Altered chemistry of oxygen and iron under deep Earth conditions

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A drastically altered chemistry was recently discovered in the Fe-O-H system under deep Earth conditions, involving the formation of iron superoxide (FeO₂Hₓ with x = 0 to 1), but the puzzling crystal chemistry of this system at high pressures is largely unknown. Here we present evidence that despite the high O/Fe ratio in FeO₂Hₓ, iron remains in the ferrous, spin-paired and non-magnetic state at 60–133 GPa, while the presence of hydrogen has minimal effects on the valence of iron. The reduced iron is accompanied by oxidized oxygen due to oxygen-oxygen interactions. The valence of oxygen is not -2 as in all other major mantle minerals, instead it varies around -1. This result indicates that like iron, oxygen may have multiple valence states in our planet’s interior. Our study suggests a possible change in the chemical paradigm of how oxygen, iron, and hydrogen behave under deep Earth conditions.
Oxygen and iron are Earth’s most abundant elements by number of atoms and by mass, respectively. They form compounds dictating major chemistry of our planet. It is conventionally accepted that the oxygen anion has an unvarying −2 valence state in mantle ferropericlase and bridgmanite throughout the deep interior, where the oxygen fugacity decreases with increasing depth. The redox states are mostly controlled by the 3d transition element Fe which could vary among three valence states, metallic Fe⁰, ferrous Fe²⁺, and ferric Fe³⁺. Recently, a series of new iron oxides have been found with varying O/Fe stoichiometry ranging from the end-member Fe³⁺₂O₃ on our planet’s highly oxidized surface to the other end-member Fe²⁺₂O₄ which should be stable at the highly reduced conditions in the deep lower mantle down to the core-mantle boundary, which include Fe₆O₇, Fe₆O₉, and Fe₆O₁₂ (refs. 2–4). High pressures in the deep lower mantle would promote the crystal field splitting of 3d orbitals of iron and cause the electronic spin-pairing transition, which can affect the physical, chemical, and transport properties of mantle phases ⁵–⁷.

The conventional wisdom, however, is facing a change in light of the recent discovery of the high-pressure pyrite-structured iron superoxide FeO₂, which has O/Fe ratio even higher than Fe₂O₃ and can hold a varying amount of hydrogen (denoted as “Py-FeO₂Hₓ” with x from 0 to 1)⁸–¹²,¹³–¹⁵. With the subducted plate carrying down water to react with the iron core to form Py-FeO₂Hₓ and release hydrogen, oxygen-rich reservoirs could be accumulated in the very reducing core-mantle boundary region ¹³–¹⁵. Such reservoirs at the mid-point (2900 km depth) of the Earth’s radius (6370 km) will certainly play a pivotal role in the global chemistry, including the generation of our present day aerobic atmosphere ⁹,¹⁶. A number of key solid-state chemistry questions on Py-FeO₂Hₓ must be understood: What are the valence states of Fe and O? What is the nature of their chemical bonding? What are the effects of hydrogen on the valence and bonding of Fe and O? Is the iron superoxide metallic? Are its d electrons spin-paired?

Assuming oxygen in the common O₂⁻ state as in other iron oxides, the valence state of iron would be ferryl (Fe⁴⁺) for FeO₂. On the other hand based on the analogy to Fe₆S₇ pyrite, in which Fe remains ferrous (Fe²⁺) with the sulfur forming S₂⁻ dimer, would FeO₂ also consist of Fe²⁺ cations and O₂²⁻ dimers? Streltsov et al.¹⁷ predicted the valence state of iron to be +3 for the hydrogen-free FeO₂ Py-phase where oxygen ions do not form O₂⁻ dimers, suggesting FeO₂ “in between” the usual dioxide oxides and peroxides, based on the density functional and dynamical mean-field theories (DFT + DMFT). By contrast, Jang et al.¹⁸ employed DFT + DMFT approaches with treating FeO₂ to presumably have O₂⁻ dimer as a complete analogue of pyrite-structured FeS₂. Thus far, theoretical calculations cannot conclude the nature of chemical bonding and state of FeO₂ without experimental constraints. Answers must be based on in situ measurements of the micron-sized Py-FeO₂Hₓ sample which cannot be preserved after releasing pressure for normal electrochemical analysis.

