sediments? Sediment --> marine sedimentary environments (cells × cm³, not mL⁻¹)
- I. 65: ...whose underlying sediments are characterized (D'Hondt et al., 2019 does not address microbial populations in the water column).
- I. 64-66: most of the deep-sea offshore cannot be considered productive. The authors likely refer to the surface ocean but productivity in the ocean offshore is limited. Coastal upwelling zones along trenches constitute specific cases. Be specific in what "spatial coupling" encompasses.
- I. 68: what are the initial sources of iron and REEs prior to reduction in the sediment and release in the pore water?
- I. 70-71: BIFs are considered chemical precipitates and this analogy seems out of context; (I) some additional words of introduction on the "Redfield ratio" and nitrogen limitation due to heterotrophic denitrification in highly productive waters are needed since this results in an accumulation of orthophosphate in bottom waters and sediments (e.g. upwelling zones, Peru and Namibian OMZs); (II) mention that phosphorus does not have a redox cycle and that this is driven by scavenging and reduction of Fe(III)-Fe(II).
- I. 73: This sentence doesn't make sense. How does metabolic degradation of organic matter prevent documenting microbial activity?
- I. 78: what about siderophores?
- I. 81: In sediments, Fe²⁺ can react with other solutes as well, after sulfate reduction (FeS₂) or fermentation (FeCO₃). The precipitation of microbially-induced pelagic magnetites requires stratified conditions and the authors should clarify when they refer to pelagic or benthic processes.
- I. 85: Iron is the main limiting nutrient in open ocean productivity, so where is it coming from? Same question for the organic matter. See comment I. 64-66.
- I. 87: what about magmatic and hydrothermal processes enriching LREE in the fluid phase? See comment in I. 51, i.e. local vs global processes
- I. 88: biogenic magnetites, you mean both or magnetosomes only. In theory, magnetite can be further reduced during DIR, the smaller the crystals the more reactive.
- I. 91: reliable biomarker? Be specific in what biogenic magnetites are. Magnetosomes constitute biomineralization, whereas magnetite precipitates are simply induced during DIR. / microbial activity --> microbial redox cycling of metals
- I. 92: unclear whether the authors refer to magnetosomes in particular. The structural Fe(III) of magnetites can be further reduced in the sediment during microbial diagenesis.
- I. 94: can one really speak of REE cycling? Except for Cerium (3+/4+) and Europium (2+/3+), REEs are not subject to redox cycling.
- I. 96: the manuscript does not present metagenomic data

Geologic background: Succinct, what about hydrogenetic nodules found around seamounts? Here, one could argue for abiotic processes of REE enrichment and provide information on past upwelling and intraplate tholeiitic volcanism.

- I. 107: zeolitic clay --> hydrothermal alteration of basalts not introduced
- I. 108: minimal organic matter with occasional terrigenous inputs --> data not shown
- I. 110: Figure 1 does not display sediment depth nor age

Results: Some introduction on the influence of the iron shuttle (sources and sinks) and reductive remobilization on $\delta^{56}\text{Fe}$ values are missing. Metagenomic data are not presented in the main text or in the supplement (a succinct table is available on zenodo for download). Sequencing data should be made available in a public repository. The authors have to better differentiate between pelagic and benthic processes.

- I. 121-127: abiotic oxidation/reduction processes also fractionate Fe isotopes, the residual phase (i.e. oxidized) being systematically enriched in the heavy Fe isotope. Moreover, $\delta^{56}\text{Fe}$ of -0.08 ‰ does not reflect an enhanced microbial fractionation compared to magmatic values (0.00 ‰). These values could also be interpreted in terms of partial oxidation of hydrothermal Fe(II) during mixing of hydrothermal fluids with seawater. As samples are from below the CCD, a depletion in carbonate-bound Fe phases is not surprising. Moreover, these are bulk measurements that do not take into account the speciation of iron phases.

- l. 131: explain what a Cerium negative anomaly implies, i.e. remains in solution under reducing conditions
- l. 137: ferromagnetic, ferrimagnetic, diamagnetic or paramagnetic minerals?
- l. 139-157: very technical part
- l. 160: magnetic particle form aggregates, could this be a preparation artifact since magnetic minerals always tend to aggregate?
- l. 168: can the authors provide information on accumulation of biogenic apatite, e.g. hard ground, condensed facies, else? Some words on forms of phosphorus (organic, inorganic, apatitic, authigenic) are also needed in order to address the transformation from organic into authigenic forms during burial. It is also worth mentioning that apatite represents the main form of authigenic phosphate in the marine environment compared to anapaite or vivianite. Then, the authors should provide some constraints on the environment and time of formation for both magnetite and apatite.

n.B. if the main source of phosphorus is actually organic and relates to past upwelling and productive conditions, this should be brought earlier in the text, not briefly mentioned at the end.

- l. 173-175: provide full names of enzymes in a supplementary table, not gene abbreviations. Moreover, there are no specific functional marker genes for dissimilatory iron reduction. These genes are involved in extracellular respiration and electron transfer via nanowires (with multiheme cytochrome c), unlikely to take place in the sediment, rather at the paleo sediment-water interface. Iron is not the only substance that can be reduced with the multiheme cytochrome. Obviously, magnetosomes are not formed in the sediment either.

n.B. metagenomic data are reported in the results, but not presented in any figure of the manuscript. Currently, these data are buried in a zenodo data dump without their corresponding metadata or accession number. Looking at this zenodo supplement, I found few information on very low number of reads assigned to Thermoanaerobaculia (identified from hydrothermal vents), Acidobacteria (high taxonomic level, no inference possible), Photobacterium sanguinicancr (bioluminescent symbiont), Photobacterium frigidophilum (facultative anaerobe common in deep-sea waters and sediments), Vibrio sp., Limnobacter sp., Muricauda sp., Stenotrophomonas nitritireducens, none of which appear to be involved in dissimilatory reduction of iron or magnetosome formation (accounting for RPKM <0.15%). Please report the FeGenie output consistently. Although detection is higher in the REE-rich layer, they are far from being overrepresented. Also, there is no evidence that the predicted metabolisms could have been active after deposition and during burial.

Discussion: The authors provide little to no evidence for microbial iron reduction as the main process leading to magnetite precipitation. They conclude on past upwelling conditions 12 Ma ago, which would likely lead to an oxygen minimum zone, but do not decipher the source of iron or how this would lead to increased redox cycling of iron.

- l. 187: in the introduction (l. 108) you mentioned that the organic content of the sediment is minimal.
- l. 193: metagenomic data not shown
- l. 194-195: "enhancement of historical microbial activity" in the water column at the time of deposition or after deposition? What is iron metabolism? Aerobic-anaerobic iron respiration, dissimilatory processes, uptake, regulation, siderophores, else? The authors ran the FeGenie pipeline (Garber et al., 2020 Front Microbiol) and could thus report more clearly on metabolic potential for aerobic-anaerobic redox Fe processes, siderophores and magnetosomes.
- l. 198-200: with more advanced bioinformatic analyses, one could fill a part of this gap.
- l. 202: what do the author mean by "bacterial iron metabolite"? Siderophores, else?
- l. 202: is it due to oceanic circulation or very low sedimentation rates?
- l. 205: these references deal with magnetosomes, not partial reaction of dissolved Fe²⁺ with amorphous hydrated iron oxides.
- l. 210: do these values correspond to fractionation factors? What are the ⁵⁶Fe values one should expect?

n.B. The authors do not mention the possibility of abiotic fractionation of Fe isotopes due to partial oxidation from ferrous to ferric Fe and assume that ⁵⁶Fe values around -0.08 ‰ constitute indubitable evidence of DIR. Also, according to the successive sorption processes theorized by the authors, the potential influence of redox shuttle has to be considered as well.

- l. 213: BIFs were formed under anoxic conditions, not under oxic to suboxic conditions. Thus, I wonder if this comparison is justified.
- l. 215: currently distal. Things may have looked different 12 Ma ago.
- l. 217-239: very technical and descriptive part reiterating results. Poorly crystalline magnetites could also form during mixing of hydrothermal fluids with seawater.
- l. 236: during deposition, here the authors assume that these magnetites are pelagic precipitates.
- l. 245: by 5700 m water depth on an abyssal plain, a detrital component is any way unlikely.
- l. 254: what is the TOC content of the sediment? Abyssal clays are usually extremely organic-lean...
- l. 262: or that reductive diagenesis of the sediment led to subsequent release of metal ions...
- l. 270: once more, in the introduction you mentioned that OM content is minimal. How can OM remineralization be substantial enough to lead to anoxic conditions? Please support this statement with bulk OM.
- l. 274: solid-phase transformation; provide reference
- l. 282: the metagenomic data are far from being compelling and are not made available to the readers.
- l. 285: due to the absence of data on sedimentary OM content and cell density, this statement remains speculative. What is the source of phosphate? To this point, the reader is left with the idea that an accumulation of macroremains of biogenic apatite is the main source causing phosphatic concretions.
- l. 303-307: ...if one assumes that ⁵⁶Fe values of -0.08 ‰ are sufficient evidence for dissimilatory iron reduction by

unidentified microorganisms. The problem is that hydrothermal fluids mixing with seawater could produce abiotic magnetites that are slightly enriched in the light Fe isotope. The authors would be then tracing the source of the fluids rather than disentangling biotic-abiotic processes.

- I. 305: "microbial iron metabolism governs secondary mineralization". Intraplate tholeiitic volcanism and hydrothermal circulation can also produce more crystalline secondary magnetite...

- I. 315: hitherto, marine productivity hotspots have not been introduced to the reader or put into context of the Pigafetta Basin 12 Ma ago.

- I. 318: microbial processes are rather defined by the substrates available after deposition at the seafloor, which is indirectly related to environmental conditions at the surface ocean.

- I. 324-331: see comment about I. 70-71 on nitrogen limitation and excess orthophosphate turning into authigenic (non-) apatitic phosphate in the sediment. P speciation would be an asset as to discriminate organic and inorganic forms of phosphates.

- I. 332-334: which indirectly argues against substantial drive by microbial dissimilatory iron reduction...

- I. 337: you mean an oxygen minimum zone? Normally, OMZs are mainly under the influence of heterotrophic denitrification (with substantial loss of fixed nitrogen). Iron is the main limiting nutrient in the modern global ocean, so where is the iron coming from?

Methods:

- I. 423: comprehensive metadata on sequence data are missing (e.g. sequencing depth, number of contigs and length, predicted genes and ORFs).

Reviewer #2 (Remarks to the Author):

The manuscript number COMSENV-25-2787 entitled "The overlooked role of microbial iron cycling for the enrichment of rare earth elements in deep-sea sediments" from Wang et al. establishes a relationship between REY enrichment in phosphates and clear evidence of enhanced Fe metabolism, supported by mineralogical characteristics, isotopic signals, and genomic data. Together, these proxies convincingly indicate that microbial Fe metabolisms are associated with diagenetic REY enrichment in sediments. Such an association of proxies is rare in sedimentology/diagenesis studies and, by itself, makes the work of great value to the literature.

From the perspective of building a genetic model for these mineral deposits and their link to a temporally constrained event, some points deserve clarification. What is the main control on REY enrichment in this case—the greater abundance of the host mineral (phosphates, as shown in Fig. 2), a paleoenvironmental factor that favored Fe metabolisms at this stratigraphic level, or both? The explanation is proposed in the last item of the discussion, but it could be better substantiated. The first key point is that REY enrichment is associated with enrichment of the host mineral (phosphates), as indicated by the bulk elemental data. From there, the investigation proceeds to the relation—which I do not contest—between the greater abundance of the host and the signatures associated with enhanced microbial Fe metabolisms.

Lines 263–265 link biomediated eodiagenetic Fe hydroxide mineralization with phosphatization, promoting remobilization and concentration of REY in authigenic phosphates. It would be important to better characterize the relative proportion of authigenic versus biogenic phosphates in this interval, rather than considering only total P abundance. Distinguishing between biogenic apatite and authigenic phosphate is essential to test this hypothesis.

The modeling of the proportion of REY enrichment associated with microbial Fe metabolisms is very interesting. As the authors discuss, this only constrains the lower bound of the role of biogeochemistry in REY concentrations, since several other metabolisms may also remobilize REY in pore waters.

The profiles of the most relevant proxies are presented only for core GC112. In the materials, two cores are cited, and it is notable that the detailed characterization is missing for GC18. Yet GC18 is used as a chronostratigraphic reference to link REY enrichment, Fe metabolisms, and phosphatization to the Middle Miocene Climate Transition (MMCT; 14.8–12.6 Ma), characterized by increased primary productivity and bottom-water oxygen depletion favoring microbial Fe metabolisms. I interpret the cause here as increased delivery of P-OM together with optimal conditions for Fe metabolisms in the substrate, leading to secondary mineralization.

Considering the complete and uncommon association of mineralogical, magnetic, geochemical, isotopic, and genomic proxies, I regard the manuscript as highly original and provocative. It opens new perspectives for investigating biogeochemical processes and the possible temporal association of REY enrichment in deep-marine sediments. This contribution will certainly advance knowledge on a topic that is strategically relevant for the energy transition and, consequently, of great interest to the readership of Communications Earth & Environment.

Reviewer #3 (Remarks to the Author):

The manuscript by Wang et al. addresses the importance of Fe cycling in marine sediments for REY cycling and thereby also REY enrichment in deep-sea sediments. While this certainly is an interesting topic, the manuscript presents very similar ideas and data to the recently published paper "Impact of iron biogeochemical cycling in deep-sea environments on rare earth element enrichment" also by Pengcong Wang in Chemical Geology. The used methods are identical and the working area is the same (although different cores). The recently published paper is not even referenced in this submitted manuscript. The figures presented here are basically the same as in the recently published paper (just a different core). I therefore suggest to reject this manuscript for now until significant changes and additions have been made to produce a substantially different manuscript to the recently published one.

Additionally, the methods lack rigorous reporting of accuracy, precision and blanks for the geochemical analyses (also see detailed comments below).

Further comments:

Discussion

L253: one of the main carriers of REY to deep sea sediments are Mn oxides (see e.g. Du et al., 2025 Nature). This should be added and discussed here.

L259 ff and Figure 2d:

pore water exhibit various different REYSN patterns in deep-sea sediments and not always the same one (see e.g. work by Haley et al., Abbott et al., Paul et al., Du et al.). This should be discussed more differentiatedly and different pore water studies should be used for comparison besides the one by Deng et al. mentioned so far.

In general: Pore water data (oxygen, nitrate, dissolved Mn, Fe, REY) for the presented core would be beneficial to support the claims about Fe and REY cycling in these deep-sea sediments.

Methods

L354ff:

precision, accuracy and blanks should be reported for the major elements, the REY and other trace elements.

L363ff: procedural blanks and replicate analyses results should be reported for Fe isotope data.

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Version 1:

Decision Letter:

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Dear Professor Deng,

Your revised manuscript titled "The biological contribution and potential climate drivers of deep-sea rare earth element enrichment: Insights from microbial iron cycling" has now been seen by our reviewers, whose comments appear below. In light of their advice we are delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Earth & Environment.

We therefore invite you to revise your paper one last time to address the remaining concerns of our reviewers. At the same time we ask that you edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work.

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Best regards,

Kai Deng
External Editor
Communications Earth & Environment

Alireza Bahadori, PhD
Senior Editor
Communications Earth & Environment
Consulting Editor
Communications Sustainability

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

Revised manuscript COMMSENV-25-2787A

The biological contribution and potential climate drivers of deep-sea rare earth element enrichment: Insights from microbial iron cycling

This is a revised version of a manuscript that I have previously reviewed. I consider that the authors have comprehensively implemented their revisions according to my comments and suggestions, which, I admit, were exhaustive. I appreciated reading the revised manuscript as well as the efforts of the authors to disentangle complex pre- and post-depositional processes. I have only minor comments and wording suggestions to support the authors' line of arguments in the introduction and discussion. I used nota bene (n.B.) where clarifications are needed. Once addressed, I can endorse acceptance of the manuscript for publication.

Yours sincerely,
Reviewer 1

Minor comments and suggestions

- I. 5-9: I would suggest inverting the order of these sentences as follows:

The migration of REY from marine particles (e.g. Fe-Mn (oxyhydr)oxides or organic matter) to apatite is a prerequisite for subsequent enrichment during early diagenesis. Thus, bioapatite and authigenic apatite act as final sinks for REY and thereby represent key reservoirs in deep-sea sediments. However, the underlying forces driving this migration process

remain unresolved.

- I.10: iron metabolism --> iron biogeochemical cycling
- I. 11 microbial element cycling --> microbial reductive diagenesis
- I. 12: Through an integrated analysis of --> Integrating...
- I. 13: there is no data documenting "activity" which implies these processes are ongoing --> reduction
- I. 14: degradation or phase transformation --> driving mineralization of marine particles after deposition
- I. 16: "This mechanism may be particularly important during periods of significant global climate variability." I find this statement a bit vague.

n.B. What I understood from the authors' answers to my comment and my lecture of the revised manuscript is that there was increased wind transport of dust particles during the Late Miocene glacial period, which combined with upwelling conditions, stimulated productivity in the Fe-limited pelagic ocean. Sedimentation of Fe-Mn oxides would scavenge orthophosphate under OMZ conditions and strong bottom currents, resulting in condensed strata acting as precursors for REY-enriched apatitic layers. If correct, could the authors rephrase to better convey this specific conditions?

- I. 44: ultimate --> final
- I. 45: The extreme concentration contrast of $\sim 10^{12}$ --> The contrast of concentrations by twelve orders of magnitude
- I. 47: cycling --> mineral phase element transfer via...
- I. 69: for Eh and pH during microbial iron reduction and diagenetic redistribution across phases via pore water, cite: Vuillemin et al. (2023) Authigenic minerals reflect microbial control on pore waters in a ferruginous analogue. *Geochem Perspect Lett* 28
- I. 71-72: not much the lowering of temperatures, but rather wind intensities and their location at higher latitudes due to the waxing of ice caps.

n.B. I realize that this is out of the scope of the manuscript, but I have a pending question related to this: Do the authors know whether increased eolian transport of dust particles during this glacial period is also involved in the increased productivity or can this argument be discarded? I tend to think that dust particles and particulate OM are correlated (i.e. iron fertilization).

- I. 77: Same here. Do the authors refer to an upwelling zone, an oxygen minimum zone, or both? ... The causes of OMZ are multiple (for instance Hawaii OMZ due to deep water stagnation, not productivity), same for the stimulation of surface productivity.

n.B. no need to extend on this topic, but please try to provide some clarifications. The TOC values argue against increased OM sedimentation. Increased dust particles could increase both productivity and scavenging of REY and phosphate during sinking.

- I. 79: I suggest to rephrase as follows: "...synergistically result in the deposition of sediment precursors promoting microbial mediation of REY release..."
- I. 81: what about sedimentation rates? --> e.g. due to very low sedimentation rates and microbial oxidative degradation of organic proxies...
- I. 90: Be careful of the order you list your arguments, i.e. magnetotactic bacteria exhibit a pelagic lifestyle and usually thrive under microaerobic conditions (i.e. oxycline, pycnocline, chemocline). Thus, they are likely not involved in the geochemical evolution of pore waters, but may point to suboxic conditions in the water column and act as early degraders of sinking OM.
- I. 99: a tracer recording past microbial activity

n.B. I have a subsidiary question (I. 147): in organic-poor pelagic sediments, sulfate reduction aborts while fermentation proceeds (e.g. D'Hondt et al. 2019 *Nat Comm* 10; Vuillemin et al., 2020 *mBio* 11). Microbial production of H₂S promotes mackinawite-pyrite formation at the expense of other Fe²⁺-bearing phases. Is sulfate reduction influential on apatite formation? FeRB are usually versatile and can also evolve as fermenters...

- I. 156: previous findings, a reference is missing
- I. 232: in the water column and at the sediment-water interface
- I. 240: in I. 222 you state that OM particles originate from surface primary productivity and here you mention organic phosphorus from riverine input. This is confusing. Does the orthophosphate necessary to apatite precipitation derives from, e.g. the sinking particulate OM or the same terrigenous dust that supplies Mn-Fe oxides, or both?
- I. 249-252: what about an accumulation of dissolved orthophosphate in OMZ waters and scavenging during sinking? It is now mentioned in the introduction, but discussed here.
- I. 264: the phosphate sink is clear, but the sources remain elusive.
- I. 269: such as condensed sediment strata? Condensed strata imply strong bottom currents consistent with upwelling. These two climatic parameters could be clearly mentioned, i.e. the contribution of strong winds and bottom currents in upwelling regions
- I. 285: cite the corresponding figure here (Fig. 2a).

n.B. I quite understand how you conclude mineral-phase transformation over reductive dissolution. However, in I. 235, you say that these elements show post-depositional decoupling, but in I. 270 you claim that migration, concentration, and sequestration are geologically instantaneous upon deposition at the seafloor. Later you argue that this is a stratigraphic transition related to past depositional (climatic) conditions, which somehow invalidates the statement in I. 235 which requires constraints on the duration of diagenetic processes.

- I. 301: see my subsidiary question on sulfate reduction in organic-poor sediment
- I. 313: mention that this corresponds to "condensed sediment strata" aka hardground. Such phosphate or glauconite condensed strata in the geological rock record are considered to correspond with past upwelling conditions

- l. 323: what about eolian transport? Upwellings are associated with stronger winds and currents
- l. 332: the focus is usually on framboidal magnetites as pelagic precipitates not related to magnetosomes.
- l. 360-372: this part is not really necessary as it doesn't convey explanations. Just keep the sentence l. 365-368 with the citation.

n.B. a word of caution about l. 367, metagenomic predictions do not prove activity (i.e. metatranscriptomes). The DNA could derive from resting stages and dormant cells, thus correspond to the stratigraphic age, not an active microbiome in subsurface sediments. It seems plausible that microbial iron reduction took place during particle sinking, at the sediment-water interface (resulting in condensation and phase transition), then likely at much slower rates during burial due to organic substrate depletion.

- l. 391-393: future work is not relevant to discussion of the data produced
- l. 394-395: delete the first half of this sentence and move to l. 391 after deletion of the sentence about future work
- l. 425: define abbreviation at first mention in the text
- l. 430: here again, the TOC argues against increased OM sedimentation. Was all the primary OM degraded during sinking? Was it reworked by strong bottom currents? Are we talking about another type of OMZ (i.e. deep water stagnation)?
- l. 455: delete " It is important to emphasize that"

Fig. 6: typos --> the "laate" Miocene "cooling" event

Reviewer #2 (Remarks to the Author):

"The biological contribution and potential climate drivers of deep-sea rare earth element enrichment: Insights from microbial iron cycling" by Pengcong Wang et al.

The authors have carefully addressed the reviewers' comments. In particular, regarding the aspect that initially drew my attention, there have been substantial improvements in the distinction and characterization between authigenic and biogenic phosphate. The revised version clearly demonstrates the predominance and significance of authigenic phosphate formation in controlling REY enrichment, as originally hypothesized. Moreover, the discussions on the climatic and diagenetic mechanisms responsible for the formation of the REY-enriched layer have been substantially improved, making the proposed hypothesis much clearer and more coherent.

For these reasons, I consider that the revision has satisfactorily addressed the previous concerns and has significantly improved the overall quality of the manuscript. I am therefore in favor of its acceptance for publication in Communications Earth & Environment.

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Dear Editor

We are grateful to you and the three reviewers for your valuable comments on our manuscript, which have been crucial for enhancing the quality of our work. We highly value this opportunity for major revision and have addressed each point raised with specific modifications in the manuscript. After careful consideration, we have updated the manuscript title to: "The biological contribution and potential climate drivers of deep-sea rare earth element enrichment: Insights from microbial iron cycling", to better reflect the refined focus of the study. For ease of review, revisions are highlighted in red within the manuscript, and our detailed point-by-point responses are provided in blue below.

Reviewer #1:

Summary

This manuscript addresses the potential role of dissimilatory iron reduction (DIR) in the migration and condensation of Rare Earth Elements (REE) from marine particulates into authigenic REE-enriched ores. Combining mineralogy of the magnetic fraction with pore water geochemistry, iron isotopes, and functional marker genes from a sediment core retrieved from 5700 m water depth in the Pigafetta Basin, western Pacific, the authors define an alternative diagenetic pathway potentially driven by microbial redox processes that can lead to an enrichment of REE in apatite concretions.

Based on the presence of multiple domain nano-magnetites, negative $\delta^{56}\text{Fe}$ values (-0.08‰), bulk sediment and pore water REE concentrations, the identification of specific taxa and functional marker genes involved in extracellular respiration, the authors claim that DIR exerts significant control on REE sorption processes, leading to in-situ formation of phosphate ores via dissolution/precipitation of transient iron oxides with adsorption in bottom waters and condensation in pore waters. Finally, global climate dynamics (i.e. productive upwelling conditions) are taken into account in the accumulation of biogenic phosphates.

