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**Ferrous Iron Under Oxygen-Rich Conditions in the Deep Mantle**

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**Abstract**

Recent experiments have demonstrated the existence of previously unknown iron oxides at high pressure and temperature including newly discovered pyrite-type FeO2 and FeO2Hx phases stable at deep terrestrial lower mantle pressures and temperatures. In the present study, we probed the iron oxidation state in high-pressure transformation products of Fe2+OOH goethite by in situ X-ray absorption spectroscopy in laser-heated diamond-anvil cell. At pressures and temperatures of ~91 GPa and 1,500–2,350 K, respectively, that is, in the previously reported stability field of FeO2Hx, a measured shift of −3.3 ± 0.1 eV of the Fe K-edge demonstrates that iron has turned from Fe3+ to Fe2+. We interpret this reductive valence change of iron by a concomitant oxidation of oxygen atoms from O2− to O−, in agreement with previous suggestions based on the structures of pyrite-type FeO2 and FeO2Hx phases. Such peculiar chemistry could drastically change our view of crystal chemistry in deep planetary interiors.

**Plain Language Summary**

Iron oxides are important end-members of the complex materials that constitute the Earth’s interior. Among them, FeO and Fe2O3 have long been considered as the main end-members of the ferrous (Fe2+) and ferric (Fe3+) states of iron, respectively. All geochemical models assume that high oxygen concentrations are systematically associated to the formation of ferric iron in minerals. The recent discovery of O2− peroxide ions in a phase of chemical formula FeO2Hx stable under high-pressure and high-temperature conditions challenges this general concept. However, up to now, the valences of iron and oxygen in FeO2Hx have only been indirectly inferred from a structural analogy with pyrite FeS2. Here we compressed goethite (FeOOH), an Fe3+−bearing mineral, at lower mantle pressure and temperature conditions by using laser-heated diamond-anvil cells, and we probed the iron oxidation state upon transformation of FeOOH in the pressure–temperature stability field of FeO2Hx using in situ X-ray absorption spectroscopy. The data demonstrate that upon this transformation iron has transformed into ferrous Fe2+. Such reduced iron despite high oxygen concentrations suggests that our current views of oxidized and reduced species in the lower mantle of the Earth should be reconsidered.

1. **Introduction**

Iron oxides are important end-members of the complex materials that constitute the Earth’s interior. Among them, wüstite (FeO) and hematite (Fe2O3) have been considered for long as the two main end-members for the ferrous (Fe2+) and ferric (Fe3+) states of iron, respectively. Magnetite (Fe3O4) has a well-defined mixed ferrous and ferric valence with a ratio of 1:2. Recent studies, however, have reported the existence under high pressures (P) and temperatures (T) of new stoichiometries such as Fe2O5, Fe3O6, and Fe7O9 (Lavina et al., 2011; Lavina & Meng, 2015; Sinmyo et al., 2016), in which iron valences are not yet known. The recent discovery of a new iron peroxide FeO2 under lower mantle P–T conditions may drastically change our understanding of iron crystal chemistry and geochemistry in deep planetary mantles (Hu et al., 2016). Indeed, if FeO2 is isostructural and isochemical with FeS2 pyrite, as proposed in Hu et al. (2016), iron would be ferrous despite the large oxygen concentrations under which it was synthesized.

