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FeO₂ and FeOOH under deep lower-mantle conditions and Earth's oxygen-hydrogen cycles

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The distribution, accumulation and circulation of oxygen and hydrogen in Earth's interior dictate the geochemical evolution of the hydrosphere, atmosphere and biosphere¹. The oxygenrich atmosphere and iron-rich core represent two end-members of the oxygen-iron (O-Fe) system, overlapping with the entire pressure-temperature-composition range of the planet. The extreme pressure and temperature conditions of the deep interior alter the oxidation states¹, spin states² and phase stabilities^{3,4} of iron oxides, creating new stoichiometries, such as Fe₄O₅ (ref. 5) and Fe₅O₆ (ref. 6). Such interactions between O and Fe dictate Earth's formation, the separation of the core and mantle, and the evolution of the atmosphere. Iron, in its multiple oxidation states, controls the oxygen fugacity and oxygen budget, with hydrogen having a key role in the reaction of Fe and O (causing iron to rust in humid air). Here we use first-principles calculations and experiments to identify a highly stable, pyrite-structured iron oxide (FeO₂) at 76 gigapascals and 1,800 kelvin that holds an excessive amount of oxygen. We show that the mineral goethite, FeOOH, which exists ubiquitously as 'rust' and is concentrated in bog iron ore, decomposes under the deep lower-mantle conditions to form FeO₂ and release H₂. The reaction could cause accumulation of the heavy FeO₂-bearing patches in the deep lower mantle, upward migration of hydrogen, and separation of the oxygen and hydrogen cycles. This process provides an alternative interpretation for the origin of seismic and geochemical anomalies in the deep lower mantle, as well as a sporadic O2 source for the Great Oxidation Event over two billion years ago that created the present oxygen-rich atmosphere.

We started with α -Fe₂O₃ (haematite) powder loaded in cryogenically condensed liquid O₂ in the sample chamber of a diamond-anvil cell (DAC) (see Methods). The pressure was initially raised to 78 GPa; no reaction between haematite and O₂ was observed at ambient temperature (~293 K). Using a Nd-doped Y₃Al₅O₁₂ laser system⁷ to heat the sample to 1,800 K *in situ* at high pressure, the sample became semi-transparent (Fig. 1b), suggesting that a chemical reaction had occurred. The X-ray diffraction (XRD) pattern shows new sets of sharp, single crystal-like diffraction spots (Fig. 1a) that are readily distinguishable from the original broad and smooth texture of the Fe₂O₃ powder pattern. Integration of the diffraction spots (Fig. 2a) shows eight peaks that do not match any known Fe₂O₃ (refs 3, 4) or O₂ phases⁸, but can be unambiguously indexed to a rather simple cubic structure (Fig. 1c) with the space group *Pa*3 (Table 1).

The spotty XRD pattern is ideally suited to the multigrain crystallography method⁹ recently adopted for high-pressure research^{10,11}. The spots are treated as diffraction from multiple single crystals, and sorted according to individual crystal orientation matrices. At least 33 single crystallites were identified by the multigrain crystallography method software. All symmetry-allowed spots for $Pa\overline{3}$ are present, and all observed spots can be accounted for by the $Pa\overline{3}$ unit cell. The details of five crystallites are presented in Extended Data Tables 1 and 2. The new phase has a structure identical to that of pyrite (FeS₂) with oxygen replacing sulphur, the next-row chalcogen element. Results from Rietveld refinement are shown in Fig. 2. For this structure, oxygen atoms not only form O–Fe bonds of 1.792 Å, but also O–O bonds of 1.937 Å (Extended Data Fig. 1 and Extended Data Table 3), that are typical of peroxide. Analogous to the archetypical pyrite, the iron in FeO₂ is considered to be ferrous. Curiously, the oxidation of Fe₂O₃ to FeO₂ reduces Fe³⁺ to Fe²⁺. This can be understood with the concurrent oxidation of O^{2–} to O^{2–} and O⁰ as indicated by the O–O bond. In other words, this material can be viewed as FeO holding extra O₂. We shall refer to the pyrite phase of *Pa*³ peroxide as the P-phase.