Reply: We are grateful for your careful review of our manuscript. Your constructive comments have been invaluable in enhancing our work. We have incorporated all of your suggestions into the revised manuscript and respond to each point in detail below.

(I) What are the major claims of the paper?

Microbial dissimilatory iron reduction could represent an alternative early diagenetic pathway explaining REE condensation and formation of authigenic ores

through sorption processes driven by iron-reducing bacteria.

Reply: We acknowledge that the original manuscript may have created ambiguity by implying that microbial iron reduction serves as an alternative pathway to early diagenesis. The revised manuscript now emphasizes the role of microbial iron metabolism, specifically dissimilatory iron reduction and magnetosome formation, as a tracer for investigating microbial contributions to deep-sea REY enrichment. While acknowledging the fundamental importance of inorganic mechanisms, we focus on microbial iron reduction and its distinctive product, biogenic magnetite, to quantitatively trace the microbial role and its underlying climate drivers in REY accumulation. Consequently, we have updated the manuscript title to: "The biological contribution and potential climate drivers of deep-sea rare earth element enrichment: Insights from microbial iron cycling."

(II) Are these claims novel, and will they be of interest to others in the community?

Biotic/abiotic and pelagic/benthic processes have to be better distinguished as to clarify the diagenetic sequence and differential timing of in-situ formation of magnetite and apatite. The authors could provide constraints in terms of sources and sinks (Fe(II)-Fe(III), organic/mineral PO_4^{3-} , REE in hydrothermal fluids and seawater).

Reply: We fully agree with your suggestion. In the updated manuscript, we propose that the transfer of REY from marine particles (e.g., Fe-Mn (oxyhydr)oxides or organic matter) to pore waters, as well as the formation of biogenic magnetite and authigenic apatite, primarily occur in surface sediments rather than in the water column, i.e., these are benthic processes.

As indicated in our responses above, we have demonstrated the limited hydrothermal influence in our study area based on several lines of evidence: its distal location from mid-ocean ridges, the absence of a significant positive Eu anomaly in REY patterns, bulk iron concentrations close to upper continental crust values and significantly lower than those in hydrothermally influenced sediments, and the consistently low dissolved iron concentrations in pore waters. This supports our interpretation that terrigenous dust is likely the primary source of Fe and REY, while phosphorus is mainly derived from riverine inputs. After entering the ocean, REY and P are scavenged by marine particles through adsorption-settlement processes, transferred to pore waters within sediments, and ultimately enriched and sequestered in authigenic minerals. Given the limited hydrothermal influence, microbial iron reduction occurring in surface sediments can be coupled with the aforementioned processes. Its characteristic products—biogenic magnetite (including extracellular nanoscale magnetite and intracellular magnetofossils), can serve as effective tracers for

microbial activity during these processes.

According to previous studies, the formation of magnetite (mediated by DIRB and MTB) and the crystallization of authigenic apatite can occur within hours to days. In contrast, the incorporation of REY into bioapatite (e.g., fish teeth) occurs on a timescale of approximately 10^3 to 10^4 years, while incorporation into authigenic apatite may be synchronous with its crystallization. Compared to the extremely low sedimentation rate in the deep sea (less than 0.5 m/Ma), these processes occurring in surface sediments can be considered geologically instantaneous.

Furthermore, abiotic fractionation of Fe isotopes due to partial oxidation of ferrous to ferric Fe could produce poorly crystalline (pelagic) magnetites exhibiting slightly negative $\delta^{56}\text{Fe}$ values during mixing of hydrothermal fluids with seawater. This has not been considered (or occulted as common knowledge?) although it is an essential part of the discussion.

Reply: As you rightly pointed out, the mixing of hydrothermal fluids with seawater can potentially precipitate poorly crystalline magnetite accompanied by negative $\delta^{56}\text{Fe}$ shifts. We acknowledge that the original manuscript's attribution of magnetite nanoparticles and the negative $\delta^{56}\text{Fe}$ signature in the sediments solely to biological processes, without adequately discussing and ruling out hydrothermal influences, may have been incomplete.

In the revised manuscript, when discussing the microbial origin of magnetite, we first dedicate a section to systematically ruling out significant hydrothermal impact on our study area from multiple perspectives, concluding that the upper continental crust is the primary iron source. Given the oxic bottom-water conditions and the relatively low degree of reduction in the surface sediments—unlike highly productive shelf environments—microbial reduction presents the most plausible source of Fe^{2+} for the magnetite found in this study. Furthermore, while distinct from the extracellularly formed, poorly crystalline magnetite nanoparticles induced by DIRB, the discovery of magnetofossils (formed via intracellular biomineralization by MTB, Fig. 4c) provides compelling evidence for a microbial origin of magnetite in our study area. Both types of biogenic magnetite can result in negative $\delta^{56}\text{Fe}$ values, although the extent of the negative shift may be attenuated by dilution from other iron-bearing components in the bulk sediment.

“The Pigafetta Basin, site of core GC112, lies far from the East Pacific Rise and shows no significant positive Eu anomaly in its REY patterns (Fig. 2d), indicating a negligible hydrothermal contribution^{4,22}. Consistent with this interpretation, the sediment iron content is close to the upper continental crust average, suggesting a dominant terrigenous dust source; this contrasts with the elevated iron levels in

hydrothermally influenced East Pacific sediments^{22,47}. Furthermore, unlike the abundant dissolved Fe^{2+} in reducing shelf settings¹⁵ and hydrothermal systems⁴, the suboxic deep-sea surface sediments in this study area exhibit consistently low porewater Fe^{2+} ¹². The structural Fe^{2+} in magnetite is therefore likely sourced from microbial iron reduction^{12,22}. Culture experiments confirm that biogenic magnetite is enriched in light iron isotopes, with DIRB-produced magnetite showing $\Delta^{56}\text{Fe}$ values of -2.6‰ to -1.3‰ relative to the substrate⁶⁶, and magnetosome magnetite a narrower range of -2.5‰ to -1.5‰⁴³. These isotopic signatures have been instrumental in identifying microbial magnetite origins in banded iron formations^{41,42}. In the hydrothermally unaffected GC112 core, the slight negative shift in whole-rock $\delta^{56}\text{Fe}$ within the REY-rich layer (Fig. 2a) may thus signal enhanced microbial iron reduction during deposition, even considering potential dilution from crustal iron sources ($\delta^{56}\text{Fe} \approx +0.082\text{‰}$)⁴⁸.” **Lines 318-335**

Although apatitic phosphate concretions are known to form as diagenetic products in marine sediments, phosphate sources, their scavenging by iron oxides prior to deposition and transformation from organic to authigenic during time of burial are not introduced either. Environmental conditions at the time of deposition (e.g. upwelling, productivity, intraplate tholeiitic iron-rich volcanism, hydrothermal activity) have to be introduced and discussed in parallel, not limited to the final part of the discussion. Otherwise, the manuscript gives the impression of being deliberately biased in favor of the research hypothesis.

Reply: Thank you for your valuable feedback. In the revised manuscript, we clarify that marine phosphorus is primarily derived from riverine inputs and detail its transport to sediments via organic matter or Fe-Mn (oxy)hydroxides, followed by release into pore waters and subsequent crystallization as authigenic apatite. Additionally, we have incorporated discussions on climatic conditions, volcanic and hydrothermal activity in the study area, and variations in surface primary productivity in the Introduction, Geological Setting, and Discussion sections. The specific revisions are outlined below.

“The strong linear correlations between whole-rock REY and P or Ca (Fig. 2c) indicate that phosphate minerals represent the ultimate sink for REY in deep-sea sediments^{12,20,23}. Marine phosphorus is primarily sourced from riverine input and delivered to sediments mainly in the form of organic phosphorus or adsorbed onto Fe-Mn (oxyhydr)oxides⁶⁰. In deep-sea settings, where conditions generally preclude minerals requiring high organic matter and strict anoxia (e.g., anapaite and vivianite), bioapatite and authigenic apatite are the dominant phosphorus sinks^{9,20,61}. Bioapatite (e.g., fossil fish teeth and bones) is a well-established host for REY, in which REY^{3+} is

*incorporated into the apatite lattice via charge-balanced coupled substitution for Ca^{2+} and P^{5+} , facilitated by Na^+ or Si^{4+} ^{9,20}. However, our statistical analysis indicates that fossil fish debris accounts for only ~0.39 wt.% of the REY-rich layer (contributing ~5.38% to total P; Table S5), implying that most phosphorus resides in transient Fe-Mn (oxyhydr)oxides associated phases or authigenic minerals ²². Supporting this interpretation, Chen et al. (2025) ⁶² reported a significant deficit between the measured and theoretical REY capacities of bioapatite, suggesting an additional phosphate-associated sink. Authigenic CFA is proposed as the most probable candidate ^{18,62}. Phosphorus delivered via organic matter or Fe-Mn (oxyhydr)oxides can be remobilized during early diagenesis, increasing porewater saturation and promoting CFA precipitation ¹⁸. As CFA is believed to control over 50% of marine phosphorus burial, it is increasingly recognized as a major potential sink for REY in deep-sea sediments, alongside bioapatite ^{18,60,62}.” **Lines 236-256***

(III) Is the work convincing, what further evidence would be required to strengthen the conclusions?

The abiotic hypothesis seems to have been dismissed a little too quickly, and the line of argumentation chosen by the authors remain highly speculative:

- Crystallographic analysis of microdomain and single-domain magnetites (assumed to reflect microbially-mediated magnetite and magnetosome, respectively) complemented by $\delta^{56}\text{Fe}$ values around -0.08‰ do not constitute sufficient evidence that enable the distinction between microbial iron reduction and mixing of hydrothermal fluids with seawater. Abiotic (oxidative) processes and sources of iron and REY are not addressed in sufficient detail.

Reply: We thank the reviewer for this constructive comment. As indicated in our responses above, the revised manuscript now includes a dedicated discussion ruling out significant hydrothermal influence in the study area prior to addressing the microbial origin of magnetite. Based on previous studies, we conclude that terrigenous dust input represents the dominant source of iron in our study area. Specific revisions are outlined below.

“The enrichment of REY in the northwestern Pacific deep sea begins with scavenging of dissolved REY by marine particles, such as Fe-Mn (oxyhydr)oxides and organic matter ^{16,22}. Organic particles originate mainly from surface primary productivity ^{16,32}, whereas terrigenous dust input likely dominates the supply of Fe-Mn (oxyhydr)oxides in the study area ^{14,47}. This interpretation is supported by the location of the Pigafetta Basin, which is far from mid-ocean ridges and shows little hydrothermal influence, as indicated by the lack of a pronounced positive Eu anomaly (Fig. 2d) and iron concentrations near the upper continental crust average (Fig. 2a) ²².”

Lines 219-226

“The Pigafetta Basin, site of core GC112, lies far from the East Pacific Rise and shows no significant positive Eu anomaly in its REY patterns (Fig. 2d), indicating a negligible hydrothermal contribution ^{4,22}. Consistent with this interpretation, the sediment iron content is close to the upper continental crust average, suggesting a dominant terrigenous dust source; this contrasts with the elevated iron levels in hydrothermally influenced East Pacific sediments ^{22,47}. Furthermore, unlike the abundant dissolved Fe^{2+} in reducing shelf settings ¹⁵ and hydrothermal systems ⁴, the suboxic deep-sea surface sediments in this study area exhibit consistently low porewater Fe^{2+12} . The structural Fe^{2+} in magnetite is therefore likely sourced from microbial iron reduction ^{12,22}.” **Lines 318-327**

- The only pore water geochemical data documented in this manuscript are REY concentrations. Rare Earth Elements being mostly redox-conservative, they may possibly reflect bottom water conditions at the time of deposition (e.g. negative anomaly of $\text{Ce}^{3+/4+}$), or release after microbial reduction of Fe(III) oxides. To infer metal reduction processes after deposition, additional pore water geochemical data are needed (e.g. Fe^{2+} , Mn^{2+} , As^{2+} , trace metals).

Reply: We fully agree with your perspective regarding the importance of porewater geochemical data for understanding post-depositional metal reduction processes. Unfortunately, corresponding porewater data were not collected or measured during our initial sampling of core GC112. To address this limitation, we have comprehensively reviewed and incorporated relevant data from previous studies. Specifically, Deng et al. (2022)¹ reported porewater Fe, Mn, and nitrate concentrations in sediments from the Pigafetta Basin—the same area as our study—which consistently show very low dissolved Fe and Mn levels. Furthermore, data from Du et al. (2025)² and D’Hondt et al. (2015)³ indicate that deep-sea sediments in highly productive regions of the northwestern and equatorial Pacific transition from oxic to suboxic conditions within the upper few centimeters, with dissolved oxygen decreasing from $>100\ \mu\text{M}$ to $<20\ \mu\text{M}$. These lines of evidence support our interpretation that REY remobilization into porewaters in our study area likely resulted from phase transformation of Fe–Mn (oxyhydr)oxides rather than reductive dissolution. The specific revisions made are outlined below.

“The transfer of REY from marine particles to porewaters occurs through two potential pathways: dissolution and mineralogical transformation ^{3,12,22}. The release of REY and phosphate from organic particles is controlled by oxidative degradation ¹⁶, which consumes dissolved oxygen in surface sediments and establishes suboxic conditions within the upper few centimeters ^{16,32}. Such conditions are common in areas

with productivity exceeding typical pelagic backgrounds, like the northwestern and equatorial Pacific ³². *Unlike reductive dissolution of Fe-Mn (oxyhydr)oxides in anaerobic, high-organic-flux environments (e.g., eastern Pacific shelf)* ^{3,15}, *suboxic deep-sea sediments favor secondary mineralization of these phases into more crystalline forms* ^{12,22}. *This recrystallization reduces the specific surface area of poorly crystalline Fe-Mn (oxyhydr)oxides by 50-80%, releasing large-radius REY³⁺ ions (1.216-0.977 Å) into porewaters via lattice exclusion* ²². *Porewater data from the Pigafetta Basin show low dissolved Fe (~1 µM) and Mn (~0 µM) in intervals with secondary REY release* ¹², *supporting the dominance of mineral-phase transformation over reductive dissolution. The preferential adsorption of MREEs and Ce⁴⁺ onto Fe-Mn (oxyhydr)oxides yields MREE-enriched patterns and a weaker negative Ce anomaly in porewaters, distinct from seawater signatures (Fig. 2d)* ²². *This finding is consistent with REY patterns in Fe-bearing porewaters from the eastern Pacific shelf* ³ *and secondary REY-release porewaters from the northwestern Pacific* ¹². *Ultimately, these geochemical signals are preserved in deep-sea sediments* ²².” Lines 271-290

- There is no characterization of the sediment organic fraction (e.g. TOC) and some contradictory statements are scattered throughout the manuscript (minimal organic content, sediment anoxic conditions due to organic mineralization). Interpretations in terms of microbial reduction of iron and organic matter mineralization have to be supported by additional downcore profiles (i.e. the authors’ own data, not literature).

Reply: We thank the reviewer for this valuable comment. In response, we conducted additional total organic carbon (TOC) measurements on core GC112.

The results indicate consistently low TOC contents throughout the core (0.2-0.4 wt.%; Fig. 2a), likely resulting from extensive oxidative degradation of organic matter at the water column or sediment-water interface. This oxygen-consuming oxidation process would induce a transition to suboxic conditions (with dissolved oxygen ranging between 20-80 µM or even below 20 µM) within the upper few centimeters of the sediment. In other words, both the very low organic carbon content and the development of suboxic conditions in the surface sediments are attributed to the oxidative degradation of organic matter. Furthermore, although the residual TOC content in the core is generally low, a slight increase is observed within the REY-rich interval, potentially linked to enhanced primary productivity during that period.

- The metagenomic data (only available for download on Zenodo) are succinct and do not clearly establish metabolic potential for dissimilatory iron reduction (DIR), or magnetosome formation. The taxa reported in this supplement are mostly aerobes, likely originating from environments that would argue against post-depositional microbial processes, i.e. oceanic bottom waters (e.g. *Limnobacter*, *Muricauda*) and

hydrothermal vents (*Thermoanaerobaculia*). The sequence data has to be submitted to a public repository and an accession number provided to the reader.

Reply: We thank the reviewer for this insightful comment. We agree that the interpretation and utilization of metagenomic data in our original manuscript remained insufficient. The current metagenomic results provide only indirect support for the core argument of the study, being largely confined to limited information on the abundance of iron-metabolism-related functional genes. Critical aspects, such as whether these functional genes are expressed, their taxonomic affiliations, and their roles in coupled biogeochemical cycling of multiple elements (e.g., C, N, P, Fe, Mn, S, and REY), remain poorly understood. However, a thorough exploration of these questions would extend beyond the central scope of this manuscript and may be more appropriately addressed in a separate study focused on microbial genomics. After careful consideration, we have therefore decided to remove the metagenomic analysis section from the revised manuscript. This revision does not compromise the core evidence presented in the study and helps sharpen the focus on the key research questions.

- In the absence of clear functional marker genes for DIR, metagenomic data was tested using the FeGenie pipeline but not consistently reported, e.g. siderophores, magnetosomes, and Fe(II/III) redox processes, Fe regulation. The few functional genes selected to identify metabolic potential for DIR were identified at very low read counts. These predicted genes relate to the multiple heme cytochrome C reductase (not specific to metal reduction) and extracellular respiration electron transfer (nanowires are not common in sediments).

Reply: As mentioned in our previous response, the interpretation of the metagenomic data in the original manuscript lacked systematic rigor, and the selection of functional gene categories was insufficiently representative or comprehensive. However, addressing these issues in depth would risk diverting attention from the primary focus of this study. Therefore, to maintain clarity without undermining the existing evidence chain, we have removed the metagenomic evidence from the revised manuscript. These data will be presented in a more specialized and systematic manner in future work.

- In the final part of the discussion, the authors mention that past upwelling conditions (ca. 12 Ma ago) could explain phosphate accumulation at the seafloor. More background information on sedimentary conditions that led to phosphate concretions are necessary. Indeed, iron oxides expelled during hydrothermal activity could trap both REY and orthophosphates. The authors have to distinguish between pelagic and benthic processes, as well as disentangle biotic-abiotic processes, in order to provide time constraints on magnetite and apatite in -situ formation.

Reply: We thank the reviewer for this constructive suggestion. In response, we have added descriptions of the sedimentary background for authigenic apatite formation in the Introduction, Geological Setting, and Discussion sections of the manuscript.

As rightly noted, although the study area is largely unaffected by hydrothermal activity, Fe–Mn (oxyhydr)oxides—mainly derived from aeolian dust—still represent one of the key carriers transporting P and REY from the water column to the sediments. Within the surface sediments (i.e., via benthic processes), both microbial activity (e.g., aerobic respiration or metal reduction) and/or abiotic processes (e.g., organic matter degradation and mineral phase transformation) could mediate the release of P and REY into pore waters, thereby creating favorable conditions for authigenic apatite formation and REY enrichment. Given the slow deep-sea sedimentation rate (<0.5 m/Myr), these processes can be considered synchronous on geological timescales.

We have elaborated on these aspects in the following sections of the manuscript:

“Potential sources of marine REY include terrigenous inputs (via runoff or dust)^{13,14}, hydrothermal activity^{4,6}, and benthic flux of porewaters^{3,15,16}. Phosphorus-bearing phases, particularly bioapatite (e.g., fossil fish teeth and bones, ideal formula $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) and authigenic apatite (mainly carbonate-fluorapatite, CFA, approximated as $\text{Ca}_{9.54}\text{Na}_{0.33}\text{Mg}_{0.13}(\text{PO}_4)_{4.8}(\text{CO}_3)_{1.2}\text{F}_{2.48}$), are recognized as the ultimate sinks for REY in deep-sea sediments, accounting for approximately 69.3–89.4% of the total REY content^{10,17–20}. The extreme concentration contrast of $\sim 10^{12}$ between seawater (REY $\sim 1.47 \times 10^{-9}$ mg/kg) and sediments implies complex enrichment processes^{3,12,21}. The element cycling driven by adsorption-desorption and crystallization-dissolution between seawater particles (e.g., Fe–Mn (oxyhydr)oxides or organic matter) and sediment porewaters likely plays a critical role^{12,22}. Marine particles with high specific surface areas effectively scavenge dissolved REY from the water column via adsorption or complexation, facilitating their transport to the seafloor^{3,12,15}. Among these, Mn (oxy)hydroxides exhibit the strongest REY scavenging capacity, followed by Fe (oxy)hydroxides and organic particles¹⁶. During early diagenesis, REY are remobilized from particles and become enriched in porewaters^{12,22}, reaching concentrations up to two orders of magnitude higher than seawater^{3,12,15}. These REY are ultimately incorporated into the apatite lattice through charge-balanced substitution reactions, such as $\text{REY}^{3+} + \text{Na}^+ \leftrightarrow 2\text{Ca}^{2+}$ and $\text{REY}^{3+} + \text{Si}^{4+} \leftrightarrow \text{Ca}^{2+} + \text{P}^{5+}$ ^{10,19}. Although the transfer of REY from particles to porewaters is crucial for enrichment^{3,12,16,22}, the underlying mechanisms remain poorly understood.” **Lines 39–59**

“The strong linear correlations between whole-rock REY and P or Ca (Fig. 2c) indicate that phosphate minerals represent the ultimate sink for REY in deep-sea sediments^{12,20,23}. Marine phosphorus is primarily sourced from riverine input and

delivered to sediments mainly in the form of organic phosphorus or adsorbed onto Fe-Mn (oxyhydr)oxides ⁶⁰. In deep-sea settings, where conditions generally preclude minerals requiring high organic matter and strict anoxia (e.g., anapaite and vivianite), bioapatite and authigenic apatite are the dominant phosphorus sinks ^{9,20,61}. Bioapatite (e.g., fossil fish teeth and bones) is a well-established host for REY, in which REY³⁺ is incorporated into the apatite lattice via charge-balanced coupled substitution for Ca²⁺ and P⁵⁺, facilitated by Na⁺ or Si⁴⁺ ^{9,20}. However, our statistical analysis indicates that fossil fish debris accounts for only ~0.39 wt.% of the REY-rich layer (contributing ~5.38% to total P; Table S5), implying that most phosphorus resides in transient Fe-Mn (oxyhydr)oxides associated phases or authigenic minerals ²². Supporting this interpretation, Chen et al. (2025) ⁶² reported a significant deficit between the measured and theoretical REY capacities of bioapatite, suggesting an additional phosphate-associated sink. Authigenic CFA is proposed as the most probable candidate ^{18,62}. Phosphorus delivered via organic matter or Fe-Mn (oxyhydr)oxides can be remobilized during early diagenesis, increasing porewater saturation and promoting CFA precipitation ¹⁸. As CFA is believed to control over 50% of marine phosphorus burial, it is increasingly recognized as a major potential sink for REY in deep-sea sediments, alongside bioapatite ^{18,60,62}.

The concentration contrast of ~10¹² between seawater and sediments points to complex, multi-stage enrichment pathways ¹². A key step is the post-depositional release of REY and phosphate from particles into porewaters ^{3,15,22}, which can enrich REY in porewaters by up to two orders of magnitude over seawater, providing a more direct source for sediment incorporation ^{3,12}. Consequently, REY patterns in the GC112 REY-rich layer (MREE-enriched) more closely match porewaters influenced by secondary REY release than seawater (Fig. 2d). Phosphate concentrated in porewaters can precipitate rapidly (hours to days) as authigenic apatite (mainly CFA), forming a key REY host ^{18,34}. The sequestration of REY from porewaters into bioapatite occurs over 10³-10⁴ years ⁶³, and incorporation into authigenic apatite may even be synchronous with its formation ¹⁸. Given the exceptionally low sedimentation rate in the northwestern Pacific (<0.5 m/Ma), the entire sequence of migration, concentration, and sequestration can be considered geologically instantaneous upon the deposition of marine particles at the seafloor ⁶³.” **Lines 236-370**

(IV) do you feel that the paper will influence conceptual understanding or technological capability?

At this stage, evidence for microbial processes of metal reduction is not compelling. Additional SEM/TEM images of magnetite could be produced as a single grain is documented (Fig. 4). Please provide additional SEM/TEM images in the

supplement.

Reply: We thank the reviewer for this suggestion. In response, we have supplemented the manuscript's Fig. 4 with TEM images of magnetosomes and SEM images of authigenic apatite.