FeO2 was first investigated with both first-principle calculations and experiments by Hu et al. (2016) who reported the reaction between Fe2O3 and O2 at P–T conditions corresponding to a depth of ~1,800 km in the Earth (76 GPa–1,500 K). FeO2 presents the same crystal structure as pyrite FeS2: an Fe atom surrounded by six O atoms makes slightly distorted FeO6 octahedra with an Fe–O average bond length of ~1.808 Å. Due to the presence of O–O covalent bonds, oxygen atoms in this new phase would have a valence of −1 (as in...
peroxide anions $O_2^{2-}$ and consequently iron would present a valence of +2 (Hu et al., 2016). If this proposed valence of iron in FeO$_2$ is confirmed, the stability of Fe$^{2+}$ under high oxygen fugacity would drastically modify our understanding of oxidation state and redox reactions that take place within the Earth’s lowermost mantle. Current models indeed assume that a high oxygen fugacity and oxidizing conditions are systematically associated to the formation of Fe$^{3+}$, and in turn, Fe$^{3+}$/Fe$^{2+}$ ratios are used for oxygen fugacity calculations. With the presence of peroxide ions, mantle redox states would need to be reconsidered. However, up to now, the valences of iron and oxygen in FeO$_2$ are still under debate and are only indirectly suggested by the structural analogy with pyrite FeS$_2$. The reported O–O distance of 1.89 Å in FeO$_2$ (Hu et al., 2016), as inferred from atomic position refinements, is larger than in molecular oxygen (1.21 Å) and in $O_2^{2-}$ peroxide ion as in BaO$_2$ and MgO$_2$ (1.49 and 1.45 Å, respectively; Koigstein et al., 1998; Lобанов et al., 2015; Streltsov et al., 2017). On this basis, one may instead expect that Fe ion in FeO$_2$ would adopt an exceptionally high oxidation state of +4, as in oxoiron (IV) compounds well known in biology and chemistry. Theoretical calculations based on the combination of density functional and dynamical mean-field theories have also proposed intermediate valences of Fe$^{3+}$ and O$^{-1.5}$ in the newly discovered FeO$_2$ phase (Streltsov et al., 2017).

Pyrite-structured iron peroxides were also synthesized starting from a common hydrous ferric mineral, α-FeOOH goethite (Boulard et al., 2018; Hu et al., 2017, 2016; Nishi et al., 2017; Zhu et al., 2017), or by reaction between Fe and H$_2$O (Liu et al., 2017; Mao et al., 2017; Yuan et al., 2018) as well as by reaction between Fe$_2$O$_3$ and H$_2$O (Hu et al., 2017; Liu et al., 2017; Mao et al., 2017). However, because the pyrite-structured phases synthesized in these studies have variable and larger unit cells than in FeO$_2$ under the same conditions, it was suggested that FeOOH transformed into pyrite-structured FeO$_2$H$_x$ with $x$ values comprised between 0.4 and 1 (Boulard et al., 2018; Hu et al., 2017; Nishi et al., 2017). In the transformation process from FeOOH to FeO$_2$H$_x$, H$_2$ or equivalent zero-valent hydrogen could be released (Hu et al., 2017), impacting the global hydrogen and water geochemical cycles. One should note, however, that there are strong divergences about the actual hydrogen content of pyrite-structured FeO$_2$H$_x$. Complete dehydrogenation of FeOOH into FeO$_2$ was initially suggested to occur at mantle conditions (Hu et al., 2016). More recently, Hu et al. (2017) and Boulard et al. (2018) advocated for a partial dehydrogenation while Nishi et al. (2017) reported no loss of H in the transformation of FeOOH. In that last scenario, one could expect the iron oxidation state to be Fe$^{3+}$ as in α-FeOOH, together with H$_{1+}$ hydrogen and O$^{-2}$ oxygen, that is, a high-pressure Fe$^{3+}$O$^{2-}$O$^{-}(\text{OH})^{-}$ hydrous polymorph of goethite with a pyrite structure containing iron, oxygen, and hydrogen with usual valences. However, if peroxide anions are involved, Fe$^{2+}$ would also be compatible with a goethite formula as in Fe$^{2+}$O$_2$$^{2-}$(OH)$_{2-}$.

To shed light on the valence states of iron in high-pressure transformation products of goethite Fe$^{3+}$OOH, we used X-ray Absorption Near Edge Structure (XANES) at the Fe K-edge in situ at high pressure and temperature. Indeed, preedge features in the Fe K-edge absorption spectra and the edge position itself are well known to be related to Fe$^{2+}$/Fe$^{3+}$ ratio and are now commonly used to determine the valence states of a wide variety of minerals (e.g., Wilke et al., 2001). Analyses were performed in a laser-heated diamond-anvil cell at high pressure and temperature upon the transformation of FeOOH in the previously reported stability field of FeO$_2$H$_x$. The same methodology was applied on pure FeO and Fe$_2$O$_3$, which were used as reference samples for Fe$^{2+}$ and Fe$^{3+}$ oxides, respectively.

