

Interactive comment on “Particulate Rare Earth Element behavior in the North Atlantic (GEOVIDE cruise)” by Marion Lagarde et al.

Anonymous Referee #1

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In this manuscript, Lagarde and colleagues present a substantial dataset for suspended particulate REEs and Y from a 2014 cruise in the NE Atlantic. The authors are commended for publishing these data, as there are too few high-quality REE datasets for ocean particles, and the interpretations have the potential to greatly increase the understanding of biogeochemical processes in general, and the ocean chemistry of REEs in particular, relative to inferences from dissolved data alone. One liability to keep in mind is that the residence time of particulate phases is generally much shorter than that of the dissolved pool, so these kinds of datasets are much more like short-term “snapshots” of distributions, especially in the upper water column, than long-term averages of regional distributions. This difference might be worth pointing out explicitly in this paper.

C1

Overall, the paper is well organized, and the figures are appropriate. This constitutes a substantive addition to the long history of effort to understand the processes affecting the distribution of REEs in the ocean, via inferences from (mostly dissolved) oceanic distributions, combined with laboratory studies that are not the focus of the current paper. I do have a fairly long list of comments and criticisms, that in sum probably suggest major revision. I list these below, in order through the manuscript. Fortunately, only a couple of the comments refer to what I deem to be serious misinterpretations of the data. These are comments #25 and 26 below (marked with *). A substantial fraction of the other comments are related to clear wording, and confusions caused by vague or inaccurate use of words and phrases. These are very important, because they are relevant to the specific processes being discussed. I have also commented extensively through the first part of the manuscript (see attached marked-up pdf, looking carefully for the small Adobe editing marks), with numerous revisions of the English word use, syntax, or grammar. However, at some point I felt that there were too many editorial needs in the use of English, and I refrained from most revisions in the interest of time, simply marking the problematic spots in yellow highlight. I leave it to the more experienced authors with good command of English (e.g. Planquette) to spend a few hours carefully improving the writing to avoid incorrect word usage and awkwardness, with the goal of making this paper much more readable. The problems with the highlighted sections should be quite obvious. One tip is that the frequent use of “one” or “ones” in a comparative sentence almost always makes for awkward English.

Once the revisions to the main body of text are completed, the authors should reconsider the content of the Abstract. As it stands, it makes the point about the long-distance transport of INLs, which I argue below is not well substantiated, and it also ends on an unsatisfyingly uncertain note with regard to Ho/Y ratio observations. I suggest deleting this last part (and perhaps the final section of the paper – see below), to end the Abstract on a stronger note.

In sum, I feel strongly that these data should be published, and will make a substantial

C2

addition to our understanding of REE behavior in the Atlantic, once the issues below are corrected, and especially when the problematic interpretations are reconsidered and revised.

1. Line 100: Methods: Were Ba and Th-232 measured on samples taken from both kinds of sampling bottles? Were conventional bottles measured by one lab and GO-FLO samples by another lab? Later it says Y was used to compare the two procedures (but also the collection method?). Not clear starting at line 100. This should also be made clear in Table 2. The authors should state what exactly is being reported here vs. related results from the same cruise that are reported in other publications. I found this description of sample types and who measured what to be confusing.

2. Line 117: Samples were rinsed with MQ water. There is possible loss of adsorbed elements as water should have been pH 5.6 if equilibrated with air. Previous workers have used NH₄OH to adjust pH of rinse water to ~8-9 to avoid this potential loss of adsorbed elements. Can the authors argue that results were not biased by loss of material from the particulate samples?