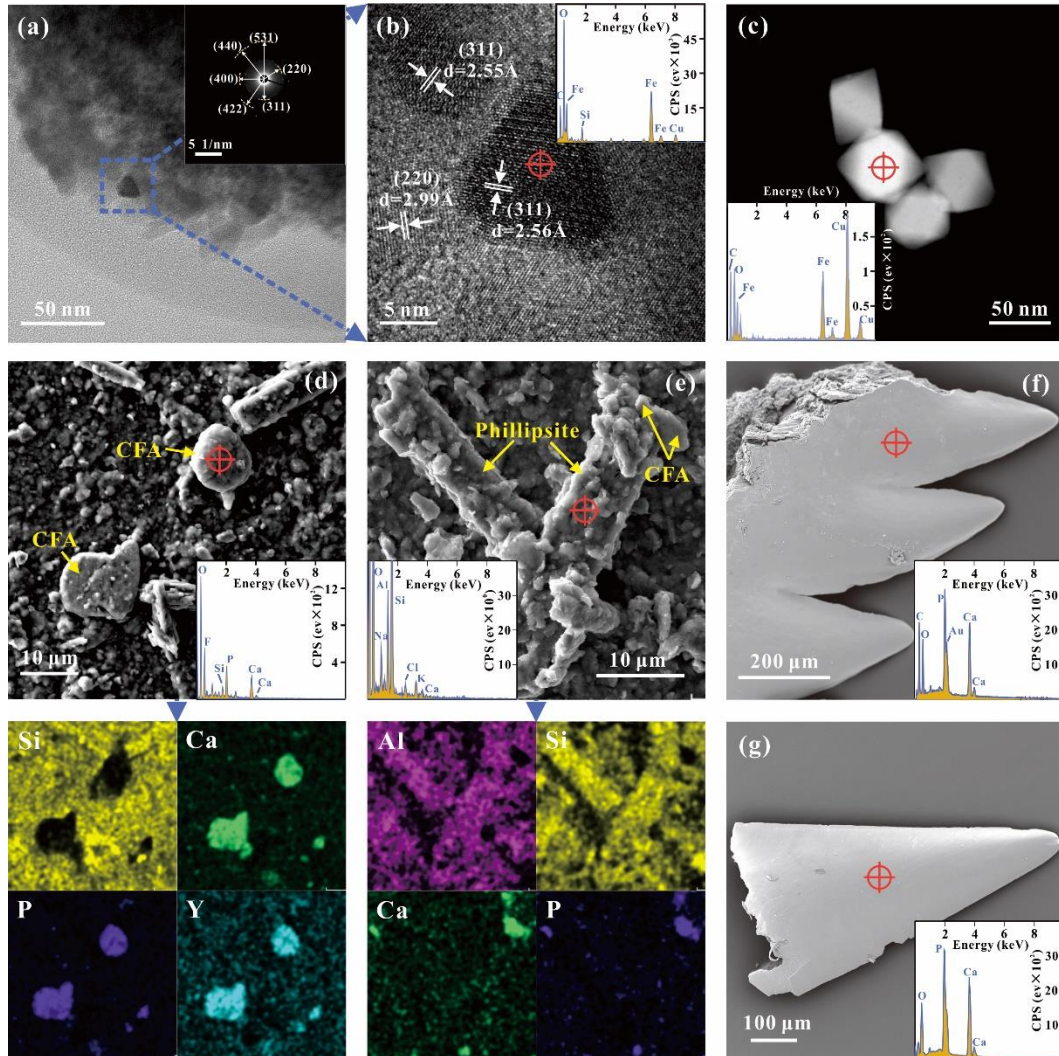


Fig. 4. (a-c) TEM images of magnetic particles extracted from REY-rich sediments via Nd-magnet separation. Corresponding selected-area electron diffraction (SAED) patterns and energy-dispersive X-ray spectroscopy (EDS) results are shown as insets. Image (b) presents a high-resolution view of the area outlined in (a). (d, e) SEM images of whole-rock samples from the REY-rich layer, with corresponding elemental maps shown below (blue arrows). (f, g) SEM images of biogenic apatite (fossil fish teeth) from the REY-rich layer. Locations of EDS point analyses are indicated by red targets.

Specific comments

Introduction: Some basic background information on REE is missing (e.g. redox

states, hydrothermal release, distribution and type of ores)

Reply: We thank the reviewer for these valuable suggestions. The Introduction has been revised accordingly, with relevant information added. Please see below for details.

- l. 24: Add “Understanding the mechanisms... is vital”

Reply: Thank you, revised.

*“Understanding REY enrichment mechanisms in deep-sea sediments is essential for both resource utilization and paleoenvironmental reconstruction.” **Lines 3-5***

- l. 27: migration rather “dissolution and subsequent incorporation”; organic matters --> organic matter

Reply: Thanks, revised.

*“The migration of REY from marine particles (e.g., Fe-Mn (oxyhydr)oxides or organic matter) to apatite is a prerequisite for subsequent enrichment during early diagenesis.” **Lines 6-8***

- l. 30: the authors do not document or report biological data per se

Reply: Deleted

- l. 31: datasets --> data

Reply: Thanks, revised. **Line 13**

- l. 33-37: this mechanism is known and referred to as “diagenetic redistribution of iron”.

Reply: We have rewritten this section in the revised manuscript.

*“Through an integrated analysis of high-resolution geochemical, magnetic, and microscopic data, we demonstrate that microbial activity promotes REY transfer into porewaters by facilitating the degradation or phase transformation of marine particles, thereby creating favorable conditions for REY enrichment. This mechanism may be particularly important during periods of significant global climate variability. Our findings provide new insights for tracing microbial contributions to deep-sea REY enrichment and for investigating their underlying drivers.” **Lines 12-19***

- l. 45: REY deposits, be more specific, what type? Polymetallic nodules, massive sulfide deposits, phosphatic concretions, else?

Reply: We have added information on REY-rich deep-sea sediments in the first paragraph of the Introduction, including their types, main distribution areas, and concentrations. Please see the details below.

“These deposits are predominantly distributed in deep-sea basins below the carbonate compensation depth (CCD) across the western, central, and southeastern Pacific, as well as the Indian Ocean, and are largely composed of zeolitic and pelagic clays⁶⁻¹⁰. Total REY (Σ REY) concentrations in these sediments range from 2000 to 8000

mg/kg, frequently characterized by distinct MREE and HREE enrichment ^{6,11}.” **Lines 31-36**

- 1. 51: what about the initial sources and mechanisms releasing REY in marine waters? Detrital sources, basalt alteration and hydrothermal vents, global versus local processes? What are the common REY concentrations in seawater? There is no mention of their very low initial concentrations and necessity to condense them to obtain minable ores, what these ores are and where they are usually found...

Reply: We thank the reviewer for this suggestion. The relevant content has been added to the second paragraph of the Introduction.

*“Potential sources of marine REY include terrigenous inputs (via runoff or dust) ^{13,14}, hydrothermal activity ^{4,6}, and benthic flux of porewaters ^{3,15,16}. Phosphorus-bearing phases, particularly bioapatite (e.g., fossil fish teeth and bones, ideal formula $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) and authigenic apatite (mainly carbonate-fluorapatite, CFA, approximated as $\text{Ca}_{9.54}\text{Na}_{0.33}\text{Mg}_{0.13}(\text{PO}_4)_{4.8}(\text{CO}_3)_{1.2}\text{F}_{2.48}$), are recognized as the ultimate sinks for REY in deep-sea sediments, accounting for approximately 69.3-89.4% of the total REY content ^{10,17-20}. The extreme concentration contrast of $\sim 10^{12}$ between seawater (REY $\sim 1.47 \times 10^{-9}$ mg/kg) and sediments implies complex enrichment processes ^{3,12,21}. The element cycling driven by adsorption-desorption and crystallization-dissolution between seawater particles (e.g., Fe-Mn (oxyhydr)oxides or organic matter) and sediment porewaters likely plays a critical role ^{12,22}. Marine particles with high specific surface areas effectively scavenge dissolved REY from the water column via adsorption or complexation, facilitating their transport to the seafloor ^{3,12,15}. Among these, Mn (oxy)hydroxides exhibit the strongest REY scavenging capacity, followed by Fe (oxy)hydroxides and organic particles ¹⁶. During early diagenesis, REY are remobilized from particles and become enriched in porewaters ^{12,22}, reaching concentrations up to two orders of magnitude higher than seawater ^{3,12,15}. These REY are ultimately incorporated into the apatite lattice through charge-balanced substitution reactions, such as $\text{REY}^{3+} + \text{Na}^+ \leftrightarrow 2\text{Ca}^{2+}$ and $\text{REY}^{3+} + \text{Si}^{4+} \leftrightarrow \text{Ca}^{2+} + \text{P}^{5+}$ ^{10,19}. Although the transfer of REY from particles to porewaters is crucial for enrichment ^{3,12,16,22}, the underlying mechanisms remain poorly understood.” **Lines 39-59***

- 1. 53: re-released --> solubilized, released and thereby concentrated in the pore water / how can REE^{3+} substitute for Ca^{2+} in the crystal lattice of apatite? How is the charge imbalance equilibrated?

Reply: The second paragraph of the Introduction has been updated accordingly. Please refer to our response to Line 51 for details.

- 1. 54: provide the normal formula of apatite; what about anapaite which commonly forms concretions in marine environment?

Reply: We have revised and supplemented the relevant content in the second paragraph of the Introduction, as detailed in our response to Line 51.

- l. 56: crystallization-dissolution, rather dissolution-precipitation cycles. Do this imply Ostwald ripening and transient phases?

Reply: Thanks, revised.

“The element cycling driven by adsorption-desorption and crystallization-dissolution between seawater particles (e.g., Fe-Mn (oxyhydr)oxides or organic matter) and sediment porewaters likely plays a critical role ” Lines 47-49

We have given careful thought to your question regarding Ostwald ripening and transient phases, and we agree that it is potential presence. For instance, poorly crystalline Fe-Mn (oxyhydr)oxides may undergo Ostwald ripening, transitioning into more crystalline phases such as goethite or hematite. This process is likely prevalent in the hydrothermally active eastern Pacific seafloor, where deep-sea iron minerals are dominated by well-crystalline goethite and hematite⁴. In the Pigafetta Basin of the western Pacific, an area with limited hydrothermal influence, as in our study, the formation of magnetite in sediments may also involve the reduction of Fe³⁺ ions. Given the relatively low degree of environmental reduction, this process is likely primarily controlled by microbial iron reduction. Furthermore, studies have shown that some poorly crystalline phosphorus-bearing phases can form on the surfaces of deep-sea phillipsite and are considered transitional precursors to authigenic apatite⁵. The transformation of these poorly crystalline phosphorus-bearing phases (e.g., observed in Fig. 4e of this study) into authigenic apatite grains (e.g., observed in Fig. 4d) may involve Ostwald ripening.

Your suggestion is highly professional and constructive. We plan to further explore and validate these mechanisms in future simulation experiments. Thank you very much.

- l. 63: are these values corresponding to cell densities in seawater or sediments? Sediment --> marine sedimentary environments (cells × cm³, not mL⁻¹)

Reply: We are grateful to the reviewer for pointing this out. The text has been amended to specify microbial density in the sediments, with the unit correctly expressed as cells cm⁻³.

“Although microbial abundance in deep-sea sediments is low (10³-10⁴ cells/cm³, two to three orders of magnitude lower than in shelf sediments), these sediments cover about 80% of the seafloor and may represent 10-50% of global subsurface microbial biomass ²⁷. ” Lines 64-67

- l. 65: ...whose underlying sediments are characterized (D'Hondt et al., 2019 does not address microbial populations in the water column).

Reply: We thank the reviewer for this correction. In the revised manuscript, we

have clarified that the microbial density refers to that in the surface sediments rather than in the water column. This section has been rewritten with appropriate citations added. Please refer to the previous response for detailed modifications.

- 1. 64-66: most of the deep-sea offshore cannot be considered productive. The authors likely refer to the surface ocean but productivity in the ocean offshore is limited. Coastal upwelling zones along trenches constitute specific cases. Be specific in what “spatial coupling” encompasses.

Reply: We thank the reviewer for this correction. Our intended meaning was to refer to regions with productivity higher than the average pelagic background levels, though still significantly lower than that of shallow-water upwelling zones, such as the equatorial Pacific or northwestern Pacific³.

The original description of "spatial coupling" may have been somewhat misleading, as our focus is on processes occurring in surface sediments rather than in the water column. Accordingly, we have thoroughly restructured this section to improve clarity. The revised text can be found in the third paragraph of the Introduction.

“Previous studies have primarily addressed inorganic mechanisms promoting REY migration into porewaters, particularly particle dissolution or phase transformation driven by variations in pH and redox conditions^{3,12,19,23,24}. Microorganisms and their metabolic activities, ubiquitous in marine settings, may also critically influence REY mobility^{22,25,26}. Although microbial abundance in deep-sea sediments is low (10^3 - 10^4 cells/cm³, two to three orders of magnitude lower than in shelf sediments), these sediments cover about 80% of the seafloor and may represent 10-50% of global subsurface microbial biomass²⁷. Preliminary evidence indicates that microbial respiration, including aerobic, nitrate, Fe-Mn, or sulfate reduction, can influence REY redistribution by mediating organic matter degradation and metal (oxy)hydroxides reduction²². Climatic influences on these processes also warrant attention. Cenozoic global cooling and steeper latitudinal temperature gradients may have intensified Pacific Walker circulation, enhancing surface ocean productivity²⁸⁻³⁰. This would enhance scavenging of REY and phosphate by marine particles derived from dust or biological sources^{16,31}. Increased organic matter flux could shift sedimentary redox conditions from aerobic (dissolved O₂ (DO) > 87.5 μM) to suboxic (DO ~ 15.6-87.5 μM)³². In accordance with the Redfield ratio (C:N:P ≈ 106:16:1), intensified heterotrophic denitrification under such conditions would further promote phosphate accumulation in deep waters and sediments^{17,32,33}. Collectively, these conditions synergistically facilitate the microbe-assisted release of REY and phosphate into porewaters and the precipitation of authigenic apatite^{22,34}. Nonetheless, due to low microbial densities and oxidative degradation of organic signals, the quantitative links

among microbial activity, REY behavior, and climate drivers in deep-sea sediments remain poorly constrained.” **Lines 60-83**

- l. 68: what are the initial sources of iron and REEs prior to reduction in the sediment and release in the pore water?

Reply: We thank the reviewer for this comment. Based on previous studies, we propose that the seawater Fe and REY in our study area are primarily derived from terrigenous dust inputs^{6,7}, while P is mainly sourced from riverine inputs⁸.

This interpretation has been elaborated in both the Introduction and Discussion sections. The revised manuscript now includes a more detailed explanation of the potential sources of Fe, P, and REY. Please refer to the following sections for specifics:

“Potential sources of marine REY include terrigenous inputs (via runoff or dust)^{13,14}, hydrothermal activity^{4,6}, and benthic flux of porewaters^{3,15,16}.” **Lines 39-40**

“The enrichment of REY in the northwestern Pacific deep sea begins with scavenging of dissolved REY by marine particles, such as Fe-Mn (oxyhydr)oxides and organic matter^{16,22}. Organic particles originate mainly from surface primary productivity^{16,32}, whereas terrigenous dust input likely dominates the supply of Fe-Mn (oxyhydr)oxides in the study area^{14,47}. This interpretation is supported by the location of the Pigafetta Basin, which is far from mid-ocean ridges and shows little hydrothermal influence, as indicated by the lack of a pronounced positive Eu anomaly (Fig. 2d) and iron concentrations near the upper continental crust average (Fig. 2a)²².” **Lines 219-226**

- l. 70-71: BIFs are considered chemical precipitates and this analogy seems out of context; (I) some additional words of introduction on the “Redfield ratio” and nitrogen limitation due to heterotrophic denitrification in highly productive waters are needed since this results in an accumulation of orthophosphate in bottom waters and sediments (e.g. upwelling zones, Peru and Namibian OMZs); (II) mention that phosphorus does not have a redox cycle and that this is driven by scavenging and reduction of Fe(III)-Fe(II).

Reply: We thank you for this correction and fully agree with your suggestion. The comparison with BIFs has been removed from the manuscript. Following your reasonable and professional advice, we have added explanations regarding how climate fluctuations and productivity changes influence the migration behavior of deep-sea REY and P. Please see the following sections for details:

“Climatic influences on these processes also warrant attention. Cenozoic global cooling and steeper latitudinal temperature gradients may have intensified Pacific Walker circulation, enhancing surface ocean productivity²⁸⁻³⁰. This would enhance scavenging of REY and phosphate by marine particles derived from dust or biological

sources^{16,31}. Increased organic matter flux could shift sedimentary redox conditions from aerobic (dissolved O₂ (DO) > 87.5 μM) to suboxic (DO ~ 15.6-87.5 μM)³². In accordance with the Redfield ratio (C:N:P ≈ 106:16:1), intensified heterotrophic denitrification under such conditions would further promote phosphate accumulation in deep waters and sediments^{17,32,33}. Collectively, these conditions synergistically facilitate the microbe-assisted release of REY and phosphate into porewaters and the precipitation of authigenic apatite^{22,34}. ” **Lines 70-80**

- 1. 73: This sentence doesn't make sense. How does metabolic degradation of organic matter prevent documenting microbial activity?

Reply: We thank you for this correction and apologize for the confusion caused by the overly indirect and absolute statements in the original manuscript. Our intended point was that the inherently low biomass in the deep sea, combined with extensive oxidative degradation of organic matter, makes direct investigation of microbial activity challenging due to material limitations. In the revised manuscript, we have refined the wording to eliminate ambiguity and overgeneralization. Please see the following sections for details:

“Nonetheless, due to low microbial densities and oxidative degradation of organic signals, the quantitative links among microbial activity, REY behavior, and climate drivers in deep-sea sediments remain poorly constrained.” **Lines 80-83**

- 1. 78: what about siderophores?

Reply: We apologize for any confusion caused by the lack of clarity in our original wording. Our intention was to illustrate how characteristic metabolic products of dissimilatory iron-reducing bacteria (DIRB) and magnetotactic bacteria (MTB) can be used to trace microbial contributions to deep-sea REY enrichment, this approach does not involve molecular biology or proteomic methods (e.g., siderophore proteins). The previous phrasing may have been overly absolute; we have therefore refined the relevant descriptions in the revised manuscript.

“Microbially mediated iron geochemistry cycling offers a key pathway to address current knowledge gaps. Iron-metabolizing bacteria, particularly dissimilatory iron-reducing bacteria (DIRB) and magnetotactic bacteria (MTB), are well-studied and ubiquitous in marine systems³⁵⁻³⁷.” **Lines 84-87**

- 1. 81: In sediments, Fe²⁺ can react with other solutes as well, after sulfate reduction (FeS₂) or fermentation (FeCO₃). The precipitation of microbially-induced pelagic magnetites requires stratified conditions and the authors should clarify when they refer to pelagic or benthic processes.

Reply: You are correct that in organic-rich, sulfidic environments (e.g., cold-seep sediments), iron reduction, sulfate reduction, and methanogenesis can interact to form

minerals such as FeS₂ or FeCO₃. However, these processes are unlikely to occur in the suboxic deep-sea sedimentary environment of our study area, which is characterized by low organic matter content and mild reducing conditions (with very low HS⁻ and CO₃²⁻ concentrations).

Furthermore, the revised manuscript now explicitly states that the formation of biogenic magnetite occurs within the surface sediments of the deep sea, representing a benthic process. The transition from oxic to suboxic conditions within the upper few centimeters of deep-sea sediments provides favorable conditions for both microbial-induced and microbial-controlled magnetite formation. Please refer to the relevant lines in the Introduction and Discussion sections for detailed revisions.

“These microorganisms transfer electrons from organic matter to Fe(III), reducing it to Fe(II) ³⁶⁻³⁸. This reduction process, coupled with organic matter degradation and iron (hydr)oxides dissolution or phase transformation, facilitates REY transfer from marine particles into porewaters ²². Although modern deep-sea bottom waters are generally well-oxygenated (DO > 100 μM) owing to limited organic input and oceanic circulation, suboxic conditions can develop within the upper few centimeters of sediment in regions with relatively higher surface productivity, such as the northwestern and equatorial Pacific ^{16,32}. These suboxic settings provide ideal niches for iron-reducing bacteria, whose metabolic activity responds sensitively to redox variations influenced by climate change and surface productivity ^{36,37}.” **Lines 87-96**

“The transfer of REY from marine particles to porewaters occurs through two potential pathways: dissolution and mineralogical transformation ^{3,12,22}. The release of REY and phosphate from organic particles is controlled by oxidative degradation ¹⁶, which consumes dissolved oxygen in surface sediments and establishes suboxic conditions within the upper few centimeters ^{16,32}. Such conditions are common in areas with productivity exceeding typical pelagic backgrounds, like the northwestern and equatorial Pacific ³². Unlike reductive dissolution of Fe-Mn (oxyhydr)oxides in anaerobic, high-organic-flux environments (e.g., eastern Pacific shelf) ^{3,15}, suboxic deep-sea sediments favor secondary mineralization of these phases into more crystalline forms ^{12,22}.” **Lines 271-280**

- l. 85: Iron is the main limiting nutrient in open ocean productivity, so where is it coming from? Same question for the organic matter. See comment l. 64-66.

Reply: We propose that the iron in our study area is primarily derived from terrigenous dust (see response to Line 68), while the organic matter originates from moderately elevated surface primary productivity under specific climatic conditions. In regions such as the equatorial Pacific or northwestern Pacific³, surface ocean productivity may be relatively high compared to the average pelagic background levels,

though still significantly lower than in shallow-water upwelling zones, with these conditions potentially being particularly pronounced during certain climatically favorable periods.

- l. 87: what about magmatic and hydrothermal processes enriching LREE in the fluid phase? See comment in l. 51, i.e. local vs global processes

Reply: We fully acknowledge that magmatic or hydrothermal processes can significantly influence REY enrichment and distribution patterns in deep-sea settings, as documented in hydrothermally affected areas near the East Pacific Rise. However, such influences are not considered significant in the Pigafetta Basin of the northwestern Pacific, the focus of our study.

Additionally, we agree with your observation regarding the potentially regional nature of our model, and we have explicitly emphasized the need for caution when considering its global applicability. The revised manuscript now includes a thorough discussion of this aspect throughout the text.

- l. 88: biogenic magnetites, you mean both or magnetosomes only. In theory, magnetite can be further reduced during DIR, the smaller the crystals the more reactive.

Reply: The term "biogenic magnetite" here refers specifically to extracellular magnetite induced by dissimilatory iron-reducing bacteria (DIRB) and intracellular magnetite formed under the controlled biomineralization of magnetotactic bacteria (MTB).

Previous studies⁹ and our prior work¹⁰ have demonstrated that in DIR environments analogous to, or even exceeding in bacterial abundance and organic matter content, deep-sea surface sediments, nanoscale magnetite particles (grain size <20 nm) can serve as electron acceptors for DIRB metabolism. In this process, Fe³⁺ within the magnetite is partially reduced without undergoing reductive dissolution; instead, the reduction is manifested only by an increased proportion of Fe²⁺ and sensitive changes in magnetic properties. Based on this evidence, we propose that once formed in deep-sea surface sediments, microbial magnetite exhibits a certain resistance to reductive dissolution, thereby favoring its preservation.

- l. 91: reliable biomarker? Be specific in what biogenic magnetites are. Magnetosomes constitute biomineralization, whereas magnetite precipitates are simply induced during DIR. / microbial activity --> microbial redox cycling of metals

Reply: Thanks, revised.

"A key advantage of the iron cycle over other microbially driven elemental cycles (e.g., O, N, S, Mn, C) is the production of biogenic magnetite [Fe(II)Fe(III)₂O₄], which can serve as a tracer for microbial activity in deep-sea environments^{22,36,39-42}. DIRB extracellularly precipitate nanoscale magnetite particles^{37,41}, whereas MTB form

intracellular magnetite chains (magnetosomes) under strict genetic control^{35,36,38}. *These biogenic minerals remain stable under mild early diagenetic conditions and retain distinctive chemical, magnetic, and mineralogical properties*^{36,39,42-44}, *making them potential proxies for identifying microbial redox cycling of metals in deep-sea geological records*^{22,36,45}." **Lines 96-105**

- l. 92: unclear whether the authors refer to magnetosomes in particular. The structural Fe(III) of magnetites can be further reduced in the sediment during microbial diagenesis.

Reply: The term "biogenic magnetite" here refers to extracellular magnetite formed via DIRB-induced mineralization and intracellular magnetite produced through MTB-controlled biomineralization. For further explanation regarding the reduction of structural Fe(III) in magnetite, please refer to our response to Line 88.

- l. 94: can one really speak of REE cycling? Except for Cerium (3+/4+) and Europium (2+/3+), REEs are not subject to redox cycling.

