Hydrogen diffusion in Ti-bearing forsterite

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Migration of point defect in ferromagnesian silicates controls the transport properties of the Earth's mantle. The geodynamic and chemical evolution is dictated by the influence of "water" (more specifically hydrogen) on the physical properties of olivine $(Fe,Mg)_2SiO_4$, which dominates the mineralogy of the upper mantle. The presence of hydrogen significantly modifies the timescale of diffusion, plastic deformation and other transport properties in olivine such as electrical conductivity or the attenuation of seismic waves. In order to understand all these processes it is essential to unravel the diffusivity of hydrous defect in nominally anhydrous minerals (NAMs). We report a new experimental approach to study hydrogen diffusion in forsterite containing key hydrous defects relevant for the upper mantle.

Synthetic titanium-bearing forsterite crystals containing 308 ± 20 ppm wt. H_2O were heated at 1273 K, 1173 K and 1073K during 296, 432 and 1304 h (ca. 1.8 months) respectively. The temporal evolution of individual peak heights related to hydroxyl (OH) stretching vibration in the infrared spectra was measured. OH-stretching bands assigned to titanium clinohumite point defects, silicon and magnesium vacancies and defects associated to trivalent cations show contrasting behaviors with time. Two different parts are distinguished during the dehydroxylation process: (1) hydrous defects related to trivalent cations and Mg-vacancies early disappear followed by hydrous defects related to Ti and Si-vacancies with a diffusion coefficients one order of magnitude slower than previously reported. The first part of the dehydroxylation is associated to the precipitation of an oriented Ti-rich phase; (2) In the second part of the dehydroxylation process, a concentration of 39-46 ppm wt. H_2O (exclusively related to Si-vacancies) is reached and remains constant until the end of the experiment. We suggest that this is related to a very slow diffusivity of Si-vacancies when other type of defects are lacking. Hydrogen extraction in forsterite and likely in other NAMs is thus far more complex than previously assumed. Unraveling these complex processes are crucial to understand the deep Earth's water cycle.

Fluorine, Cl, Br & I in serpentinites

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The abundance of F, Cl, Br and I in serpentinites were examined to evaluate their behaviour in subduction zones. Samples include (1) unmetamorphosed, obducted hydrated abyssal peridotites, (2) subducted abyssal peridotites to depth of ~30 km, (3) forearc mantle serpentinites from shallow depth (<30 km) and (4) mantle wedge serpentinites from ~140 km depth in the Himalayas. Samples (1,2,3) from Dominican Republic are composed of lizardite (low temp. serpentine). The Himalayan samples consist of antigorite (high temp. phase). Abyssal peridotites contain high (<530 ppm) Cl but they lose Cl during their subduction. In the mantle wedge, elevated (<880 ppm) Cl in shallow serpentinites suggests transfer of Cl from subducting slab to the overlying mantle wedge. Lower Cl values (≤50 ppm) in deep mantle wedge serpentinites indicate loss of Cl either by pressure increase or transition from lizardite to antigorite. The Br/Cl ratios for obducted abyssal peridotites are comparable to that of seawater, confirming their serpentinization on or near the ocean floor. Bromine appears to mimic Cl in its behaviour; abyssal peridotites partially lose Br during subduction and there is high Br content in shallow mantle wedge serpentinites. However, the degree of Br loss is less than that of Cl with increasing depth, as illustrated by the elevated Br/Cl ratio ($<12 \times 10^{-3}$) in the deep mantle wedge. Hydrated abyssal peridotites contain relatively high I/Cl ratios up to 240 times seawater. Our results are consistent with data from sea floor serpentinites [1]. The content of I remains relatively constant during their shallow subduction. In the mantle wedge, shallow and deep forearc serpentinites contain similar amounts of I, indicating retention of I during the lizardite to antigorite phase transition.

Fluorine shows significantly different behaviour from the other halogens. The content of F is low (≤20 ppm) in abyssal peridotites, as expected from low F content in seawater. Upon shallow subduction, F content increases in hydrated abyssal peridotites, likely incorporated from shallow water sediments. Similar F-enhancement is observed for shallow forearc peridotites. Fluorine is further enriched in deep mantle wedge peridotites (<160 ppm) by incorporating F released from slabs and sediments.

Serpentinites likely contribute to the transfer of F and I into the deep mantle, whereas Br and Cl likely have shallow cycles in subduction zones.

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