

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

Comment: “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 depositions? The point here is that results from whole-sediment geochemical analysis may be challenging when addressing specific elemental ratios and linking

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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 analyzed detrital fraction and detrital-bioturbated sample separately to compare Y/Ho ratios.

Reply: Detrital minerals are primary magmatic minerals or sedimentary ones. The former are formed in high temperature conditions that usually allow to chondritic signatures of Y-Ho fractionations. The latter crystallize under “sedimentary conditions involving both Y-Ho behaviour driven by CHARAC processes (Bau, 1996; Contrib. Mineral. Petrol. 123, 323-333) and Y-Ho decoupling due to different behaviour of these elements as regards of surface complexations (see Bau, 1999; Geochim. Cosmochim. Acta 63, 67-77). Theoretically speaking, if detrital minerals are stable in studied brines their surfaces can induce some Y and Ho scavenging. According to the X-Ray determinations, detrital minerals consist of quartz, biogenic and abiogenic calcite and gypsum. Recently Roberts et al. (2012; Geochim. Cosmochim. Acta 94, 57–71) suggested that surface REE complexation onto biogenic carbonates could allow as carbonate complexes. Luo and Byrne (2004; Geochim. Cosmochim. Acta 68, 691–699) estimated complexation constants for dissolved carbonate complexes finding that these values were slightly higher for Y (102.85-108.03) than for Ho (102.78-107.66) for carbonate and di-carbonate complexes, respectively). At the same time Jordan et al. (2013; Journal of Phys. Chem. A 115, 14438-14445) found a preferential Y<sup>3+</sup>, La<sup>3+</sup> and Gd<sup>3+</sup> partitioning on amorphous silica surfaces in chloride medium. Therefore Y-Ho scavenging onto quartz and carbonates should allow to a superchondritic signature in these solids. On the other hand Stojanovic et al. (2009; Chemie der Erde 69, 223-234) found higher REE contents in sediments in contact with lower ionic strength waters, in agreement with the competitive effects of major ions with respect to REE during scavenging onto surfaces of detrital minerals. These features suggest that in brine sediments studied here, effects of Y-Ho decoupling due to surface complexation concur with the presence of detrital minerals to allow to a chondritic signature of several stud-

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ied samples. On the other hand also dissolved Y-Ho speciation and the presence of biological surface can limit the extent of Y-Ho fractionations. According to X-ray analyses, presented data suggest that authigenic minerals are limited to Mg-rich carbonates and halides, rather than the occurrence of limited amount of sulphates in parageneses cannot be excluded. The trace element incorporations in crystallizing minerals consist of an early migration of elements from parent solution to mineral surfaces followed by the incorporation of these elements into crystal lattice. Qu et al. (2009; *Geochem. Jour.* 43, 403-414) report the preferential Ho incorporation into CaCO<sub>3</sub> (both calcite and aragonite) with respect to Y, implying a potential subchondritic Y/Ho signature of these minerals. This evidence is also confirmed by data from Tanaka et al. (2004; *Geochem. Jour.* 38, 19-32) showing a preferential Y enrichment in dissolved phase during the calcite crystallization with respect to Ho that is explained in terms of different covalency of Ho-CO<sub>3</sub> and Y-CO<sub>3</sub> bonding in carbonates (Tanaka et al., 2008; *Chem. Geol.* 248, 104-113). As regards of halides Steimann and Stille (1998, *C.R. Acad. Sci. Paris* 327, 173-180) suggest a larger stability of [YCl]<sub>3</sub><sup>+</sup> complex with respect to [HoCl]<sub>3</sub><sup>+</sup> in brines in order to explain observed REE distributions in NaCl formed close to a basaltic intrusion. Further confirmations of Y-Ho decoupling during depositions of salt minerals come from analyses of silvite and kainite crystals (Censi et al., in preparation). Therefore a sub-chondritic signature could be expected in Mg-carbonate and halide rich sediments. Although the recognition of the geochemical significance of a specific REE signature in whole-sediment analyses, this result can be achieved in the studied assemblages where authigenic carbonates and halides were simultaneously investigated from different sequences where they represent the only authigenic occurring minerals.

"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."