To assess the stability of the P-phase under pressure, we calculated the volume change of the reaction at 76 GPa as follows:

$$2Fe_2O_3 + O_2 = 4FeO_2 \tag{1}$$

Here we used molar volumes of 35.69 Å³ for Fe₂O₃ in the *Aba2* structure⁴, 12.79 Å³ for O₂ in the O₈ cluster¹², and 20.76 Å³ for the P-phase. The reaction has a volume shrink of $\Delta V/V = -1.4\%$. Pressure lowers the Gibbs free energy of the reaction by $\Delta G = \int \Delta V dP$, thus favouring the formation of FeO₂ at increasing pressure. The P-phase is non-quenchable to ambient conditions; its XRD peaks disappear below 31 GPa during pressure release at 300 K (Extended Data Fig. 2).

We expanded our study from the O–Fe binary to the O–Fe–H ternary, and showed that the P-phase could also be synthesized under moderately reducing conditions coexisting with H₂. We studied the Fe₂O₃–H₂O join, in which the most stable compound FeOOH occurs ubiquitously as rust on Earth's surface, in the deep ocean, on meteorites, on other planets, and on moons, in the α -, β -, γ -, δ -, or ϵ -FeOOH forms. It concentrates in bog iron ore deposits, which have been used as a copious, renewable resource of iron ever since the Iron Age. The α -FeOOH (goethite) transforms to the ϵ -phase at high pressure and decomposes to Fe₂O₃+H₂O at high temperature. Its pressure–temperature phase boundaries and pressure–volume–temperature equations of state have been previously determined up to 29.4 GPa and 523 K (ref. 13).

We compressed goethite in Ne pressure medium to 92 GPa and laser-heated it to 2,050 K. XRD clearly shows the conversion to the P-phase (Fig. 2b), indicating the following reaction:

$$2FeOOH = 2FeO_2 + H_2 \tag{2}$$

The H₂ at 92 GPa and 2,050 K is far above its melting temperature of 900 K (ref. 14), and the H₂ fluid is highly mobile. Raman spectroscopy is used to search for H₂, and clearly observed H₂ vibron peaks at 5,180 cm⁻¹ (Fig. 3), corresponding to H₂ in the Ne pressure medium¹⁵. The production of free H₂ indicates a moderately reducing condition.

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Figure 1 | **The FeO**₂ **phase. a**, A two-dimensional XRD image of the Fe₂O₃ + O₂ experiment at 76 GPa after laser heating, collected at $\omega = -8.5^{\circ}$, with X-ray wavelength of 0.6199 Å. The original image in $2\theta - \eta$ polar coordination is converted into Cartesian coordinates. The newly developed sharp spots are from several single crystals of FeO₂, while smeared powder rings are from the remaining Fe₂O₃. Four selected diffraction spots and their Miller indices from the P-phase are shown below. Their observed Bragg angles (2θ), rotation angles (ω) and azimuthal angles (η) are listed in Extended Data Table 1. **b**, A microphotographic image of FeO₂.

As a chemical equivalent of $Fe_2O_3 + H_2O$, the goethite reaction (2) demonstrates that the water in deep Earth¹⁶ can provide an abundant source of O_2 , that is:

$$Fe_2O_3 + H_2O = 2FeO_2 + H_2$$
 (3)

Although the exact quantity of H_2O in the mantle is uncertain, the existence of H_2O there in hydrates or other forms is well accepted^{17–19}.

We were initially motivated by our computational predictions. A first-principles-based structure-searching algorithm²⁰ allows us to investigate the energy landscape of Fe–O compounds under pressure. At 100 GPa and 300 GPa, we conducted extensive prediction of Fe–O compounds using this model, and FeO₂ appears as one of the most stable phases. In the convex hull curve (Fig. 4a and b), FeO₂ stands out as energetically extremely favourable (the deepest hull). Our phonon calculations of FeO₂ show stable phonons at all pressure (Fig. 4c). The experimentally observed structural parameters of the P-phase FeO₂ agree exactly with the *ab initio* prediction (Table 1). Electron localization function calculations and Bader analysis shed light on the chemical bonding nature of FeO₂. Valence electrons near anionic O are highly localized and electron localization function minima are located between Fe and O atoms.

The P-phase has been previously predicted at 100–465 GPa by a computational search for high-pressure iron oxides²¹. It is clearly one of the most prominent phases in the convex hull curve at all of the calculated pressures, which are thought to occur at Earth's centre.