We take the challenge by combining a variety of recently enabled synchrotron X-ray spectroscopic techniques¹⁹, and obtain intriguing answers from direct high-pressure experiment supplemented by first-principles simulations with the self-consistent linear-response approach. Here we find many unexpected chemical behaviors in Py-FeO₂Hₓ samples (Supplementary Figures 1–5), where iron is in the reduced, spin-paired ferrous state and the valence state of oxygen varies around −1, instead of at −2 in common iron oxides, while hydrogen is weakly bonded in the structure. Our results suggest that other than iron, oxygen can occupy multiple valence states in our planet’s interior, leading to a chemical paradigm change in the deep Earth.

Results

Valence states of iron and oxygen in FeO₂Hₓ. The valence state of Fe can be characterized by near-edge X-ray absorption spectroscopy (XAS) features at energy slightly below the iron K-edge ²⁰. Because of the strong absorption of 7 keV X-ray by diamond anvils, the XAS spectra were collected in the partial fluorescence yield (PFY) geometry for the iron superoxide at 53–133 GPa. That is, the incident X-ray beam passes through one diamond anvil, and then the X-ray fluorescence exists in the radial direction through the Be gasket to avoid double diamond absorption. The peak position and intensity distribution are diagnostic probes for valence state, spin state, geometry, and the ligand–ligand interactions for Fe atoms ²⁰. The iron K pre-edge feature that is related to the 1s → 3d electronic transition, is particularly sensitive to the valence state of iron ²¹. Our XAS-PFY measurements of other representative iron compounds at ambient conditions explicitly show that the position of iron K pre-edge absorption increases with increasing valence state (Fig. 1a top). The position of iron K pre-edge of the iron superoxide FeO₂ is very close, but slightly below, that of Fe²⁺ compounds. That is, the valence state of iron in FeO₂ is plausibly close to +2. Its position remains almost constant from 53 to 81 GPa, suggesting a minimal pressure dependence on the valence state of iron ²², consistent with mantle ferropericlase and bridgmanite. Furthermore, it is intriguing that the iron valence state of the hydrogen-free iron superoxide is similar to that of the hydrogen-bearing Py-FeO₂Hₓ with x = 0.5–0.7 at 133 GPa. These observations indicate that the hydrogen content has minimal effects on the valence state of iron in the superoxide (Fig. 1a).

With the valence state of iron slightly under +2, the valence state of oxygen for the Py-FeO₂ would have to be nearly −1, suggesting that oxygen atoms must interact with each other in the iron superoxide. Such interaction can be observed experimentally from the oxygen K-edge spectroscopy. We note that the edge at 540 eV is in a very soft X-ray region inaccessible to XAS in DAC experiments. Instead, we can access the oxygen K-edge by X-ray Raman scattering (XRS) using hard X-ray in and hard X-ray out method, where the energy loss is measured due to inelastic Raman shift ²³,²⁴. For XRS measurements on the oxygen K-edge, we deliberately used LiF as a pressure transmitting-medium, instead of water or O₂, to assure XRS signals of oxygen only from the Py-FeO₂Hₓ (Supplementary Figure 3). In the XRS at 110 GPa, we observed a sharp oxygen n⁺ peak near 531 eV and a broad φ⁺ peak at 540–550 eV (Fig. 1b). These peaks represent the O electron transition from 1s core orbitals to the antibonding 1σ* and 3σ* orbitals, respectively (termed as n⁺ and φ⁺ transitions). The strong n⁺ transition indicates the presence of the O–O dimer.