### 2. Materials and Methods

Starting materials consisted of a natural sample of crystalline goethite (α-FeOOH) from a lateritic soil of Central African Republic provided by the collection of University Pierre et Marie Curie. Pellets of α-FeOOH were loaded in diamond anvil cells (DAC) either in neon (Ne) gas or between two dry potassium chloride (KCl) disks. Ne and KCl acted both as pressure media as well as thermal insulators. Complementary high-pressure and high-temperature experiments were performed on the two endmember oxides, α-Fe$^{3+}$O$_3$ and Fe$^{2+}$O, which served as references for the two iron valence states at high pressure and temperature. To our knowledge, no previous XANES data exist on FeO and Fe$_2$O$_3$ at both high-pressure and high-temperature conditions. For these experiments, we used synthetic starting materials purchased from Sigma-Aldrich with >99.9 and 99.7% purity, respectively, loaded in-between oven-dried KCl disks.
X-ray absorption spectroscopy measurements at the Fe K-edge were performed at the beamline ID24 of the European Synchrotron Radiation Facility (Kantor et al., 2014, 2018; Pascarelli et al., 2016). XANES spectra were collected in situ at high pressure and temperature by coupling a DAC and a double-sided laser heating setup. For each sample, XANES spectra were first collected during compression at ambient temperature, then in situ at high pressure and temperature and after quench to ambient temperature. Due to the X-ray absorption setup used, no simultaneous X-ray diffraction could be performed; we thus assume the phases present from previous X-ray diffraction measurements on the same assemblages and at the same pressure and temperature conditions (e.g., Bykova et al., 2016; Fischer et al., 2011; Hu et al., 2016). Extended description of the experimental methods and spectrum analysis can be found in the supporting information (Akahama & Kawamura, 2004; Benedetti & Loubeyre, 2004; Boccatto et al., 2017; Boubnov et al., 2015; Dewaele et al., 2008; Dräger et al., 1988; Galoisy et al., 2001; Giampaoli et al., 2018; Waychunas et al., 1983; Max Wilke et al., 2005).

3. Results

3.1. Compression at Ambient Temperature of α-FeOOH

XANES spectra collected during compression at ambient temperature of FeOOH goethite loaded into Ne are shown in Figure 1. The XANES features of the Fe K-edge collected at 14 GPa are in good agreement with the literature related to Fe K-edge of α-FeOOH (Piquer et al., 2014; Wilke et al., 2001), which is the thermodynamically stable phase at ambient conditions. As expected for slightly distorted octahedrally coordinated Fe$^{3+}$, the preedge presents two main features near 7,113 and 7,115 eV associated with electronic transitions to the $t_{2g}$ and $e_g$ empty Fe 3d orbitals, respectively (Wilke et al., 2001). The crystal field splitting energy obtained from the splitting between the two preedge features shows a linear increase from 1.6 at 14 GPa up to 2.1 eV at 39 GPa interpreted as due to the compression of FeO$_6$ octahedra with pressure. In the meantime, the preedge’s centroid is observed to move toward lower energies: from 7,114.8 eV at 33 GPa to 7,114.0 eV at 64 GPa (Figure S2). The white line of the edge is also modified with the appearance of a shoulder around 7,124 eV for pressures above 33 GPa, and the feature A is shifted by +3 eV (Figure 1).

Compressibility of α-FeOOH at ambient temperature has been previously studied by X-ray diffraction, and it is known that α-FeOOH undergoes an iso-structural phase transition at ~49 GPa upon the spin-crossover of iron from high spin (HS) to low spin (LS), a pressure-induced electronic process that is accompanied by hydrogen bond symmetrization and FeO$_6$ octahedra becoming regular (Gleason et al., 2013; Reagan et al., 2016; Xu et al., 2013). Since the preedge feature is sensitive to the $t_{2g}$ and $e_g$ components of the 3d band through hybridization effects, it is directly connected to the population of the HS and LS spin states. Here modifications in the preedge and edge XANES features between 33 and 39 GPa at ambient temperature show similarities with data collected upon the Fe spin transition in Fe$_2$O$_3$ (Figure S3; Badro et al., 2002; Mao et al., 1996; Narygina et al., 2009; Sanson et al., 2016; Wang et al., 2010). Therefore, we attribute the modifications of the preedge observed in this pressure range to the pressure-induced iron spin-crossover in α-FeOOH. These compression data show that Fe$^{2+}/$Fe$^{3+}$ quantitative analysis of the preedge centroid position and intensity as developed by Wilke et al. (2001) is not systematically possible due to the structural and/or spin transition and related modifications in the preedge at high pressures. However, this does not prevent qualitative and unambiguous observation of the valence state evolution.

