

Oxidation of slab mantle due to dehydration of serpentinite

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The oxygen fugacity in subduction zones controls the speciation of C-O-H-bearing fluids and phase equilibria in metamorphic processes. It is therefore important to quantify the oxidation states in the Earth's interior. This study used X-ray absorption near edge structure (XANES) spectroscopy to investigate changes in redox state that accompany the dehydration of serpentinite. A run product (Atg02) of our previous deformation experiment (Shimizu et al., 2011) was used for the analysis.

The starting material of the experiment was dark-green natural serpentinite (from Oeyama, Kyoto Prefecture, Japan) consisting mainly of antigorite and accessory wustite. A cylindrical sample of serpentinite (diameter 10 mm, height 15 mm) was enclosed in Ni and Ag sheets, and was set in confining mediums of talc and pyrophyllite. High-pressure and high-temperature deformation experiments were conducted with a piston-cylinder type apparatus. The confining pressure was kept at 800 MPa during the experiments. A graphite furnace was used to heat the sample to 700°C. After the constant strain-rate experiment, the color of the sample had changed to pink or red, and forsterite and talc had grown in the antigorite matrix. Small particles of hematite were identified in the matrix by optical microscope and micro-Raman spectroscopy.

The oxidation state of the serpentinite before and after the experiments was investigated by the Fe-K edge XANES spectra acquired at BL9A, Photon Factory, KEK (Tsukuba, Japan), using Fe standards of FeS₂, fayalite, magnetite (Fe₃O₄), FeO, *a*-FeOOH, and *a*-Fe₂O₃. Following Wilke et al. (2001), the ratio $X(\text{Fe}^{3+}) = \text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ was calculated from the Fe-K pre-edge centroid positions. The results show that $X(\text{Fe}^{3+})$ increased from 7% of the original sample to 23% in the reacted sample. It is probable that the oxidation state of the sample was buffered by a large amount of free water liberated by the following dehydration reaction: antigorite => forsterite + talc + H₂O.

The mechanical data of the antigorite-serpentinite showed drastic dehydration weakening. This result supports the hypothesis that intermediate-depth earthquakes in subduction slabs are triggered by the dehydration instability of serpentinite. If this hypothesis holds true, then the subducting slab mantle must be largely serpentinitized.

In general, the oxygen fugacity of peridotites is equilibrated near the fayalite-magnetite-quartz (FMQ) buffer at the top of the upper mantle, and decreases with increasing depth (Frost and McCammon, 2008). However, if large parts of the slab mantle are serpentinitized and if free water is released by the breaking down of antigorite, the reaction front of antigorite would be highly oxidized. The redox states in the subducting oceanic crust and the wedge mantle would be also influenced by water supplied from the slab mantle.

References

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