Formation of Fe-rich volatile-bearing phases in the deep lower mantle and the implications for deep Earth volatile cycles

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Inclusions in deep diamonds provide a window to the actual deep mantle processes. The observation of hydrous ringwoodite with ~1 wt.% H_2O as a diamond inclusion indicates the transition zone is, at least locally, very wet [1]. Furthermore, the recent discovery of Ice-VII and halite inclusions at pressures as high as 24 GPa in diamonds provides direct evidence for the existence of saline fluid at least down to the shallow lower mantle [2]. To understand the interaction of water and Cl with the Fe-bearing lower mantle, we performed experiments to simulate the behavior of volatile-bearing systems in laser-heated diamond anvil cells (DACs) under high pressure-temperature (*P-T*) conditions corresponding to the deep lower mantle. The phase assemblages were determined by a combination of *in-situ* synchrotron-based X-ray diffraction (XRD) and *ex situ* transmission electron microscope (TEM) analysis. In the system MgO-Al_2O_3-Fe_2O_3-SiO_2-H_2O containing ~7 wt.% water, the hydrous Fe-bearing δ-phase coexists with both bridgmanite (Bdg) and post-perovskite (pPv) in a broad *P-T* range of 104-126 GPa and 1900-2500 K, whereas the pyrite-type (py) FeOOH phase was observed coexisting with the pPv phase. *In situ* XRD data further revealed that saline fluid reacts with Fe-bearing pPv to form a previously unknown cubic phase of $FeCl_2$ that adopts the identical space group of *Pa3* with the py-phase FeOOH. The TEM chemical analysis revealed that the composition of the pPv phase contains 3.5 wt.% Na_2O and 16.5 wt.% FeO after the reaction with the oversaturated saline fluid. Formation of the very dense Fe-rich volatile-bearing phases in the lowermost mantle provides clues for the deep storage of water and Cl and may contribute to the chemical heterogeneities in this region.

[1] D. G. Pearson *et al.*, Nature **507** (2014).
[2] O. Tschauner *et al.*, Science **359** (2018).

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