Magnetic and electronic spin states of iron in FeO₂Hₓ. Magnetic ordering and spin state of Fe in iron superoxide can be investigated using synchrotron Mössbauer scattering (SMS) and X-ray emission spectroscopy (XES), respectively. ⁵⁷Fe is a Mössbauer active isotope with nuclear resonant energy of 14.41 keV. A series of SMS spectra of the iron superoxide were collected upon decompression in steps from 118 GPa down to 32 GPa (Fig. 2a), and the experiment was repeated in three separated runs (Supplementary Figures 6–8) of FeO₂Hₓ with different x (Supplementary Table 1). SMS spectra were analyzed using CONUSS program ²⁵ to extract the quadrupole splitting (QS) and isomer shift (IS) of iron in the Py-phase which is compared with that of standard samples of ferrous pyrite FeS₂, ferrous Fe₉₆Mg₀.₅₂O, and ferric Fe₂O₃ (Fig. 2b). The QS of iron in the Py-phase barely
increased with increasing pressure, whereas the IS displayed an opposite trend. The pressure dependence of QS and IS for iron in the superoxide is comparable to that for ferrous iron (Fe$^{2+}$) in ferropericlase (Mg, Fe)O in the low-spin state (refs. 26,27), likely due to the ferrous nature of the iron superoxide. It is noted that the spin transition could largely affect the QS of iron in (Mg, Fe)O (refs. 27,28). Furthermore, the values of the QS and IS of iron in the superoxide extrapolated to ambient conditions are about 0.27 and 0.55 mm s$^{-1}$, in excellent agreement with that in pyrite FeS$_2$ (ref. 29).

Our SMS spectra in Fig. 2a consistently showed that the Py-phase remained in the non-magnetic state represented by the clean, single beat spectra, regardless of the content of hydrogen in the lattice. SMS data with multiple time beats indicating magnetic ordering appeared only below 40–50 GPa when the iron superoxide decomposed into a magnetic phase under decompression. We note that the full width at half maximum (FWHM) for the diffraction peaks for the iron superoxide broadened significantly below 65 GPa and the peak intensity continually decreased until they finally disappeared around 40 GPa upon decompression at room temperature. Furthermore, the QS and IS values of iron in the magnetic phase are close to that in hematite (Fe$_2$O$_3$) at 32 GPa. It is consistent with our recent X-ray diffraction (XRD) observations where the new diffraction peaks can be indexed to hematite below 40 GPa.

The magnetic spin states of 3$d$ electrons are also directly probed by XES spectra of the Fe $K_\alpha$ fluorescence lines (refs. 30) of the iron superoxide between 40 and 133 GPa (Fig. 3). The intensity of the $K_\alpha$ satellite peak of iron in the superoxide decreased between 45 and 60 GPa and disappeared completely at 60–65 GPa where the total spin momentum ($S$) of iron in the Py-phase approached zero, indicating that iron in the Py-phase undergoes a gradual electronic spin-pairing transition below 65 GPa from high-spin to low-spin states (Supplementary Figure 9). We note that the XES spectra were collected with decreasing pressure and thus the spin transition pressure may be higher due to pressure hysteresis on the spin crossover upon decompression (ref. 31). These observations also suggest that the iron superoxide is not stable in the high-spin state and would decompose into oxygen and hematite across the electronic spin transition of iron, associated with the valence change in oxygen and iron at the same time.

**Oxygen bonding and charge transfer in FeO$_2$ and FeO$_2$H.** For pyrite-type structures, the covalent nature is mainly controlled by the anion–anion distance ($D_{ab}$). We followed previous strategies (refs. 32,33) and used the fractional coordination $y$ of oxygen to compare O–O distance at different pressures:

$$y = \frac{1}{2} \cdot \frac{\sqrt{3}D_{ab}}{6a},$$

where $a$ is the lattice parameter as a function of pressure. The archetypal pyrite FeS$_2$ with $y = 0.385$ forms solid anion dimers with divalent Fe cations at ambient conditions. In contrast, conventional dioxides with tetravalent cations (e.g. RuO$_2$ and OsO$_2$) have a smaller value of 0.34–0.35 for $y$ in the pyrite-type structure (ref. 33). Our previous experimental XRD data showed $y = 0.371$ with $D_{ab} = 1.937$ Å in the iron superoxide at 75 GPa which lies between conventional dioxides and peroxides (refs. 9,33). Due to the importance of the O–O bond length, we collected XRD patterns on a nearly pure FeO$_2$ sample at 96 GPa, which have been further analyzed by using the Rietveld method for the primary phase of FeO$_2$ and the LeBail method for the weaker O$_2$ and Fe$_2$O$_3$ phases. The final refinement factors are $R_I = 0.069$ and $wR_2 = 0.14$. The bond length ($D_{0}$) for FeO$_2$ is $\sim 1.87(1)$ Å and the lattice parameter is $4.2855(3)$ Å with $y = 0.374$ at 96 GPa. Therefore, compared with various peroxides synthesized at ambient pressure (ref. 34), the O–O bonding length in the iron superoxide is relatively longer. With $0.35 < y < 0.39$, iron–oxygen octahedrons are chained by the O–O bonding as shown in Fig. 4a.

