An experimental study on stable isotope fractionation of rare earth elements during the adsorption on iron and manganese oxides

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Recent development of analytical instruments, especially multiple collector (MC) ICP-MS, has enabled us to discuss the mass-dependent isotopic fractionation of heavy elements. Although several rules controlling the isotopic fractionation has have been suggested, it is still insufficient to discuss which chemical properties are the most important factor to evaluate bond stiffness in the equilibrium isotopic fractionation. This study, therefore, exhibits the results of stable isotopic fractionation of rare earth element (REE) during the adsorption experiment to discuss the cause of the isotopic fractionation among REE.

Lanthanum, Ce, Nd, and Sm chloride solutions with various concentrations were respectively added to both synthesized ferrihydrite and δ-MnO$_2$ suspensions. In all the systems, pH was adjusted to 5.00 ($\pm$0.05) and shaken for 6 hours before the filtration. Stable isotope ratios in both liquid and solid phases were determined using MC-ICP-MS. REE-Cl$_3$ solutions used in the adsorption experiment were employed as standard solutions and the isotope ratio of each element was expressed in epsilon notation relative to the average standards, which is shown in the equation as follows: $\varepsilon = (R_{sample}/R_{STD} - 1) \times 10^4$, where R was defined as $^{139}La/^{138}La$, $^{142}Ce/^{140}Ce$, $^{145}Nd/^{143}Nd$, or $^{149}Sm/^{147}Sm$, respectively. For the solid phase, K-edge EXAFS of filtered samples was measured at BL01B1 in SPring-8 to obtain the information of the coordination environment.

Though accurate determination of La isotope ratio was difficult due to the large difference in the isotopic abundance between ^{138}La and ^{139}La, a broad trend obtained in this study suggested that the lighter La isotope was selectively partitioned into the solid phase. In Ce system, it is clearly shown that the lighter isotope was partitioned into solid phase, whereas in Nd and Sm systems, lighter isotopes remained in the liquid phase, suggesting that physicochemical factors have been changed between Ce and Nd. According to the EXAFS analysis, split first shell (La-O bond) was observed for La-adsorption system, suggesting that the first coordination sphere is distorted in the system. Such distortion was also expected for Ce-adsorption system from their EXAFS results. On the other hand, split first shell was not observed for Nd and Sm systems. Thus, it is expected that the slight change in coordination environment, which can also cause the difference in their hydration numbers, affects the direction and degrees of mass-dependent isotope fractionations among REE.

Mechanism and conditions for strain softening in gabbro

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Introduction

Weakening of lower crustal rocks due to fluid infiltration and metamorphism is responsible for the development of ductile shear zones. In this contribution, we describe the mechanism of formation of ductile shear zones in a granulite facies gabbro, followed by fabric formation during retrogression after eclogite facies metamorphism in rocks from Flakstadøy, Lofoten, Norway [1].

Results

Several mm to cm wide ductile shear zones are observed within the leuco-gabbro. Pl$_0$, Ol$_0$ and Opx$_0$ form the cumulus igneous texture. Opx$_1$ and Grt$_1$ corona around Pl$_0$ and Ol$_0$ indicate granulite facies metamorphism (M$_1$). Alternate bands of mafic (Opx$_0$+ Omp + Grt$_{I/II}$) and felsic (Pl + Amp + Spl) layers characterize the shear zone. The Opx$_0$ porphyroclasts are mantled by recrystallized Opx$_{II}$ grains (20-30 mm) and show asymmetrical σ-porphyroclast indicative of sinistral sense of shear (D$_1$). Static overgrowth of Omp $\pm$ Grt$_{II}$ around Opx$_{0/II}$ is the peak pressure metamorphic stage (M$_{2A}$). Subsequently, Cpx - Pl symplectite (M$_{2B}$) form at the outer rim the Omp. Breakdown of Grt$_{I/II}$ to Amph $\pm$ Pl (An rich) $\pm$ Spl with opposite shear sense in the Opx$_{0/II}$ defined fabric characterize M$_3$ metamorphism.

Alternate bands of mafic (Cpx + Pl + Qtz + Grt$_{II}$ − Ol$_0$ - Opx$_0$ - Omp) layer ($\approx$M$_{2B}$)and felsic (Pl+ Amp + Cz − Spl) layer characterize the fabric in the retrograde eclogite. Amp and Cz overgrows at the contact between the mafic and felsic layers ($\approx$ M$_3$).

In the ductile shear zone, chemical similarity and CPO data of Opx$_0$ and Opx$_{II}$ indicate that Opx$_0$ deformed by cracking (D$_1$) at the onset of M$_1$-metamorphism. The fine-grained Pl shows a strong CPO indicative of inheritance of the CPO from D$_1$ deformation. The CPO of amphibole suggests that amphibole re-orients by rigid body rotation forming aligned (100) planes during post D$_1$ deformation.

In the retrograde variety, the CPO data of Cpx from the mixed phase mafic layers is consistent with the (010) [001] dominant slip system but is interpreted as oriented-growth-fabric during diffusion creep, because the mixed-phase-fabric does not indicate dislocation creep microstructures. CPO data of recrystallized plagioclase in the mono-mineralic felsic layers indicate (010) [100] as dominant slip system during dislocation creep.

Conclusions

This study indicates that deformation of Opx via cracking (D$_1$) requires very high differential stress at lower crustal conditions [3] during M$_1$ stage. However, in the retrograde eclogite, Omp breakdown will produce fine-grained Cpx+Pl mixtures [4] and promotes diffusion creep accommodated fabric formation.

[1] Markl & Bucher (1997) *Lithos* **42**, 15-35. [2] Kretz (1983) *Am. Min.* **68**, 277-279. [3] Steltolphel et al. (2006) *Geosphere* **2**, 61-72. [4] Anderson & Mocher (2007) *Contrib. Min. Pet.* **154**, 253-277.