Journal: **BIOGEOSCIENCE**

Title: Authigenic phases and biomass contents drive Zr, Hf and REE distributions in anoxic lake sediments

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General comments

The study of the fractionation and interplay between trace and rare earth elements with authigenic and biogenic phases as well as detritic components in such exciting environments like seafloor brines from deep-sea Mediterranean basins is very worth reading. Thereby, to receive this paper for revision was very interesting because I found the subject quite promising, although you cannot get the subject from just the title because it doesn't mention that the "lakes" are in reality deep-sea hypersaline basins of the Mediterranean. So, my first recommendation to the authors is to change the title and to include these terms.

I really encourage the authors to improve this manuscript since the research is quite new and interesting for the scientific community, but firstly, some issues have to be addressed and changed. So, please, read comments below.

Specific comments and technical corrections

Abstract

MREE usually denotes "middle" rare earth element better than "intermediate" see Page 8978 line 15, Page 8985 line 22

Introduction

In the literature when you study together lanthanide rare earth elements (REE) and Yttrium (Y), they are usually referred as REY but no just REE (you can also write YREE). So please, correct the sentence in page 8980 line 6

Page 8980 lines 12-17. I think that in "the aim of this work" you should indicate that you are going to study these solid-liquid processes in hypersaline anoxic deep-sea basins since you do not compare your results with any other marine environment. Therefore, I miss this comparison in your discussion and I strongly recommend you to achieve it in order to improve this knowledge you wish for.

Materials and methods

Bortoluzzi et al. (2011) do not describe sediments from Kryos, Thetis and Medee as you suggest in page 8981 line 5-8. Only sediments from Medee show these sandy products while Kryos is "undisturbed, laminated, gray to black muddy sediment" and Thetis is "undisturbed, laminated, gray-greenish muddy sediment". So please, check your descriptions and correct the text and interpretations.

Please correct resistivity units of Ultrapure or high-purity water (it should be 18.2 MΩ·cm) in page 8981 line 17 and 8982 line 27

The method you use for mineral identification (page 8981) is not quantitative so you have to indicate it somewhere. Therefore, I wonder if the numbers provide in the supplement-1 are in wt% or any other unit, so please indicate the concentration units. Moreover, do you realise that mineral content of Kryos and Thetis basins are not in this supplement-1? I guess you also analysed these samples, so please check it. Finally, I also miss bischofite in supplement-1 since you consider this mineral very important in the results of your samples. Is it maybe included in halides column? but in mineralogy results you indicate that soluble salt minerals are halite and bischofite. You have to clarify this matter.

Page 9892 (chemical analyses) you give many details about the procedure you follow but you do not indicate either precision or accuracy after ICP-MS measurements. Please, do it.

Page 8982 line 24. I do not understand why you use as a blank a solution of 1M HCl when all procedures indicate that blanks should have the same quantities of all chemical reagents, in your case a solution of 1:1 HNO_3-H_2O_2. Please justify or clarify why you have changed it.

The same for the working standard solutions (page 8983 line 4)

I think the information you provide from Page 8982 line 26-29 is no use because you already mentioned the reagents. Better indicate accuracy and precision of the analysis.

Page 8983 line 15. correct …centrifuged at "7000 g" by "7000 rpm", and line 17 correct "5'" for "5 min." In supplement-1 can you specify the units of biomass content?

Results. Mineralogy

Page 8984

Lines 3-7. You indicate monotonous mineralogical composition and minerals presents in all samples, but in supplement-1 there are data only from Tyro and Medee. I know salt minerals were removed from Kryos and Thetis, but there are no data of other mineral assemblage to corroborate the sentence at the beginning of the paragraph.

Lines 25-27. About Medee basin. I cannot find in supplement-1 the large amounts of low-Mg calcite below 25 cm depth. There are just 2 values and they are lower than those above. I cannot see either in supplement-1 the decreasing you mention in shallowest sediments, in fact they show an increasing.

From line 27 to line 4 (next page), you indicate values and assemblages that there are not in supplement-1, because there are no mineralogical data from Thetis and Kryos, so I cannot see what you mention in your results.

Results. Geochemistry

You mix up results with interpretation and discussion in this section quite often (i.e. page 8985, from line 15 to 18; page 8986, from line 7 to 18, and so on)

Page 8985 line 24. I do not see the progressive enrichment from Eu to Ho but from Nd to Gd in WS sediments. So the progressive HREE depletion starts also from Gd to Lu.

I suggest you to include Gd anomaly values in supplement-1 since this is one of the main features you use to discriminate samples coming from different basins (see page 8986 line 3-6). It would be also very interesting to comment the behaviour of Ce anomaly since your samples are taken in anoxic basins and this rare earth element is quite sensitive to redox conditions.

I recommend you to find some more possibilities for MREE enrichments, see i.e. Johannesson et al. (1996), Johannesson and Zhou (1999), Hannigan and Sholkovitz (2001), Verplanck et al. (2004), among others, because to compare just with estuarine sediments is very poor for this discussion paper, since the environmental conditions are completely different. Dubinin (2004) shows MREE enrichment (together with a positivie Ce anomaly) in pelagic clays that could be present in your samples as well.

Page 8986 lines 15-18. The positive relationship you show in fig.4 between HREE/MREE and biomass is a bit forced (see also the low correlation index of 5.6) because there are two samples (one of Medee and one of Tyro) that depict very far from the general tendency of the others and make you draw a fictitious correlation line. I also guess that organic matter plays a major role in these sediments but you have to find another way to relate this characteristic with REE behaviour to set this statement.