We further conducted first-principles simulations (see Methods) to construct the charge density landscape at 100 GPa (Fig. 4). Following the Bader charge division scheme, we determined the charge of the Fe atoms are 6.38 e by DFT + U and 6.32 e by the
Heyd-Scuseria-Ernzerhof (HSE) screened hybrid functional (screening variable of 0.15) free of the empirical Hubbard parameter $U$. Based on our experimental observations that Py-FeO$_2$Hx is in the non-magnetic state, the O–O bond length values from our GGA + $U$ calculations are consistent with our XRD experimental results as well as Lu et al.$^{35}$. We note that the O–O bonding length is sensitive to computational and physical environments and that either antiferromagnetic or ferromagnetic configurations would yield a longer O–O bond by ~10%.$^{35}$. The valence state of iron is $+1.62$ (DFT + $U$) or $+1.68$ (HSE) and that of oxygen is $-0.81$ (DFT + $U$) or $-0.84$ (HSE) for FeO$_2$ (Table 1). It is known that Bader analysis may underestimate the charge transfer between anions and cations.$^{36}$ Our calculations may not indicate the exact valence values, but clearly show charge transfer between anions, which has also been seen in the calculations of archetypal pyrite FeS$_2$ (ref. $^{37}$). In hydrogen-bearing Py-FeO$_2$H, hydrogen is equally bonded with two nearest oxygen atoms.$^{38}$ As a result, hydrogen is calculated to be $+0.64$ at 100 GPa. Oxygen atoms adopt electrons from hydrogen and become $-1.13$ while the valence state of iron remains around $+1.63$ for the Py-FeO$_2$H. Therefore, hydrogen only donates electrons to oxygen atoms and has a minimal effect on the valence state of iron.

**Discussion**

Looking at individual properties, FeO$_2$ and FeO$_2$Hx may appear similar to pyrite FeS$_2$ in their crystal structure, cation and anion valences, and spin-pairing state. Assimilating the comprehensive experimental and theoretical investigations, however, points to fascinating changes of high-pressure crystal chemistry above 70 GPa which corresponds to roughly the pressures beyond 1700 km depth, which is the midpoint separating the Earth’s mass into two equal halves. At higher pressures, the valence of oxygen in oxides is no longer fixed to $-2$, but becomes variable. The valence of iron becomes more dependent on the crystal structure and pressure rather than the oxygen stoichiometry. Hydrogen is no longer bonded to oxygen as OH, but becomes mobile. FeO$_2$ and FeO$_2$Hx do not exactly belong to the pyrite FeS$_2$ type structure with interactive anion dimer, nor the PdF$_2$ type structure without interactive anion dimer, but represent a new structure type in the Pn3 MA$_2$ family with...
partially interactive anion dimer. These issues have been previously noted as separate enigmas in other studies of O, Fe, and H under high pressures, such as formation of O₂ molecules39, the redox paradox of ferric iron40, and mobility of hydrogen in ice41,42. With the integrated study here, now the overall picture clearly indicates a chemical paradigm change under deep Earth conditions.

At zero pressure without external constraint, the O–O interaction type can be empirically determined by their distance33,34, 1.29–1.53 Å for bonded dimers in peroxides and 2.45–2.72 Å for non-interactive oxygen in PdF₂-type dioxides. Under pressures, however, the intermolecular interactions are further controlled by additional external forces that can generate additional intermolecular bonds. For instance, O₂ transform to the high pressure ε-O₈ phase with two types of bond length D₀ = 1.20 Å and 2.18 Å, respectively. The O–O dimer of D₀ = 1.89 Å (refs. 24,39,43), the reduced valence of oxygen in FeO₂ and FeO₂Hx, and the formation of new type of Pa₃ peroxide are a natural consequence of high-pressure chemistry.