3. Line 127: Analytical Methodology: The text implies that 2.0mL from a 3.0mL total digest solution was used for REE, Y, Ba and Th analyses. But what was the dilution of this solution for analysis? Was HF included in this solution, and was an HF-compatible ICP-MS introduction system used? Were standard curve solutions match to the acid mixture and concentrations in the (diluted?) samples? What was the % correction for oxides for each of the REEs, especially those generated by Ba and the LREE? How were isobaric interferences avoided; it may be useful to list in a table the isotopes analyzed. What mass resolution settings on the HR-ICPMS were used for the various analytes? The reported 20-30% uncertainty in final PREE concentrations seems very high. What was the largest contributor to the uncertainty? Fig. S2A implies that the largest source of error was cutting the filter exactly in half (or sample heterogeneity on the filter surface). The highly variable and relatively large error associated with the measurement (Fig. S2A) is odd because cps should have been quite high given the

C3

sample volume and final digest volume, unless the primary digest solution was over-diluted (if so, why?). Reading between the lines, one could guess that a dry-down step was not desired, so digests may have been diluted to acceptable acid concentrations for the ICP-MS introduction, leading to low counts per second and high uncertainties based on signal counting statistics. Alternatively, filter blanks may have been high and/or variable (this is not mentioned – what was the range of % filter blank?). This needs much more explanation, because 20-30% uncertainty is very high, and is belied by the relative smoothness of the profiles shown Fig. 3 for example. This stated measurement uncertainty should have yielded noticeably “bouncy” vertical profiles. I think the data are not as uncertain as the authors’ assessment, which may be more theoretical than empirical, since true sample replication was not practical.

4. Line 155: To compare concentrations between the two analytical labs, the regression slope is only partially helpful. Please give the mean % difference for all samples, and indicate if this % shows any trend with sample concentration (e.g. higher concentrations agree better?).

5. Line 159: Why did Y agree much better between the two sampling systems (and labs?) than Ba, which has much higher particulate concentrations? Was this related to the filter type used for each sampling effort, or differences in the digestion methods used by the two labs? This comparison is again quite unclear. If this cannot be explained in simple terms, please put all the information in a table, with columns of collection bottle type, filter used, digest method, analytical method, lab where analyses were made, and final results from each lab, etc.

6. Line 167: “Ce oxidation onto particles” suggests a poor understanding of whether pCe is dominated by adsorbed Ce⁴⁺ or by an independent phase e.g. CeO₂. If Ce forms or forms within an independent oxidized authigenic mineral, then “prevents adsorption” is not the right phrase. Please clarify and expand this explanation of the unique behavior of Ce.

C4

7. Line 171: This section describing pCe distributions is very hard to follow because no figures are referred to. Also the terms epipelagic and mesopelagic need to be re-defined by depth intervals as a reminder to the reader, so that “bottom of the epipelagic” can be understood relative to the depth scale of Figure 2.

8. Line 184: The Station 44 maxima at 120m and 160m are defined by only one point each, so I think it is quite possible that they are uniquely contaminated with Ce, unless the contextual data can provide a clue as to a possible source in this region at those depths. See further related comment on Ce anomalies below.

9. Line 200: Section 3.4 has a big problem because the heading says Nd/Yb but Fig. 4 shows Yb/Nd, the inverse. One of these headings is wrong, and I suspect it is the section heading. I would expect that near-surface particles have a greater biogenic component and a smaller crustal component, so that Yb/Nd will be higher, reflecting the LREE-depleted seawater source for the particulate uptake, which is only partially compensated by preferential LREE removal by biological particle production, and by particle scavenging in general. In other words, I would expect PAAS-normalized REE patterns for particles in the euphotic zone to be “seawater-like”, but somewhat less LREE-depleted. Thus my guess is that Fig. 4 is correct, and the text throughout section 3.4 is wrong. Please correct this. The following two comments should be taken in this light.

10. Line 202: I don't see any values of Yb/Nd of 0.01 in Fig. 4. Visually, it looks like the minimum value is about 0.2.

11. Line 204: It is stated that the highest Yb/Nd value is in the epipelagic of Sta. 21, but Figure 4 shows a single subsurface value three times as high in the epipelagic of Sta. 13. This needs to be corrected. The last sentence of this paragraph says that at this relative high Yb/Nd point at Sta. 21, four of the LREE are also at high concentration. This sounds odd, because high LREE would be expected to drive HREE/LREE, and thus Yb/Nd, to low ratios, not high. If this sentence is highlighting a surprising result

C5

(high HREE/LREE at high [LREE]) then this should be pointed out. I can see from Fig. 2A that pCe has a single point maximum – is that single point the one that generates the high Yb/Nd?

