Unraveling the controls on the silica metasomatic reactions during serpentinization using the exchange Monte Carlo method.

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In the oceanic lithosphere, a large amount of mass transfer occurs as observed as reaction zoning around the crust–mantle boundary. The amounts and distribution of serpentinized peridotite in the oceanic lithosphere are critical to constraining the water budget in the Earth’ s interior: however, the detailed relationship between mass transport and surface reactions during serpentinization have been unclear. The metasomatic zoning of forsterite–serpentine–talc–quartz has been modeled by diffusional mass transport processes coupled with multiple precipitation–dissolution reactions (Lichtner *et al.*, 1986). These models, which assume the local equilibrium between fluid and minerals, predict the development of the monomineralic layers of serpentine and talc, but the detailed mechanism for the development of the silica metasomatic zone has not been examined experimentally. For understanding the temporal and spatial variation of progress on serpentinization in the oceanic lithosphere, the effects of silica transport on serpentinization rate needs to be constrained.

In this study, we conducted hydrothermal experiments (300°C, 8.6 MPa) on olivine (Ol)–quartz (Qtz)–H_2O system, as analogues of crust-mantle boundary. By using tube-in-tube type hydrothermal experiments vessel, spatial distribution of minerals (reactant and product) was observed.

After the experiments, the mineralogy of the reaction products in the Ol-hosted region changed with increasing distance from the Ol–Qtz boundary, from talc to serpentine + magnetite + brucite. Talc was formed 3.2 mm from the Ol–Qtz boundary in Ol-hosted region. On the other hand, in Qtz-hosted region, no minerals were formed after the experiments.

The observed mineral distribution was modeled by reaction-diffusion equation. To model our experiments, we set eight reaction rate constants; diffusion constant for $SiO_{2(aq)}$ and rate constants for olivine→talc, olivine→serpentine, olivine→brucite, serpentine→talc, talc→serpentine, serpentine→ brucite, and brucite→serpentine. The unknown parameters were optimized by using exchange Monte Carlo method (Hukushima and Nemoto, 1996). The surface area of minerals in the reaction-diffusion model (reactant or product) were selected by 2-hold cross validation method.

By using the exchange Monte Carlo method, the observed mineral distribution in the Ol-Qtz-H_2O experiments was reproduced by numerical reactive transport model. The second Damkőhler number (Da_{II}) of each reaction changed from Da_{II}<<1 at 1000 h to Da_{II} >> 1 at 2000 h reaction, suggesting that the rate-limiting processes during Si-metasomatic reaction was changed in time and space from surface-controlled reaction to transport-controlled reaction. Our experiments and kinetic analysis suggests that the dynamic changes in rate law from transport- to surface controlled reaction, and vice versa, would be responsible for the spatial-temporal evolution of the metasomatic zone at the crust-mantle boundary in the oceanic lithosphere.

References

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