3.2. Transformation Into ε-FeOOH at ~64 GPa and 1,600–1,800 K

α-FeOOH was pressurized up to ~64 GPa in Ne and transformed by laser heating at temperatures of ~1,600 K. The corresponding XANES Fe K-edge spectra collected before and after heating are presented in Figure 2. Table S1 summarizes the spectral positions of the main Fe K-edge features of FeOOH, FeO, and Fe$_2$O$_3$ before and after laser heating at 64 GPa. Within a few seconds of laser heating, the A spectral feature of the XANES spectra was shifted toward higher energies (by about +1 eV). The flank of the edge and feature B were also modified. The position of the white line did not evolve but the centroid position of the preedge shifted from 7,114.0 to 7,114.4 eV (Figure S2). Further heating up to 1,800 K at this pressure condition and then temperature quenching did not result in any significant changes. The modification of the XANES Fe K-edge spectra at ~64 GPa and 1,600–1,800 K is to be related to the transformation of α-FeOOH into ε-FeOOH, a rutile-type structure that has been reported to occur at these $P$-$T$ conditions (Gleason et al., 2008; Suzuki, 2010; Figure 2).
For comparison, XANES spectra were collected on FeO at 47 GPa (ambient temperature) and on Fe₂O₃ at 54 GPa and ~1,500–2,000 K. The edge positions of FeOOH and Fe₂O₃ after laser heating are close to each other and ~4 eV higher than the Fe K-edge position in FeO (Figure 2 and Table S1). Using in situ Mössbauer spectroscopy at high pressure, Bykova et al. (2016) have reported that iron in η-Fe₂O₃, the stable polymorph of Fe₂O₃ at these conditions, is indeed Fe³⁺. Therefore, we can conclude that iron is also in a Fe³⁺ valence state in ϵ-FeOOH.

3.3. Transformation Into FeO₂Hₓ at ~91 GPa and 1,500–2,350 K

FeOOH was compressed at ambient temperature directly at 91 GPa in KCl and at 87 GPa in neon, respectively, before transformation under laser heating at temperatures ranging from 1,500 to 2,350 K. As presented in Figure 3, drastic changes in the XANES spectra are observable. In addition to the modifications of postedge features, a clear shift of the edge by about 3.3 eV toward lower energies took place together with a ~2-eV shift of the maximum intensity position of the XANES spectrum. We observed no evidence of a shift in the centroid position of the preedge, which remained at about 7,114 eV (Figure S2). Again, these modifications in the Fe K-edge XANES were observed within a few seconds of laser heating at 1,800 K and no evolution occurred in the spectra upon heating over longer durations or at higher temperatures, up to 2,350 K. The ~3.3-eV energy shift of the absorption threshold that is observed at ~90 GPa and 1,500–2,350 K is consistent with a change in oxidation state of the Fe ions from Fe³⁺ to Fe²⁺. The new edge position is indeed close to that in Fe²⁺O at the same P–T conditions and about 4.5 eV below that of the edge position in Fe³⁺₂O₃ (Figures 3 and S4; Bykova et al., 2016; Fischer et al., 2011; Ozawa et al., 2010) and below the edge position expected for an oxoiron (Fe⁴⁺)-bearing phases (e.g., England et al., 2014; Rohde et al., 2004). Postedge features are different from those of FeO; the synthetized phase is therefore different from wüstite. Moreover, several previous experimental (X-ray diffraction) and theoretical studies have shown that at these pressure and temperature, FeOOH transforms into the pyrite-structured FeO₂Hₓ phase (Boulard et al., 2016).
et al., 2018; Hu et al., 2017, 2016; Nishi et al., 2017). Our results therefore suggest that in FeO$_2$H$_x$, part of the FeO$_6$ octahedra are connected by O–O bonds resulting in the formation of the peroxide dimer O$_2^{2−}$. This observation agrees with previous experimental and theoretical work who suggested the presence of O$^{1−}$ and Fe$^{2+}$ in this P–T range of the Fe–O–H phase diagram (Boulard et al., 2018; Hu et al., 2017, 2016; Jang et al., 2017; Mao et al., 2017). This observation would also be consistent with the release of H as zerovalent hydrogen from symmetrically hydrogen-bonded ϵ-FeOOH upon transformation to the pyrite-structured FeO$_2$H$_x$ according to reaction (1) as reported by Zhu et al. (2017).

