



	Experiment title: Oxidation states of FeO ₂ and FeO ₂ H _x at high pressure	Experiment number: ES-693
Beamline: ID-24	Date of experiment: from: 01/11/2017 to: 07/11/2017	Date of report: 03/03/2018
Shifts: 18	Local contact(s): Sakura Pascarelli	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Boulard Eglantine * ¹ ; Harmand Marion * ¹ ; Fiquet Guillaume * ¹ ; Guyot François * ¹ ; Morard Guillaume * ¹ ¹ Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, IRD. Institut de Minéralogie, Physique des Matériaux et Cosmochimie - IMPMC, 4 Place Jussieu, 75005 Paris, France		

Report:

In a recent experimental study, Hu et al. (2016) demonstrated that a new pyrite-structured with a composition of FeO₂ is synthesized above 76 GPa-1500 K (~1800 km depth) from Fe₂O₃ + O₂. The particularity of this new phase is the presence of covalent oxygen-oxygen bonds inferred from the atomic positions and suggesting, by analogy to FeS₂ pyrite, that oxygen in this new phase has a valence of -1 (peroxide anion O₂⁻²) while iron valence is Fe²⁺ (Hu et al., 2016). Increasing the plausibility of the presence of such anomalous oxygen valences in the Earth, Hu et al (2017) and Boulard et al (in press) have synthesized from FeOOH goethite, a phase present in subducted materials, a FeO₂H_x in which hydrogen is not present at the +1 redox state as in H₂O but as zero valent as in molecular H₂. Unlike the dehydration process that releases hydrogen as H₂O, here, if the oxygen valency in that new phase is really -1, H₂ would be released from dehydrogenation of FeOOH (Hu et al., 2017).

The discovery of these new pyrite-structured phases may have profound implication 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⁺. However, so far, these new oxidation states of oxygen and iron have only been indirectly suggested by x-ray diffraction measurements which do not allow to directly probe the oxidation state or local environment of elements.

In this report, we present first XANES spectra collected at the Fe K-edge on these new pyrite-structured oxides at lower mantle conditions. We used the unique capabilities of ESRF on beamline ID-24 in order to collect XANES *in situ* at high pressure and temperature through laser heated diamond anvil cell.

We performed 5 runs of experiment at pressures up to 106 GPa and temperatures up to 2500 K using the double-sided laser heating system of ID-24 (Table 1). Fe K-edges spectra were collected upon the compression, as well as before, during and after laser heating. In order to help with the interpretation of

the Fe K-edge spectra of the new phases, we collected further Fe K-edge on different standards of iron oxides at ambient pressure and temperature: FeO, Fe₃O₄, α -Fe₂O₃, γ -Fe₂O₃, FeOOH and FeS₂.

Table 1:

#Exp	Samples	Pressure and Temperature conditions
1	Fe ₂ O ₃ + O ₂	92 GPa – 2500 K
2	FeOOH in Ne	87 GPa – 2200 K
3	FeOOH in Ne	64 GPa – 1600 K and 86 GPa- 2200 K
4	FeOOH in KCl	106 GPa – 2400 K
5	Fe ₂ O ₃ in KCl	82 GPa – 2500 K

- **XANES in FeO₂**

Hematite (α -Fe₂O₃) was loaded into O₂ by cryogeny in order to synthesized FeO₂. For comparison, one run was performed on α -Fe₂O₃ loaded in KCl. We observed evidence of reducing of iron upon laser heating in α -Fe₂O₃+O₂ as FeO₂ was form (Figure 1).

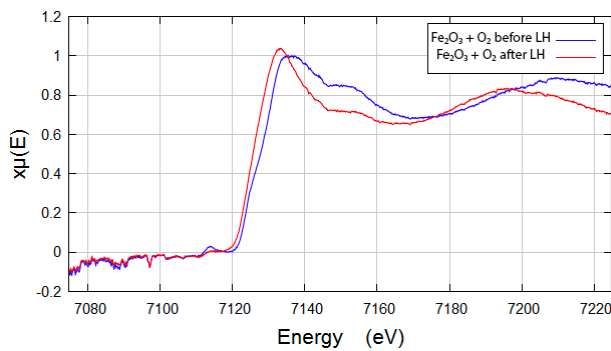


Figure 1 : Fe K-edge XANES spectra collected at 92 GPa, before and after laser heating (LH) of α -Fe₂O₃ + O₂.

- **XANES in FeO₂H_x**

There are strong divergences about the hydrogen content of the pyrite-structured FeO₂H_x. It was first proposed that complete dehydrogenation of FeOOH into FeO₂ take place at mantle conditions (Hu et al., 2016) and H₂ would be release into the mantle. In 2017, Hu et al. (2017) and Boulard et al. (in press) reported partial dehydrogenation of FeOOH into FeO₂H_x while Nishi et al. (2017) observed no dehydrogenation. In these studies, the hydrogen content, which cannot be determine directly, was inferred by the unit cell volume from x-ray diffraction. Although in all of these studies FeO₂H_x was synthesized from FeOOH, different pressure mediums (KCl, Ar and Ne) were used and lead to different observations. Therefore, here we performed runs on FeOOH loaded either in Ne or in KCl. Upon preliminary analyses, we observed no differences between the two kind of pressure mediums. As for FeO₂, we observed however, evidence of reducing of iron upon the phase transition into FeO₂H_x (Figure 2).

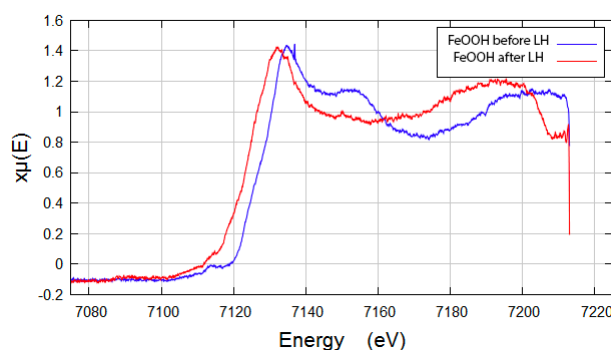


Figure 2: Fe K-edge XANES spectra collected at 92 GPa, before and after laser heating (LH) of FeOOH loaded in KCl.

Further work are in progress on a detailed analyses of the pre-edge of Fe K-edge in order to get insight on the Fe oxidation state (Wilke et al., 2004). Theoretical calculation of XANES spectra are also in progress in order to help with the interpretation of the new spectroscopic signatures. Ex situ analyses will also be performed by Scanning Electron Microscopy as well as Transmission Electron Microscopy on selected samples. Based on this study, one publication is in preparation.

References:

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