

Tale of water in Earth's lower mantle

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Earth's lower mantle has been considered to be the driest layer in Earth's interior. Recent studies indicate that the lower mantle may not be as dry as we expected, as the trace of water has been found inside diamonds that likely come from Earth's lower mantle (Tschauer *et al*, *Science* 2018). Our recent experimental studies in a multi-anvil press indicate that water solubility in bridgmanite increases with pressure, and the lower mantle may turn out to be capable to hold water equivalent to the mass of a few to ten oceans. Furthermore, our experimental data of laser-heated diamond anvil cells indicate that $\text{FeOOH}_{0.75}$ is stable in pyrite-type structure at the bottom of the lower mantle to host significant amount of water. In-situ P-V-T data unveils that this pyrite-type phase may give rise to the ultra-low velocity zone (ULVZ) at the core-mantle boundary.

The multi-anvil experiments were conducted on aluminous magnesium silicate bridgmanite as a function of pressure up to 33 GPa at temperature of 1900°C. The starting material for these experiments was a mixture of oxides ($\text{Mg}(\text{OH})_2$, Al_2O_3 and SiO_2) with equivalent of about 5 mol % of Al_2O_3 and 15 wt % of H_2O . The structure and composition of the perovskite phase after high P/T syntheses were examined using x-ray diffraction (XRD) and electron probe microanalysis (EPMA). Water concentration in the sample was measured using secondary ion mass spectroscopy (SIMS) and Fourier transform infrared spectroscopy (FTIR). The measurements yield that the aluminous magnesium silicate bridgmanite with about 2 wt% of Al_2O_3 may take as much as 0.13 wt % of H_2O at the P/T condition of the top of the lower mantle and this solubility increases significantly with pressure. At the bottom of the lower mantle, the solubility may reach nearly a couple of weight percent of water according to simple extrapolation of the experiment result.

Time resolved *in situ* x-ray diffraction of FeOOH was conducted at pressures of 110 GPa and 120 GPa and temperature of 2200 K. The phase transitions from α - FeOOH to pyrite-type FeOOH_x and a new hexagonal phase are observed. After the formation of the pyrite-type FeOOH_x phase, the sample is kept at 2200 K and x-ray diffraction is collected as a function of time. The sample is cooled down to room temperature periodically during the heating to stabilize the system and to measure the lattice parameter of the sample at room temperature. The accumulated period of laser heating is about 12 hours. We observed that the volume of pyrite-type FeOOH_x reduces during the heating and approaches $x=0.75$ while the LiF lattice remains constant. The x value decreases slightly when the pressure increases to 120 GPa. Fitting the 2nd order Birch-Murnaghan EOS to the P-V-T data yields $K_0 = 268 \pm 17$ GPa, $dK/dT = -0.054$ GPa/K, $a_0 = 5.9 \times 10^{-5}$ and $a_1 = 1.3 \times 10^{-8}$. Estimated P- and S-wave velocities of this pyrite-type FeOOH_x based on these data and theoretical calculation are significantly lower than that of PREM, and therefore become a possible origin of the ULVZ (as shown in the figure).