Reply: As suggested, we have refined the phrasing to: "*Therefore, elucidating the connection between microbial iron cycling and REY mobilization provides a novel framework for understanding the microbial role and its drivers in deep-sea REY enrichment.*" **Lines 105-107**

- l. 96: the manuscript does not present metagenomic data

Reply: As mentioned in our previous response, this content has been removed.

Geologic background: Succinct, what about hydrogenetic nodules found around seamounts? Here, one could argue for abiotic processes of REE enrichment and provide information on past upwelling and intraplate tholeiitic volcanism.

Reply: We thank the reviewer for this suggestion. Accordingly, we have supplemented this section with information on the distribution of seamounts in the study area, described the primary periods of volcanic activity, and briefly explained the genesis of crusts and their hiatus infillings on these seamounts. This information provides fundamental support for subsequently ruling out volcanic-hydrothermal influences and elucidating material sources.

- l. 107: zeolitic clay --> hydrothermal alteration of basalts not introduced

Reply: Thanks, revised.

"Its upper 0-40 m of sediment consists mainly of brown zeolitic clays, deposited from the Late Cretaceous to Pliocene, with potential sources including eolian dust and weathered basaltic seamount material." **Lines 128-130**

- l. 108: minimal organic matter with occasional terrigenous inputs --> data not shown

Reply: We have measured the total organic carbon (TOC) content of core GC112, and the results are presented in Fig. 2a.

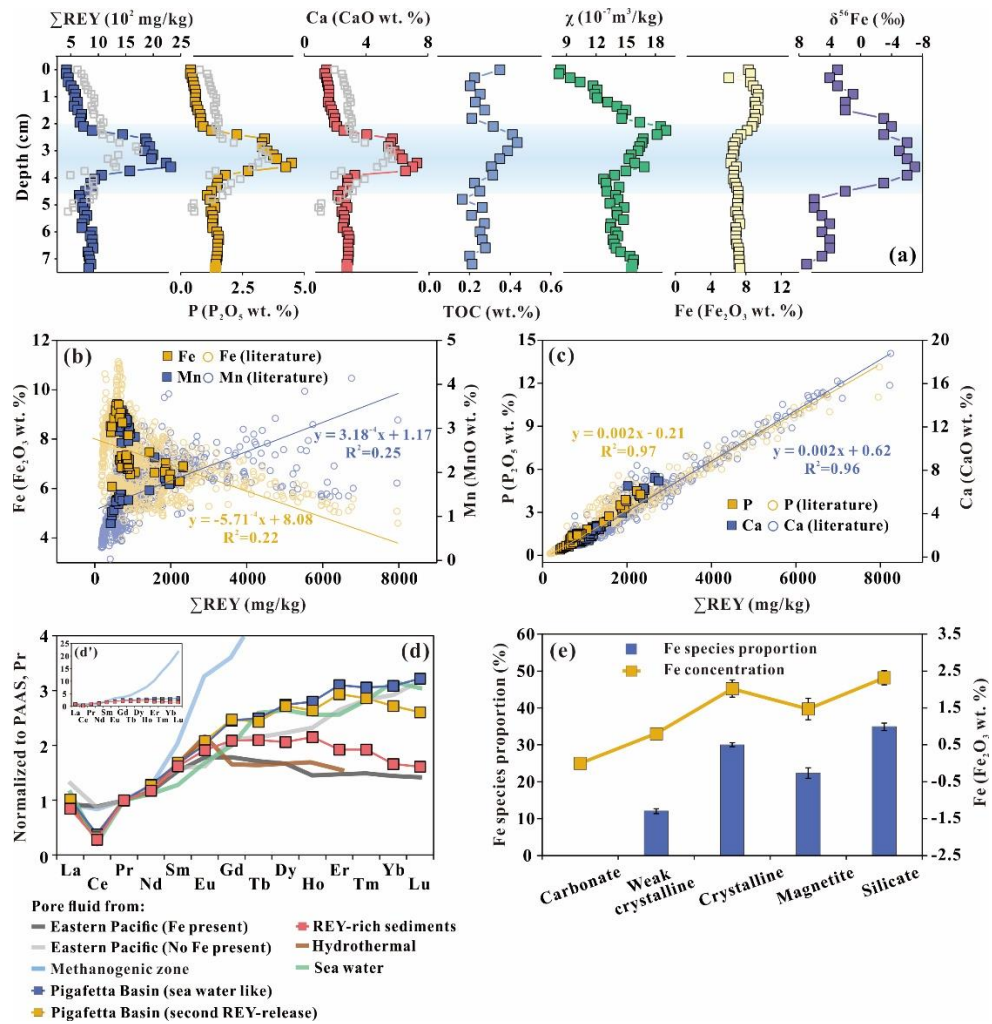


Fig. 2. (a) Downcore variations of elemental concentrations, total organic carbon (TOC), magnetic susceptibility, and Fe isotope ratios in core GC112. The light blue shaded area denotes REY-rich layers ($\Sigma\text{REY} > 700$ mg/kg)⁶. Data from core GC18 are shown for comparison (gray hollow squares). (b, c) Correlation plots of ΣREY versus Fe and Mn (b), and versus P and Ca (c). Data from this study (solid squares) and compiled literature (hollow circles) are plotted; the full dataset is available at <https://doi.org/10.5281/zenodo.12685586>. (d) REY distribution patterns of the REY-rich layer in core GC112, normalized to Post-Archean Australian Shale (PAAS) and Pr^{3,49}. Patterns from representative hydrothermal fluids, seawater, and various porewater types are shown for comparison^{3,4,12,15,50,51}. (e) Iron phase distribution in the REY-rich layers (n=3); background sediment data are provided in Table S2.

- 1. 110: Figure 1 does not display sediment depth nor age

Reply: We have added this information to the main text (Fig. 1).

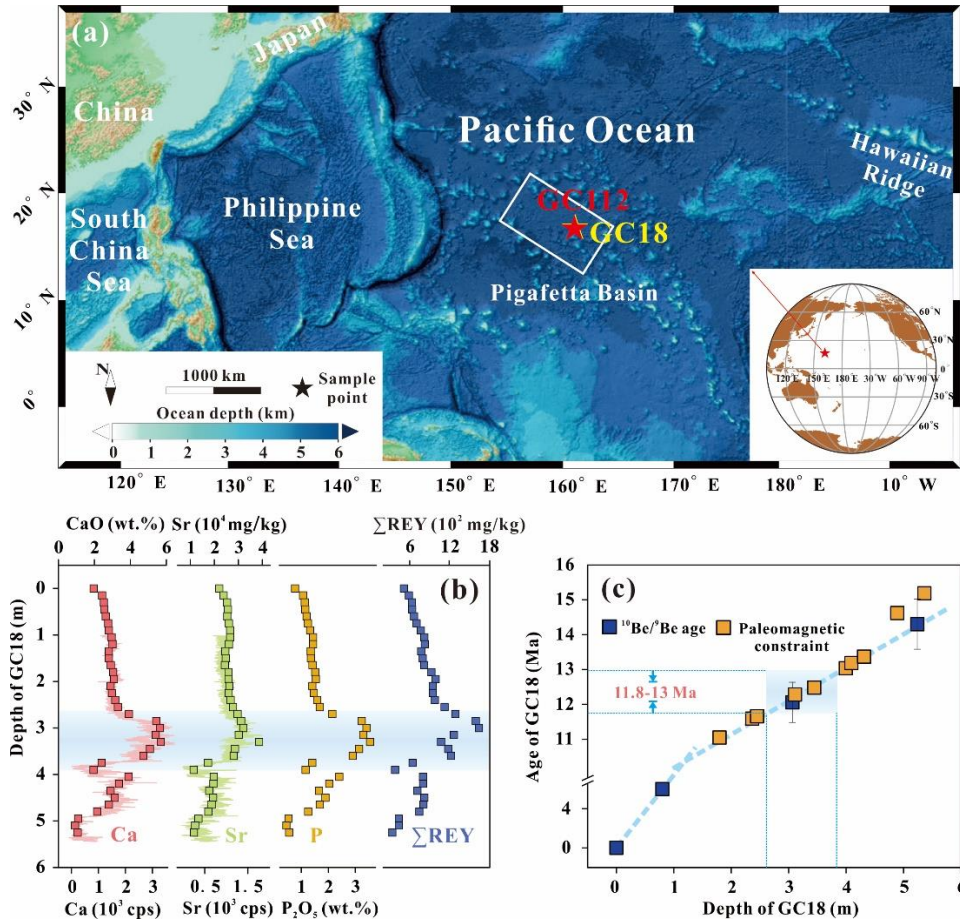


Fig. 1. (a) Sampling locations of deep-sea sediment cores GC112 and GC18⁴⁷ in the Pigafetta Basin, western Pacific. (b) Downcore variations of Ca, Sr, P, and REY concentrations in core GC18. Light-colored lines denote high-resolution X-ray fluorescence (XRF) scanning data⁴⁷; solid squares represent whole-rock chemical analyses. (c) Chronostratigraphic framework for the Pigafetta Basin deep-sea sediments, established by integrated $^{10}\text{Be}/^9\text{Be}$ dating and paleomagnetic data from core GC18⁴⁷. The REY-rich interval is constrained to an age of 11.8-13 Ma.

Results: Some introduction on the influence of the iron shuttle (sources and sinks) and reductive remobilization on $\delta^{56}\text{Fe}$ values are missing. Metagenomic data are not presented in the main text or in the supplement (a succinct table is available on zenodo for download). Sequencing data should be made available in a public repository. The authors have to better differentiate between pelagic and benthic processes.

Reply: We thank the reviewer for their constructive suggestions on this section. In response, we have undertaken the following revisions: supplementing the manuscript with TOC measurements, refining the magnetic analysis to improve clarity for non-specialist readers, and removing the preliminary metagenomic data which were not

central to the main argument. Please note that, as the Results section is reserved for objective data presentation, some of the contextual interpretations have been incorporated into the revised Discussion. Detailed point-by-point responses are provided below.

- 1. 121-127: abiotic oxidation/reduction processes also fractionate Fe isotopes, the residual phase (i.e. oxidized) being systematically enriched in the heavy Fe isotope. Moreover, $\delta^{56}\text{Fe}$ of -0.08 ‰ does not reflect an enhanced microbial fractionation compared to magmatic values (0.00 ‰). These values could also be interpreted in terms of partial oxidation of hydrothermal Fe(II) during mixing of hydrothermal fluids with seawater. As samples are from below the CCD, a depletion in carbonate-bound Fe phases is not surprising. Moreover, these are bulk measurements that do not take into account the speciation of iron phases.

Reply: We thank the reviewer for this professional and insightful feedback. We fully acknowledge that abiotic redox processes, such as those in certain anaerobic shelf settings or cold-seep systems, as well as partial oxidation during the mixing of hydrothermal Fe(II) with seawater, can indeed lead to iron isotope fractionation. In response, we have added a focused discussion on this issue.

Overall, we posit that although the flux of organic matter to the surface sediments during the REY-enrichment period in our study area was elevated compared to background layers (resulting in suboxic conditions within the upper few centimeters), it remained significantly lower than in shelf upwelling zones or cold-seep environments. This level of organic input was insufficient to trigger the strong reductive dissolution of Fe seen in those settings. This interpretation is supported by previous assessments of sediment oxygen levels^{2,3} and the consistently low dissolved iron concentrations in our porewater data¹¹. Furthermore, we have rigorously evaluated and discounted significant hydrothermal influence in our study area based on several lines of evidence: its distal location from mid-ocean ridges, the absence of a pronounced positive Eu anomaly in REY patterns, bulk iron concentrations approximating upper continental crust values and being markedly lower than those in hydrothermally influenced sediments, and the stable, low dissolved iron levels in pore waters. These observations collectively support a dominant terrigenous dust source for Fe^{6,7}.

Regarding the negligible fractionation of the $\delta^{56}\text{Fe}$ value (-0.08 ‰) relative to the magmatic baseline (0.00 ‰), we have provided a detailed explanation in the second and third parts of the Discussion. The current study is based on bulk sediment iron isotope analysis, where the negative $\delta^{56}\text{Fe}$ shift potentially caused by biological activity is likely masked by other iron-bearing components (e.g., crustal iron sources with $\delta^{56}\text{Fe} \approx +0.082$ ‰). Nevertheless, the observed negative shift in the REY-rich layer relative

to the background still offers tentative support for our hypothesis. Future work will focus on single-mineral or phase-specific iron isotope analysis to enable a more quantitative assessment of the microbial contribution.

- l. 131: explain what a Cerium negative anomaly implies, i.e. remains in solution under reducing conditions

Reply: We thank the reviewer for this comment. We have now added an explanation for the observed negative Ce anomaly in the Discussion section. Seawater exhibits a distinct negative Ce anomaly. As noted, under oxic conditions (e.g., in the water column), Ce is preferentially scavenged and enriched onto the surfaces of Fe–Mn (oxy)hydroxides. The subsequent transfer of this relatively enriched Ce into sediments and pore waters, and its ultimate sequestration into authigenic minerals, would partially mitigate the pronounced negative Ce anomaly characteristic of seawater. This results in a bulk-rock Ce anomaly that is less pronounced than that of seawater, exhibiting an intermediate signature between seawater and pore waters affected by REY remobilization. The relative enrichment of MREEs in the sediments compared to seawater may also be influenced by the above mechanism.

Please refer to the specific modifications in the Discussion section.

“The preferential adsorption of MREEs and Ce⁴⁺ onto Fe-Mn (oxyhydr)oxides yields MREE-enriched patterns and a weaker negative Ce anomaly in porewaters, distinct from seawater signatures (Fig. 2d)²². This finding is consistent with REY patterns in Fe-bearing porewaters from the eastern Pacific shelf³ and secondary REY-release porewaters from the northwestern Pacific¹². Ultimately, these geochemical signals are preserved in deep-sea sediments²².” **Lines 285-290.**

- l. 137: ferromagnetic, ferrimagnetic, diamagnetic or paramagnetic minerals?

Reply: The minerals have now been explicitly identified as ferrimagnetic minerals.
Line 177

- l. 139-157: very technical part

Reply: We apologize for the overly technical language in the original version of this section. In the revised manuscript, we have added clear, concluding statements for each magnetic analysis and improved the logical flow between them to reduce technical complexity and enhance readability.

“The temperature-dependent magnetic susceptibility (κ -T) heating curves dropped to zero near the Curie temperature of magnetite ($T_C \sim 580^\circ\text{C}$), confirming its presence (Fig. 3a)⁵². The most rapid decrease in χ occurred near 475°C , significantly lower than the standard T_C for standard magnetite (Fig. 3a), likely reflecting fine grain size or imperfect crystallinity⁵². First-order reversal curve (FORC) diagrams of the REY-rich layers displayed a dominant central ridge and a negative region in the lower left-

hand corner (blue dashed box, Fig. 3b), together diagnostic of biogenic magnetite in the single-domain (SD, 25-80 nm) size range^{36,53,54}. Compared to background sediment, FORC diagrams of REY-rich layers showed no vertical spread along the B_u axis and a stronger central ridge (Fig. S1), indicating minimal coarse-grained magnetite particles (e.g., pseudo-single-domain, PSD, >80 nm, and multi-domain, MD, μ m-scale micrometer-sized) and a higher SD proportion^{36,53,54}. The absence of a clear Verwey transition near 120 K, a cubic-to-monoclinic phase change in magnetite usually seen in larger grains, in the zero-field-cooled (ZFC) and field-cooled (FC) curves further indicates limited PSD/MD abundance (Fig. 3c)³⁶. FORC contours extending from the origin ($B_c = 0$ mT) suggest superparamagnetic (SP, <25 nm) magnetite particles⁵³. Hysteresis loops showed a coercivity increase from ~7.7 mT at 300 K to ~20.3 mT at 10 K (Fig. 3d), consistent with SP to SD transition upon cooling⁵⁵. Low-temperature alternating current (AC) susceptibility confirmed higher SP concentrations (10-15 nm) in REY-rich layers than in background sediment (Fig. 3e)⁵⁶. Isothermal remanent magnetization (IRM) acquisition curves were dominated by low-coercivity components, with two soft magnetic phases ($B_{1/2} = 19.0$ mT, 75.7%; 6.38 mT, 18.5%; Fig. 3f) and no detectable high-coercivity fraction.” **Lines 179-201**

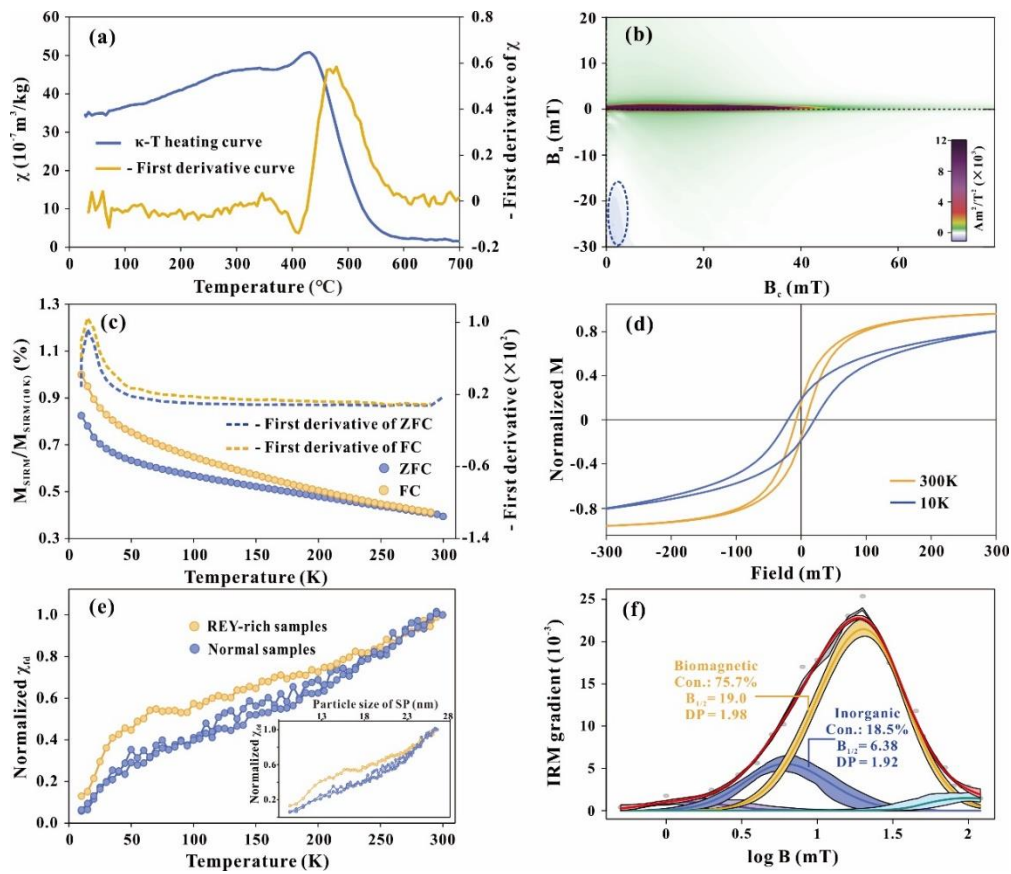


Fig. 3. Magnetic properties of REY-rich samples: (a) κ -T heating curve, (b) FORC diagram, (c) ZFC and FC curves, (d) hysteresis loops, (e) Low-temperature AC

susceptibility of REY-rich and background samples (Inset: Maximum-normalized χ_{fd} versus SP particle size, with analytical method follows Liu et al. (2005)⁵⁶), and (f) IRM coercivity component analysis. Background layer results are provided in Fig. S1.

- l. 160: magnetic particle form aggregates, could this be a preparation artifact since magnetic minerals always tend to aggregate?

Reply: Due to their small particle size, the superparamagnetic (SP) magnetite grains inevitably underwent aggregation during magnetic separation using a neodymium magnet (as shown in Fig. 4a). However, in the whole rock samples, these magnetic particles are dispersed and uniformly distributed. In the revised manuscript, we have also included TEM images showing chain-structured magnetosome particles. We clarify that all magnetic analyses were performed on whole rock samples, whose magnetic characteristics are therefore unaffected by aggregation effects.

- l. 168: can the authors provide information on accumulation of biogenic apatite, e.g. hard ground, condensed facies, else? Some words on forms of phosphorus (organic, inorganic, apatitic, authigenic) are also needed in order to address the transformation from organic into authigenic forms during burial. It is also worth mentioning that apatite represents the main form of authigenic phosphate in the marine environment compared to anapaite or vivianite. Then, the authors should provide some constraints on the environment and time of formation for both magnetite and apatite.

Reply: We thank the reviewer for this suggestion. In the revised manuscript, in addition to bioapatite (fish debris), we have supplemented the micro-characterization of authigenic phosphorus-bearing phases in the bulk samples. These authigenic phosphorus phases occur either as relatively large particles (likely mature aggregates of CFA) or in an amorphous form associated with phillipsite surfaces (possibly precursors to CFA)⁵.

Furthermore, we have expanded the Discussion to include a more detailed description of phosphorus speciation in the deep sea, as well as its formation environment and processes. Particular emphasis is placed on constraining the temporal relationship between phosphorus formation and the enrichment of magnetite and REY.

“The strong linear correlations between whole-rock REY and P or Ca (Fig. 2c) indicate that phosphate minerals represent the ultimate sink for REY in deep-sea sediments^{12,20,23}. Marine phosphorus is primarily sourced from riverine input and delivered to sediments mainly in the form of organic phosphorus or adsorbed onto Fe-Mn (oxyhydr)oxides⁶⁰. In deep-sea settings, where conditions generally preclude minerals requiring high organic matter and strict anoxia (e.g., anapaite and vivianite),

bioapatite and authigenic apatite are the dominant phosphorus sinks^{9,20,61}. Bioapatite (e.g., fossil fish teeth and bones) is a well-established host for REY, in which REY³⁺ is incorporated into the apatite lattice via charge-balanced coupled substitution for Ca²⁺ and P⁵⁺, facilitated by Na⁺ or Si⁴⁺^{9,20}. However, our statistical analysis indicates that fossil fish debris accounts for only ~0.39 wt.% of the REY-rich layer (contributing ~5.38% to total P; Table S5), implying that most phosphorus resides in transient Fe-Mn (oxyhydr)oxides associated phases or authigenic minerals²². Supporting this interpretation, Chen et al. (2025)⁶² reported a significant deficit between the measured and theoretical REY capacities of bioapatite, suggesting an additional phosphate-associated sink. Authigenic CFA is proposed as the most probable candidate^{18,62}. Phosphorus delivered via organic matter or Fe-Mn (oxyhydr)oxides can be remobilized during early diagenesis, increasing porewater saturation and promoting CFA precipitation¹⁸. As CFA is believed to control over 50% of marine phosphorus burial, it is increasingly recognized as a major potential sink for REY in deep-sea sediments, alongside bioapatite^{18,60,62}.”

n.B. if the main source of phosphorus is actually organic and relates to past upwelling and productive conditions, this should be brought earlier in the text, not briefly mentioned at the end.

Reply: We thank the reviewer for this suggestion. In the revised manuscript, this point is now addressed at the beginning of the Discussion section rather than at the end.

- 1. 173-175: provide full names of enzymes in a supplementary table, not gene abbreviations. Moreover, there are no specific functional marker genes for dissimilatory iron reduction. These genes are involved in extracellular respiration and electron transfer via nanowires (with multiheme cytochrome c), unlikely to take place in the sediment, rather at the paleo sediment-water interface. Iron is not the only substance that can be reduced with the multiheme cytochrome. Obviously, magnetosomes are not formed in the sediment either.

Reply: As indicated in our earlier response, we believe the current analysis and interpretation of the metagenomic data are insufficient to serve as key evidence supporting the main arguments of this study. After careful consideration, we have decided to remove this section for now. These data will be presented in a subsequent article more suited to molecular biology, following a specialized, rigorous, and comprehensive analysis.

Furthermore, we fully agree with and have incorporated your point that the processes discussed in this paper occur within the surface sediments of the deep sea (within the upper few centimeters below the paleo-sediment-water interface). In this environment, microorganisms can utilize nitrate, iron, manganese, and sulfate for

respiration, although our study focuses specifically on iron reduction and its products. This point has been clearly articulated in the revised manuscript.