At zero pressure, the valence of iron or ferric/ferrous ratio is generally correlated to the oxygen fugacity. The correlation is weakened by the additional control by the crystal structure of high-pressure phases. For instance, the paradoxical correlation of lower oxygen fugacity with higher Fe³⁺ abundance40 reflects the ability of the high-pressure perovskite structure to accommodate more Fe³⁺ iron44. Here the new high-pressure iron superoxide structure is able to keep its iron in ferrous state by reducing the oxygen valence, and fits well in the reducing environment of the core-mantle boundary. The spin-paired non-magnetic Fe²⁺ also fits the high-pressure chemistry of the deep lower mantle5,30.

At zero pressure, hydrogen is present as H⁺ and replaces other cations without affecting the anion valence. Here, the addition of hydrogen has negligible effects on the chemical and magnetic properties of the iron in FeO₂Hx, but mainly affects the oxygen valence. This shows the change of hydrogen from strong OH covalent bond at low pressures to weak interaction in the Py-FeO₂Hₓ lattice. Hydrogen chemistry in H₂O is known to have a very important change at high pressures to become symmetrically hydrogen bonded at low temperature42 and superionic at high temperature41,43; both result in weakening the OH bonding. The present observation indicates the weakened interaction of hydrogen is not limited to H₂O but is a general high-pressure chemical trend that has many important consequences, including loss of hydrogen in the formation of Py-FeO₂Hₓ (ref. 39), spontaneous splitting of H₂O into hydrogen and oxygen43, and separation of water and hydrogen cycles in the deep Earth49.

Our study demonstrates that under extreme pressures of the deep mantle, the structure type becomes a main controlling factor of valence states, and the conventional sense of valence of elements could be altered to fit the structure. The new type of structure has the unexpected valence state of oxygen that is different from the O²⁻ state in primary mantle oxides and silicates, and the ferrous, spin-paired, and non-magnetic state of iron that would affect Mg–Fe partitioning between mantle phases46,47. We may expect the new iron superoxide in pyrite structure to accommodate and form solid solutions with other divalent and trivalent cations such as Mg²⁺ and Al³⁺ (ref. 48) and with anions, such as sulfur and halogens. We may further expect that the Pa₃ peroxide structure is only one example of the possible compositions in the deep Earth, and that additional structure types with different valence and spin, such as the recently discovered hexagonal phase48, will emerge.

**Methods**

**Sample synthesis and characterization.** The five samples of the pyrite-type phase have been synthesized and further probed by X-ray spectroscopic techniques in this study (Supplementary Table 1). Iron superoxide samples of FeO₂ or FeO₂Hₓ were synthesized from goethite (FeOOH) or ⁵⁷Fe-enriched hematite (Fe₂O₃) mixture with O₂ and water H₂O, respectively, at 1800–2200 K under target pressures in laser-heated DACs at 16IDB, 13ID-D and High Pressure Synergetic Consortium (HP5ync) of the Advanced Photon Source of Argonne National Laboratory. In order to avoid any signal contamination from other phases in the sample and to assure complete transition, the whole starting materials of goethite (FeOOH) or hematite (Fe₂O₃) have been laser-heated repeatedly for 2–3 h at target pressures to synthesize a pure pyrite-structured FeO₂Hₓ (x = 0–1) phase.

XRD patterns were collected with the mapping steps of 4 μm for the whole-synthesized samples at beamlines 13ID-D or 16ID-B of Advanced Photon Source (APS), Argonne National Laboratory (ANL), confirming that the whole sample is the pyrite-type phase without any detectable amount of starting materials goethite or hematite left in the DACs (Supplementary Figures 1–5). The hydrogen content (x) of the iron superoxide samples that were synthesized from FeOOH or Fe₂O₃
with H2O was estimated to be 0.5–0.8 based on the unit-cell parameter calibration10 (Supplementary Table 1). In particular, a relatively small size of starting materials were selected to be 25–30 μm in diameter with a thickness of 6–8 μm, which can reduce the synthesis time. We note that the X-ray beam was focused down to 5–7 μm in the full-width at half-maximum (FWHM) at the sample position. Thus the sample center was deliberately probed in order to achieve a relatively high efficiency of the spectroscopic measurements. That is, about one fifth of the volume of the synthesized samples was probed in the spectroscopic measurements.