\[
\text{Fe}^{3+}\text{OOH} \rightarrow \text{Fe}^{2+}\text{O}_2\text{H}_x + (1-x)/2 \text{H}_2
\]

We stress, however, that the present XANES measurements do not give any direct insight on the actual hydrogen content in the high-pressure phases studied. A Fe$_{2}^{2+}$O$_2^{2−}$-(OH)$_2^{−}$ phase with no H loss with respect to a goethite composition would be equally consistent with the X-ray absorption data of the present study.

### 4. Implications

Here we report unambiguous observation of Fe$^{2+}$ in high-pressure high-temperature transformation products of Fe$^{3+}$OOH goethite at ~91 GPa and 1,500–2,350 K. Although we could not get a structural determination of the phase simultaneously to the measurement of the X-ray absorption, we notice that at least three experimental studies carried out under similar or identical conditions obtained a pyrite-structured FeO$_2$H$_x$ phase (x comprised between 0.4 and 1) in this region of the Fe–O–H phase diagram (Boulard et al., 2018; Hu et al., 2018; Hu et al., 2017, 2016). Our results therefore suggest that in FeO$_2$H$_x$, part of the FeO$_6$ octahedra are connected by O–O bonds resulting in the formation of the peroxide dimer O$_2^{2−}$. This observation agrees with previous experimental and theoretical work who suggested the presence of O$^{1−}$ and Fe$^{2+}$ in this P–T range of the Fe–O–H phase diagram (Boulard et al., 2018; Hu et al., 2017, 2016; Jang et al., 2017; Mao et al., 2017). This observation would also be consistent with the release of H as zerovalent hydrogen from symmetrically hydrogen-bonded ϵ-FeOOH upon transformation to the pyrite-structured FeO$_2$H$_x$ according to reaction (1) as reported by Zhu et al. (2017).
et al., 2017, 2016; Lu & Chen, 2018; Nishi et al., 2017). We thus propose that the present study provides experimental evidence of ferrous iron in pyrite-structured FeO$_2$H$_x$.

The possibility of stabilizing ferrous iron in oxygen-rich compositions (as goethite or hematite) had been previously proposed based on structural data obtained by X-ray diffraction (e.g., Hu et al., 2016; Mao et al., 2017). Here we report the first direct spectroscopic evidence of this valence state of iron in such oxygen-rich compositions at P-T conditions achievable both in very cold and hot descending slabs in the lower mantle (Figure 4). This observation will have to be taken into account for modeling the oxygen fugacity, that is, redox state of the Earth’s lower mantle which is usually based on the Fe$^{3+}$/Fe$^{2+}$ ratios. The O$_2$$^2$$^-$/O$_2$$^-$ redox couple which likely interacts with Fe$^{3+}$/Fe$^{2+}$ will most likely have to be taken into account as well.