“Multiple independent lines of evidence suggest enhanced microbial iron metabolism (such as dissimilatory iron reduction or magnetosome mineralization) coincident with REY enrichment in core GC112, implying a microbial contribution to deep-sea REY accumulation. However, the coupled biogeochemical cycling of multiple elements (e.g., C, O, N, S, Mn) mediated by diverse microorganisms may play a more substantial role. A microbiome-based approach could help clarify the associated microbial activities and elemental pathways. Reconstructing these processes remains challenging, however, due to low microbial biomass and poor preservation of genetic material in deep-sea sediments. Previous metagenomic studies report higher gene abundance and elevated metal-reduction gene levels in REY-rich layers than in background sediments, indicating enhanced microbial activity during formation and partially supporting our hypothesis²². A priority for future work is to resolve these complex biogeochemical pathways qualitatively and quantitatively using microbiome tools. It is important to note that metagenomic data reflect genetic potential, not gene expression or activity; thus, correlative analysis and validation of microbial metabolic products with multidisciplinary methods are crucial.” **Lines 356-371**

n.B. metagenomic data are reported in the results, but not presented in any figure of the manuscript. Currently, these data are buried in a zenodo data dump without their corresponding metadata or accession number. Looking at this zenodo supplement, I found few information on very low number of reads assigned to Thermoanaerobaculia (identified from hydrothermal vents), Acidobacteria (high taxonomic level, no inference possible), Photobacterium sanguinanceri (bioluminescent symbiont), Photobacterium frigidiphilum (facultative anaerobe common in deep-sea waters and sediments), Vibrio sp., Limnobacter sp., Muricauda sp., Stenotrophomonas nitritireducens, none of which appear to be involved in dissimilatory reduction of iron or magnetosome formation (accounting for RPKM <0.15%). Please report the FeGenie output consistently. Although detection is higher in the REE-rich layer, they are far from being overrepresented. Also, there is no evidence that the predicted metabolisms could have been active after deposition and during burial.

Reply: As you correctly noted, the identified microbial taxa fall outside the typical taxonomic range of classical DIRB and MTB. Moreover, other metabolic pathways could indeed be characterized in greater detail using metagenomic data. As mentioned above, we have prudently decided to temporarily remove this section, and plan to address these aspects more comprehensively in a separate, dedicated study.

Discussion: The authors provide little to no evidence for microbial iron reduction as the main process leading to magnetite precipitation. They conclude on past upwelling conditions 12 Ma ago, which would likely lead to an oxygen minimum zone, but do not decipher the source of iron or how this would lead to increased redox cycling of iron.

Reply: We thank the reviewer for their careful reading and constructive comments. In the revised manuscript, based on the exclusion of significant hydrothermal and inorganic reduction influences in our study area, we have integrated multiple independent lines of evidence, including iron isotope analysis, magnetic characterization, and microscopic observations (particularly TEM images of magnetofossils), to demonstrate the microbial origin of magnetite in the REY-rich layers. In response to your suggestions, we have completely restructured the Discussion section into the following four parts:

- REY enrichment processes in the northwestern Pacific deep sea;
- The microbial role in deep-sea REY enrichment: insights from iron cycling;
- Quantifying the microbial contribution to deep-sea REY enrichment;
- Potential climatic mechanisms of deep-sea REY enrichment.

The revised manuscript now presents our core arguments through a clear logical framework addressing material sources, depositional processes, microbial involvement and contribution, and underlying climatic background.

- l. 187: in the introduction (l. 108) you mentioned that the organic content of the sediment is minimal.

Reply: We propose that the increased organic matter input in the REY-rich layers likely results from moderately elevated surface primary productivity under specific climatic conditions. For instance, in regions such as the equatorial Pacific or northwestern Pacific³, surface ocean productivity may be relatively high compared to the average pelagic background levels, though still significantly lower than that of shallow-water upwelling zones, with these conditions being particularly pronounced during certain periods of climatic variability.

- l. 193: metagenomic data not shown

Reply: Deleted

- l. 194-195: “enhancement of historical microbial activity” in the water column at the time of deposition or after deposition? What is iron metabolism? Aerobic-anaerobic iron respiration, dissimilatory processes, uptake, regulation, siderophores, else? The authors ran the FeGenie pipeline (Garber et al., 2020 Front Microbiol) and could thus report more clearly on metabolic potential for aerobic-anaerobic redox Fe processes, siderophores and magnetosomes.

Reply: In the original manuscript, the phrase "enhancement of historical microbial

activity" refers to microbial activity within the surface sediments at the time of deposition. "Iron metabolism" here denotes the processes by which DIRB and MTB form magnetite through extracellularly induced mineralization and intracellularly controlled biomineralization, respectively, at redox interfaces. This section has been rewritten in the revised manuscript. To maintain focus on the core objective of this paper (identifying microbial processes in REY enrichment), detailed mechanisms such as aerobic/anaerobic iron respiration, dissimilatory pathways, uptake, regulation, siderophore or magnetosome metabolic potential, and other microbial elemental metabolisms will be thoroughly analyzed using metagenomic data and presented in a subsequent study.

- 1. 198-200: with more advanced bioinformatic analyses, one could fill a part of this gap.

Reply: To maintain focus on identifying microbial processes in REY enrichment, more detailed bioinformatic analyses will be addressed in future work.

- 1. 202: what do the author mean by "bacterial iron metabolite"? Siderophores, else?

Reply: This refers specifically to microbial-derived magnetite. To prevent potential misunderstanding caused by unclear phrasing, we have revised the text in the updated manuscript to read: "*microbial iron cycling and its diagnostic byproduct, biogenic magnetite.*" **Lines 302-303**

- 1. 202: is it due to oceanic circulation or very low sedimentation rates?

Reply: We propose that both factors may be involved. In our study area, which is unaffected by significant hydrothermal activity, ocean circulation maintains generally oxic conditions in the water column. At the same time, the extremely low sedimentation rate results in the extensive oxidative degradation of organic matter—already far lower than in shelf environments—during its settling process, with only a small fraction reaching the surface sediments. This limited organic input is insufficient to create the strongly anaerobic conditions typical of shelf settings, leading instead to suboxic conditions in the deep-sea sediments. Under these circumstances, the Fe^{2+} in deep-sea sediments is primarily derived from microbial iron reduction, rather than from the reductive dissolution of iron oxides, which is widespread in shelf environments.

"The Pigafetta Basin, site of core GC112, lies far from the East Pacific Rise and shows no significant positive Eu anomaly in its REY patterns (Fig. 2d), indicating a negligible hydrothermal contribution^{4,22}. Consistent with this interpretation, the sediment iron content is close to the upper continental crust average, suggesting a dominant terrigenous dust source; this contrasts with the elevated iron levels in hydrothermally influenced East Pacific sediments^{22,47}. Furthermore, unlike the

*abundant dissolved Fe^{2+} in reducing shelf settings ¹⁵ and hydrothermal systems ⁴, the suboxic deep-sea surface sediments in this study area exhibit consistently low porewater Fe^{2+12} . The structural Fe^{2+} in magnetite is therefore likely sourced from microbial iron reduction ^{12,22}.” **Lines 318-327***

- l. 205: these references deal with magnetosomes, not partial reaction of dissolved Fe^{2+} with amorphous hydrated iron oxides.

Reply: We have updated the literature citations, including references describing DIRB-induced magnetite mineralization ^{4,12} and MTB-controlled magnetosome biomineralization ^{12,13} as tracers of microbial activity.

- l. 210: do these values correspond to fractionation factors? What are the $\delta^{56}\text{Fe}$ values one should expect?

Reply: You are correct that these values refer to the fractionation factors of the respective systems. We have clarified this point in the revised manuscript. Additionally, the expected $\delta^{56}\text{Fe}$ value of the bulk sample is related to its end-member mixing, which we have elaborated on in detail in the third section of the Discussion.

*“After preliminarily tracing microbial activity in deep-sea REY enrichment via iron metabolism, we applied a two-end member iron isotope mixing model to quantify the microbial contribution. Using the upper continental crust ($\text{Fe} = 3.52 \text{ wt.}\%$, $\delta^{56}\text{Fe} = +0.082\text{‰}$) ⁴⁸ and microbial magnetite ($\text{Fe} = 72.36 \text{ wt.}\%$, $\delta^{56}\text{Fe} = -0.4\text{‰}$) ⁶⁸ as end-members, the model indicates a microbial contribution ranging from 0 to 2% (Fig. 5). In the simulation, a conservative $\delta^{56}\text{Fe}$ value of -0.4‰ was adopted for microbial magnetite (less fractionated than the -2‰ reported in pure-culture studies) yet the model still yields a detectable microbial signal, providing partial support for the core hypothesis. Nevertheless, we consider these estimates likely underestimated for several reasons: 1) The simplified end-member assumption overlooks the integrated nature of whole-rock $\delta^{56}\text{Fe}$, which represents a mixture of multiple iron phases; 2) Unconstrained isotopic variability in other sediment phases (e.g., clays or oxides), if distinct from the crustal value, would affect model accuracy. For instance, higher $\delta^{56}\text{Fe}$ in non-microbial phases would further suppress the calculated microbial contribution; 3) Laboratory-cultured microbial magnetite may not fully replicate in situ biomineralization conditions. Despite these potential masking effects, the REY-rich layers show consistently higher modelled microbial contributions than the background sediments (Fig. 5), lending moderate support to the proposed mechanism. Future work will focus on developing single-mineral and phase-specific iron isotope analyses to improve the precision of microbial contribution estimates using iron isotope mixing models.” **Lines 373-392***

n.B. The authors do not mention the possibility of abiotic fractionation of Fe

isotopes due to partial oxidation from ferrous to ferric Fe and assume that $\delta^{56}\text{Fe}$ values around -0.08 ‰ constitute indubitable evidence of DIR. Also, according to the successive sorption processes theorized by the authors, the potential influence of redox shuttle has to be considered as well.

Reply: As mentioned in our previous response, the investigation and characterization of the sedimentary environment have largely ruled out the influence from hydrothermal activity and reductive dissolution of Fe^{2+} .

- l. 213: BIFs were formed under anoxic conditions, not under oxic to suboxic conditions. Thus, I wonder if this comparison is justified.

Reply: You are correct that over-reliance on analogies with BIFs formation mechanisms is inappropriate for interpreting the processes in our study area. In the updated discussion, we have downplayed this comparison, presenting it only as background context to illustrate how iron isotopes can help identify microbial activity in geological settings.

“These isotopic signatures have been instrumental in identifying microbial magnetite origins in banded iron formations ^{41,42}.” Lines 330-331

- l. 215: currently distal. Things may have looked different 12 Ma ago.

Reply: Your concern is well-founded. Based on relevant studies, considering the east-to-west directed subduction of the Pacific Plate beneath adjacent plates, the REY-rich layer in core GC112 from the northwestern Pacific was also deposited in a deep-sea environment at approximately 12 Ma, with a paleo-position relatively close to its present location (Fig. R1).

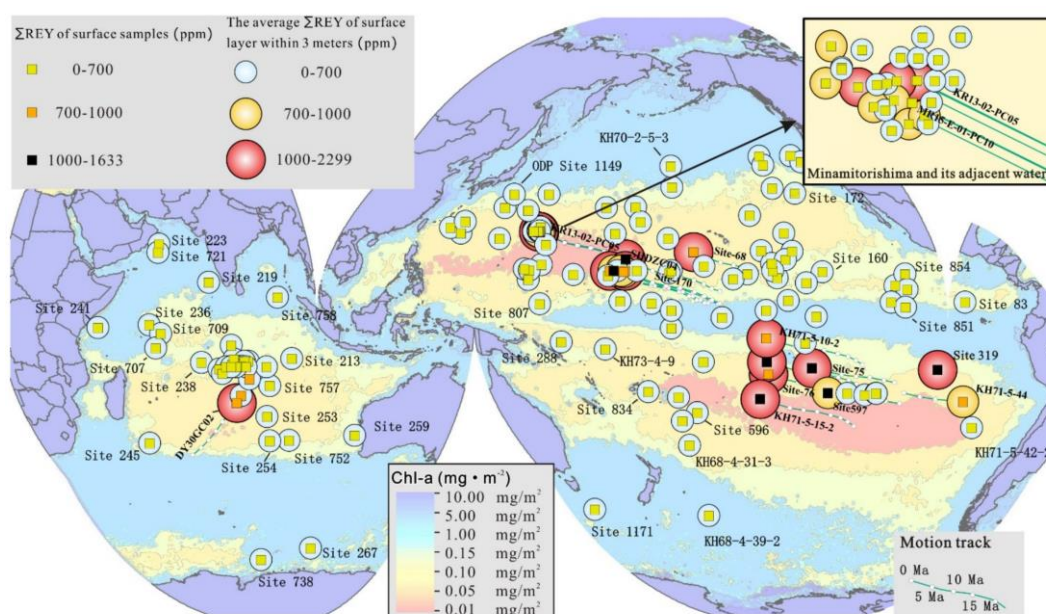


Fig. R1. Depth profiles of ΣREY concentrations in surface and subsurface samples (within the upper 3 m) from deep-sea sediments in the Pacific and Indian Oceans

(data from Ren et al., 2021) ¹⁴. The green line with white dots depicts the palaeopositional evolution of REY-enriched sites, with consecutive dots representing 5 Myr intervals.

- l. 217-239: very technical and descriptive part reiterating results. Poorly crystalline magnetites could also form during mixing of hydrothermal fluids with seawater.

Reply: We have rewritten this section to avoid mechanical repetition of the Results. The potential contribution of hydrothermally derived inorganic magnetite has been previously addressed and ruled out in earlier sections.

“Size-dependent magnetic properties and distinct crystallographic features provide key diagnostic criteria for biogenic magnetite ^{22,36,45}. Magnetosomes formed via MTB-controlled biomineralization typically display SD behavior (grain size ~25-80 nm at room temperature), characterized by high coercivity and stable remanence resulting from uniform magnetic alignment ^{35,36,38}. In contrast, DIRB-induced magnetite generally occurs in the SP state (<25 nm at room temperature), exhibiting negligible coercivity and no remanence at room temperature due to rapid magnetic randomization under thermal energy ^{45,56}. DIRB-synthesized magnetite also commonly shows poor crystallinity, further diminishing magnetic stability owing to the absence of membrane constraints during extracellular formation ^{37,38,45}. In this study, κ -T heating curves confirmed magnetite by a T_c near 580 °C ⁵². Additional room- and low-temperature magnetic analyses revealed that magnetite in REY-rich intervals is predominantly composed of SD and SP particles. The SD fraction likely derives from disaggregated magnetosome chains ^{36,45}, while the SP particles are attributed to extracellular precipitation by DIRB, with sizes confined to 10-15 nm (Fig. 3f) ^{37,56}. These results are corroborated by TEM imaging (Fig. 4a-4c). Furthermore, the FORC diagram pattern (Fig. 3b), the absence of a Verwey transition in ZFC/FC curves (Fig. 3e), and IRM unmixing results (indicating 75.7% biogenic contribution; Fig. 3c) collectively suggest that the contribution of detrital grains characterized by PSD/MD magnetite is negligible relative to the dominant SD/SP biogenic magnetite ^{55,67}.” **Lines 336-355**

- l. 236: during deposition, here the authors assume that these magnetites are pelagic precipitates.

Reply: We have rewritten this section to emphasize the microbial origin of magnetite, which primarily formed within deep-sea surface sediments.

- l. 245: by 5700 m water depth on an abyssal plain, a detrital component is any way unlikely.

Reply: We fully agree with your observation. Our magnetic and microscopic analyses confirm that detrital magnetite is virtually absent.

- l. 254: what is the TOC content of the sediment? Abyssal clays are usually extremely organic-lean...

Reply: Through additional measurements, we have determined that the TOC content of core GC112 ranges between 0.2 and 0.4 wt.%, which is consistent with previously reported low TOC values for deep-sea sediments².

- l. 262: or that reductive diagenesis of the sediment led to subsequent release of metal ions...

Reply: You are correct that inorganic reductive diagenesis in sediments can indeed lead to the release of metal ions. Specifically regarding Fe (oxyhydr)oxides, the environmental conditions in our study area may not have reached the threshold required to trigger their reductive dissolution. Furthermore, the transformation of Fe (oxyhydr)oxides to magnetite in our study area likely required microbial reduction to supply electrons. Therefore, we propose that REY remobilization into pore waters in this region resulted from the combined effects of inorganic and microbial processes, with microbial iron reduction serving as a tracer for the microbial contribution (though not representing the entire microbial contribution).

- l. 270: once more, in the introduction you mentioned that OM content is minimal. How can OM remineralization be substantial enough to lead to anoxic conditions? Please support this statement with bulk OM.

Reply: By incorporating previous data and additional TOC measurements from our core GC112, we conclude that the input of organic matter in our deep-sea study area can induce a transition to suboxic conditions within the upper few centimeters of surface sediments^{2,3}, providing an ideal environment for microbial iron reduction. This phenomenon would have been more pronounced during periods of elevated surface productivity driven by climate fluctuations, resulting in marginally higher residual TOC in the sediments compared to background layers (Fig. 2a).

- l. 274: solid-phase transformation; provide reference

Reply: The relevant references have been added.

- l. 282: the metagenomic data are far from being compelling and are not made available to the readers.

Reply: The metagenomic-related content has been removed. Please refer to our earlier response for details.

- l. 285: due to the absence of data on sedimentary OM content and cell density, this statement remains speculative. What is the source of phosphate? To this point, the reader is left with the idea that an accumulation of macroremains of biogenic apatite is the main source causing phosphatic concretions.

Reply: We have supplemented the sediment TOC content data. Furthermore, we

propose that phosphate is derived from the input of organic matter and Fe-Mn (oxy)hydroxides from seawater into the sediments. Subsequently, this phosphate is released into pore waters and contributes to an important phosphorus sink in the deep sea, in addition to bioapatite (fish debris), namely, authigenic apatite represented by CFA (Fig. 4d and 4e).

- 1. 303-307: ...if one assumes that $\delta^{56}\text{Fe}$ values of -0.08 ‰ are sufficient evidence for dissimilatory iron reduction by unidentified microorganisms. The problem is that hydrothermal fluids mixing with seawater could produce abiotic magnetites that are slightly enriched in the light Fe isotope. The authors would be then tracing the source of the fluids rather than disentangling biotic-abiotic processes.

Reply: As mentioned in our previous response, multiple lines of evidence have effectively ruled out the influence of hydrothermal Fe^{2+} .

- 1. 305: “microbial iron metabolism governs secondary mineralization”. Intraplate tholeiitic volcanism and hydrothermal circulation can also produce more crystalline secondary magnetite...

Reply: We clarify that active volcanism in the study area was largely confined to the Cretaceous to Eocene¹¹. As indicated previously, the region was largely unaffected by hydrothermal activity during the formation of the REY-rich layer. Furthermore, images of chain-structured magnetosomes included in the revised manuscript provide supporting evidence for the formation of biogenic magnetite.

- 1. 315: hitherto, marine productivity hotspots have not been introduced to the reader or put into context of the Pigafetta Basin 12 Ma ago.

Reply: In the revised manuscript, we have enhanced the Introduction by incorporating the linkages among climatic conditions, ocean productivity, and REY enrichment, thereby setting the stage for the subsequent discussion.

- 1. 318: microbial processes are rather defined by the substrates available after deposition at the seafloor, which is indirectly related to environmental conditions at the surface ocean.

Reply: We fully agree with this perspective. In the revised manuscript, we have more clearly delineated the impact of variations in surface productivity on the flux of marine particles to the deep sea, and have confined the primary site of REY migration and transformation to the surface sediments of the deep sea.

- 1. 324-331: see comment about 1. 70-71 on nitrogen limitation and excess orthophosphate turning into authigenic (non-) apatitic phosphate in the sediment. P speciation would be an asset as to discriminate organic and inorganic forms of phosphates.

Reply: By supplementing TEM images of authigenic phosphorus-bearing phases

in deep-sea sediments and performing statistical analysis of the relative proportions of total sediment P, bioapatite P, and authigenic apatite P, we preliminarily find that authigenic forms of phosphorus represent the dominant contributor to the total sedimentary phosphorus pool⁸. This observation aligns with previous studies suggesting that, in addition to bioapatite (e.g., fish debris), authigenic apatite may serve as a more significant host mineral for deep-sea REY enrichment¹⁵.

“However, our statistical analysis indicates that fossil fish debris accounts for only ~0.39 wt.% of the REY-rich layer (contributing ~5.38% to total P; Table S5), implying that most phosphorus resides in transient Fe-Mn (oxyhydr)oxides associated phases or authigenic minerals²². Supporting this interpretation, Chen et al. (2025)⁶² reported a significant deficit between the measured and theoretical REY capacities of bioapatite, suggesting an additional phosphate-associated sink. Authigenic CFA is proposed as the most probable candidate^{18,62}. Phosphorus delivered via organic matter or Fe-Mn (oxyhydr)oxides can be remobilized during early diagenesis, increasing porewater saturation and promoting CFA precipitation¹⁸. As CFA is believed to control over 50% of marine phosphorus burial, it is increasingly recognized as a major potential sink for REY in deep-sea sediments, alongside bioapatite^{18,60,62}. ” **Lines 245-256**

- l. 332-334: which indirectly argues against substantial drive by microbial dissimilatory iron reduction...

Reply: In the revised manuscript, we have emphasized the role of microbial iron reduction as a tracer, rather than a primary driver, of microbial processes in deep-sea REY enrichment. We further clarify that REY enrichment results from the synergistic effects of both inorganic and microbial processes.

“It is important to emphasize that while microbial iron cycling provides a novel perspective for tracing microbial contributions, deep-sea REY enrichment results from a complex interplay of abiotic and microbial processes^{12,22,31}. The detailed mechanisms underlying this synergy require further qualitative and quantitative clarification. Furthermore, the significant spatial and temporal heterogeneity of microbial roles in REY enrichment warrants future investigation²². Nonetheless, this study highlights the crucial yet underestimated contribution of biological processes to deep-sea REY enrichment and offers new insights into the links between REY-rich deposits, marine productivity, and climate change. ” **Lines 454-462**

- l. 337: you mean an oxygen minimum zone? Normally, OMZs are mainly under the influence of heterotrophic denitrification (with substantial loss of fixed nitrogen). Iron is the main limiting nutrient in the modern global ocean, so where is the iron coming from?

Reply: In the revised manuscript, this section has been refined to indicate that climatic

drivers not only promote productivity increases and subsequent oxygen minimum zone (OMZ) expansion, but also lead to a relative increase in deep-sea organic matter input. This input shallows the dissolved oxygen penetration depth in surface sediments, resulting in a transition from oxic to suboxic conditions within the upper few centimeters.

The source of iron, as elaborated in our previous response, is primarily attributed to terrigenous dust inputs.

Methods:

- 1. 423: comprehensive metadata on sequence data are missing (e.g. sequencing depth, number of contigs and length, predicted genes and ORFs).

Reply: As mentioned in our previous response, the metagenomic analysis has been temporarily removed. These data will be presented in future work following more detailed and specialized molecular biological analysis.

Reviewer #2

The manuscript number COMMSENV-25-2787 entitled “The overlooked role of microbial iron cycling for the enrichment of rare earth elements in deep-sea sediments” from Wang et al. establishes a relationship between REY enrichment in phosphates and clear evidence of enhanced Fe metabolism, supported by mineralogical characteristics, isotopic signals, and genomic data. Together, these proxies convincingly indicate that microbial Fe metabolisms are associated with diagenetic REY enrichment in sediments. Such an association of proxies is rare in sedimentology/diagenesis studies and, by itself, makes the work of great value to the literature.

Reply: We thank you for your positive assessment of our manuscript. Your suggestions have been essential in helping us improve the work. We have addressed each of your comments in the revised manuscript, and a detailed point-by-point response is provided below.

From the perspective of building a genetic model for these mineral deposits and their link to a temporally constrained event, some points deserve clarification. What is the main control on REY enrichment in this case—the greater abundance of the host mineral (phosphates, as shown in Fig. 2), a paleoenvironmental factor that favored Fe metabolisms at this stratigraphic level, or both? The explanation is proposed in the last item of the discussion, but it could be better substantiated. The first key point is that REY enrichment is associated with enrichment of the host mineral (phosphates), as indicated by the bulk elemental data. From there, the investigation proceeds to the relation—which I do not contest—between the greater abundance of the host and the signatures associated with enhanced microbial Fe metabolisms.

Reply: We thank the reviewer for their expert suggestions. We propose that REY enrichment in our study area is significantly associated with both an increase in host minerals and enhanced microbial activity. Against the backdrop of climate fluctuations leading to elevated marine primary productivity, a greater amount of REY and phosphorus from seawater is transported to deep-sea sediments via marine particles (e.g., Fe-Mn (oxyhydr)oxides or organic matter). Within the surface sediments of the deep sea, early diagenesis — integrating both abiotic processes (e.g., oxidative degradation of organic matter or inorganic phase transformations of Fe-Mn (oxyhydr)oxides) and microbial activity (e.g., aerobic respiration, nitrate reduction, Fe-Mn reduction, and sulfate reduction)—can facilitate the release of particle-bound REY and phosphate into pore waters. This process leads to the enrichment of REY in pore waters and, concurrently, promotes the crystallization of key host minerals, such as authigenic apatite represented by CFA.

