

Interactive comment on “Authigenic phases and biomass contents drive Zr, Hf and REE distributions in anoxic lake sediments” by P. Censi et al.

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I have read the interesting paper on “Authigenic phases and biomass contents drive Zr, Hf and REE distributions in anoxic lake sediments” by Censi and co-authors

This paper addresses REE, Y, Zr and Hf fractionations in hypersaline, anoxic seafloor sediments from Eastern Mediterranean deep-sea basins.

Censi and co-authors bring together in this paper a challenging mixture of components or processes to assess REE and HFSE mobility: brines, biological activity and sedimentary processes in deep-sea environments. This type of work is always very welcome and builds up on a large literature on trace element distribution and mobility

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in the continental crust.

Looking at this study as a whole, some issues should be addressed or articulated more extensively. Interpretations given to explain Y/Ho and Zr/Hf fractionations would benefit if they would be better defined and supported.

The conclusions are structured and discussed in a manner that leaves other possibilities open that could give an explanation for the same elemental fractionations (see comments below). For example, is the biologic activity responsible of the fractionation, or the carbonate precipitation, the brine activity in the basin, or this is an inherited geochemical feature from the sediment and source areas?

There is some literature that explains REE and HFSE fractionation in many different ways, depending on processes and conditions. Therefore, if the fractionations described in this study are linked with specific processes or mineral precipitation, a discussion arguing why other processes are not involved would strength the argument of the manuscript.

A more detailed mineralogy to further develop the link between REE-HFSE signatures and fractionations would help significantly the discussion.

The abstract needs polishing its structure and be more clearly written.

Results are combined with interpretations that are re-discussed in the discussion section.

As written, some sections are difficult to follow.

Some more literature on REE-HFSE fractionation and abundances related to fine-grained sediments, carbonates and sea-floor sediments could be discussed to enhance the argument.

Please see some comments below.

***Abstract P. 15

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“Y/Ho ratios are clustered around chondritic values justified by the occurrence of detritic Minerals”

Chondritic Y/Ho values can be detrital or be part of a new mineral phase formed after deposition of the sediment, under conditions that do not fractionate Y from Ho.

Which detrital mineral grains are these Chondritic Y/Ho values associated with?

Are there no chondritic Y/Ho values in the rest of the minerals precipitated after deposition?

The point here is that results from whole-sediment geochemical analysis may be challenging when addressing specific elemental ratios and linking them with mineral phases.

Once the main carrier of the Y/Ho is linked to the mineralogy in the detrital sample and in the post-depositional/bioturbated fraction, then the estimation of where Y/Ho changes could be easier to perform.

Another suggestion for this comparison would be to analyze detrital fraction and detrital-bioturbated sample separately to compare Y/Ho ratios.

P. 15-20

“Negative Gd anomalies, subchondritic Y/Ho and Zr/Hf values are found in Mg-carbonate rich samples suggesting that authigenic Mg-carbonates partition Ho and Hf with respect to Y and Zr during their crystallization from brines.”

Y/Ho, Zr/Hf and REE fractionation has been reported to happen due to element mobility under alkaline oxidizing brines with no bioturbation activity or influence, for example:

Kerrick, Renault, and Bonli, 2002. Trace-element composition of cherts from alkaline lakes in the east African rift: a probe for ancient counterparts. In: Sedimentation in Continental Rifts. Soc. Sed. Geol., Boulder, CO, pp. 277–298, Spec. Publ. 73.

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González-Álvarez and Kerrich, 2010. REE and HFSE mobility due to protracted flow of basinal brines in the Mesoproterozoic Belt-Purcell Supergroup, Laurentia. Precambrian Research, 177, 291-307

P. 25

“These first data suggest that Zr/Hf ratio and REE distributions can represent tracers of biological activity in sediments.”

Definitely, the points presented above can lead to this possibility. However, as presented, so far there are not criteria for discrimination if the Zr/Hf ratio and REE distributions reported in this study is directly related to biological activity in sediments, or to the effect of the brines as reported in other studies.

***Results section: Geochemistry

Results and interpretations are blended in this section.

P. 5

“REE, Zr and Hf concentrations measured in sediments are reported in Supplement The recognised concentrations are always higher in Tyro and Medee sediments” which is interpreted as : “These differences indicate that the investigated trace elements are concentrated both in soluble halides and in minerals forming FWSS”

This is a very good interpretation if the sediments from the other basins were the same.

The authors may want to consider addressing this by analyzing for REE, Zr and Hf the Tyro and Medee sediments with and without the halides and FWSS, which I understand it was not carried out.

The point here is that even if the sediment from the Thetis and Kryos seem the same mineralogically, the clay composition could vary and/or the sorting of the heavy minerals during deposition. This could bring different REE and HFSE signatures to the sediments from the different basins sampled.

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Other studies report no effect on REE and HFSE sedimentary signatures of rich-carbonate sedimentary packages (e.g., Schieber J.A. studies in 80's among others).

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For MREE enrichment, any possibility that that would be associated with the post-depositional precipitation of apatite?

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"This evidence suggests a preferential Ho partitioning in solids with respect to Y during authigenic carbonate crystallizations, in agreement with experimental evidence"

Is there any other evidence that the Y/Ho fractionation is associated to the carbonate precipitation and not by the brine effect in the sediments?

Fig. 5

It looks that the black dots define two sample compositions for each Y/Ho and Zr/Hf.

Are the "out of the clusters" black dots with bioturbation associated and the other samples not?

***Discussion

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It is first time in the paper that foraminifera are mentioned.

It would be informative for the reader if the carbonate sources for the samples are described in detail previously, since the paper addresses the importance of that component in the sample for REE and some HFSE signatures.

P. 15-20

"Therefore subchondritic Y/Ho values recognised in sediments enriched in low-Mg bio20 clastic calcite from Thetis and Kryos basins (Supplement 1) suggest that Ho

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is preferentially partitioned in calcite with respect to Y also in biogenic carbonates"

To be completely sure of this maybe it would have been better to only analyze the biogenic carbonate, then the saline component of the sediments and then the sediments themselves independently, and then compare results?

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"a further sediment component should be invoked to justify Gd/Gd**"

Gd/Gd* anomalous values are not explained related to any process or sediment "component". Does this refer to any specific mineral, post-depositional process, and sedimentation sorting effect...?

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"In 5 contrast, the higher affinity of Zr and Hf for organic surfaces with respect to REE and other metals (Monji et al., 2008),"

Zr/Hf very rarely fractionate when looking into the rich organic sedimentary packages rich in clay. Monji's study was for acidic solutions and plants if I understood correctly. Is Monji's study framework comparable with this work?

***Some references that the authors may find interesting:

Schieber J. A., 1988. Chem. Geol. 69, 111-126.

Kato et al. 011, Nature letters.

Laenan et al. 1997, PALAEO 132, 325-342.

Gonzalez-Alvarez and Kerrich, 2011, Geochim. Cosmochim. Acta 75, 1733-1756.

Plank and Langmuir 1998, Chem Geol. 145, 325-394.

Williams-Jones et al. 2013, Elements, 8, 355-360.

Best regards,

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