Comment: "Y/Ho Zr/Hf and REE fractionation has been reported to happen due

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to element mobility under alkaline oxidizing brines with no bioturbation activity or influence, for example Kerrich, Renaut, and Bonli, 2002. Trace-element composition of cherts from alkaline t in the east African rift: a probe for ancient counterparts. In: *Sedimentation in Continental Rifs. Soc. Sed. Geol., Boulder, CO*, pp. 277-298, Spec. Publ. 73. Gonzalez-Alvarez and Kerrich, 2010. REE and HFSE mobility due to protracted inflow of basinal brines in the Mesoproterozoic Belt-Purcell Supergroup, Laurentia. *Precambrian Research*, 177, 291-307

Reply: Although Kerrich et al. (2002) and Gonzalez-Alvarez and Kerrich (2010) represent two very important papers of the scarce literature about REE, Zr and Hf mobility under near-surface conditions and alkaline conditions can increase trace element mobilities as occurs along some African reef lakes (Kerrich et al. 2002), these authors recognise these effects by means of analyses of chert, rather than from analyses of dissolved phase. On the contrary here Y/Ho, Zr/Hf and REE behaviour are investigated in carbonate- and halide-bearing sediments in contact with brines under slight acidic rather than alkaline conditions as reported in De Lange et al. (1990; *Mar. Chem.* 31, 63-88). Moreover in these brines authigenic carbonate and halide depositions occur and this fact involves some differences in terms of Y behaviour. In studied brines the deposition of authigenic carbonates allows to the Ho partitioning onto carbonate surfaces and/or co-precipitated with Ca-carbonates whereas Y is preferentially scavenged onto authigenic chert under alkaline conditions with respect Ho. Moreover deep-sea brines should have that agree with REE speciation based on chloride complexes (according to PHREEQC calculations).

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

Comment: "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.

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Reply: I agree with the suggestions of Dr. Gonzalez-Alvarez also because values of Zr/Hf ratio could be influenced by crystallization of authigenic minerals. Therefore I change this phase as follows: "These first data suggest that Zr/Hf ratio and REE distributions are also influenced by the biological activity in sediments."

"REE, Zr and Hf concentrations measured in sediments are reported in Supplementary information. 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".

Comment: "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 mineralogy, 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. 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). For MREE enrichment, any possibility that that would be associated with the post-depositional precipitation of apatite?"

Reply: Recent analyses of saline minerals from K and Na salt mines in Sicily where saline domes of Miocene age are exploited, found that these minerals are able to contain REE, Zr and Hf with concentrations ranging from 0.4 and 7.9  $\mu\text{g kg}^{-1}$  for REE, from 0.1 to 0.2  $\mu\text{g kg}^{-1}$  for Zr and from 0.04 to 0.1  $\mu\text{g kg}^{-1}$  for Hf (Ragusa, 2013). Moreover these data evidence a larger capability to concentrate the above mentioned elements in sulphates, rather than in chlorides with a tendency to preferentially concentrate Ho and Hf with respect to Y and Zr, respectively. Furthermore, I cannot rule out that some mineralogical differences can occur between sediments from Thetis, Kryos, Tyro and Medee basins, even if REE distributions in brines from Tyro, Thetis and Medee basins

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show very similar features (Censi et al., 2013a). Certainly, as you report, authigenic carbonates and salt minerals are not the best examples of phases to incorporate REE, Zr and Hf in their crystal lattices. Therefore, could be difficult to accept that the occurrence of these minerals in sediment can influence the composition of these elements in sediments. So I would change the previously reported interpretation of the recognised REE, Zr and Hf distributions in studied sediments as follows: "These differences suggest that the investigated trace elements are also contained both in soluble halides and in minerals forming FWSS". On the other hand many researches carried out investigating the REE distributions in sedimentary assemblages were mainly focused on the recognition of source materials of sedimentary assemblages, rather than to investigate authigenic parageneses in newly-forming sediments with respect to parent solutions. Then these studies cannot evaluate REE fractionations between authigenic minerals and coexisting fluids also because post depositional diagenetic effects on the original compositions of sedimentary assemblages cannot ruled out. Only recently, some studies have been carried out on fractionations of REE, Zr and Hf in natural systems crystallizing authigenic minerals (mainly Fe- and Mn oxyhydroxides, see Bau and Koschinsky, 2006; *Earth Plan. Sc. Lett.* 241, 952–961; Moller and Dulski, 1983; *Chem. Geol.* 40, 1-12). These and further studies showed that Zr and Hf concentrations can change in carbonate-rich mineralogical assemblages as a consequence of secondary processes as hydrothermal alteration, metasomatic reactions, etc. (Ganino et al., 2013 and reference therein; *Geoscience Frontiers* 4, 535-546). Although MREE-bulge feature in normalised REE patterns have been interpreted as a consequence of apatite occurrence in mineralogical assemblages (Hannigan and Sholkovitz, 2001; *Chem. Geol.* 175, 495-508) neither Apatite, nor other phosphates were recognised in X-ray analyses. On the other hand MREE incorporation in minerals also occurs in authigenic carbonates (Himmeler et al., 2010; *Chem. Geol.* 277, 126-136) due to crystal-chemical considerations (Terakado and Masuda, 1988; *Chem. Geol.* 69, 103-110; Zhao and Jones, 2013; *Sed. Geol.* 284-285, 26-38).