Microbial iron reduction acts primarily as a tracer in the above process for three main reasons:

1. It couples with organic matter degradation, and both processes favor REY release into pore waters.
2. The ideal environmental condition for microbial iron respiration is suboxia. The relative increase in organic matter input under the described climate background can shift deep-sea sediments to suboxic conditions within the upper few centimeters, making microbial iron reduction highly sensitive to climate variability and productivity changes.
3. Most importantly, within the context of our study area, microbial iron reduction produces unique and readily identifiable biogenic magnetite, which remains relatively stable during early diagenesis.

Based on these points, microbial iron reduction represents a highly promising pathway for tracing the microbial contribution to deep-sea REY enrichment. We have clarified these aspects in the Introduction and Discussion sections of the revised manuscript. Please refer to the specific locations below.

“Microbially mediated iron geochemistry cycling offers a key pathway to address current knowledge gaps. Iron-metabolizing bacteria, particularly dissimilatory iron-reducing bacteria (DIRB) and magnetotactic bacteria (MTB), are well-studied and ubiquitous in marine systems³⁵⁻³⁷. These microorganisms transfer electrons from organic matter to Fe(III), reducing it to Fe(II)³⁶⁻³⁸. This reduction process, coupled with organic matter degradation and iron (hydr)oxides dissolution or phase transformation, facilitates REY transfer from marine particles into porewaters²². Although modern deep-sea bottom waters are generally well-oxygenated ($DO > 100 \mu M$)

owing to limited organic input and oceanic circulation, suboxic conditions can develop within the upper few centimeters of sediment in regions with relatively higher surface productivity, such as the northwestern and equatorial Pacific ^{16,32}. These suboxic settings provide ideal niches for iron-reducing bacteria, whose metabolic activity responds sensitively to redox variations influenced by climate change and surface productivity ^{36,37}. A key advantage of the iron cycle over other microbially driven elemental cycles (e.g., O, N, S, Mn, C) is the production of biogenic magnetite [Fe(II)Fe(III)₂O₄], which can serve as a tracer for microbial activity in deep-sea environments ^{22,36,39-42}. DIRB extracellularly precipitate nanoscale magnetite particles ^{37,41}, whereas MTB form intracellular magnetite chains (magnetosomes) under strict genetic control ^{35,36,38}. These biogenic minerals remain stable under mild early diagenetic conditions and retain distinctive chemical, magnetic, and mineralogical properties ^{36,39,42-44}, making them potential proxies for identifying microbial redox cycling of metals in deep-sea geological records ^{22,36,45}. Therefore, elucidating the connection between microbial iron cycling and REY mobilization provides a novel framework for understanding the microbial role and its drivers in deep-sea REY enrichment.” **Lines 84-107**

“Under such climate variability, increased fluxes of marine particles (derived from dust or primary production) promoted the transfer of REY and phosphate from the water column to deep-sea sediments ¹⁶. Subsequent microbial-mediated organic matter degradation and Fe-Mn (oxyhydr)oxides phase transformation in surface sediments, alongside abiotic processes, facilitated the release of REY and phosphate into porewaters, creating favorable conditions for their ultimate sequestration into phosphate phases (Fig. 6a) ^{22,31}. Although most microbial signatures are obscured by organic degradation, the suboxic conditions resulting from oxygen consumption provided an ideal niche for microbially driven iron cycling ^{22,28,32}. The concurrent enhancement of microbial iron reduction in REY-rich layers offers a potential tracer for quantifying the biological contribution to REY enrichment.” **Lines 434-444**

Lines 263–265 link biomediated eodiagenetic Fe hydroxide mineralization with phosphatization, promoting remobilization and concentration of REY in authigenic phosphates. It would be important to better characterize the relative proportion of authigenic versus biogenic phosphates in this interval, rather than considering only total P abundance. Distinguishing between biogenic apatite and authigenic phosphate is essential to test this hypothesis.

Reply: We fully agree with your perspective. Following your suggestion, we have quantified the mass fraction of fish debris across different intervals of core GC112 (Table S5) and analyzed the proportion of fish debris-derived phosphorus relative to

total phosphorus. Our results indicate that authigenic phosphorus forms represent the dominant contribution to the total sedimentary phosphorus pool⁸ and likely serve as another major host for REY. This finding aligns with previous reports noting a significant discrepancy between the theoretical and measured REY contents in bioapatite (fish debris)¹⁵. Furthermore, we have supplemented the manuscript with TEM images of authigenic phosphorus-bearing phases in the deep-sea sediments, confirming the morphological characteristics of these authigenic components. These results collectively indicate that, alongside fish debris, authigenic apatite (represented by CFA) constitutes a more important sink for both REY and phosphorus in the deep-sea environment.

“However, our statistical analysis indicates that fossil fish debris accounts for only ~0.39 wt.% of the REY-rich layer (contributing ~5.38% to total P; Table S5), implying that most phosphorus resides in transient Fe-Mn (oxyhydr)oxides associated phases or authigenic minerals²². Supporting this interpretation, Chen et al. (2025)⁶² reported a significant deficit between the measured and theoretical REY capacities of bioapatite, suggesting an additional phosphate-associated sink. Authigenic CFA is proposed as the most probable candidate^{18,62}. Phosphorus delivered via organic matter or Fe-Mn (oxyhydr)oxides can be remobilized during early diagenesis, increasing porewater saturation and promoting CFA precipitation¹⁸. As CFA is believed to control over 50% of marine phosphorus burial, it is increasingly recognized as a major potential sink for REY in deep-sea sediments, alongside bioapatite^{18,60,62}. ” **Lines 245-256**

The modeling of the proportion of REY enrichment associated with microbial Fe metabolisms is very interesting. As the authors discuss, this only constrains the lower bound of the role of biogeochemistry in REY concentrations, since several other metabolisms may also remobilize REY in pore waters.

Reply: We fully concur with your perspective. Given the diverse microbial metabolic activities potentially present in the deep sea (e.g., aerobic respiration, nitrate reduction, Mn reduction, sulfate reduction), the microbial contribution estimated based solely on iron reduction likely represents only a lower-bound estimate. Meanwhile, distinguishing the relative proportions of microbial versus inorganic contributions remains a challenging task for future research. We have explicitly addressed these points in the revised manuscript; please refer to **Line 408-412** for details.

“It should be noted that this value represents a lower-bound estimate of the microbial contribution. If currently unquantified microbial processes are considered, such as microbial goethite formation³⁹, Mn(IV) reduction^{16,69}, organic carbon mineralization^{3,15}, and clay mineral neoformation/dissolution^{59,64}, the total microbial contribution is likely higher.”

The profiles of the most relevant proxies are presented only for core GC112. In the materials, two cores are cited, and it is notable that the detailed characterization is missing for GC18. Yet GC18 is used as a chronostratigraphic reference to link REY enrichment, Fe metabolisms, and phosphatization to the Middle Miocene Climate Transition (MMCT; 14.8–12.6 Ma), characterized by increased primary productivity and bottom-water oxygen depletion favoring microbial Fe metabolisms. I interpret the cause here as increased delivery of P-OM together with optimal conditions for Fe metabolisms in the substrate, leading to secondary mineralization.

Reply: We thank the reviewer for this suggestion. In the revised manuscript, we have supplemented data from core GC18 to enhance the reliability of its chronological constraints. In addition to citing previous element trends obtained via XRF core scanning, we have also performed new geochemical measurements of bulk Ca, Sr, P, and REY concentrations. Our results show that the REY-rich layers in core GC18 largely overlap with those in GC112 (Fig. 2a), supporting the reasonably reliable age constraints based on the former.

Furthermore, we fully agree with the view that a combination of climatic forcing, increased input of phosphorus and organic matter, and enhanced microbial activity in surface sediments collectively promotes deep-sea REY enrichment. Guided by this conceptual framework, we have rewritten the Introduction and Discussion sections accordingly.

Considering the complete and uncommon association of mineralogical, magnetic, geochemical, isotopic, and genomic proxies, I regard the manuscript as highly original and provocative. It opens new perspectives for investigating biogeochemical processes and the possible temporal association of REY enrichment in deep-marine sediments. This contribution will certainly advance knowledge on a topic that is strategically relevant for the energy transition and, consequently, of great interest to the readership of Communications Earth & Environment.

Reply: Once again, we sincerely appreciate your positive feedback on our manuscript.

Reviewer #3

The manuscript by Wang et al. addresses the importance of Fe cycling in marine sediments for REY cycling and thereby also REY enrichment in deep-sea sediments. While this certainly is an interesting topic, the manuscript presents very similar ideas and data to the recently published paper "Impact of iron biogeochemical cycling in deep-sea environments on rare earth element enrichment" also by Pengcong Wang in Chemical Geology. The used methods are identical and the working area is the same (although different cores). The recently published paper is not even referenced in this

submitted manuscript. The figures presented here are basically the same as in the recently published paper (just a different core). I therefore suggest to reject this manuscript for now until significant changes and additions have been made to produce a substantially different manuscript to the recently published one.

Reply: We sincerely thank you for reviewing our manuscript and apologize for any confusion caused by the initial version's failure to sufficiently highlight the distinctions from our previous publication. Following your suggestions, we have substantially restructured the entire manuscript to emphasize these differences and have incorporated key evidence that was missing in the earlier version.

To clarify, this study represents a significant extension of our recent work published in *Chemical Geology*. The previously published article provided a preliminary comparative tracing of microbial roles in deep-sea REY enrichment in both the eastern and western Pacific using a multidisciplinary approach. The present study focuses specifically on the Pigafetta Basin in the northwestern Pacific—a deep-sea environment largely unaffected by significant hydrothermal activity—and aims to trace microbial contributions and assess their magnitude in deep-sea REY enrichment using microbial iron cycling as a key investigative pathway. It also explores the potential climatic drivers behind these processes. Specifically, we consider the main advancements of this study compared to our prior work to be as follows:

1. Expanded Tracer Evidence: In addition to characterizing microbial-induced magnetite mediated by dissimilatory iron-reducing bacteria (DIRB), this study includes characterization of microbial-controlled magnetite formed by magnetotactic bacteria (MTB). The latter exhibits distinct magnetic and microstructural signatures and is widely used as a tracer for microbial activity in marine environments, thereby providing stronger support for identifying the microbial role in deep-sea REY enrichment.

2. Quantitative Assessment of Microbial Contribution: This study conducted higher-resolution iron isotope analysis on sediment core GC112 and applied a two-endmember mixing model to preliminarily quantify the microbial contribution. The results suggest that the microbial contribution estimated from bulk rock iron isotope analysis is likely a significant underestimate. Isotopic analysis of individual minerals or iron phases will be essential for improving accuracy in future work. Furthermore, using a combined approach of iron speciation analysis and IRM coercivity unmixing, we constrained a lower-bound estimate for the microbial contribution to REY enrichment (which may primarily reflect iron-reducing microbes). Considering other microbial metabolisms (e.g., aerobic respiration, nitrate reduction, manganese reduction, or sulfate reduction), the actual contribution could be higher.

3. Investigation of Climatic Drivers: Building on existing chronological

frameworks, this study constrains the formation age of the REY-rich layer in core GC112 to 11.8-13 Ma, coinciding with the Middle Miocene Climate Transition (MMCT). This allows a preliminary analysis of the linkages between REY enrichment, enhanced microbial activity, and climatic conditions. We propose that increased primary productivity during global climate perturbations likely stimulated microbial activity at the deep-sea sediment-water interface, positively influencing the migration, transformation, and enrichment of REY and phosphate.

Based on these substantial developments, we have updated the manuscript title to: "The biological contribution and potential climate drivers of deep-sea rare earth element enrichment: Insights from microbial iron cycling" to better reflect its distinct focus. Corresponding modifications and additions have been made throughout the main text.

Additionally, the methods lack rigorous reporting of accuracy, precision and blanks for the geochemical analyses (also see detailed comments below).

Reply: We thank the reviewer for their rigorous and professional suggestions. The manuscript has been revised and supplemented accordingly in response to each of the specific comments provided. Please see below for details.

Further comments:

Discussion

L253: one of the main carriers of REY to deep sea sediments are Mn oxides (see e.g. Du et al., 2025 Nature). This should be added and discussed here.

Reply: We sincerely appreciate your suggestion. The recommended literature has been extremely valuable in helping us refine the discussion on marine elemental cycling processes. Moreover, the high-quality deep-sea sediment and porewater data reported in this excellent reference have significantly strengthened our evidentiary framework.

"The element cycling driven by adsorption-desorption and crystallization-dissolution between seawater particles (e.g., Fe-Mn (oxyhydr)oxides or organic matter) and sediment porewaters likely plays a critical role^{12,22}. Marine particles with high specific surface areas effectively scavenge dissolved REY from the water column via adsorption or complexation, facilitating their transport to the seafloor^{3,12,15}. Among these, Mn (oxy)hydroxides exhibit the strongest REY scavenging capacity, followed by Fe (oxy)hydroxides and organic particles¹⁶." **Lines 47-53**

L259 ff and Figure 2d: pore water exhibit various different REYSN patterns in deep-sea sediments and not always the same one (see e.g. work by Haley et al., Abbott et al., Paul et al., Du et al.). This should be discussed more differentiatedly and different pore water studies should be used for comparison besides the one by Deng et al. mentioned so far.

Reply: We thank the reviewer for this suggestion. In the revised manuscript, we have incorporated previously reported porewater data from the eastern Pacific shelf (including both Fe-bearing and Fe-depleted systems), methane seep environments, and the Pigafetta Basin in the northwestern Pacific (our study area) encompassing both secondary REY-release porewaters and seawater-dominated porewaters. These data have been compared and discussed alongside the REY patterns of the REY-rich intervals in our study. These additions significantly strengthen the evidence chain of our work and substantially enhance the robustness and persuasiveness of our arguments.

“The REY distribution patterns of the REY-rich layer in core GC112, normalized to Post-Archean Australian Shale (PAAS) and Pr^{3,49}, displayed relative MREE enrichment and a negative Ce anomaly (red squares in Fig. 2d). These patterns were distinct from Fe-rich hydrothermal fluids (positive Eu anomaly; brown line in Fig. 2d)⁴ and methane-rich sulfidic settings (HREE-enriched; light blue line in Fig. 2d)⁵⁰. Compared to eastern Pacific shelf sediments, the MREE-enriched signature more closely resembled Fe-bearing porewaters (dark gray line in Fig. 2d) than Fe-depleted porewaters (light gray line in Fig. 2d)^{3,15}. Similarly, the MREE/MREE ratio (1.45 ± 0.03) was comparable to secondary REY-released porewaters from the Pigafetta Basin (1.32; yellow squares in Fig. 2d)¹², but distinct from seawater (0.74; light green line in Fig. 2d)⁵¹ and seawater-dominated porewaters (0.83; blue squares in Fig. 2d)¹², both of which showed HREE enrichment. The negative Ce anomaly ($Ce/Ce^* = 0.33 \pm 0.10$) was intermediate between seawater (0.07)⁵¹ and secondary REY-released porewaters (0.42)¹², lying closer to the latter (Fig. 2d).”* **Lines 156-169**

“The preferential adsorption of MREEs and Ce⁴⁺ onto Fe-Mn (oxyhydr)oxides yields MREE-enriched patterns and a weaker negative Ce anomaly in porewaters, distinct from seawater signatures (Fig. 2d)²². This finding is consistent with REY patterns in Fe-bearing porewaters from the eastern Pacific shelf³ and secondary REY-release porewaters from the northwestern Pacific¹². Ultimately, these geochemical signals are preserved in deep-sea sediments²².” **Lines 285-290**

In general: Pore water data (oxygen, nitrate, dissolved Mn, Fe, REY) for the presented core would be beneficial to support the claims about Fe and REY cycling in these deep-sea sediments.

Reply: As you rightly noted, porewater data play a crucial role in supporting interpretations of iron and rare earth element cycling in deep-sea sediments. Since porewater geochemical parameters (e.g., Fe, Mn, dissolved oxygen) were not measured during the sampling of core GC112, we have addressed this gap by referencing relevant previous studies. Specifically, Deng et al. (2022)¹ reported porewater Fe, Mn, and nitrate data from sediments in the Pigafetta Basin—the same area as our study.

Furthermore, data from Du et al. (2025)² and D'Hondt et al. (2015)³ indicate that deep-sea sediments in highly productive regions of the northwestern and equatorial Pacific transition from oxic to suboxic conditions within the upper few centimeters, with dissolved oxygen declining from >100 μM to <20 μM . These datasets collectively provide robust supporting evidence for our findings.

Methods

L354ff: precision, accuracy and blanks should be reported for the major elements, the REY and other trace elements.

Reply: The precision, uncertainty, and blank values for the major and trace element analyses have been added to the Materials and Methods section and the Supporting Information (Table S1).

“Procedural blanks were below the instrument detection limits, and analytical precision was better than 5% for all elements (Table S1). Analytical accuracy, verified using the GSD-9 reference standard, showed uncertainties ranging from -3.5% to +4.1% for all elements (Tables S1).” **Lines 476-479**

L363ff: procedural blanks and replicate analyses results should be reported for Fe isotope data.

Reply: The procedural blanks, internal precision, and external reproducibility for the iron isotope analyses have been supplemented in the Materials and Methods section and the Supporting Information (Table S2).

“For Fe isotope analysis, aliquots (50 mg) of samples were sequentially digested with 1:1 (v/v) HF-HNO₃ and 3:1 (v/v) HCl-HNO₃ mixtures, followed by evaporation to dryness. The residues were dissolved in 1 mL of 8 M HCl containing 0.001% H₂O₂ and purified using AG-MP-1M resin. Matrix elements (e.g., Na, Mg, Al, K, Ti, Mn, Ni, Ba, REY) were eluted with 9 mL of the same solution, Cu with 28 mL, and Fe was collected with 16 mL of 0.5 M HCl ⁷¹. Iron isotopes were measured using a Nu Plasma 1700 multi-collector ICP-MS (MC-ICP-MS; Nu Instruments, UK), with procedural blanks confirming negligible contamination. Mass bias and instrumental drift were corrected by sample-standard bracketing using IRMM-14. Repeat analyses yielded internal precision better than 0.03‰ (2 σ) and external reproducibility better than 0.04‰ (2 σ ; Table S2).” **Lines 484-494**

References

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- 2 Du, J. H. *et al.* Abyssal seafloor as a key driver of ocean trace-metal biogeochemical cycles. *Nature* **642**, (2025).

- 3 D'Hondt, S. *et al.* Presence of oxygen and aerobic communities from sea floor to basement in deep-sea sediments. *Nat. Geosci.* **8**, 299-304, (2015).
- 4 Wang, P. C. *et al.* Impact of iron biogeochemical cycling in deep-sea environments on rare earth element enrichment. *Chem. Geol.* **692**, 122951, (2025).
- 5 Fan, W. X. *et al.* Carbonate fluorapatite coatings on phillipsite represent a significant sink of phosphorus in abyssal plains of the western Pacific Ocean. *PNAS* **122**, e2407683122, (2025).
- 6 Wang, H. F. *et al.* Dominant eccentricity cycles in paleoenvironmental variabilities recorded by pelagic sediments in the Western Pacific during 15-11 Ma. *Palaeogeogr. Palaeocl.* **628**, 111776, (2023).
- 7 Liu, Y., Jing, Y. T. & Zhao, W. C. Distribution of rare earth elements and implication for Ce anomalies in the clay-sized minerals of deep-sea sediment, Western Pacific Ocean. *Appl. Clay Sci.* **235**, 106876, (2023).
- 8 Zhao, M. *et al.* Drivers of the global phosphorus cycle over geological time. *Nat. Rev. Earth Env.* **5**, 873-889, (2024).
- 9 Byrne, J. M. *et al.* Redox cycling of Fe(II) and Fe(III) in magnetite by Fe-metabolizing bacteria. *Science* **347**, 1473-1476, (2015).
- 10 Wang, P. C. *et al.* Changes in magnetic properties of magnetite nanoparticles upon microbial iron reduction. *Geochem. Geophys. Geosy.* **23**, e2021GC010212, (2022).
- 11 Deng, Y. N. *et al.* Early diagenetic control on the enrichment and mobilization of rare earth elements and transition metals in buried ferromanganese crust. *Mar. Geol.* **469**, 107238, (2024).
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- 13 Chang, L., Heslop, D., Roberts, A. P., Rey, D. & Mohamed, K. J. Discrimination of biogenic and detrital magnetite through a double Verwey transition temperature. *J. Geophys. Res.-sol. Ea.* **121**, 3-14, (2016).
- 14 Ren, J. B. *et al.* Mechanism and influencing factors of REY enrichment in deep-sea sediments. *Minerals* **11**, 196, (2021).
- 15 Chen, Y. *et al.* In-situ geochemistry of fish teeth in REE-rich mud: Indicating missing REE-bearing mineral phases for mass balance. *Ore Geol. Rev.* **184**, 106746, (2025).

Dear Editor

We would like to extend our sincere gratitude to you and the reviewers for the thorough and constructive feedback on our manuscript. Your comments have been invaluable in significantly improving the quality of our work. We have taken this revision opportunity very seriously and have addressed all the points raised by you and the reviewers point-by-point in the revised manuscript.

In accordance with the journal's formatting guidelines regarding titles (specifically, the preference to avoid punctuation such as colons), we have carefully revised the title to: “**Microbial iron cycling illuminates the biological contribution and potential climate drivers of deep-sea rare earth element enrichment**”. We believe this updated title adheres to the journal's style while fully retaining the original meaning. All changes made within the manuscript have been highlighted in red for easy identification. Our detailed point-by-point responses to the comments are provided in blue text below. Furthermore, we have addressed your editorial suggestions regarding manuscript formatting in the “Editorial Requests Table”.

Overall, it has been a rewarding experience submitting our work to your journal. We deeply admire the professionalism and dedication demonstrated by you and the reviewers. Thank you once again for your time and effort.

Reviewer #1:

This is a revised version of a manuscript that I have previously reviewed. I consider that the authors have comprehensively implemented their revisions according to my comments and suggestions, which, I admit, were exhaustive. I appreciated reading the revised manuscript as well as the efforts of the authors to disentangle complex pre- and post-depositional processes. I have only minor comments and wording suggestions to support the authors' line of arguments in the introduction and discussion. I used nota bene (n.B.) where clarifications are needed. Once addressed, I can endorse acceptance of the manuscript for publication.

Reply: We sincerely thank you for your thorough and insightful review of our manuscript. Your valuable comments have been crucial in refining and enhancing the quality of this work. Moreover, several of your thought-provoking perspectives have provided meaningful inspiration for our future research directions. We genuinely appreciate your efforts. In response to your suggestions, we have carefully addressed

each point in the revised manuscript and provide our detailed responses below.

Minor comments and suggestions

- 1. 5-9: I would suggest inverting the order of these sentences as follows:

The migration of REY from marine particles (e.g. Fe-Mn (oxyhydr)oxides or organic matter) to apatite is a prerequisite for subsequent enrichment during early diagenesis. Thus, bioapatite and authigenic apatite act as final sinks for REY and thereby represent key reservoirs in deep-sea sediments. However, the underlying forces driving this migration process remain unresolved.

Reply: We fully concur with your suggestion, as it is instrumental in significantly enhancing the logical flow of the abstract. We appreciate your guidance.

In line with your comments and in accordance with the journal's guidelines on abstract structure, we have thoroughly reorganized the content of the abstract. The revised version aims to achieve an optimal balance among professionalism, logical coherence, readability, and conciseness. The specific modifications are detailed below.

“Deep-sea sediments enriched in rare earth elements represent important potential resources and paleoceanographic archives. The transfer of these elements from marine particles (e.g., Fe-Mn (oxyhydr)oxides or organic matter) to phosphate phases is essential for their enrichment during early diagenesis. However, the biogeochemical processes driving this transfer remain unresolved. Here we investigate how microbial reductive diagenesis influences rare earth element enrichment in deep-sea sediments of the northwestern Pacific. By integrating geochemical, magnetic, and microscopic analyses of iron biogeochemical cycling and its signature mineral, biogenic magnetite, we demonstrate that microbial reduction drives the post-depositional mineralization of sinking marine particles. This process releases rare earth elements into porewater, thereby promoting their uptake into bioapatite or authigenic apatite. This mechanism was likely enhanced during past global cooling events that increased ocean productivity. Our findings provide valuable insights for tracing microbial contributions to deep-sea rare earth element enrichment and for investigating their underlying drivers.” **Lines: 2-16.**

- 1.10: iron metabolism --> iron biogeochemical cycling

Reply: We thank you for your valuable suggestion. It has been implemented in the

revision. *Line 9.*

- l. 11 microbial element cycling --> microbial reductive diagenesis

Reply: Thank you for your suggestion. Revised. *Line 7.*

- l. 12: Through an integrated analysis of --> Integrating...