Our experiments and theoretical calculations demonstrate that if the surface assemblage FeOOH or $Fe_2O_3 + H_2O$ is thrust deeper than 1,800 km (into the deep lower mantle), it will form the P-phase. The frequent occurrence of such assemblages in the down-going slabs suggests that reaction (2) could have started as early as the accretion of the early Earth from planetesimals of assorted compositions. The water-rich and iron-oxide-rich fragments would release H_2



Figure 2 | Integrated XRD pattern and Rietveld refinement of the pyrite-type FeO₂ phase. a, FeO₂ synthesized from Fe₂O₃ and O₂ at 76 GPa with *R* indices $R_1 = 0.0663$ and $wR_2 = 0.171$. Blue stars belong to the *Aba2* phase of Fe₂O₃. We attribute the residual peaks to post-perovskite-type (pPv) Fe₂O₃ and O₂. b, FeO₂ synthesized from FeOOH at 92 GPa, with *R* indices, $R_1 = 0.0541$ and $wR_2 = 0.167$. Red stars refer to residual ϵ -FeOOH. Similar results are reproduced in multiple experiments for each composition.

and convert to the P-phase when pressure exceeds 76 GPa. With its high density (7.026 g cm⁻³ at 76 GPa) in comparison to the density (5 g cm⁻³) of the mantle according to the Preliminary Reference Earth Model²², the P-phase would normally settle at depth, while the light and mobile hydrogen would diffuse, infiltrate, or react to form other volatiles, and work its way up to complete the hydrogen cycle. A portion of the H₂ might eventually escape into space. Plate



Figure 3 | Raman peak of the hydrogen Q_1 vibron in dense neon. Data points (blue circles) below 45 GPa and the top inset are taken from Loubeyre's hydrogen vibron measurements of H_2 in the Ne matrix¹⁵. The blue dashed curve is the fourth-order polynomial fitting given by ref. 15. Data points (red squares) above 80 GPa and the bottom inset are taken from the present results of our FeOOH experiment after laser heating and during decompression to 80 GPa. The sharp hydrogen vibron peak at $5,180-5,170 \,\mathrm{cm^{-1}}$ clearly indicates the hydrogen H_2 in the neon matrix. Errors of frequency are calculated from the full-width half-maximum of the Raman peak. Pressure uncertainty is derived from multiple measurements of diamond line shifts at the centre of the culet.



Figure 4 | **Crystal structure search results. a**, 100 GPa; **b**, 300 GPa. The convex hull graph referenced by a dashed line shows each compound's stability with respect to decomposition into individual Fe and O elements. Solid squares show the formation enthalpy of each compound possessing the lowest enthalpy within fixed stoichiometry and chemical formula (red

tectonics would have continued to supply FeOOH, Fe₂O₃, and H₂O to the down-going slabs, thus accumulating P-phase to form patches of oxygen reservoirs in the deep lower mantle and at the same time sustaining the hydrogen cycle. The high mobility and rapid cycling of hydrogen would help to build up substantial patches of the P-phase, possibly detectable as seismic anomalies in the D["] layer and other deep lower-mantle regions.

Occasionally, the P-phase-rich patches could have been swept up by plumes or other large-scale mantle dynamic processes. Once they reached the middle lower mantle at depths of less than 1,500 km, the P-phase would decompose according to the reversal of equation (1) to provide a sporadic source of extra O₂.

The idea of such P-phase-rich patches is in harmony with the general concept of an overall reducing lower mantle. First, reaction (2) shows that FeO_2 can coexist with H_2 , indicating a moderately reducing condition in spite of its high oxygen content. Second, our knowledge of oxygen fugacity in the deep Earth is based on very limited sampling from the lower mantle (with none from the deep lower mantle). Sampling is chemically selective towards cratonic lithosphere²³. Considering the geochemical diversity of the mantle²⁴, the major

Table 1 \mid Indexed peaks of the XRD pattern from the P-phase at 76 GPa

hkl	d _{obs} (Å)	d _{cal} (Å)	Δd (Å)	d _{simu} (Å)
111	2.5190(1)	2.5189	-0.0001	2.500
200	2.1817(5)	2.1814	-0.0003	2.165
210	1.9508(3)	1.9511	0.0003	1.937
211	1.7821(15)	1.7811	-0.0010	1.768
220	1.5421(4)	1.5425	0.0004	1.531
311	1.3151(5)	1.3154	0.0003	1.306
222	1.2600(7)	1.2594	-0.0006	1.250
320	1.2093(12)	1.2100	0.0007	1.201