12. Line 231: “react preferentially with biogenic phases”. Can the authors be more specific? Are they suggesting that Yb would be adsorbed preferentially to Nd on POM? On bSi? This phrase is too vague. Best to be more specific about the phase invoked, and to cite references appropriately.

13. Line 241: This is the first place in the manuscript where I finally understood that the samples being discussed were collected in the standard Niskin bottles. This should be abundantly clear in the Methods. See comment above.

14. Line 244: Rock types in the crust are likely more variable in Th content than in Al content. A rough estimation of the uncertainty in the %Lithogenic fraction calculated in this manner should be presented. Are the uncertainties large enough that the %Lithogenic should be viewed only as a relative scale?

15. Line 258: A finding of >100% lithogenic fraction using the Th-232 method suggests that ALL estimates of lithogenic fraction may be overestimates, and are at least probably not underestimates. This should be acknowledged in the text as a potential unidirectional bias in % lithogenic fraction.

16. Line 262: The patterns of PAAS normalized lithogenic fractions are called “flat” but the plots in Fig. S3 are on a log scale. This hides the fact that most of the patterns are MREE-enriched. Could the authors comment on this observation? I encourage plotting REE patterns on a linear scale whenever possible; this highlights the quality of the data and inter-element pattern details more clearly.

17. Line 276: The enrichment in LREEs is interesting, and this enrichment appears larger where the absolute pREE concentration is higher (greater depths). The authors imply that this is because of the “lower solubility” of the LREE relative to the HREE,

C6

and that this depth difference in LREE enrichment is caused by the adsorbed fraction. Yet the % lithogenic increases with depth as well. Can the authors eliminate the possibility that the LREE-enrichment is a function of the difference in REE composition of source rocks (or the fraction of source rocks that survives chemical weathering) and PAAS? Also, as noted in comments on the pdf, “solubility” is not the right term to use to describe the LREE, if the process being referred to is adsorptive scavenging, not the solubility of a unique solid phase. Admittedly, this chemically inaccurate language is used often in the marine chemistry community.

18. Line 276: “these maxima” . It is not clear here that you are referring now to the Iberian margin maxima in % lithogenic fraction. This is because the start of the paragraph refers to BOTH margins. Please add words to make it clear that you are shifting your focus to the Iberian margin here. And the Fig. 6 caption needs to explain the white arrows in the figure. I think they are supposed to show a density similarity between relative maxima in the profiles from the various stations, but for Sta. 26, for example, the arrow from Sta. 21 does not point to a relative maximum; the maximum is one depth lower at 200m. Similarly, the lower arrow pointing from Sta. 26 to Sta. 32 shows the % lithogenic increasing from ~60% (not a relative max) to ~100% at Sta. 32. I don't see how the lithogenic fraction could increase unless biogenic particles are preferentially lost to sinking (not likely) or another source of lithogenic particles exists at Sta. 32. I suspect that these differences are all related to the uncertainties inherent in the Th-232 normalization. The authors need to do more work to justify their interpretation that Iberian margin suspended particles are advected NW along isopycnals. Where are currents going at various depths? What about the possible influence of the broad shelf-slope region around the British Isles?

19. Line 303: “no particular lithogenic lithogenic contribution” is used to describe agreement between the PFe and PMn results from Gourain et al., as compared to the PREE results presented here. But Sta. 53 HREE have a substantially higher %lithogenic than Sta. 51 (Fig. 5), indicating that there IS in fact an increase in lithogenic fraction at Sta.

C7

53 only. So the phrase in quotes does not represent an observation “in agreement with our results”. This needs clarification and re-wording. The word “particular” is not clear in the above – do you mean “unusual”? Note also that authigenic contributions of Mn and Fe from shelf sediments may mask an increase in lithogenic Mn and Fe, when looking only at %lithogenic as a metric. This may be less true for REE, especially HREE, leading to the differences between Sta.'s 51 and 53 as noted above.

