Local structures of Y and Ho in calcite and its relevance to Y fractionation from Ho

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The behavior of Y and Ho in most igneous activities is very close due to the similarity in their ionic radii, while Y fractionates from Ho in marine systems. In this study, in order to elucidate Y-Ho fractionation observed in marine systems in terms of structural chemistry, we examined Ho L_{III}-edge and Y K-edge EXAFS study for two partitioning systems, namely, 1) calcite-aqueous solution (Y-Ho fractionation system) and 2) strong acid cation exchange resin-aqueous solution (non Y-Ho fractionation system). The results of the EXAFS analysis did not show significant differences in interatomic distances to the most neighboring O atoms between Ho and Y for all the samples (Table 1).

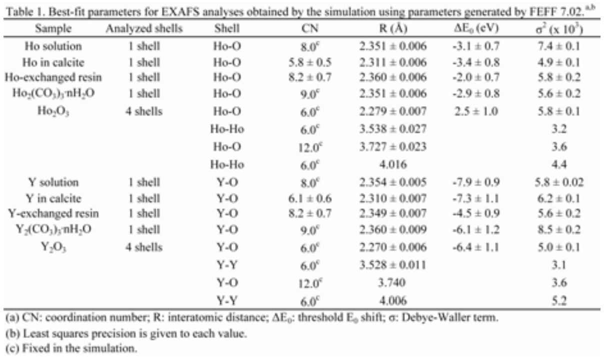

Table 1. Best-fit parameters for EXAFS analyses obtained by the simulation using parameters generated by FEFF 7.02.[a,b]

Sample	Analyzed shells	Shell	CN	R (Å)	ΔE_0 (eV)	σ^2 (x 10^3)
Ho solution	1 shell	Ho-O	8.0^c	2.351 ± 0.006	-3.1 ± 0.7	7.4 ± 0.1
Ho in calcite	1 shell	Ho-O	5.8 ± 0.5	2.311 ± 0.006	-3.4 ± 0.8	4.9 ± 0.1
Ho-exchanged resin	1 shell	Ho-O	8.2 ± 0.7	2.360 ± 0.006	-2.0 ± 0.7	5.8 ± 0.2
$Ho_2(CO_3)_3 \cdot nH_2O$	1 shell	Ho-O	9.0^c	2.351 ± 0.006	-2.9 ± 0.8	5.6 ± 0.2
Ho_2O_3	4 shells	Ho-O	6.0^c	2.279 ± 0.007	2.5 ± 1.0	5.8 ± 0.1
		Ho-Ho	6.0^c	3.538 ± 0.027		3.2
		Ho-O	12.0^c	3.727 ± 0.023		3.6
		Ho-Ho	6.0^c	4.016		4.4
Y solution	1 shell	Y-O	8.0^c	2.354 ± 0.005	-7.9 ± 0.9	5.8 ± 0.02
Y in calcite	1 shell	Y-O	6.1 ± 0.6	2.310 ± 0.007	-7.3 ± 1.1	6.2 ± 0.1
Y-exchanged resin	1 shell	Y-O	8.2 ± 0.7	2.349 ± 0.007	-4.5 ± 0.9	5.6 ± 0.2
$Y_2(CO_3)_3 \cdot nH_2O$	1 shell	Y-O	9.0^c	2.360 ± 0.009	-6.1 ± 1.2	8.5 ± 0.2
Y_2O_3	4 shells	Y-O	6.0^c	2.270 ± 0.006	-6.4 ± 1.1	5.0 ± 0.1
		Y-Y	6.0^c	3.528 ± 0.011		3.1
		Y-O	12.0^c	3.740		3.6
		Y-Y	6.0^c	4.006		5.2

(a) CN: coordination number; R: interatomic distance; ΔE_0: threshold E_0 shift; σ: Debye-Waller term.
(b) Least squares precision is given to each value.
(c) Fixed in the simulation.

However, the first shell Ho-O and Y-O distances in the Y-Ho doped calcite were shorter than those in the aqua ion. In contrast, the first shell Ho-O and Y-O distances in the Y-Ho doped resin were similar to those in the aqua ion. Previous studies have suggested that lanthanide (Ln) is more covalent due to 4f orbital participation in bonding relative to Y. Spectroscopic studies on various Ln^{3+} complexes show that Racah parameters for 4f electron repulsion in Ln^{3+} ions decrease with an increase in covalency of bonding of Ln^{3+} ions with anionic ligands. Therefore, our EXAFS results suggest that Y-Ho fractionation in partitioning is possibly attributed to the difference of change in covalency associated with the ligand exchange between Y and Ho, which we have observed as differences in partition coefficients between calcite and aqueous solution.

[1] Tanaka *et al.* (2008) *Chem. Geol.* **248**, 104-113.

Lead isotope systematics of olivine-hosted melt inclusions from Hawaiian lavas

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We present new data on Pb isotopic compositions of olivine-hosted melt inclusions from Kilauea, Mauna Loa and Koolau lavas with those previously reported [1]. Only olivine grains that were >1 mm in size, which should have high dislocation densities [2] were selected for melt inclusion studies. The Pb isotopic compositions of olivine-hosted melt inclusions show a systematic increase in $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ in the order Kilauea < Mauna < Koolau Makapuu, with considerable overlap with each other in general. However, several melt inclusions extend beyond their whole-rock field of each volcano or even of whole ranges of all Hawaiian lavas. Since the deformed olivines that crystallized from previous magmas could have been trapped from the conduit wall or magma chamber into the magma, the analyzed Pb isotopic compositions of melt inclusions should carry the signatures of the previous magma(s) in the same volcano from which they crystallized. The evolution of magmas that eventually erupted to form the Kilauea, Mauna Loa and Koolau volcanoes could be explained by the supply of batches of magmas of similar or different chemical and/or isotopic compositions into magma chambers where olivine crystallization, fractionation, deformation and subsequent entrainment occurred. We propose that the batches of magma in the preceding stages of the Kilauea volcano had Kilauea- and Loihi-like compositions. Likewise, Mauna Loa volcano recorded the exhaustion of Kilauea-/Loihi-like and Loa components and the initiation of Loa component, which is chemically and isotopically different from the previous Loa component. The Koolau volcano probably recorded the history of three batches of magma. Kilauea-like magma dominated early Main shield stage, which was followed by low $^{207}Pb/^{206}Pb$ MORB-like magmas, and finally the high $^{207}Pb/^{206}Pb$ magma typically found in Makapuu-stage lavas. These evidences suggest that the Hawaiian olivine-phyric lavas contains significant amount of earlier-stage olivine grains that crystallized from magma that has different geochemical characteristics from the host magma.

[1] Kobayashi *et al.* (2004) *Chem. Geol.* **212**, 143-161.
[2] Sakyi *et al.* (2008) *GCA*, this volume.