The lattice parameter is calculated to be a = 4.3628(1) Å. The wavelength of the synchrotron X-ray is 0.4344 Å. The d-spacings at 76 GPa are as follows: d_{obs} are the observed peak positions; d_{cal} is calculated from the averaged lattice parameter; $\Delta d = d_{cal} - d_{obs}$; and d_{simu} is the first-principles simulation. The estimated standard deviations are included in parentheses.

line is a guide to the eye). c, Phonon dispersion relations sampling along high-symmetry points in the Brillouin zone $(\Gamma - X - M - \Gamma - R)$ at 76 GPa. d, The electron localization function distribution modelled in the FeO₂ crystal lattice.

elements can vary greatly in regions of subduction $\operatorname{crust}^{25}$, upwelling plumes²⁶, D" layer²⁷, and many other small patches. Solid diffusion is extremely inefficient²⁸, and cannot eliminate the oxygen inhomogeneity between a P-phase-rich patch and the adjacent rocks kilometres away, even at the mantle temperatures occurring through geological time. The oxygen fugacity in the deep lower mantle is probably as inhomogeneous as that in the crust, which ranges from the oxygen fugacity of the iron-wüstite buffer²⁹ to that of free O₂ in the air. The oxygen-rich P-phase could exist in pockets, locally or regionally.

The scenarios of spatial and temporal heterogeneity of oxygen in the deep lower mantle have far-reaching implications. The oxygen-rich patches may lead to new phase assemblages with very different mineralogical, chemical and physical signatures from the nominally bridgmanite-ferropericlase mantle. The new phase assemblages may be responsible for many unexplained seismic and geochemical anomalies in the deep lower mantle and the D" layer. The new scenario introduces a complex picture of the deep lower mantle that calls for in-depth study of the P-phase.

The Great Oxidation Event marked the permanent rise of the O_2 level in the atmosphere, which did not previously contain free O_2 . It is thought to have occurred 2.4–2.1 billion years ago^{30} , on the basis of evidence such as the appearance of highly oxidized red soil, the disappearance of easily oxidized FeS₂ pyrite³¹, and the disappearance of distinctive non-mass-dependent sulphur isotope fractionations³². In addition to the proposed biogenic origin of the O_2 , the emergence of P-phase-bearing patches could provide an extra, eventful, abiotic source of O_2 . Whether the strong uprising of the P-phase patches 2.4–2.1 billion years ago was an accidental, sporadic event or was triggered by some geodynamic instability would be very interesting to know. Exploration of these hypotheses, however, requires further investigations of the physical, chemical, and mineralogical properties of the P-phase under the deep lower-mantle conditions.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.



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Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to H.-K.M. (hmao@gl.ciw.edu).

METHODS

XRD of haematite in O₂. Angular dispersive XRD experiments were performed at the 16-BMD and 16-IDB stations of the High-Pressure Collaborative Access Team (HPCAT) and the 13BM-C station of the GeoSoilEnviroCARS, at the Advanced Phonon Source, Argonne National Laboratory.

High-purity Fe₂O₃ powders from Alfa Aesar (MFCD00011008, 99.99% purity) were annealed at 1,296 K for 12 h to eliminate the absorbed water. The dehydrated samples were compressed into patties of size $60 \mu m$ (length) × $60 \mu m$ (width) × $10 \mu m$ (thickness), and loaded in a DAC. We use diamond anvils with culets of 200 μm to access pressures above 70 GPa. The sample chamber was a 100- μm -diameter hole drilled in a pre-compressed rhenium gasket. The DAC was placed in a sealed container immersed in liquid nitrogen. O₂ gas was piped into the container. Liquefied O₂ infused into the sample chamber, and served as both oxidant and pressure medium after the chamber was sealed by compression. The initial pressure after loading O₂was 8 GPa.

