

Hydrogen in Al-bearing stishovite

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Hydrogen content of stishovite synthesized in the natural eclogitic system was investigated at the pressure of 10 and 15 GPa and at the temperature range of 1200 to 1400 degrees Celsius in order to consider the incorporation mechanism of hydrogen with respect to its relations to other minor element. The hydrogen content of stishovite in an eclogitic system depends on aluminum content and is much higher than in a simple alumina-silica-water system. It is expected that significant quantities of hydrogen might be incorporated into stishovite to charge balance aluminum with increasing pressure. Stishovite could be a major hydrous phase in the deep mantle including subducting slab.

Rossman and Smyth (1990) observed that rutile of mantle origin contains considerable amounts of H. Rutile is isostructural, and contains a high-pressure phase of SiO₂, stishovite. It can therefore be used to examine the manner in which stishovite accommodates H. Pawley et al. (1993) reported that Al-bearing stishovite can contain more H₂O than Al-free stishovite and that the H₂O content of synthetic Al-containing stishovite reaches 500 ppm for 1.51 wt. percent alumina at 10 GPa and 1200 degrees Celsius. Ono (1999) observed that the Al content of stishovite in a simple alumina-silica-water system increased with increasing temperature and Al₂O₃ up to about 9 wt. percent. These results in a simple alumina-silica-water system indicate that a considerable amount of water is likely to dissolve into stishovite in compared to Al₂O₃, and that stishovite could be an important water reservoir in the lower mantle which is too hot for hydrous minerals to be stable. To reconsider the mechanism of H incorporation into stishovite and the effect of Al₂O₃ contents on hydrogen concentration of stishovite in a natural system, we have investigated stishovite synthesized in an eclogitic system.

Natural MORB quenched glasses, with water contents of 10±3 wt. percent (HB13) and 0.9±0.2 wt. percent (HB1) were used as starting materials for high-pressure experiments. Stishovite samples were obtained by using an MA-8 type apparatus (ERI 2000). Stishovite crystals coexisting with majoritic garnet and jadeitic clinopyroxene were obtained at 10 and 15 GPa, and 1200-1400 degrees Celsius. Chemical analyses of recovered experimental charges were done by a JEOL JXA-8800 electron microprobe. Most of stishovite single crystals were acicular and the grain size was typically smaller than 30 μm. IR absorption was measured using a micro FTIR spectrophotometer (Spectrum 2000, Perkin Elmer) and water content was calculated according to Beer-Lambert equation.

The Al₂O₃ content of stishovite was found to be 0.83-1.35 wt. percent and was dependent on the temperature, coexisting phases and water content of starting materials. It increases with temperature, and stishovite in the run charges of HB13 has more Al₂O₃ content than HB1. It contained 0.05~0.5 wt. percent of divalent cations, dominated by Fe and Ca, and ~0.05 wt. percent of monovalent cations, dominated by Na. IR absorption spectra of single crystals showed the incorporation of H into stishovite. Absorption at 3111 cm⁻¹ due to OH-stretching vibration indicates the structural OH. Polarized spectra confirm that OH dipole is oriented perpendicular to the c axis of the stishovite, the same orientation as found for rutile. Therefore, H and Al are substituted for Si in octahedral site, as in rutile. Calculated water content of stishovite synthesized at 15GPa is 5 times more than that obtained in a simple system by Pawley et al (1993), but Al content is slightly lower than that in the simple system. The high H content in an eclogitic system would seem to be due to the effects of pressure on H incorporation into stishovite. The absence of other impurities may also contribute to the increase of H incorporation into stishovite. H incorporation linked to other impurities in rutile was examined by Vlassopoulos et al. (1993). However, despite the effects of pressure on H incorporation into stishovite, the H content is significantly less than required for Al charge balance. A possible charge balance mechanism to the high Al content may be the substitution of other impurities or by oxygen vacancy from the previous works, but compositional systematics on H and other impurities in a natural system needs to be reexamined further.

Our results suggest that stishovite in an eclogitic system could store more H to charge-balance Al than that expected in a simple alumina-silica-water system and that stishovite may be a major hydrous phase in the lower mantle and the deep subducting slab.