



	Experiment title: Influence of water on mineralogy of the lower mantle	Experiment number: ES-1255
Beamline: ID15B ID18	Date of experiment: from: 14 September 2022 to 18 September 2022 (ID15B) from: 14 November 2021 to 19 November 2022 (ID18)	Date of report: 18/09/2023
Shifts: 12 (ID15b) 15 (ID18)	Local contact(s): Michael Hanfland (ID15b), Georgios Aprilis (ID18)	<i>Received at ESRF:</i>
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Report:

The aim of the current project is to advance our understanding of high-pressure (HP)-high-temperature (HT) interactions between rock-forming minerals of lower mantle (*i.e.* ferroperricite, (Mg,Fe)O (Fp) and bridgmanite, (Mg,Fe)SiO₃ (Bgr)) and water by means of *in situ* synchrotron-based X-Ray diffraction (XRD) and Synchrotron Mössbauer Source (SMS). This beamtime was a continuation of the proposal ES-1071. While previous experimental session aimed to study reactions taking place in the uppermost lower mantle, during this beamtime we aimed to investigate 1) possible reactions occurring in the lowermost lower mantle; 2) to compare HP-HT behaviour of Fp in dry and hydrous environment (in order to illuminate effects observed in ES-1071). Several diamond anvil cells have been prepared at the Bayerisches Geoinstitut (BGI) and ESRF prior to the beamtime. A single crystal of ferroperricite and enstatite glass powder (as a precursor of bridgmanite) were loaded inside DACs. Water or Ne were loaded as a pressure-transmitting medium in order to simulate hydrous and dry lower mantle, respectively.

The strategy of the experiment was following: 1) XRD and SMS measurements of the compressed samples at ID15b and ID18 beamlines, respectively, prior to laser-heating (LH) sessions; 2) performance of LH at ID18 beamline and collection of SMS data on the heated spot; 3) XRD mapping of the heated area with collection of the powder and single crystal XRD at ID15b beamline; 4) depending on the sample – pressure increase or DAC reload.

The results on Fp in the pressure range 30–110 GPa and temperature range 1400–2300 K are summarised in the Figure 1. We have discovered that depending on the pressure and temperature conditions, Fp decomposes into a variety of structurally different oxides. While hydrous environment facilitates more rich

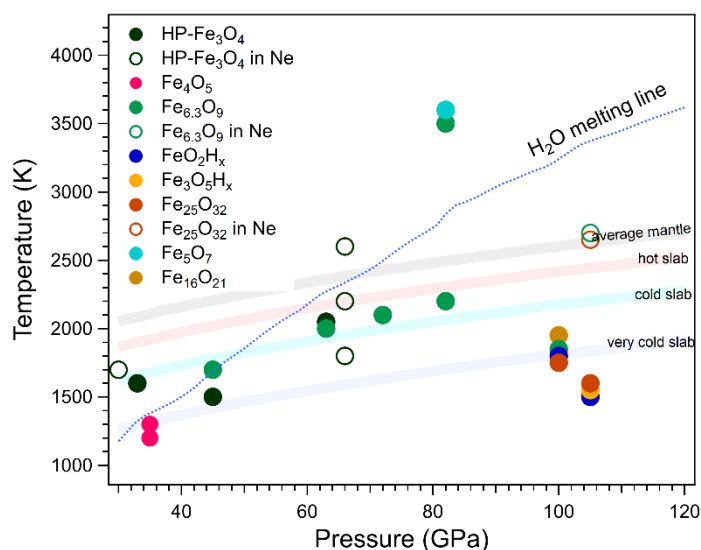


Figure 1. Iron oxides and hydroxides formed after laser-heating of ferroperricite at different P-T conditions in water and Ne.

mineralogical assembly, fewer iron oxides are formed as decomposition of Fp in dry environment. Interestingly, in hydrous environment, we have observed formation of a novel $\text{Fe}_3\text{O}_5\text{H}_x$ hydroxide at the lowermost lower mantle conditions. This H-storage phase crystallized in orthorhombic symmetry, with unit cell parameters $a = 7.8666(11)$, $b = 2.5671(4)$, and $c = 11.041(2)$ Å (at 105 GPa) and $Pnma$ space group. Usage of multi-grain SCXRD allowed us to solve and refine its crystal structure that is given in the Figure 2. The crystal structure features channels running along the b axis. Bond valence analysis and DFT-calculation have supported presence of hydrogen within these channels. Upon decompression, $\text{Fe}_3\text{O}_5\text{H}_x$ phase has been observed down to ~ 20 GPa. Another interesting observation is formation of $(\text{Fe}, \text{Mg})_{6.3}\text{O}_9$ both in dry and hydrous environments. This phase features the channels as well (see Figure 3) and it was long-debated

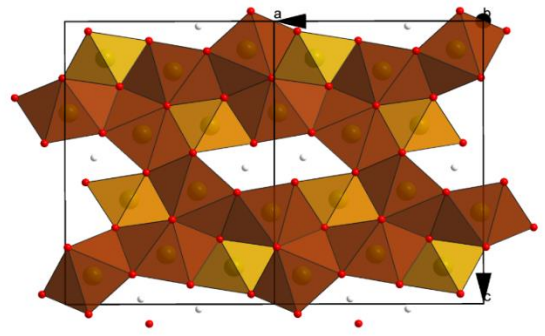


Figure 2. The crystal structure of the novel H-bearing phase that we discovered to form upon alternation of Fp and Brg by H_2O at the conditions of the lowermost lower mantle. FeO_n polyhedra are given in dark-brown and light-brown while H atoms are given as grey spheres.

whether

disordered hydrogen or iron atoms are stored within these channels. Our observation of $(\text{Fe}, \text{Mg})_{6.3}\text{O}_9$ being formed in Ne PTM, excludes possibility of H-storage in this phase.

Our results on decomposition of bridgmanite $(\text{Mg}, \text{Fe})\text{SiO}_3$ in water-rich environment at pressures 30-100 GPa and 1500-2500 K show formation of such decomposition products as stishovite, phase D and novel $\text{Fe}_3\text{O}_5\text{H}_x$ hydroxide, depending on the HP-HT conditions.

The present project demonstrates that the chemical reactions taking place in the Earth's deeps are more complicated than previously thought. Mineralogy of the lower mantle and properties of the constituting rocks are strongly affected on the presence of water. The preparation of the manuscript with the detailed characterisation of the observed phases and geological implications is ongoing.

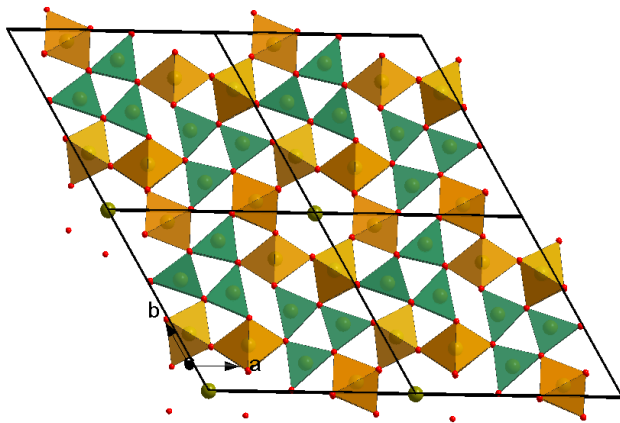


Figure 3. Crystal structure of $\text{Fe}_{6.3}\text{O}_9$ oxide that was found to form upon decomposition of Fp both with usage of H_2O and Ne as PTM. The structure features the channels running along the c axis and partially occupied by Fe atoms.