The compression rate from 8 to 78 GPa was as slow as 5 GPa per hour. During compression, the Raman signals from samples reproduce the literature results of Fe₂O₃ (ref. 33) and solid O₂ (ref. 8). We checked the structure of compressed Fe₂O₃ at 78 GPa, and verified that the diffraction pattern agreed with the Rh₂O₃-type Fe₂O₃ phase^{3,4}. The sample was then heated by a double-sided laser system⁷ to promote chemical reaction. The heating temperature reached 1,800 K on both sides of the sample, measured by fitting the black-body radiation curve. After laser heating and quenching to ambient temperature, the sample pressure was equilibrated at 76 GPa.

To confirm the synthesis conditions for FeO₂, we implemented separate runs at different pressures (56–81 GPa) using the same assemblage. We gradually increase the laser-heating power and monitor the change of XRD pattern. FeO₂ was observed above 75 GPa when the temperature was raised above 1,600 K, which represented the kinetic barrier of the reaction. FeO₂ was not observed at pressures below 72 GPa even at temperatures as high as 2,050 K, thus defining the lower stability limit of FeO₂ (Extended Data Fig. 3a).

Diffraction patterns performed at 16-BMD (HPCAT) with a monochromatic X-ray energy of 40.1 keV were collected on a Mar 345 image plate detector while the DAC was rotated so that the sample-beam angle varied from -7° to 7° . The P-phase is identified (Fig. 2). We performed additional XRD experiments at 13BM-C with rotation angle -13.0° to 12.5° and X-ray energy of 28.5 keV. Observation of the P-phase was well reproduced with the same experimental conditions. Pressure was determined by calibrating the derivative shift of the diamond Raman mode in an offline Raman system, confirmed by the vibron mode frequency of ε -O₂ (ref. 8). The pressure uncertainty is up to ± 3 GPa, derived from the difference between diamond line shifts and O₂ vibron mode shifts.

Decompress FeO₂. The sample was decompressed to the ambient condition from 76 GPa at a rate of 8 GPa per hour. The P-phase was recognized in diffraction patterns until 41 GPa, where the signature (111) and (200) becomes weak in intensity. The FeO₂ structure is eventually invisible at 31 GPa (Extended Data Fig. 2). Three newly emerged peaks are possibly associated with the low-pressure haematite.

Multigrain single-crystal XRD. To identify the new unit cell of an unknown phase, the conventional powder XRD method uses only the Miller indices–Bragg angle relationship ($hkl-2\theta$) and the answer is often non-unique. Like the single-crystal XRD method, the multigrain crystallography method requires all observable Miller indices simultaneously to satisfy the stringent geometrical relation among 2θ , ω (rotation axis perpendicular to the incident X-ray beam), and η (rotation axis parallel to the incident X-ray beam) within a tight uncertainty range, so the unit-cell assignment is absolutely definitive. In addition, the multigrain crystallography method has the statistical advantage over the single-crystal XRD owing to the number of multiple crystals and the coverage advantage enabling the access of full orientations that can be blocked for a single crystal by the limited DAC opening.

Multigrain single-crystal XRD experiments were implemented at BL15U1 station, the Shanghai Synchrotron Radiation Facility and 13BM-C, GeoSoilEnviroCARS. At Shanghai Synchrotron Radiation Facility, diffraction patterns were collected on a charge-couple device detector with nano-focusing incident beam (beam size of $1.5 \,\mu\text{m} \times 2 \,\mu\text{m}$) and beam energy of 20.0 keV. A total number of 50 images were collected by rotating the sample beam angle from -12.5° , to 12.5° , with a scanning step of 0.5° . For experiments performed at 13BM-C, the incident X-ray is $15 \,\mu\text{m} \times 15 \,\mu\text{m}$ in beam size and $28.5 \,\text{keV}$ in energy. The sample beam angle is -13.0° to 12.5° . The diffraction peak indexing and *d*-spacing for five selected FeO₂ crystal grains are summarized in the Extended Data Table 1a–e

respectively. A short summary of the multigrain diffraction results is shown in Extended Data Table 2.

XRD experiment on FeOOH. For the FeOOH experiment, angular dispersive XRD experiments were performed at the 16-IDB station of HPCAT and the 13BM-C station of GeoSoilEnviroCARS. High-purity α -FeOOH powders were purchased from Alfa Aesar (MFCD00064782, 99+% purity). The powder sample was pre-compressed to 35 μ m (length) × 35 μ m (width) × 10 μ m (thickness) and quickly loaded into the DAC without annealing. Diamond anvils with culet diameter of 150 μ m (bevelled from 300 μ m) were used to reach high pressures. The sample was placed in a hole of diameter 95 μ m, and sealed with rhenium gasket. Neon was loaded as hydrostatic pressure medium and thermal insulator. The pressure after gas-loading was 0.9 GPa, derived from the lineshift of ruby fluorescence.