20. Line 307: “At station #13 at 200m, no lithogenic maximum is identified”. The authors need to clarify whether they are still referring to Ac-227 data or are now referring to REE data. Indeed, Fig. 6 shows this depth to be a relative min. in %lithogenic Nd, but there are relative max's just above and below. Please clarify language so it is fully clear which data you are referring to. Also, please use “lithogenic” and “%lithogenic” appropriately. It is possible to have high lithogenic concentrations but low %lithogenic, for example near a margin where weathering particles might combine with higher biogenic particles resulting from high productivity. In the quote above, I think you mean “%lithogenic”.

21. Line 308: “merging of the two maxima observed eastward”. Please clarify where the two maxima are and do you mean eastward of Sta. 13 or some other station? Also, Fig. 4 does not show anything about isopycnals; should this be citing Fig. 6?

22. Line 322: The concluding paragraph should sum up the REE results. As it stands, it restates more general processes at ocean margins that have been established through previous studies. It would be better to summarize the central findings related to REE marine geochemistry.

23. Line 327: “less prone to desorption”. This phrase is not fully accurate because my understanding is that Ce, once oxidized, has a higher Kd, which describes an equilibrium state where adsorption and desorption rates are equal, but distribution of Ce is more strongly in favor of the solid surface. See for example Ohta and Kawabe, GCA, 2001. Also, the literature contains some discussion whether adsorption or coprecipita-

C8

tion best describes the association of Ce(IV) with authigenic Fe and Mn oxyhydroxides. The nature of the anomalous redox behavior of Ce deserves a more complete introduction here, including its relative K_d via adsorption to MnO₂ and FeOOH, from abundant published experimental data. It is important to understand as well as possible which major authigenic mineral phase is most responsible for REE adsorption or coprecipitation, and for Ce oxidation.

24. Line 329: "authigenic Ce adsorbed on". An adsorbed species must first be in solution, and "authigenic" usually refers to a mineral in solid phase, so this wording is incorrect. Whether Ce(III) is first adsorbed, then oxidized, or whether a discrete mineral (CeO₂?) forms independently or in a co-precipitation process with a more abundant oxide is to my mind an open question, but the authors may wish to briefly summarize their understanding of the literature on this point. This reinforces the importance of the terminology referred to in the last comment.

25.* Line 338: The paragraph starting on this makes some assumptions that I think may not be true. First it is stated that Ce oxidation only occurs below the surface layer. In fact, without dissolved REE data, the authors cannot prove the Ce does not have a positive anomaly relative to the dissolved REEs. The authors seem to have been caught in the trap of interpreting the Ce anomaly in absolute terms rather than in relation to the dissolved pool from which the REEs are adsorbed onto or absorbed into the biogenic particles. This dissolved pool has itself a very negative Ce anomaly throughout most of the ocean. Very likely then, the only way to achieve a positive Ce anomaly in marine suspended matter is via advection of sedimentary particles that have had very long time periods during which to undergo substantial REE cycling and fractionation, or as the authors suggest, preferential loss of the strictly trivalent REEs upon POM remineralization. The authors also suggest, however, that a strong (positive) Ce anomaly could result from high particle concentrations. But a higher concentration of reactive surfaces would affect all REEs similarly; I don't see how high particle loads by themselves would lead to preferential Ce oxidation and retention on the particles.