Reply: Thank you for your suggestion. Revised. *Line 8.*

- l. 13: there is no data documenting “activity” which implies these processes are ongoing --> reduction

Reply: Thank you for your suggestion. Revised. *Line 10.*

- l. 14: degradation or phase transformation --> driving mineralization of marine particles after deposition

Reply: Thank you for your suggestion. Revised. *Lines 10-11.*

- l. 16: “This mechanism may be particularly important during periods of significant global climate variability.” I find this statement a bit vague.

n.B. What I understood from the authors’ answers to my comment and my lecture of the revised manuscript is that there was increased wind transport of dust particles during the Late Miocene glacial period, which combined with upwelling conditions, stimulated productivity in the Fe-limited pelagic ocean. Sedimentation of Fe-Mn oxides would scavenge orthophosphate under OMZ conditions and strong bottom currents, resulting in condensed strata acting as precursors for REY-enriched apatitic layers. If correct, could the authors rephrase to better convey this specific conditions?

Reply: We thank you for this suggestion. We fully concur with your perspective. Accordingly, we have revised the abstract to explicitly state the positive role of global cooling-induced increases in marine primary productivity in promoting deep-sea rare earth element enrichment.

“This mechanism was likely enhanced during past global cooling events that increased ocean productivity.” **Lines 13-14.**

- l. 44: ultimate --> final

Reply: Thank you for your suggestion. Revised. *Line 40.*

- l. 45: The extreme concentration contrast of $\sim 10^{12}$ --> The contrast of concentrations by twelve orders of magnitude

Reply: Thank you for your suggestion. Revised. *Line 42 and Line 265.*

- l. 47: cycling --> mineral phase element transfer via...

Reply: Thank you for your suggestion. Revised. *Line 44.*

- l. 69: for Eh and pH during microbial iron reduction and diagenetic redistribution across phases via pore water, cite: Vuillemin et al. (2023) Authigenic minerals reflect microbial control on pore waters in a ferruginous analogue. *Geochem Perspect Lett* 28

Reply: We appreciate your valuable suggestion. We have thoroughly reviewed the referenced study and refined our manuscript's description accordingly.

“Under specific geochemical conditions (e.g., particular pH and Eh ranges), microbial respiration processes such as aerobic, nitrate, Fe-Mn, and sulfate reduction may be key drivers of REY redistribution, primarily by facilitating the degradation of organic matter and the reduction of metal (oxyhydr)oxides^{23,30}.” **Lines 64-68.**

- l. 71-72: not much the lowering of temperatures, but rather wind intensities and their location at higher latitudes due to the waxing of ice caps.

Reply: We thank you for your valuable suggestion. We fully concur with your professional assessment and have refined the relevant passages in the manuscript accordingly.

“Against the backdrop of Cenozoic global cooling, the expansion of polar ice sheets enhances surface ocean productivity by intensifying and shifting global surface wind fields (due to a steeper latitudinal temperature gradient)³¹⁻³³.” **Lines 69-71.**

n.B. I realize that this is out of the scope of the manuscript, but I have a pending question related to this: Do the authors know whether increased eolian transport of dust particles during this glacial period is also involved in the increased productivity or can this argument be discarded? I tend to think that dust particles and particulate OM are correlated (i.e. iron fertilization).

Reply: We sincerely thank you for raising this profound and thought-provoking question. Your insightful speculation regarding the potential role of enhanced dust flux

during glacial periods in stimulating marine productivity through the “iron fertilization effect” aligns well with current understanding of dust-climate feedback mechanisms, and we fully concur with this perspective.

A recent study published in *Nature Reviews Earth & Environment*¹, which synthesized global marine core records, clearly indicates a stepwise increase in dust flux against the backdrop of Late Cenozoic global cooling. The study emphasizes that dust served as a key iron source in glacial oligotrophic oceans, effectively boosting marine primary productivity. In light of this evidence, we agree that the “iron fertilization effect” resulting from increased dust input represents a plausible factor contributing to elevated productivity during glacial intervals.

While, as you rightly noted, a detailed demonstration of this process may extend beyond the primary scope of our initial manuscript, we have incorporated and acknowledged this important perspective in the revised Discussion section. This allows for a more comprehensive presentation of potential drivers behind glacial productivity changes. Furthermore, your comment has provided significant inspiration for our future research directions. We truly appreciate your valuable input, which has been crucial in enhancing the depth and breadth of our study.

- l. 77: Same here. Do the authors refer to an upwelling zone, an oxygen minimum zone, or both? ... The causes of OMZ are multiple (for instance Hawaii OMZ due to deep water stagnation, not productivity), same for the stimulation of surface productivity.

n.B. no need to extend on this topic, but please try to provide some clarifications. The TOC values argue against increased OM sedimentation. Increased dust particles could increase both productivity and scavenging of REY and phosphate during sinking.

Reply: We thank you for this suggestion, with which we fully agree. In the revised manuscript, we now explicitly state that increased marine primary productivity significantly influences both the expansion of the oxygen minimum zone and the alteration of redox conditions at the sediment-water interface. We further emphasize that marine particles, particularly organic aggregates derived from this productivity and dust particles from aeolian input, play a crucial role in scavenging rare earth elements and phosphate, a process that was significantly enhanced under this specific climatic background.

“The resultant increase in marine organic matter flux enhances ocean reductivity, manifested by an expanded oxygen minimum zone and a shift in surface sediments from

aerobic (dissolved O_2 (DO) > 87.5 μM) to suboxic (DO ~ 15.6-87.5 μM) conditions ³⁴. In accordance with the Redfield ratio (C:N:P $\approx$ 106:16:1), intensified heterotrophic denitrification under such conditions promotes phosphate accumulation in deep waters ^{21,34,35}. Furthermore, increased surface ocean productivity and/or enhanced eolian dust input under this climatic background enhances the scavenging of REY and phosphate by marine particles ^{23,36}. These conditions act synergistically, leading to the deposition of sedimentary precursors that enhance microbially mediated release of REY and phosphate into porewater, facilitating authigenic apatite precipitation ^{23,36}.” **Lines 71-81.**

- l. 79: I suggest to rephrase as follows: “...synergistically result in the deposition of sediment precursors promoting microbial mediation of REY release...”

Reply: Thank you for your suggestion. Revised.

“These conditions act synergistically, leading to the deposition of sedimentary precursors that enhance microbially mediated release of REY and phosphate into porewater, facilitating authigenic apatite precipitation ^{23,36}.” **Lines 79-81.**

- l. 81: what about sedimentation rates? --> e.g. due to very low sedimentation rates and microbial oxidative degradation of organic proxies...

Reply: We thank you for this suggestion. As highlighted in both the 'Geological Background' and 'Discussion' sections of our manuscript, deep-sea sedimentation rates are indeed very slow, with a rate of <0.5 m Myr⁻¹ documented in our study area. In accordance with your comment, we have revised the text and added the appropriate references.

“Nonetheless, due to very low sedimentation rates and microbial oxidative degradation of organic proxies ^{12,37}, the quantitative links among microbial activity, REY behavior, and climate drivers in deep-sea sediments remain poorly constrained.” **Lines 81-84.**

- l. 90: Be careful of the order you list your arguments, i.e. magnetotactic bacteria exhibit a pelagic lifestyle and usually thrive under microaerobic conditions (i.e. oxycline, pycnocline, chemocline). Thus, they are likely not involved in the geochemical evolution of pore waters, but may point to suboxic conditions in the water column and act as early degraders of sinking OM.

Reply: We sincerely thank you for this valuable and highly insightful comment. Your logical clarification regarding the ecological niche of magnetotactic bacteria and its biogeochemical implications is precise, and we fully agree with your perspective.

To address the less precise wording in the original manuscript, we have revised the relevant text in the updated version to state: *“By coupling organic matter degradation and iron (oxyhydr)oxides dissolution or phase transformation, this process plays a critical role in the mobilization and cycling of REY and phosphate among the water column, marine particles, sediments, and porewater²³.”* **Lines 89-92.**

- l. 99: a tracer recording past microbial activity

Reply: Thank you for your suggestion. Revised. **Line 101.**

n.B. I have a subsidiary question (l. 147): in organic-poor pelagic sediments, sulfate reduction aborts while fermentation proceeds (e.g. D'Hondt et al. 2019 Nat Comm 10; Vuillemin et al., 2020 mBio 11). Microbial production of H₂S promotes mackinawite-pyrite formation at the expense of other Fe²⁺-bearing phases. Is sulfate reduction influential on apatite formation? FeRB are usually versatile and can also evolve as fermenters...

Reply: We thank you for this critical question. You are correct that fermentation occurs in both deep-sea and shelf environments alongside respiration. In these settings, fermentation likely serves to break down complex organic macromolecules into simpler substrates (e.g., acetate, lactate, monosaccharides, or amino acids). These smaller molecules may represent more crucial electron donors for microbial respiration than the less bioavailable macromolecules.

We fully concur with the reviewer's perspective that sulfate reduction-promoted pyritization is a key process competing with microbial iron reduction. However, the manifestation, intensity, and ultimate outcome of this competition differ significantly between deep-sea and shelf environments:

1. Shelf environments, rich in organic matter, provide ample electron donors for both sulfate reducers and iron reducers. The resultant H₂S rapidly consumes dissolved Fe²⁺, leading to efficient sequestration as mackinawite-pyrite.
2. In organic-poor deep-sea sediments, electron donor scarcity limits microbial activity. Most labile organic matter is consumed in the upper sediment layers by aerobic respiration, denitrification, and iron/manganese reduction, leaving limited substrates

for sulfate reducers. Consequently, H₂S production is low, resulting in minimal iron sulfide formation.

Despite these stark differences, sulfate reduction, by coupling with organic matter degradation similar to other respiratory pathways, can still contribute to phosphate release into porewater and apatite crystallization. Nevertheless, this role is likely predominant in organic-rich shelf settings (e.g., upwelling zones, cold seeps) and plays a more subtle part in the oligotrophic deep sea.

- l. 156: previous findings, a reference is missing

Reply: Thank you for your suggestion. Revised. *Line 157.*

- l. 232: in the water column and at the sediment-water interface

Reply: Thank you for your suggestion. Revised. *Lines 235-236.*

- l. 240: in l. 222 you state that OM particles originate from surface primary productivity and here you mention organic phosphorus from riverine input. This is confusing. Does the orthophosphate necessary to apatite precipitation derives from, e.g. the sinking particulate OM or the same terrigenous dust that supplies Mn-Fe oxides, or both?

Reply: We sincerely thank you for this valuable comment and apologize for any confusion caused by the imprecise wording in our original manuscript.

You correctly pointed out the ambiguity regarding the sources of organic phosphorus. Following your suggestion, we have revised the relevant sentence to: *“Marine phosphorus is primarily derived from riverine inputs and subsequently transported to deeper layers via processes such as the biological pump and particle scavenging⁶³. For instance, compared to surface waters, the oxygen minimum zone exhibits relative phosphate enrichment due to pronounced nitrogen limitation^{21,34,35}. Ultimately, phosphorus is incorporated into sediments as organic particles or associated with Fe-Mn (oxyhydr)oxides⁶³.”* **Lines 243-248.**

This revision aims to clarify that: 1) riverine input is the primary initial source of marine phosphorus; and 2) this phosphorus is transported to sediments through pathways such as incorporation into organic particles by primary producers or adsorption onto marine particles like Fe-Mn oxides. Therefore, the orthophosphate involved in apatite precipitation can be derived from either the degradation of sinking particulate organic matter or the release of phosphorus associated with terrigenous dust-

derived Fe-Mn oxides. Both pathways can serve as sources of phosphate in pore waters.

We are grateful for your rigorous review, which has significantly improved the accuracy of our manuscript.

- l. 249-252: what about an accumulation of dissolved orthophosphate in OMZ waters and scavenging during sinking? It is now mentioned in the introduction, but discussed here.

Reply: We thank you for this correction. As suggested, we have supplemented the relevant content in the revised manuscript as follows:

“For instance, compared to surface waters, the oxygen minimum zone exhibits relative phosphate enrichment due to pronounced nitrogen limitation^{21,34,35}. Ultimately, phosphorus is incorporated into sediments as organic particles or associated with Fe-Mn (oxyhydr)oxides⁶³.” Lines 245-248.

- l. 264: the phosphate sink is clear, but the sources remain elusive.

Reply: We thank you for this correction and fully agree with your suggestion. To avoid the overly definitive description regarding phosphorus sources in the original manuscript, we have revised the relevant sentence in the updated version as follows:

“Phosphate entering the porewater can precipitate as authigenic apatite (mainly CFA) within hours to days, thus forming a key sink for REY^{18,36}.” Lines 271-273.

- l. 269: such as condensed sediment strata? Condensed strata imply strong bottom currents consistent with upwelling. These two climatic parameters could be clearly mentioned, i.e. the contribution of strong winds and bottom currents in upwelling regions

Reply: We thank you for this suggestion, with which we fully agree. The relevant content has been incorporated into the revised manuscript.

“Intensified ocean circulation and extremely low sedimentation rates ($<0.5 \text{ m Ma}^{-1}$) may promote REY enrichment via enhanced phosphorus burial, a process mechanistically similar to the formation of condensed strata⁶⁷.” Lines 275-278.

- l. 285: cite the corresponding figure here (Fig. 2a).

Reply: We thank you for pointing this out and apologize for the confusion caused by our unclear phrasing. The porewater data referenced here are from previous studies and

are not displayed in Fig. 2a. To eliminate any potential misunderstanding, we have revised the relevant text in the updated manuscript to read:

“As reported by previous studies, porewaters from the Pigafetta Basin intervals experiencing secondary REY release exhibit low concentrations of dissolved iron (~1 μM) and manganese (~0 μM), evidence which supports the dominance of mineral phase transformation versus reductive dissolution¹².” **Lines 290-294.**

n.B. I quite understand how you conclude mineral-phase transformation over reductive dissolution. However, in l. 235, you say that these elements show post-depositional decoupling, but in l. 270 you claim that migration, concentration, and sequestration are geologically instantaneous upon deposition at the seafloor. Later you argue that this is a stratigraphic transition related to past depositional (climatic) conditions, which somehow invalidates the statement in l. 235 which requires constraints on the duration of diagenetic processes.

Reply: We sincerely thank you for this extremely insightful and critical comment, and we apologize for the confusion caused by the ambiguous phrasing in our original manuscript.

Regarding “post-depositional decoupling”: Based on data from this study and previous work, we observed a weak correlation between REY and Fe-Mn (especially when compared to the strong correlation between REY and P-Ca). This led us to hypothesize that REY and Fe-Mn (oxy)hydroxides become decoupled during the early diagenetic stage after deposition. We acknowledge that, with the current data, the exact duration of this process remains unconstrained. It may be influenced by a combination of factors, including the timescales required for the secondary mineralization (or potential reductive dissolution) of Fe-Mn (oxy)hydroxides, the formation of authigenic apatite, and the equilibrium redistribution of REY into the apatite lattice.

Regarding “geologically instantaneous”: As noted, the diagenetic processes involving the release of REY and phosphate from carrier particles and their sequestration from porewater into minerals can occur over highly variable timescales, ranging from hours to thousands of years. For instance, REY incorporation into authigenic apatite may be synchronous with its formation (although subsequent enrichment is possible), whereas stable redistribution of REY into fish teeth may require 10^3 - 10^4 years. Nevertheless, compared to the geological time required to form a recognizable stratigraphic unit (on the order of millions of years in deep-sea sediments,

which may record a specific climatic event), these processes are relatively rapid and could thus be considered “instantaneous” within a stratigraphic context.

However, we recognize that the term “geologically instantaneous” used in the original manuscript was potentially misleading to readers and is not central to the main scientific questions addressed in our study. Consequently, we have omitted this specific phrasing from the revised manuscript.

- 1. 301: see my subsidiary question on sulfate reduction in organic-poor sediment

Reply: We thank you for this suggestion. The role of fermentation has now been incorporated into the revised manuscript, along with explanations regarding the factors that constrain different microbial metabolic processes in various environments.

“Under suboxic or anoxic conditions, microbial metabolisms such as fermentation, nitrate, Fe-Mn, or sulfate reduction and methanogenesis may also facilitate REY mobilization from particles into porewaters⁵³. The dominant metabolic pathways, however, are strongly governed by sedimentary conditions such as the abundance and type of available substrates^{28,53}.” **Lines 308-312.**

- 1. 313: mention that this corresponds to “condensed sediment strata” aka hardground. Such phosphate or glauconite condensed strata in the geological rock record are considered to correspond with past upwelling conditions

Reply: We thank you for pointing this out. The corresponding content has been supplemented in the revised manuscript.

“The concomitant degradation of organic matter and release of phosphate during these processes further promote REY release and authigenic apatite crystallization^{16,18,23,62}, a phenomenon potentially driven by enhanced deep-sea phosphorus burial under low sedimentation rates and intensified ocean circulation, analogous to the genesis of condensed sediment strata⁶⁷.” **Lines 319-323.**

- 1. 323: what about eolian transport? Upwellings are associated with stronger winds and currents

Reply: We thank you for this observation. The role of eolian transport has been duly noted and incorporated into the revised manuscript. As you rightly pointed out, this process likely exhibited an intensified trend under the specific climatic context discussed in our study. We agree that future investigations should incorporate additional

parameters and techniques to trace this process in greater detail, and we appreciate your insightful suggestion in this regard.

“Consistent with this interpretation, the sediment iron content is close to the upper continental crust average, suggesting a dominant terrigenous eolian dust source; this contrasts with the elevated iron levels in hydrothermally influenced East Pacific sediments^{23,37}.” **Lines 331-334.**

- l. 332: the focus is usually on framboidal magnetites as pelagic precipitates not related to magnetosomes.

Reply: We thank you for this observation and fully agree with your perspective. In the revised manuscript, we have reorganized the logical flow of these sentences to address the lack of rigor in the original phrasing and citations.

“Culture experiments confirm that biogenic magnetite is enriched in light iron isotopes, with DIRB-produced magnetite showing $\Delta^{56}\text{Fe}$ values of -2.6‰ to -1.3‰ relative to the substrate⁷⁰. These isotopic signatures have been instrumental in identifying microbial magnetite origins in banded iron formations^{42,44}. In contrast, magnetosome magnetite exhibits a narrower range of -2.5‰ to -1.5‰ ⁴⁶.” **Lines 338-342.**

- l. 360-372: this part is not really necessary as it doesn't convey explanations. Just keep the sentence l. 365-368 with the citation.

Reply: We thank you for this correction. The manuscript has been revised accordingly based on your suggestion.

n.B. a word of caution about l. 367, metagenomic predictions do not prove activity (i.e. metatranscriptomes). The DNA could derive from resting stages and dormant cells, thus correspond to the stratigraphic age, not an active microbiome in subsurface sediments. It seems plausible that microbial iron reduction took place during particle sinking, at the sediment-water interface (resulting in condensation and phase transition), then likely at much slower rates during burial due to organic substrate depletion.

Reply: We are deeply grateful for this profound and crucial insight. You have correctly highlighted the essential distinction between metagenomic predictions and the demonstration of actual microbial activity, while also providing a more compelling

interpretation of the temporal scale of microbial iron reduction. We fully accept your perspective and sincerely apologize for any misunderstanding caused by the original text.

Following your suggestion, we have revised the manuscript. The updated version now clearly states that the metagenomic data indicate the presence of relevant microbial functional genes, without directly equating this with active metabolic processes. Furthermore, the role of microbial iron reduction is now specifically constrained to the mineralization period to avoid confusion with subsequent burial stages.

Your invaluable comments have significantly enhanced the rigor and scientific accuracy of our discussion. We have fully incorporated these suggestions into the revised manuscript and wish to express our sincere gratitude once again for your thorough and rigorous review.

“A higher abundance of metal-reduction genes in REY-rich layers compared to background sediments, as shown by prior metagenomic studies ²³, implies a potentially more active role of microbial metal reduction during mineralization, offering partial support for our hypothesis.” Lines 370-373.

-l. 391-393: future work is not relevant to discussion of the data produced

Reply: Thank you for your suggestion. Revised.

- l. 394-395: delete the first half of this sentence and move to l. 391 after deletion of the sentence about future work

Reply: Thank you for your suggestion. Revised.

- l. 425: define abbreviation at first mention in the text

Reply: Thank you for your suggestion. Revised. *Line 422.*

- l. 430: here again, the TOC argues against increased OM sedimentation. Was all the primary OM degraded during sinking? Was it reworked by strong bottom currents? Are we talking about another type of OMZ (i.e. deep water stagnation)?

Reply: We are profoundly grateful for this extremely insightful and critical comment. As you rightly highlighted, deep-sea organic matter undergoes extensive degradation during settling and early diagenesis. Although data indicate that this organic matter is not completely consumed (TOC is very low but not zero), intense degradation masks

the signal of productivity increases during certain climatic events, resulting in minimal vertical variation in the ultimately buried organic carbon pool in deep-sea sediments. For example, in our study, the TOC in productivity-enhanced intervals (i.e., REY-enriched layers) is only marginally higher than in background layers.

We propose that the REY enrichment process likely depends more on the *flux* of organic matter settling induced by climatic factors (e.g., sea surface wind intensity, terrigenous weathering input, bottom current intensity) rather than the final *burial amount*. Even if most organic matter is rapidly consumed during settling and at the sediment-water interface, its degradation is sufficient to drive microbial reduction reactions in the shallow subsurface, thereby triggering the release of key ore-forming elements (REY and P).

We strongly agree with your point regarding the impact of vigorous bottom current reworking. The tectonic and paleoceanographic setting of the study area supports the presence of strong bottom currents. Their winnowing action removes fine-grained particles, and the dissolved oxygen they carry supports the oxidative degradation of organic matter. This reworking perfectly explains the combination of high organic matter degradation flux (supporting mineralization) and low final organic matter burial (low TOC) during the REY enrichment period.

Furthermore, we posit that the redox environment in this region was primarily controlled by water column chemistry and sediment-water interface processes, rather than large-scale deep-water stagnation and anoxia. The suboxic conditions required for mineralization were created locally, at micro-scales, by microbial metabolism within the sediments.

Your invaluable comments have compelled us to make crucial refinements to our model. The revised discussion no longer treats the low TOC content as counter-evidence but integrates it as an inevitable consequence of the high-degradation, intense-reworking depositional environment. This makes the overall metallogenic model more dynamic and compelling. We extend our sincere thanks once again for your rigorous and insightful review.

“Under these conditions, increased nutrient supply from both deep waters and terrigenous eolian dust stimulated primary productivity, leading to an elevated flux of organic matter to the seafloor (Fig. 6a) ^{31-33,35,76}. The consequent rise in oxygen consumption during organic matter mineralization contributed to an expansion of the oxygen minimum zone and a shoaling of the oxygen penetration depth in deep-sea

sediments^{16,34}. This sequence of processes began in the eastern Pacific (~15.1 Ma) and propagated westward on a million-year scale, reaching the western Pacific by ~13.6 Ma³¹. ” **Lines 426-433.**

“Subsequent microbial-mediated organic matter degradation and Fe-Mn (oxyhydr)oxides phase transformation in surface sediments, alongside abiotic processes (e.g., sorting and reworking by vigorous deep-water circulation^{35,37}), facilitated the release of REY and phosphate into porewaters, creating favorable conditions for their ultimate sequestration into phosphate phases (Fig. 6a)^{23,76}. ” **Lines 436-440.**

- l. 455: delete “It is important to emphasize that”

Reply: Thank you for your suggestion. Revised.

Fig. 6: typos --> the “laate” Miocene “coooling” event

Reply: Thank you for your suggestion. Revised.

Reviewer #2:

"The biological contribution and potential climate drivers of deep-sea rare earth element enrichment: Insights from microbial iron cycling" by Pengcong Wang et al.

The authors have carefully addressed the reviewers' comments. In particular, regarding the aspect that initially drew my attention, there have been substantial improvements in the distinction and characterization between authigenic and biogenic phosphate. The revised version clearly demonstrates the predominance and significance of authigenic phosphate formation in controlling REY enrichment, as originally hypothesized. Moreover, the discussions on the climatic and diagenetic mechanisms responsible for the formation of the REY-enriched layer have been substantially improved, making the proposed hypothesis much clearer and more coherent.

For these reasons, I consider that the revision has satisfactorily addressed the previous concerns and has significantly improved the overall quality of the manuscript. I am therefore in favor of its acceptance for publication in *Communications Earth & Environment*.

Reply: We are delighted to learn that the reviewers support the publication of our manuscript in *Communications Earth & Environment*. We extend our sincere gratitude

to the editor and reviewers for the time, profound insights, and constructive guidance provided throughout the peer-review process. The positive feedback from the reviewers, particularly their recognition of the significant improvements in distinguishing authigenic phosphate phases and the clearer discussion of the climate-diagenesis mechanism, has been greatly encouraging. We are pleased that the revisions have successfully addressed the previous concerns and enhanced the overall quality of the paper.

