**Water Storage capacity of dense, lower mantle minerals.** B. Grocholski[1] and E. Cottrell[1]
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**Introduction:** Surface water on the Earth is in large part due to the inability of mantle minerals to dissolve hydrogen into their crystal structures. The amount of water we may expect to find on a terrestrial exo-planet will in part depend on the water storage capacity of dense, lower mantle silicate minerals such as stishovite or magnesium perovskite. These types of minerals become more important as the size of the planet increases, as perovskite or the closely related post-perovskite structure should comprise increasingly larger fractions of a planetary mantle.

Experimental measurements of structurally bound hydrogen at lower mantle pressure have been elusive. Previous investigators have made room pressure measurements of the water content of perovskites synthesized at high pressure. The estimates for the water content using IR aborption in this way range from under 2 ppm to >1000 ppm [1-3], dramatically impacting the role the lower mantle may play in the large scale cycling of water through geologic time.

We have new IR absorption measurement that show two sharp, reproducible, high energy, pressure-dependent O-H stretching peaks up to 80~GPa. The stretching vibration is structurally bound to either stishovite or perovskite, both of which we find in our sample after laser heating. We can conclude that the water content of perovskite is on the lower end of the previous estimates, with the implication of a small lower mantle water storage capacity per unit mass.

**Experimental Methods:** Hydrous iron-aluminous pyroxene crystals were synthesized in the piston cylinder device with stoichiometric amounts of oxides plus excess silica. Pyroxene crystals were doubly polished to under 20 microns and cryogenically loaded with argon in the diamond cell (Fig 1).

Samples were compressed to above 25 GPa and converted to perovskite by infrared laser heating. X-ray diffraction at the Advances Photon Source (beamline 13-IDD) confirmed the formation of perovskite plus small amounts of stishovite in the laser heated sample. The stishovite is likely a contaminant from loading the spacer grains (Fig. 1) to prevent the sample from directly touching the diamond culets.

Infrared absorption measurements were made at the U2A beamline the at National Synchrotron Light Source. The absorption of radiation in the 3000-4000 $cm^{-1}$ region is due to the O-H stretching vibration and is proportional to the number of O-H bonds in the sample [4].

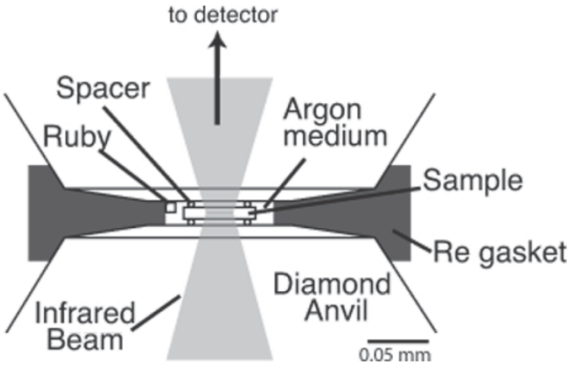


**Figure 1** Sample schematic. Pressure is determined by the shift in fluorescence by illuminating the ruby chip with a green laser. Argon surrounds the sample to maintain a hydrostatic environment during heating. Infrared absorption of the sample is determined by using the argon medium as the background.

**Results:**

The infrared absorption spectra from our experiments at high pressure show a broad

region of increased absorption between 2800 $cm^{-1}$ and ~3400 $cm^{-1}$ with two peaks from structurally bound O-H stretching vibrations near ~3750 $cm^{-1}$ and ~3820 $cm^{-1}$. The source of the absorption in the broad region is unclear and difficult to quantify due to uncertainty in the background subtraction. However, the region has been previously interpreted by some researchers as structurally bound water [2, 3]. The lack of sharp peaks over the broad region suggests water is not structurally bound and therefore potentially irrelevant for planetary interiors. In contrast, the two sharp peaks at higher energy are a clear indication of structurally bound hydrogen.

The shift of the high energy peaks in response to pressure change show the O-H vibrations are from a mineral in the sample chamber and not due to external contaminants. Further, the two peaks are resolvable in three different sample loadings. The peak locations are consistent with the high coordination environment of either stishovite or perovskite.

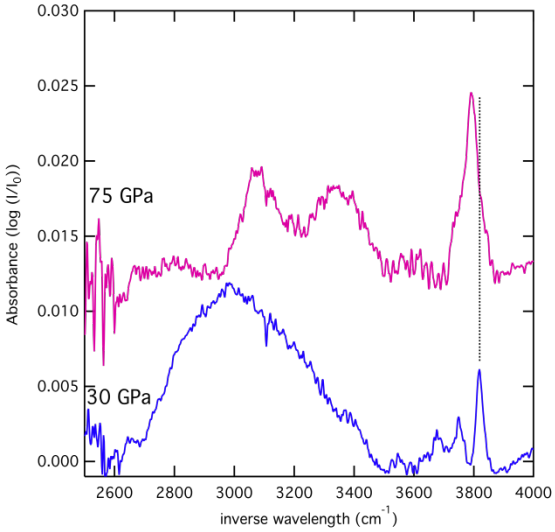


**Figure 2** Example of high-energy O-H stretching peaks at 30 and 75 GPa. Dashed line shows the shift of the large peak to lower energy at the higher pressure.

**Implications:** The ambiguity of the source of the sharp O-H stretching peaks makes it difficult to quantify the role of the lower mantle in the global water supply. If the peaks are due to stishovite instead of perovskite, the mineral could be an important source for introducing water into the deep interior of planets if basaltic material can be subducted deeper than the transition zone, as has been suggested by some studies [5, 6].

Regardless of the crystal the water is dissolved into, the water storage capacity of perovskite is likely to be low. The storage capacity of the lower mantle consequently would be under 0.5 oceans of water if we assume the sharp O-H absorption peaks are from hydrogen locked up in the perovskite structure. If the hydrogen is in the stishovite structure, the lower mantle of terrestrial planets may be exceedingly dry.

**References:**

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