C9

The authors assert that a positive Ce anomaly is not observed in the ARCT and NADR regions because export is strong and particle residence time is short, but Fig. 7 does show positive Ce anomalies at various depths in these regions, so this assertion seems untrue and needs more thorough examination and explanation. If Ce is preferentially removed under all scavenging scenarios, then it is reasonable to expect that a productive region with rapid export would deplete dissolved Ce in the mixed layer in both absolute and relative terms, through the course of a weeks-long bloom, leading potentially to strongly negative Ce anomalies in the dissolved state and increasingly negative (though positive relative to the dissolved pool) in the near-surface particles sampled at some advanced bloom stage. I encourage the authors to examine whether this scenario has been shown or disproven in other productive regions. Even if Ce oxidation were not favored in the sunlit ocean, I would guess that the dissolved REE pool would show a fairly strongly negative Ce anomaly, inherited during previous deep winter mixing. In sum, I would expect for most oceanic regions that Ce anomaly to be negative for biogenic particles in the euphotic zone in general, unless there were an admixture of authigenic particles (perhaps resuspended from shelf sediments) overwhelming the biogenic effect. The authors may be able to refute this idea based on published data, in which case this should be stated as part of the discussion in this section. These two particle sources are often mixed in highly variable ratios in ocean margins, and I would think that alone would make total particulate REE data difficult to interpret. I think this is the reason why the authors have so much trouble in the last few sentences of this paragraph seeing consistent correlations between Ce anomaly and Mn behavior, particle concentration, particle residence time, etc. Finally, I think the very sharp strong single-point maxima in Ce anomaly (Fig. 7A, B; e.g. Sta. 32, 440m and Sta. 13 600m) are very likely a result of Ce-specific contamination. Unless the authors can justify these oceanographically surprising features, those data points should be deleted from the graphs, and the data table values marked as likely contaminated values. See similar comments below.

26.* Line 360: The opening sentence of this paragraph seems incorrect to me, and

C10

gets the reasoning behind the interpretation of REE patterns in biogenic particles off on the wrong foot, affecting the rest of this discussion section. The LREE's likely have a larger lithogenic fraction than do the HREEs NOT because the LREE's are not preferentially taken up by (or onto) the biogenic particles, but simply because the surface seawater dissolved REE pool is so LREE-depleted relative to PAAS. The degree of LREE-depletion cannot be known for the stations investigated here because no dissolved REE data are presented, but even with preferential LREE scavenging, a mixture of crustal minerals and biogenic surface particles would always show the observed larger lithogenic component for the LREE, because the preferential LREE uptake on the biogenic particles cannot come close to compensating for how depleted the LREEs are in the dissolved pool. This depletion might be especially true for a surface layer that has already seen substantial growth and export in the preceding weeks, which could cause the surface layer to be even more LREE-depleted than it was immediately following winter mixing. I encourage the authors to "borrow" dissolved REE data from elsewhere in the Atlantic (no one measure them on GEOVIDE??), assume a degree of preferential LREE uptake based on published laboratory adsorption experiments or papers showing both dissolved and particulate data for euphotic zones in other regions, and do the calculation themselves. Without looking exhaustively at the literature, it is evident from dissolved REE data near Bermuda (see deBaar et al., GCA, 2018, Fig. 10) that dissolved Nd/Yb decreases from deep water up to the surface. In sum, a "seawater-like" pattern does not necessarily imply a unique LREE/HREE fractionation, or absorption vs. adsorption, it simply means short-term uptake from a very LREE-depleted pool, without significant admixture of authigenic minerals or refractory lithogenic particles, which are so important to the total PREE patterns below the surface layer. I think it is a mistake and is misleading to refer to "HREE enrichment" because PAAS-normalization has little relevance for biogenic marine particles, and this term implies preferential HREE uptake, relative to LREE. I also think that the speculations about REE patterns implying some kind of control by biogenic carbonate vs. silica is poorly reasoned and not convincing; I would argue that the vast majority of REEs in

C11

biogenic particles (mostly living cells in productive surface waters) is associated with organic matter, as is true for nearly all trace metals. In sum, I strongly disagree with the interpretations in section 4.4 and I urge the authors to reconsider and rewrite this entire section. As a related side observation, I see from Fig. 5 that the REE pattern of near-surface particles from Sta. 53 shows high concentrations (relative to Sta. 51) and strong LREE-enrichment (shown log scale). This station was dismissed in the first sentence of the section as distinct from most other stations which form the basis of the discussion in Section 4.4. But the question remains how this LREE-enrichment might occur. Is this a result of preferential LREE scavenging from a "flat" dissolved REE pattern, or does it reflect mineral particles from sediments or the continent that are already LREE-enriched, for example the authigenic products of previous long-term particle-seawater interactions?