**Synchrotron X-ray diffraction experiments.** XRD experiments were carried out at beamlines 13-ID-D and 16-IDB of the Advanced Photon Source, Argonne National Laboratory. A high-quality monochromated incident X-ray beam was used with an energy of 30.49 keV (0.3738 Å), 33.17 keV (0.3738 Å), or 37.08 keV (0.3534 Å). The incident X-ray beam reached the sample position with a beam size of 2–5 μm in FWHM. For laser-heating XRD, two infrared laser beams were focused down to ~15 μm and 25–30 μm in the flat top area of the heating profile on both sides of the sample at beamlines 13-ID-D and 16-IDB, respectively. With the help of the X-ray induced luminescence on the sample and/or ruby, both laser beams were co-axially aligned with the incident X-ray beam. The temperature of the samples was calculated through fitting the measured thermal radiation spectra with the gray-body approximation57,58. The temperature uncertainty is 100–200 μK. A tiny piece of gold was placed in the sample chamber and its lattice parameters of gold were applied to determine pressure and uncertainty57.  

**Synchrotron Mössbauer spectroscopy experiments.** The SMS spectra of Fe2O3 and H2O or O2 approximately at 90 K were collected, a thin stainless-steel foil or a platelet of ~2 μm in thickness was probed in the spectroscopic measurements. From Fe2O3 and H2O approximately at 100 GPa and 2000 K. The XES measurement of FeO2 has attracted many computational studies. However, an accurate description about its electron-correlation part in calculating the total energy still remains a challenging task. Based on previous studies, O 2p orbitals may hybrid with Fe 3d orbitals at the Fermi surface. It may cause O electrons to contribute to the electron-correlation portion in calculating the total energy. We note the linear-response method is excellent in dealing with the electron-exchange–correlation energy for one atom species (e.g. Fe), although it may encounter issues for two types of atoms at the same time. Therefore, the use of Hubbard parameter U gives a first-order approximation to this energy portion. Combined with the self-consistent linear-response approach59,60, many experimental observations can be reproduced by theory.

First-principles calculations based on density function theory using the package VASP were carried out using the projector-augmented wave (PAW) pseudopotential and a plane-wave cutoff energy of 600 eV. The exchange-correlation functional employs the parameterization by Perdew, Burke, and Ernzerhof under the Generalized Gradient Approximation. We follow our previous computational recipe60 to approximate the on-site Coulomb interaction by the Hubbard method (U = 5.0 and J = 0.8 eV). In parallel, we also employed the Heyd-Scuseria-Ernzerhof screened hybrid functional (HSE) that was recently adopted for a variety of iron-oxides and calculated reliable structural, magnetic, and electronic properties61,62. For HSE-type functional, the screening parameter was set to 0.15 since it produces reasonable values in other Fe–O minerals like wüstite, magnetite, hematite, and goethite. We generated k-point in gamma centered Monkhorst-Pack grids of 7 × 7 × 7 throughout our simulation. The structures were relaxed for atomic position, cell shape, and volumes for target pressures until the force acting on each atom was smaller than 0.01 eV/Å. Following the Bader charge division scheme, we are able to determine the valence state of Fe and O atoms from the electron charge density (Table S1). Calculated valence states definitely are against ferric (Fe3+) or ferric (Fe2+) state of iron. Iron and oxygen atoms in pyrite-structured FeO2 exhibit partial covalent feature, which is recognized as a common feature in pyrite FeS2 model63. Therefore, our simulation results confirm that the valence state of iron in the Py-phase is close to Fe2+ with O–O bonding.

**Data availability**

The datasets generated during and/or analysed during the current study are available from the corresponding authors and J.L. (Jin.Liu@hpstar.ac.cn).

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Author contributions
J.L., Q.H., L.Y., X.Y., P.C., Y.M., and V.B.P carried out the experiment. J.L., W.B., Q.H., W.L.M., and H.K.M. performed the experimental data analysis and interpretation. Q.H performed the theoretical simulation. J.L., W.L.M., and H.K.M. conceived and designed the experiment. J.L., Q.H., W.L.M., and H.K.M. wrote the manuscript. All authors contributed to the discussion of the results and revision of the manuscript.