"This evidence suggests a preferential Ho partitioning in solids with respect to Y during

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authigenic carbonate crystallizations, in agreement with experimental evidence".

Comment: "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?"

Reply: A very interesting paper about the Y-Ho decoupling induced by crystallizations of Ca-carbonates was published by Qu et al. (2009; *Geochem. Jour.* 43, 403-414). In this paper a similar behaviour of Y and Ho fractionations is recognised during the crystallization of Aragonite and Calcite, resulting Ho preferentially incorporated in solids with respect Y with larger extent for aragonite than for calcite. Results obtained by Qu and co-workers also agreed with those from previous investigations limited to calcite-water equilibria (Zhong and Mucci, 1995; *Geochim. Cosmochim. Acta* 59, 443-453; Tanaka and Kawabe, 2006; *Geochem. Jour.* 40, 425-435).

Comment: "It looks that the black dots define two sample composition for each Y/Ho and Zr/Hf. Are the "out of clusters" black dots with bioturbation associated and the other samples not?"

Reply: Your observation could be right. As reported in the enclosed "Fig. 5 (modified)" a group of 4 samples highlighted with red ellipses represent samples with the lowest contents in low-Mg bioclastic calcite in studied samples from Tyro basin. It is hard to establish if these samples are related to more "bioturbated" levels.

Comment: "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."

Reply: A more detailed description of sediment will be reported in the revised text.

"Therefore subchondritic Y/Ho values recognised in sediments enriched in low-Mg bioclastic calcite from Thetis and Kryos basins (Supplement 1) suggest that Ho is preferentially partitioned in calcite with respect to Ho also in biogenic carbonates".

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

Reply: I fully agree with your idea. But, we did not analyse single fractions being them hard to separate without direct manual separation with binocular microscope. Moreover I was not able to find analyses of REE (with yttrium) of living biogenic carbonates. It could represent an interesting test to establish if Y-Ho decoupling also occurs in biogenic carbonates or if some "vital effect" can occur.

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

Comment: "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. ...?"

Reply: Apart from any anthropogenic contribution (see Kulaksiz and Bau, 2013 for a comprehensive review; *Earth Plan. Sc. Let.* 362, 43-50) Gd positive anomalies have been recognised in seawater and justified as a consequence of preferential dissolved Gd partition in seawater during equilibria with suspended particulate matter (Erel and Stolper, 1993; *Geochim. Cosmochim. Acta* 57, 513-518). On the other hand positive Gd anomalies are also shown in several brines worldwide where these fluids attain to crystallize chlorides and other salts. Therefore, if these minerals are depleted in Gd with respect to its neighbours along the REE series, the observed positive Gd anomaly in coexisting brine would be explained.

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

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

Reply: Although pH measurements in brines are poorly significant, conditions occur-

ring in these deep-sea hypersaline solutions are slightly acidic (De Lange et al., 1990; Mar. Chem. 31, 63-88) but less acidic than those occurring during Monji's experiments, as you correctly evidenced. But bacterial colonies usually produce extracellular polymeric substances (EPS) that do not occur in the organic substances used by Monji and co-workers. These EPS consist of densely packed, multispecies populations, encased in a cell-synthesized polymeric coating bacterial cell surfaces having a negative surface charge due to their anionic nature (Rendueles et al., 2013; Environmental Microbiology 15, 334-346). According to PHREEQC calculations in hypersaline brines the most abundant Zr and Hf species should be  $Zr(OH)_4$  and  $Hf(OH)_5^-$ . The different anionic character of these species could explain the observed fractionation between Zr and Hf being the former preferentially bound to anionic EPS with respect to the negatively charged  $Hf(OH)_5^-$  species. Analogous evidences of Zr-Hf decoupling have been recently shown in thermal springs during crystallization of silica-rich stromatolites in presence of bacterial activity (Censi et al., 2013b; Gondwana Research, under review). Therefore I would integrate the revised version of the text with these considerations, if you agree.

Many thanks for your contribution Sincerely yours

Paolo Censi

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