



	Experiment title: Probing New Oxygen Valence at Lower Mantle	Experiment number:
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Shifts: 15	Local contact(s): Emmanuelle De Clermont Gallerande	<i>Received at ESRF:</i>

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Report:

Recent experimental studies have reported unusual stoichiometries in the Fe-O system that take place at high pressure and temperature such as Fe₄O₅, Fe₅O₆, Fe₇O₉, and in particular, FeO₂H_x (with x between 0 and 1) which was synthesized above 76 GPa-1500 K (~1800 km depth)¹⁻⁴. Since FeO₂H_x crystallizes in a pyrite-type structure, it was proposed, by analogy with FeS₂ pyrite, that oxygen in this new phase has a valence of -1 (peroxide anion O₂²⁻) while iron valence is Fe²⁺. The discovery of this new pyrite-structured phase may have profound implications in terms of planetary science as it challenges many general conceptions such as the fact that only O²⁻ oxide ion takes place over the whole mantle and under oxygen rich conditions iron is of valence Fe³⁺. XANES spectra collected at the Fe K-edge indicate an iron valence of Fe²⁺⁵, while X-ray diffraction

measurements suggest O-O distance deduced by X-ray diffraction of ~1.93 Å at 76 GPa seems incompatible with typical O-O covalent bonds of 1.29 - 1.49 Å expected for peroxide groups¹. Recent theoretical studies using density functional and dynamical mean-field theories concluded to an unusual valence of Fe³⁺ and O^{1.5-} in FeO₂ due to oxygen-metal negative charge transfer, with no O₂ dimer⁶. While other theoretical studies support the idea of Fe²⁺ and O₂ dimer longer than usual, forming unusual soft covalent bonds^{7,8}. To resolve this ongoing argument, we have collected O K-edge at high pressure through diamond anvil cells (DAC) on FeO₂H_x, FeOOH and ZnO₂, a peroxide phase that crystallizes in the pyrite-type structure at ambient conditions.

The initial incident energy was of 9.7 keV with the use of a post-monochromator, however as we noticed that little or no signal was measurable for iron-rich compositions in these conditions, different tests were performed on both FeOOH and ZnO₂ crystals placed on a needle for incident energies of 6.4, 9.7 and 12.9 keV with and without the use of the post-monochromator. Finally the best signal was measured for 12.9 keV without the post-monochromator and this configuration was used for the rest of the beamtime. The lack of a post-monochromator reduces the energy resolution but increases the signal. These different tests took up to 6 shifts.

1) α -FeOOH (Goethite) under compression

In a first experiment, O K-edges were collected upon the compression up to 31 GPa at room temperature of α -FeOOH loaded with He as pressure medium in two different panoramic DACs (noted as 02 and 04 in figure 1). Pressure was measured using the ruby fluorescence before and after the measurements. As the signal becomes weaker at higher pressure (above 20 GPa), correct normalization of the spectra becomes complicated. At 0 GPa, the O -K edge is characterized by a prepeak and a broad edge at higher energy. The former results from the hybridization of the Fe 3d and O 2p and it usually splits into t_{2g} and e_g states by the ligand field. Here we cannot distinguish these two states and the prepeak is observed around 531.6 eV which is higher in

energy than in literature on O K-edge measured by ELNES in TEM⁹. The broad edge is composed of density of states from oxygen p character hybridized with Fe 4s and 4 p states.

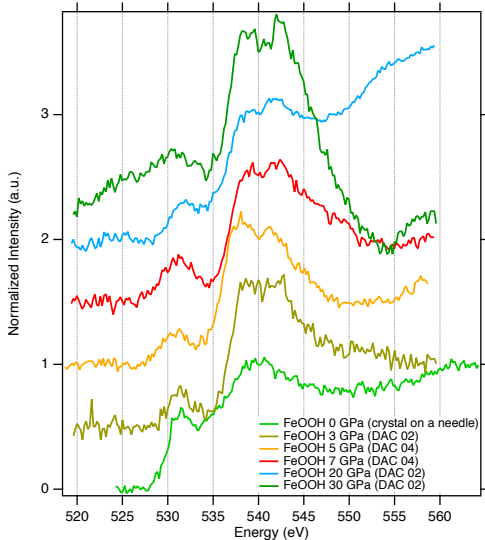


Figure 1 : XRS signals at the O K-edges collected upon compression of α -FeOOH

As pressure increases, the prepeak becomes weaker. Several changes in the broad edge can be observed as pressure increases. Above 3-5 GPa two features can be distinguished around 538.8 and 541.8 eV. Above 7 GPa one more feature is observed at higher energy (around 545.6 eV). Interestingly, these changes take place at similar pressures (4 and 8 GPa) to the recent report of changes in the Raman spectra and electrical spectroscopy while X-Ray diffraction show no structural changes^{10,11}. The nature of these transition is still under debate.

2) ZnO₂ under compression

ZnO₂ was used as a reference for a pyrite-structured peroxide. Particular attention has been draught to the use of pure nano-particules of ZnO₂ without ZnO as usually commercially found. The spectrum collected at ambient pressure shows a prepeak at 532.7 eV typical of O₂²⁻ bonding as in peroxides. Spectra were collected upon compression up to 9 GPa.

3) FeO₂H_x at high pressure after laser heating

FeO₂H_x was synthesized prior to the beamtime at our laboratory IMPMC by pressurizing α -FeOOH in DAC up to 94 GPa and used infra-red laser heating at 2300 K for 10 minutes in order to transform it into FeO₂H_x (Table 1). O K-edge were collected through the DAC at high pressure at room temperature. For these synthesis, we used “miniature-diamond anvils” in order to reduce the absorption from the diamond¹² during the XRS measurements. Due to a lack of time, only DAC1 and DAC2 could be tested and not DAC3.

Table 1: P-T conditions for the synthesis of FeO₂H_x

miniature DAC1:	α -FeOOH	P = 88 GPa	T = 2300 K for 5 min
miniature DAC2:	α -FeOOH embedded in KCl disks	P = 85 GPa	T = 2000-2300 K for 10 min
miniature DAC3:	α -FeOOH embedded in KCl disks	P = 94 GPa	T = 2000-2200 K for 5 min

Outputs:

The results of this beamtime are part of an on-going PhD thesis. Further work on the optimization during the extraction of the XRS signal and normalization is ongoing for each of the compositions. In addition, theoretical calculation will also be crucial to carefully interpret these signals. X-ray diffraction and Raman spectroscopy have been performed on the DAC1-DAC2 and DAC3. Ideally, complementary beamtime will be necessary to analyze the sample in DAC3.

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