Furthermore, according to reaction (1), production of ferrous iron in FeO$_2$H$_x$ is linked to dehydrogenation of FeOOH when $x > 1$. In this case, hydrogen atoms will be released as zero-valent (H$^0$) such as in H$_2$. For example, at least 60% of the hydrogen atoms initially present in goethite from a subducting banded iron formation (Dobson & Brodholt, 2005) would be released as H$^0$ (Boulard et al., 2018; Hu et al., 2017; Zhu et al., 2017). This process differs from the release of hydrogen as H$,^+$ often as H$_2$O, when heating H-bearing mantle minerals. Unlike H$_2$O, H$_2$ may be dissolved in lower mantle silicates (Yang et al., 2016). H$^0$, in whatever form, may also ascend to Earth’s surface through the mantle, thus completing a reduced loop of the hydrogen cycle. H$^0$ may also react with other volatiles, giving rise, for example, to hydrocarbons, thus impacting the carbon oxidation state in the lower mantle and the associated deep carbon cycle. In particular, interaction of these newly discovered iron oxides with CO$_2$ might change the hydrogen cycle (Boulard et al., 2018); more generally, their evolution in a volatile-bearing silicate lithology should be further studied.

Subduction of FeOOH is geophysically relevant (e.g., Dobson & Brodholt, 2005) but might be limited due to possible dehydration of goethite at shallow depth (e.g., Gleason et al., 2008). However, crystalline-bounded

Figure 3. Normalized Fe-K edge XANES spectra collected at ~90 GPa before, during, and after laser heating (LH) of FeOOH loaded into KCl. For comparison, spectra collected in FeO and Fe$_2$O$_3$ at similar pressure after laser heating are also represented. A shift of $-3.3$ eV of the Fe K-edge is observed as $\alpha$-FeOOH transformed into FeO$_2$H$_x$. Hydrogen atoms are not represented in the crystal structure of the FeO$_2$H$_x$. 

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water almost certainly survive shallow subduction and is recycled to large depth, particularly in cold slabs (Van Keken et al., 2011). Therefore, reactions between iron and water are likely even at lower mantle conditions and the present study on FeOOH transformations is relevant for modeling these interactions at depth. Moreover, other contexts than subduction generate a broad geophysical interest for studying the Fe–O–H system at high pressure. Pyrite-structured FeO₂Hₓ was indeed reported to result from the reaction of water with metallic iron (Liu et al., 2017; Mao et al., 2017; Yuan et al., 2018), a reaction that may have taken place during core formation resulting in the delivery of hydrogen to the Earth’s core (Yuan et al., 2018). Iron hydride FeHₓ indeed satisfies density and sound velocities constraints in the Earth’s core (e.g., Tagawa et al., 2016). In addition, dehydration melting of transition zone materials swept down to the lower mantle by mantle convection or melting of dense hydrous magnesium phases in subducting slabs that are stagnating near 660-km seismic discontinuity could produce deep hydrous melts at the top of the lower mantle. Reaction of these deep hydrous melt with the metallic iron-rich lower mantle material (Frost et al., 2004) may produce FeO₂Hₓ in the lower mantle (Yuan et al., 2018). The dense FeO₂Hₓ peroxide-bearing phase would sink to the core-mantle boundary where it would accumulate. In any case, large amount of FeO₂Hₓ could be produced at the core-mantle boundary when residual hydrated subducted materials meet metallic iron-rich outer core (Mao et al., 2017). Sound velocity measurement on FeO₂Hₓ at the core-mantle boundary pressure conditions show that a mixture of FeO₂Hₓ with the ambient mantle could be a good candidate for the distinct ultralow-velocity zone (Liu et al., 2017). Moreover, a (Mg,Fe)O₂Hₓ solid solution would reduce the density such that ultralow-velocity

Figure 4. Pressure-induced change of valence state of Fe, O, and H in the lower mantle. FeO₂Hₓ is likely to be produced in descending slabs that transport hydrated material and where oxidizing conditions exist. Model paths of the hottest (orange) and coldest (blue) slabs from Syracuse et al. (2010) are represented by arrows and their hypothetical extrapolation (orange and blue lines). Mantle geotherm is after Ono (2008).
zone might be entirely composed of Mg-bearing pyrite structured FeO₂H₄ (Liu et al., 2017). This solid solution has not yet been tested; however Lobanov et al. (2015) have shown that a magnesium peroxide (MgO₂) is stable at the pressure–temperature conditions of the lowermost mantle. Beyond the pure FeOOH stoichiometry the actual valence of iron in realistic lower mantle complex compositions and the resulting physical properties must now be explored.

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