Under my point of view, the same happens in Page 8987 lines 4-6 (Fig.6a) in relation to Y/Ho and Biomass content. I mean, the general tendency of the samples do not follow the correlation line.

Sorry, but I don't know the meaning of all parameters you show in page 8986 line 21. Please, specify them in the text or in the figure (the same for page 8987 lines 1-2).

I wonder why you do not comment anything about the behaviour of the same parameters (HREE/MREE, Y/Ho, Zr/Hf and biomass content) in Thetis and Kryos basins. Even when there is no correlation, you should comment that and also try to explain what you think about the different behaviour among sediments of the different basins. Of course, this has to be written in the discussion section. In fact, you mention the subchondritic values of Y/Ho and Zr/Hf in these basins at the beginning of the discussion section but there is nothing about that in the result section.

Page 8987

Lines 11-12. The agreement between Gd/Gd* > 1 and low-Mg calcite you mention cannot be observed because the lack of mineralogical data of Thetis and Kryos (supplement-1). Again, I think you should include a column with Gd anomalies of your samples because is a key feature of your study.

Lines 19-23. I cannot see this relation because of the lack of mineralogical data in Thetis and Kryos (supplement-1).

Page 8988 lines 13-16. You mention that brines associated display G enrichment (Censi et al., 2013) as well as other brines worldwide. Can you please include drawing of their patterns in order to compare them with your samples? I would find it very interesting to improve this manuscript.

Page 8989 lines 1-4. I do not understand this comment about the co-variation of Y/Ho and Zr/Hf of your samples with carbonatites that get this relation from magmatic differentiation processes. They are completely different environments so, what would you like to point out with this sentence?

Conclusions

Page 8990.

Lines 1-7. First paragraph is too long and a bit confusing, please re-write it.

Lines 7-9. Sorry, but I do not get this conclusion after reading the manuscript, I thought both indices have a similar behaviour.

This section is a bit difficult to follow and there are some discussions included. I strongly recommend you to revise and rewrite it, moving some sentences to the discussion section.

Figures and tables

Fig.1) please include a better figure where you can see the basins in more detail, like a bathymetric map from GEBCO or even better from the MAMBA cruise or another cruise of the project.

Fig.2) What do you mean with "strong" detrital carbonate fraction?

You have repeated (f) in the table caption, please correct it

Fig.3) you mention "the dashed area represents…", which dashed area? Maybe you forgot it.

Fig.5) I suggest you to change some details

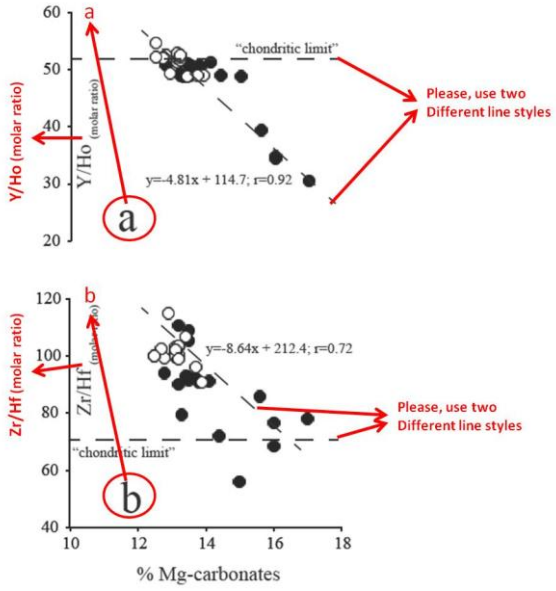

Fig. 5. Relationships between Y/Ho **(a)** and Zr/Hf **(b)** values with respect to the contents of authigenic Mg-carbonates (dolomite + Mg-calcite) in studied assemblages. Symbols as in Fig. 4.

Fig.7) I find this figure vey interesting and quite synthetic of the behaviour of these brine sediment samples.

Supplement-1) there are some suggestions and comments about this document along this revision. If possible, include units of the measured parameters (i.e. biomass, mineral contents). If you have the content of bischofite and halite, please indicate them separately instead of the common occurrence as halides. I think that to include a column with Gd/Gd* is very much worth it. Include mineralogical data of Kryos and Thetis. Additionally, correct the name of Medee basin.

Some references suggested in this revision

Dubinin, A.V., 2004. Geochemistry of Rare Earth Elements in the Ocean. Lithology and Mineral Resources 39, 289–307.

Johannesson, K.H., Zhou, X., 1999. Origin of middle rare earth elements enrichments in acid waters of a Canadian High Artic lake. Geochimica et Cosmochimica Acta 61, 153–165.

Hannigan, R.E., Sholkovitz, E.R., 2001. The development of middle rare earth element enrichments in freshwaters: weathering of phosphate minerals. Chemical Geology 175, 495–508.

Johannesson, K.H., Lyons, W.B., Yelken, M.A., Gaudette, H.E., Stetzenbach, K.J., 1996. Geochemistry of the rare-earth elements in hypersaline and dilute acidic natural terrestrial waters: complexation behaviour and middle rare-earth element enrichments. Chemical Geology 133, 125–144.

Verplanck, P.L., Nordstrom, D.K., Taylor, H.E., Kimball, B.A., 2004. Rare earth element partitioning between hydrous ferric oxides and acid mine water during iron oxidation. Applied Geochemistry 19, 1339–1354.