

High-pressure dehydration of antigorite-serpentinite and its effect on boron isotope fractionation in the shallow mantle wedge.

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The ultramafic rocks of Cerro del Almirez Massif in Spain preserve field evidence for the subduction-related, prograde transition from antigorite-serpentinite (ant-serp) to chlorite-harzburgite (chl-harz) [1]. This study investigates the influence of dehydration reactions on B isotope fractionation in the sub-arc region, where fluid loss accompanies prograde metamorphism under well constrained P-T conditions (650 °C, 1.7 GPa [2]).

B isotopes are strongly fractionated during the dehydration of ant-serp, with a sharp decrease of $\delta^{11}\text{B}$ across the ant-serp to chl-harz isograd. Ant-serp has a $\delta^{11}\text{B}$ of +22.6 ‰ (± 1.6 ; n=2), similar to the heaviest $\delta^{11}\text{B}$ in forearc serpentinites of the active Mariana subduction zone [3, 4]. Transitional ant-chl-ol-opx serpentinite samples preserve a $\delta^{11}\text{B}$ of +3.3 ‰ (± 0.3), and the dehydration reaction product, granofels-textured chl-harz, has a $\delta^{11}\text{B}$ of -3.5 ‰ (± 0.3). Spinifex-textured chl-harz formed by crystallisation of atg-breakdown products and sampled some distance from the isograd, has a $\delta^{11}\text{B}$ of +2.7 ‰ (± 0.4). The anomalously heavy $\delta^{11}\text{B}$ of the spinifex-textured chl-harz may be attributable to interaction with a second, boron-bearing fluid associated with the formation of the spinifex textures or to a less efficient fractionation process due to the fast mineral and textural transformations that took place.

The drop in $\delta^{11}\text{B}$ approaching the isograd demonstrates that massive B isotope fractionation occurs in the shallow segments of the slab-mantle interface during the dehydration of ant-serp. Moreover, the effects survive to higher P-T conditions. The continuing stability of chlorite beyond the antigorite breakdown reaction limits the release of H₂O, and therefore B, to about 6–7 wt% H₂O, whereas without the “chlorite-in” reaction the dehydration would yield > 12 wt% H₂O loss and thus a larger B flux). This likely results in a chlorite-hosted, B-rich reservoir with a heterogeneous $\delta^{11}\text{B}$. This reservoir may contribute B to the fluids necessary to trigger melting under volcanic arcs and in addition to the proposed deeply subducted serpentinite [5] may contribute to the heavy and often very heterogeneous $\delta^{11}\text{B}$ signatures of island arc volcanoes

[1] Trommsdorff et al. (1998) *Contrib. Min. Petrol.* **132**, 139-148.

[2] Padrón-Navarta et al. (2011) *J. Petrol.* **52**, 2047-2078. [3] Savov

et al. (2007), *J. Geophys. Res.*, doi:10.1029/2006JB004749.[4]

Pabst et al. (2012) *Lithos* **133**, 162-179. [5] Ullmer & Trommsdorff (1995) *Science* **268**, 858-861.

Identification and characterization of phase governing Eu(III) uptake in granite by microscopic observations

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Sorption behaviors of trace elements on single mineral surface have been extensively studied. However, there have been very few researches for the trace elements sorption on complex mineral assemblages such as rocks, sediments and soils. In order to make predictions for the trace elements migration on geologic media, it is crucial to understand the molecular-scale interaction of trace elements with complex mineral assemblages, and to construct the thermodynamic sorption models based on the molecular-scale information. In the present study, the sorption of trace level of Eu(III) on complex mineral assemblages, slightly altered granite, as function of pH was studied by microscopic approaches.

The granite sample was collected from a borehole at a depth of 400m from the Mizunami Underground Research Laboratory constructed by Japan Atomic Energy Agency in central Japan. The granite sample was visually fresh. However, the microscope observation as well as the X-ray diffraction patterns of clay fraction shows that the occurrences of smectite, chlorite, vermiculate, calcite and hydrous iron oxides. The thin sections of the granite were prepared for Eu(III) sorption experiments. The thin sections were reacted for 24 hours in solutions of which pH were adjusted to 4, 5 and 6 under 0.01 M NaCl support electrolyte and analyzed by electron probe micro analyzer (EPMA). Then, the same thin sections were reacted for 24 hours in solutions of which 1.5 ppm of Eu(III) was added into solutions mentioned above. The resulting thin sections were served for observation and analyses by EPMA.

EPMA analyses of the thin sections after Eu(III) sorption shows that the Eu contents in quartz, plagioclase, K-feldspar, chlorite, calcite and iron hydroxide were less than detection limit. In contrast, smectite always contains up to 4 wt% of Eu. Part of biotite grains also contains up to 8 wt% of Eu. Because the Eu concentration in solution is 1.5 ppm, the concentrated factors of Eu in smectite and biotite are more than ten thousands. Quantitatively, the amount of smectite in the granite is negligible. We concluded that biotite is most important phase governing Eu(III) uptake on the granite. The texture of Eu enriched parts in the biotite grain were different from the original texture. The Eu enriched parts were distorted and the distinct cleavages appear. There is good negative correlation between K and Eu in the affected biotite grain. The relationship shows the uptake mode of Eu on biotite is ion-exchange of K in biotite and Eu(III) in solution. The number of the Eu affected biotite grain increases with decreasing pH. This indicates that the intercalation of Eu(III) to K in biotite favors at low pH conditions. The macroscopic sorption behavior of Eu(III) on granite (Maeda et al. this volume) is consistent with the microscopic observations.

Ref.: K. Maeda, K. Fukushi, Y. Hasegawa, Y. Yamamoto, D. Aosai and T. Mizuno: “Modeling Eu(III) sorption on granite, In this volume.