

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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Introduction

Although several authors used the acronym REE to indicate elements from La to Lu, IUPAC recommendations for nomenclature of chemical elements indicate them as Lanthanides. In the same publication Lanthanides plus Sc and Y are defined Rare Earths or Rare Earth Elements (REE). Similarly these element group is defined in the preface to the first volume of the “Handbook of Physics and Chemistry of Rare Earths (Gschneidner and Eyring, 1979). So I would more precisely change the definition given in the introduction as follows in the revised version of the manuscript: “REE (hereafter

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referred to lanthanides and yttrium without Sc)”. Done. The “aim of this work” was changed.

Materials and methods

The method used for mineral identification is not quantitative, but the analysis of mineralogical composition carried out with the DiffracPlus TOPAS[®] based on the Rietveld refinement method is quantitative and the values reported in Supplement-1 are weight %. In Kryos and Thetis sediments the mineralogical composition was investigated only after the removal of soluble minerals. For these materials the mineralogical composition of the FWSS fraction has been reported in the new Supplement-2. Halite and bischofite are the soluble halides that very often (mainly halite) occur in studied sediments. Therefore, their contents are included in the halide column. The paragraph describing procedures to determine precision and accuracy of chemical analyses is now enclosed in the revised version of the manuscript and in Supplement-3 The 1 M HCl solution running during analyses between a sample and one another represents a washing solution, erroneously defined “blank”. Investigated elements are usually considered refractory with a strong reactivity towards surfaces and can be scavenged onto surfaces of tubes and pumping inlet system of ICP-MS. In order to avoid this effect that involves severe problems during analyses, an acid and complexing HCl solution able to increase the mobility of refractory elements (especially Zr and Hf) is used to wash the inlet system. The same reason allowed me to prefer a chloride environment for the working standard solution in order to avoid any precipitation of Zr and Hf and their solution complexation in chloride form. Indeed, although chloride complexes of Zr and Hf are less stable with respect to OH-, F-, CO₃²⁻- and PO₄³⁻- complexes (Aja et al., 1995; Appl. Geochem. 10, 603-620) these are the most stable dissolved Zr and Hf species under strong acid conditions. The paragraph was removed in the revised version of the manuscript.

Results. Mineralogy

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In Kryos and Thetis sediments the mineralogical composition was investigated only after the removal of soluble minerals. For these materials the mineralogical composition of the FWSS fraction has been reported in the new Supplement-2. Mineralogical results for investigated samples have been revised according to the suggestion of the anonymous referee 2. These values are reported in Supplement-2.

Results. Geochemistry

Also Dr. Ignacio Gonzalez-Alvarez suggested me to avoid to mix results and their discussion. I hope to have removed these problems in the revised version of the manuscript. Suggested changes in description of patterns were reported in the revised version.

Discussion and conclusions

Gd/Gd* and Ce/Ce* values are now reported in Supplement-2 and the latter presented in the text. Possible explanations of observed MREE enrichments have been included in the revised version of the manuscript. Fig. 4 was changed. Also graph related to Y/Ho vs biomass contents was changed and re-presented in Results. The meaning of expressions at lines 1-2 pag. 8997 have been clarified in the caption of the new Fig. 6 Features of Y/Ho, Zr/Hf and MREE enrichments are now commented in the version of the manuscript. The explanation of observed positive Gd anomalies has been rewritten. Mineralogical data for FWSS sediment fractions are now enclosed in Supplement-3. Gd positive anomalies that I mentioned in the BGD manuscript are now treated differently. $Gd/Gd^* > 1$ in brines worldwide are not enclosed in the revised version because not necessary. But a brief collection of shale-normalised REE data and related positive Gd anomalies are reported in the file "Brines worldwide.xlsx" enclosed in the revised version for commodity of the Reviewer 2. To recognise Zr/Hf values measured in carbonates is very rare. Only in carbonatites these analyses can be found together with Y/Ho ratios. So, in the early version of the manuscript these values in brine sediments have been compared with analyses of Alberti et al. (1999)

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and Bizimis et al., 2003. Anyway, being environment occurring in deep-sea brine very different from those occurring during carbonatitic emplacements the paragraph was changed. The first paragraph of conclusions was rewritten Conclusions were rewritten, as requested.

Figures and tables Fig. 1 was changed "strong" was removed "f" was substituted with "g" Dashed area was incorrect Fig. 5 was redrawn. Units are now enclosed

As regards to the suggested papers I know them and some have been cited in the revised version of the manuscript. On the other hand several of these papers justify observed MREE enrichments as due to phosphate (Hannigan and Sholkovits, 2001) and/or oxyhydroxide components (Johannesson and Zhou, 1999; Johannesson et al., 1996; Verplanck et al., 2004) in sediments the are not reported in our data. Dubinin (2004) reports a review of REE behaviour in ocean water that takes in account effects of REE input from detrital atmospheric materials. In any case in the paper I provide both reference and direct evidences of a composite origin for the MREE enrichment mainly due to salt minerals occurring in WS sediment fractions.

Best Wishes Paolo Censi

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