27. Line 426: The meaning of "dynamic scavenging" used here and above, and how it can generate a positive Ce anomaly, should be explained further. My understanding of the authors' meaning is that that successive cycles of adsorption and desorption accompanied by progressive Ce oxidation, can increase the Ce anomaly until it is strongly positive. But could remineralization of organic matter, and loss of the associated REE, leaving MnO₂ and other authigenic oxyhydroxides as a greater fraction of the overall particulate REE, have the same effect, as long as refractory lithogenic particles (no Ce anomaly) were not an important part of the mix? This is not the same process as repeated cycles of adsorption and desorption on a constant particle population.

28. Line 429: "and then a stronger scavenging of REEs". It is not clear what this phrase means. Is this proposed to be the second step occurring at this depth interval, after "intensive exchanges", or does "then" mean further down the water column. I'm not clear how one achieves the combination of high P_{Ho} enrichment and strong positive Ce anomaly. Could the responsible processes be occurring independently, involving different particle types within the suspended particle mixture? Overall, it seemed to me that this section dutifully follows a pattern of discussion points in other REE papers from

C12

the senior author's group, and is interesting on theoretical grounds, but did not advance understanding of the relative behavior of Ho and Y in the ocean to a significant degree. The variations in Fig. 8 seem barely interpretable in any cohesive way. The authors should reconsider whether this section truly adds to the impact of the paper. To my reading, it makes the paper end on a somewhat vague note.

Comments on Figures:

Fig. 2: make all white water mass labels in bold and possibly larger font as they are very difficult to read. Also the inset white scale and axis labels for Station 53 should be as bold and large as possible – very difficult to read especially in print where blowing up the image is not possible. Overall, the very narrow profiles do not allow the subtleties of the profiles to be visualized very well. It would help if a separate figure showed all the profiles on one graph with a clear y-axis at concentration = 0. Right now many of the points cannot be distinguished visually from zero. Figure caption: Delete “the” before “station” and replace “map” with “section view”.

Fig. 4: I understand the color coding of the regions, but the different shades of symbols within each panel are hard to distinguish from each other. Perhaps symbol shapes could be different as well to help with this?

Fig. 5: The labels on the exterior panels are small and quite difficult to read. I fear this will be true in the print version as well. Those reading online can blow up the magnification to read these labels, but those with access only to the print version should be able to read the axes labels. I think these could be made a bit larger and bolder to increase readability. Also the vertical axis label of the pattern plots says “(PYREE/YREE)” but Y is not shown in the pattern. These should all therefore be revised to “(PREE/YREE)”. Finally, the profile plots for the ARCT region should be labeled Sta. 53 on left and Sta. 51 on right. The middle label “51 & 53” makes the reader think that the profiles are the reverse.

Fig. 6: Caption should explain the white arrows. See also the comment above about

C13

the appropriateness of the specific data points that are connected by the arrows.

Fig. 7: The very strong Ce anomaly maxima should not be plotted in the fig. 7A section view (where they generate very distracting and misleading “blobs” of high value) and should be labeled as potentially contaminated in the profiles, as well as in Fig. 2A, as discussed above. This of course leaves the question as to whether the fairly high positive Ce anomalies in the upper 200m are real or are also contamination. There appears to be some tendency for more instances of positive Ce anomaly at stations where PCe is generally at low concentration in the upper 200m, increasing the relative importance of minor contamination (or particulate carry-over from an earlier high-particle margin station?). But at least there are multiple instances of these anomalies, increasing the chances that they are real features. But the authors then need to explain why they should be such isolated maxima, in general. It would also help if all of the panels in Fig. 7B had the same x-axis maximum (4.0 would work), while allowing the >10 value to be marked with an arrow and a symbol for potential contamination.

Fig. 8: I had a very hard time visually to take any message away from this figure, and this is reflected in the speculative nature of the discussion. The variations with depth and province are not very systematic.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2019-462/bg-2019-462-RC1-supplement.pdf>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2019-462>, 2020.

C14