References

- 1 Zan, J. B. *et al.* Global dust impacts on biogeochemical cycles and climate. *Nat. Rev. Earth Env.*, (2025).

The overlooked role of microbial iron cycling for the enrichment of rare earth elements in deep-sea sediments

Summary

This manuscript addresses the potential role of dissimilatory iron reduction (DIR) in the migration and condensation of Rare Earth Elements (REE) from marine particulates into authigenic REE-enriched ores. Combining mineralogy of the magnetic fraction with pore water geochemistry, iron isotopes, and functional marker genes from a sediment core retrieved from 5700 m water depth in the Pigafetta Basin, western Pacific, the authors define an alternative diagenetic pathway potentially driven by microbial redox processes that can lead to an enrichment of REE in apatite concretions.

Based on the presence of multiple domain nano-magnetites, negative $\delta^{56}\text{Fe}$ values (-0.08‰), bulk sediment and pore water REE concentrations, the identification of specific taxa and functional marker genes involved in extracellular respiration, the authors claim that DIR exerts significant control on REE sorption processes, leading to in-situ formation of phosphate ores via dissolution/precipitation of transient iron oxides with adsorption in bottom waters and condensation in pore waters. Finally, global climate dynamics (i.e. productive upwelling conditions) are taken into account in the accumulation of biogenic phosphates.

(I) What are the major claims of the paper?

Microbial dissimilatory iron reduction could represent an alternative early diagenetic pathway explaining REE condensation and formation of authigenic ores through sorption processes driven by iron-reducing bacteria.

(II) Are these claims novel, and will they be of interest to others in the community?

Biotic/abiotic and pelagic/benthic processes have to be better distinguished as to clarify the diagenetic sequence and differential timing of in-situ formation of magnetite and apatite. The authors could provide constraints in terms of sources and sinks (Fe(II)-Fe(III), organic/mineral PO_4^{3-} , REE in hydrothermal fluids and seawater).

Furthermore, abiotic fractionation of Fe isotopes due to partial oxidation of ferrous to ferric Fe could produce poorly crystalline (pelagic) magnetites exhibiting slightly negative $\delta^{56}\text{Fe}$ values during mixing of hydrothermal fluids with seawater. This has not been considered (or occulted as common knowledge?) although it is an essential part of the discussion.

Although apatitic phosphate concretions are known to form as diagenetic products in marine sediments, phosphate sources, their scavenging by iron oxides prior to deposition and transformation from organic to authigenic during time of burial are not introduced either. Environmental conditions at the time of deposition (e.g. upwelling, productivity, intraplate tholeiitic iron-rich volcanism, hydrothermal activity) have to be introduced and discussed in parallel, not limited to the final part of the discussion. Otherwise, the manuscript gives the impression of being deliberately biased in favor of the research hypothesis.

(III) Is the work convincing, what further evidence would be required to strengthen the conclusions?

The abiotic hypothesis seems to have been dismissed a little too quickly, and the line of argumentation chosen by the authors remain highly speculative:

- Crystallographic analysis of microdomain and single-domain magnetites (assumed to reflect microbially-mediated magnetite and magnetosome, respectively) complemented by $\delta^{56}\text{Fe}$ values around -0.08‰ do not constitute sufficient evidence that enable the distinction between microbial iron reduction and mixing of hydrothermal fluids with seawater. Abiotic (oxidative) processes and sources of iron and REE are not addressed in sufficient detail.

- The only pore water geochemical data documented in this manuscript are REY concentrations. Rare Earth Elements being mostly redox-conservative, they may possibly reflect bottom water conditions at the time of deposition (e.g. negative anomaly of $\text{Ce}^{3+/4+}$), or release after microbial reduction of Fe(III) oxides. To infer metal reduction processes after deposition, additional pore water geochemical data are needed (e.g. Fe^{2+} , Mn^{2+} , As^{2+} , trace metals).
- There is no characterization of the sediment organic fraction (e.g. TOC) and some contradictory statements are scattered throughout the manuscript (minimal organic content, sediment anoxic conditions due to organic mineralization). Interpretations in terms of microbial reduction of iron and organic matter mineralization have to be supported by additional downcore profiles (i.e. the authors' own data, not literature).
- The metagenomic data (only available for download on Zenodo) are succinct and do not clearly establish metabolic potential for dissimilatory iron reduction (DIR), or magnetosome formation. The taxa reported in this supplement are mostly aerobes, likely originating from environments that would argue against post-depositional microbial processes, i.e. oceanic bottom waters (e.g. *Limnobacter*, *Muricauda*) and hydrothermal vents (*Thermoanaerobaculia*). The sequence data has to be submitted to a public repository and an accession number provided to the reader.
- In the absence of clear functional marker genes for DIR, metagenomic data was tested using the FeGenie pipeline but not consistently reported, e.g. siderophores, magnetosomes, and Fe(II/III) redox processes, Fe regulation. The few functional genes selected to identify metabolic potential for DIR were identified at very low read counts. These predicted genes relate to the multiple heme cytochrome C reductase (not specific to metal reduction) and extracellular respiration electron transfer (nanowires are not common in sediments)..
- In the final part of the discussion, the authors mention that past upwelling conditions (ca. 12 Ma ago) could explain phosphate accumulation at the seafloor. More background information on sedimentary conditions that led to phosphate concretions are necessary. Indeed, iron oxides expelled during hydrothermal activity could trap both REY and orthophosphates. The authors have to distinguish between pelagic and benthic processes, as well as disentangle biotic-abiotic processes, in order to provide time constraints on magnetite and apatite in -situ formation.

(IV) do you feel that the paper will influence conceptual understanding or technological capability?

At this stage, evidence for microbial processes of metal reduction is not compelling. Additional SEM/TEM images of magnetite could be produced as a single grain is documented (Fig. 4). Please provide additional SEM/TEM images in the supplement.

Specific comments

Introduction: Some basic background information on REE is missing (e.g. redox states, hydrothermal release, distribution and type of ores)

- l. 24: Add "Understanding the mechanisms... is vital"
- l. 27: migration rather "dissolution and subsequent incorporation"; organic matters --> organic matter
- l. 30: the authors do not document or report biological data *per se*
- l. 31: datasets --> data
- l. 33-37: this mechanism is known and referred to as "diagenetic redistribution of iron".
- l. 45: REY deposits, be more specific, what type? Polymetallic nodules, massive sulfide deposits, phosphatic concretions, else?
- l. 51: what about the initial sources and mechanisms releasing REY in marine waters? Detrital sources, basalt alteration and hydrothermal vents, global versus local processes? What are the common REY concentrations in seawater? There is no mention of their very low initial concentrations and necessity to condense them to obtain minable ores, what these ores are and where they are usually found...

- l. 53: re-released --> solubilized, released and thereby concentrated in the pore water / how can REE³⁺ substitute for Ca²⁺ in the crystal lattice of apatite? How is the charge imbalance equilibrated?
- l. 54: provide the normal formula of apatite; what about anapaite which commonly forms concretions in marine environment?
- l. 56: crystallization-dissolution, rather dissolution-precipitation cycles. Do this imply Oswald ripening and transient phases?
- l. 63: are these values corresponding to cell densities in seawater or sediments? Sediment --> marine sedimentary environments (cells × cm³, not mL⁻¹)
- l. 65: ...whose underlying sediments are characterized (D'Hondt et al., 2019 does not address microbial populations in the water column).
- l. 64-66: most of the deep-sea offshore cannot be considered productive. The authors likely refer to the surface ocean but productivity in the ocean offshore is limited. Coastal upwelling zones along trenches constitute specific cases. Be specific in what "spatial coupling" encompasses.
- l. 68: what are the initial sources of iron and REEs prior to reduction in the sediment and release in the pore water?
- l. 70-71: BIFs are considered chemical precipitates and this analogy seems out of context; (I) some additional words of introduction on the "Redfield ratio" and nitrogen limitation due to heterotrophic denitrification in highly productive waters are needed since this results in an accumulation of orthophosphate in bottom waters and sediments (e.g. upwelling zones, Peru and Namibian OMZs); (II) mention that phosphorus does not have a redox cycle and that this is driven by scavenging and reduction of Fe(III)-Fe(II).
- l. 73: This sentence doesn't make sense. How does metabolic degradation of organic matter prevent documenting microbial activity?
- l. 78: what about siderophores?
- l. 81: In sediments, Fe²⁺ can react with other solutes as well, after sulfate reduction (FeS₂) or fermentation (FeCO₃). The precipitation of microbially-induced pelagic magnetites requires stratified conditions and the authors should clarify when they refer to pelagic or benthic processes.
- l. 85: Iron is the main limiting nutrient in open ocean productivity, so where is it coming from? Same question for the organic matter. See comment l. 64-66.
- l. 87: what about magmatic and hydrothermal processes enriching LREE in the fluid phase? See comment in l. 51, i.e. local vs global processes
- l. 88: biogenic magnetites, you mean both or magnetosomes only. In theory, magnetite can be further reduced during DIR, the smaller the crystals the more reactive.
- l. 91: reliable biomarker? Be specific in what biogenic magnetites are. Magnetosomes constitute biomineralization, whereas magnetite precipitates are simply induced during DIR. / microbial activity --> microbial redox cycling of metals
- l. 92: unclear whether the authors refer to magnetosomes in particular. The structural Fe(III) of magnetites can be further reduced in the sediment during microbial diagenesis.
- l. 94: can one really speak of REE cycling? Except for Cerium (3+/4+) and Europium (2+/3+), REEs are not subject to redox cycling.
- l. 96: the manuscript does not present metagenomic data

Geologic background: Succinct, what about hydrogenetic nodules found around seamounts? Here, one could argue for abiotic processes of REE enrichment and provide information on past upwelling and intraplate tholeiitic volcanism.

- l. 107: zeolitic clay --> hydrothermal alteration of basalts not introduced
- l. 108: minimal organic matter with occasional terrigenous inputs --> data not shown
- l. 110: Figure 1 does not display sediment depth nor age

Results: Some introduction on the influence of the iron shuttle (sources and sinks) and reductive remobilization on $\delta^{56}\text{Fe}$ values are missing. Metagenomic data are not presented in the main text or in the supplement (a succinct table is available on zenodo for download). Sequencing data should be made available in a public repository. The authors have to better differentiate between pelagic and benthic processes.

- l. 121-127: abiotic oxidation/reduction processes also fractionate Fe isotopes, the residual phase (i.e. oxidized) being systematically enriched in the heavy Fe isotope. Moreover, $\delta^{56}\text{Fe}$ of -0.08 ‰ does not reflect an enhanced microbial fractionation compared to magmatic values (0.00 ‰). These values could also be interpreted in terms of partial oxidation of hydrothermal Fe(II) during mixing of hydrothermal fluids with seawater. As samples are from below the CCD, a depletion in carbonate-bound Fe phases is not surprising. Moreover, these are bulk measurements that do not take into account the speciation of iron phases.
- l. 131: explain what a Cerium negative anomaly implies, i.e. remains in solution under reducing conditions
- l. 137: ferromagnetic, ferrimagnetic, diamagnetic or paramagnetic minerals?
- l. 139-157: very technical part
- l. 160: magnetic particle form aggregates, could this be a preparation artifact since magnetic minerals always tend to aggregate?
- l. 168: can the authors provide information on accumulation of biogenic apatite, e.g. hard ground, condensed facies, else? Some words on forms of phosphorus (organic, inorganic, apatitic, authigenic) are also needed in order to address the transformation from organic into authigenic forms during burial. It is also worth mentioning that apatite represents the main form of authigenic phosphate in the marine environment compared to anapaite or vivianite. Then, the authors should provide some constraints on the environment and time of formation for both magnetite and apatite.

n.B. if the main source of phosphorus is actually organic and relates to past upwelling and productive conditions, this should be brought earlier in the text, not briefly mentioned at the end.

- l. 173-175: provide full names of enzymes in a supplementary table, not gene abbreviations. Moreover, there are no specific functional marker genes for dissimilatory iron reduction. These genes are involved in extracellular respiration and electron transfer via nanowires (with multiheme cytochrome c), unlikely to take place in the sediment, rather at the paleo sediment-water interface. Iron is not the only substance that can be reduced with the multiheme cytochrome. Obviously, magnetosomes are not formed in the sediment either.

n.B. metagenomic data are reported in the results, but not presented in any figure of the manuscript.

Currently, these data are buried in a zenodo data dump without their corresponding metadata or accession number. Looking at this zenodo supplement, I found few information on very low number of reads assigned to Thermoanaerobaculia (identified from hydrothermal vents), Acidobacteria (high taxonomic level, no inference possible), Photobacterium sanguinicancris (bioluminescent symbiont), Photobacterium frigidophilum (facultative anaerobe common in deep-sea waters and sediments), Vibrio sp., Limnobacter sp., Muricauda sp., Stenotrophomonas nitritireducens, none of which appear to be involved in dissimilatory reduction of iron or magnetosome formation (accounting for RPKM <0.15‰). Please report the FeGenie output consistently. Although detection is higher in the REE-rich layer, they are far from being overrepresented. Also, there is no evidence that the predicted metabolisms could have been active after deposition and during burial.

Discussion: The authors provide little to no evidence for microbial iron reduction as the main process leading to magnetite precipitation. They conclude on past upwelling conditions 12 Ma ago, which would likely lead to an oxygen minimum zone, but do not decipher the source of iron or how this would lead to increased redox cycling of iron.

- l. 187: in the introduction (l. 108) you mentioned that the organic content of the sediment is minimal.
- l. 193: metagenomic data not shown

- l. 194-195: “enhancement of historical microbial activity” in the water column at the time of deposition or after deposition? What is iron metabolism? Aerobic-anaerobic iron respiration, dissimilatory processes, uptake, regulation, siderophores, else? The authors ran the FeGenie pipeline (Garber et al., 2020 Front Microbiol) and could thus report more clearly on metabolic potential for aerobic-anaerobic redox Fe processes, siderophores and magnetosomes.
- l. 198-200: with more advanced bioinformatic analyses, one could fill a part of this gap.
- l. 202: what do the author mean by “bacterial iron metabolite”? Siderophores, else?
- l. 202: is it due to oceanic circulation or very low sedimentation rates?
- l. 205: these references deal with magnetosomes, not partial reaction of dissolved Fe^{2+} with amorphous hydrated iron oxides.
- l. 210: do these values correspond to fractionation factors? What are the $\delta^{56}\text{Fe}$ values one should expect?
n.B. The authors do not mention the possibility of abiotic fractionation of Fe isotopes due to partial oxidation from ferrous to ferric Fe and assume that $\delta^{56}\text{Fe}$ values around -0.08 ‰ constitute indubitable evidence of DIR. Also, according to the successive sorption processes theorized by the authors, the potential influence of redox shuttle has to be considered as well.
- l. 213: BIFs were formed under anoxic conditions, not under oxic to suboxic conditions. Thus, I wonder if this comparison is justified.
- l. 215: currently distal. Things may have looked different 12 Ma ago.
- l. 217-239: very technical and descriptive part reiterating results. Poorly crystalline magnetites could also form during mixing of hydrothermal fluids with seawater.
- l. 236: during deposition, here the authors assume that these magnetites are pelagic precipitates.
- l. 245: by 5700 m water depth on an abyssal plain, a detrital component is any way unlikely.
- l. 254: what is the TOC content of the sediment? Abyssal clays are usually extremely organic-lean...
- l. 262: or that reductive diagenesis of the sediment led to subsequent release of metal ions...
- l. 270: once more, in the introduction you mentioned that OM content is minimal. How can OM remineralization be substantial enough to lead to anoxic conditions? Please support this statement with bulk OM.
- l. 274: solid-phase transformation; provide reference
- l. 282: the metagenomic data are far from being compelling and are not made available to the readers.
- l. 285: due to the absence of data on sedimentary OM content and cell density, this statement remains speculative. What is the source of phosphate? To this point, the reader is left with the idea that an accumulation of macroremains of biogenic apatite is the main source causing phosphatic concretions.
- l. 303-307: ...if one assumes that $\delta^{56}\text{Fe}$ values of -0.08 ‰ are sufficient evidence for dissimilatory iron reduction by unidentified microorganisms. The problem is that hydrothermal fluids mixing with seawater could produce abiotic magnetites that are slightly enriched in the light Fe isotope. The authors would be then tracing the source of the fluids rather than disentangling biotic-abiotic processes.
- l. 305: “microbial iron metabolism governs secondary mineralization”. Intraplate tholeiitic volcanism and hydrothermal circulation can also produce more crystalline secondary magnetite...
- l. 315: hitherto, marine productivity hotspots have not been introduced to the reader or put into context of the Pigafetta Basin 12 Ma ago.
- l. 318: microbial processes are rather defined by the substrates available after deposition at the seafloor, which is indirectly related to environmental conditions at the surface ocean.
- l. 324-331: see comment about l. 70-71 on nitrogen limitation and excess orthophosphate turning into authigenic (non-) apatitic phosphate in the sediment. P speciation would be an asset as to discriminate organic and inorganic forms of phosphates.
- l. 332-334: which indirectly argues against substantial drive by microbial dissimilatory iron reduction...
- l. 337: you mean an oxygen minimum zone? Normally, OMZs are mainly under the influence of heterotrophic denitrification (with substantial loss of fixed nitrogen). Iron is the main limiting nutrient in the modern global ocean, so where is the iron coming from?

Methods:

- 1. 423: comprehensive metadata on sequence data are missing (e.g. sequencing depth, number of contigs and length, predicted genes and ORFs).

The biological contribution and potential climate drivers of deep-sea rare earth element enrichment: Insights from microbial iron cycling

I consider that the authors have comprehensively implemented their manuscript according to my comments and suggestions, which, I admit, were exhaustive. I appreciated reading the revised manuscript as well as the effort of the authors to disentangle complex pre- and post-depositional processes. I have only minor comments and wording suggestions to support the authors' line of arguments in the introduction and discussion. I used nota bene (n.B.) where clarifications are needed. Once addressed, I can endorse acceptance of the manuscript for publication.

Yours sincerely,

Reviewer 1

Minor comments and suggestions

- l. 5-9: I would suggest inverting the order of these sentences as follows:

The migration of REY from marine particles (e.g. Fe-Mn (oxyhydr)oxides or organic matter) to apatite is a prerequisite for subsequent enrichment during early diagenesis. Thus, bioapatite and authigenic apatite act as final sinks for REY and thereby represent key reservoirs in deep-sea sediments. However, the underlying forces driving this migration process remain unresolved.

- l. 10: iron metabolism → iron biogeochemical cycling

- l. 11 microbial element cycling → microbial reductive diagenesis

- l. 12: Through an integrated analysis of → Integrating...

- l. 13: there is no data documenting “activity” which implies these processes are ongoing → reduction

- l. 14: degradation or phase transformation → driving mineralization of marine particles after deposition

- l. 16: “This mechanism may be particularly important during periods of significant global climate variability.” I find this statement a bit vague.

n.B. What I understood from the authors' answers to my comment and my lecture of the revised manuscript is that there was increased wind transport of dust particles during the Late Miocene glacial period, which combined with upwelling conditions, stimulated productivity in the Fe-limited pelagic ocean. Sedimentation of Fe-Mn oxides would scavenge orthophosphate under OMZ conditions and strong bottom currents, resulting in condensed strata acting as precursors for REY-enriched apatitic layers. If correct, could the authors rephrase to better convey this specific conditions?

- l. 44: ultimate → final

- l. 45: The extreme concentration contrast of $\sim 10^{12}$ → The contrast of concentrations by twelve orders of magnitude

- l. 47: cycling → mineral phase element transfer via...

- l. 69: for Eh and pH during microbial iron reduction and diagenetic redistribution across phases via pore water, cite: Vuillemin et al. (2023) Authigenic minerals reflect microbial control on pore waters in a ferruginous analogue. *Geochemical Perspectives Letters*, 28, 20-26. [doi: 10.7185/geochemlet.2339](https://doi.org/10.7185/geochemlet.2339)

- l. 71-72: not much the lowering of temperatures, but rather wind intensities and their location at higher latitudes due to the waxing of ice caps.

n.B. I realize that this is out of the scope of the manuscript, but I have a pending question related to this: Do the authors know whether increased eolian transport of dust particles during this glacial period is also involved in the increased productivity or can this argument be discarded? I tend to think that dust particles and particulate OM are correlated (i.e. iron fertilization).

- l. 77: Same here. Do the authors refer to an upwelling zone, an oxygen minimum zone, or both? ... The causes of OMZ are multiple (for instance Hawaii OMZ due to deep water stagnation, not productivity), same for the stimulation of surface productivity.

n.B. no need to extend on this topic, but please try to provide some clarifications. The TOC values argue against increased OM sedimentation. Increased dust particles could increase both productivity and scavenging of REY and phosphate during sinking.

- l. 79: I suggest to rephrase as follows: "...synergistically result in the deposition of sediment precursors promoting microbial mediation of REY release..."

- l. 81: what about sedimentation rates? → e.g. due to very low sedimentation rates and microbial oxidative degradation of organic proxies...

- l. 90: Be careful of the order you list your arguments, i.e. magnetotactic bacteria exhibit a pelagic lifestyle and usually thrive under microaerobic conditions (i.e. oxycline, pycnocline, chemocline). Thus, they are likely not involved in the geochemical evolution of pore waters, but may point to suboxic conditions in the water column and act as early degraders of sinking OM.

- l. 99: a tracer recording past microbial activity

n.B. I have a subsidiary question (l. 147): in organic-poor pelagic sediments, sulfate reduction aborts while fermentation proceeds (e.g. D'Hondt et al. 2019 Nat Comm 10; Vuillemin et al., 2020 mBio 11). Microbial production of H₂S promotes mackinawite-pyrite formation at the expense of other Fe²⁺-bearing phases. Is sulfate reduction influential on apatite formation? FeRB are usually versatile and can also evolve as fermenters...

- l. 156: previous findings, a reference is missing

- l. 232: in the water column and at the sediment-water interface

- l. 240: in l. 222 you state that OM particles originate from surface primary productivity and here you mention organic phosphorus from riverine input. This is confusing. Does the orthophosphate necessary to apatite precipitation derives from, e.g. the sinking particulate OM or the same terrigenous dust that supplies Mn-Fe oxides, or both?

- l. 249-252: what about an accumulation of dissolved orthophosphate in OMZ waters and scavenging during sinking? It is now mentioned in the introduction, but discussed here.

- l. 264: the phosphate sink is clear, but the sources remain elusive.

- l. 269: such as condensed sediment strata? Condensed strata imply strong bottom currents consistent with upwelling. These two climatic parameters could be clearly mentioned, i.e. the contribution of strong winds and bottom currents in upwelling regions

- l. 285: cite the corresponding figure here (Fig. 2a).

n.B. I quite understand how you conclude mineral-phase transformation over reductive dissolution. However, in l. 235, you say that these elements show post-depositional decoupling, but in l. 270 you claim that migration, concentration, and sequestration are geologically instantaneous upon deposition at the seafloor. Later you argue that this is a stratigraphic transition related to past depositional (climatic)

conditions, which somehow invalidates the statement in l. 235 which requires constraints on the duration of diagenetic processes.

- l. 301: see my subsidiary question on sulfate reduction in organic-poor sediment
- l. 313: mention that this corresponds to “condensed sediment strata” aka hardground. Such phosphate or glauconite condensed strata in the geological rock record are considered to correspond with past upwelling conditions
- l. 323: what about eolian transport? Upwellings are associated with stronger winds and currents
- l. 332: the focus is usually on framboidal magnetites as pelagic precipitates not related to magnetosomes.
- l. 360-372: this part is not really necessary as it doesn’t convey explanations. Just keep the sentence l. 365-368 with the citation.

n.B. a word of caution about l. 367, metagenomic predictions do not prove activity (i.e. metatranscriptomes). The DNA could derive from resting stages and dormant cells, thus correspond to the stratigraphic age, not an active microbiome in subsurface sediments. It seems plausible that microbial iron reduction took place during particle sinking, at the sediment-water interface (resulting in condensation and phase transition), then likely at much slower rates during burial due to organic substrate depletion.

- l. 391-393: future work is not relevant to discussion of the data produced
- l. 394-395: delete the first half of this sentence and move to l. 391 after deletion of the sentence about future work
- l. 425: define abbreviation at first mention in the text
- l. 430: here again, the TOC argues against increased OM sedimentation. Was all the primary OM degraded during sinking? Was it reworked by strong bottom currents? Are we talking about another type of OMZ (i.e. deep water stagnation)?
- l. 455: delete “ It is important to emphasize that”

Fig. 6: typos → the “late” Miocene “cooling” event