During the compression process, pressure was first calibrated by ruby fluorescence and cross-checked by diffraction peaks of solid neon³⁴ and the rhenium gasket edge. At higher pressures, while ruby fluorescence modes were hard to detect, the lowest derivative value of diamond Raman peak was taken as additional calibration. After laser heating, diffraction peaks of neon were shifted, owing to the presence of hydrogen, and could not be used as a reliable pressure calibrate. Therefore only the lowest derivative of the diamond Raman peak and diffraction pattern taken at the edge of rhenium gasket were considered for pressure calibration. The pressure uncertainty is as large as ± 5 GPa.

XRD patterns were collected at stations 13BM-C of GeoSoilEnviroCARS and 16-IDB of HPCAT. FeOOH powder on Ne was compressed to 92 GPa (compression rate ~10 GPa per hour). The compressed sample was laser heated for 10 min. Sample pressure decreased to 87 GPa after quenching to ambient temperature. A Raman peak around 5,180 cm⁻¹ (Fig. 3) associated with the Q₁ vibron of hydrogen was observed, showing the diffusion of hydrogen into neon crystals^{15,35}. A portion of the heated sample had transformed into FeO₂ (Fig. 2b and Extended Data Fig. 4).

Additional *in situ* laser heating experiments were conducted to investigate the stability field of FeOOH. From 58–114 GPa, the sample was heated by a double-sided laser and we probe the P-phase by both XRD and Raman spectroscopy. We constrained the decomposition pressure of FeOOH between 78 GPa and 87 GPa (Extended Data Fig. 3b).

Ab initio crystal structure searching. The first-principles calculations were performed in the framework of density functional theory^{36,37} through package VASP³⁸. The generalized gradient approximation of Perdew, Burke, and Ernzerhof was implemented to describe the exchange correlation functions^{39,40}. Pseudopotentials were used with eight valence electrons for Fe atoms ($3d^74s^1$) and six for O atoms ($2s^22p^4$). Energy convergence and *k*-points mesh. For the crystal structure search, we used USPEX²⁰ with a plane-wave basis set cutoff energy of 800 eV.

Phonon dispersion curves from first-principles. Phonon calculations were conducted based on density functional perturbation theory⁴¹ implemented in VASP software in connection with the Phonopy software⁴². $8 \times 8 \times 8$ *q*-mesh (phonon momentum space) was used for mapping a $2 \times 2 \times 2$ supercell of FeO₂. We found that phonon dispersions are also stable at 0 GPa and 300 GPa, as shown in Extended Data Fig. 5.

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Extended Data Figure 1 | **Bonding lengths and angles in pyritetype FeO₂ at 76 GPa.** The structure is viewed along the x axis of the experimental FeO₂ unit cell.



Extended Data Figure 2 | **XRD pattern series by decompressing the P-phase.** The P-phase becomes weak in intensity at 41 GPa and totally disappears at 31 GPa and below. The decompressed sample eventually recovered to the α -Fe₂O₃ phase at low pressure. P indicates the P-phase FeO₂; O indicates solid O₂; H indicates α -Fe₂O₃ (haematite). Fe₂O₃ contains post-perovskite type and *Aba2*-structured high-pressure phases.



Extended Data Figure 3 | **Synthesis pressure-temperature conditions for FeO**₂**. a**, Open circles indicate the coexistence of Fe₂O₃ and O₂. Solid squares indicate the appearance of P-phase FeO₂. FeO₂ was synthesized between 72 GPa and 75 GPa. **b**, Open circles indicate FeOOH.

Decomposition pressure was constrained between 78 GPa and 87 GPa. Sample temperature was measured using the spectroradiometric method and errors are estimated from the goodness of fit to the spectroradiometric profile.



Extended Data Figure 4 | XRD patterns of FeOOH through the experimental pressure-temperature path. a, Goethite sample (G) in neon and Re gasket at 0.9 GPa. **b**, As in **a**, compressed to 35 GPa. The XRD peaks include goethite, solidified Ne, and the Re gasket. **c**, As in **a**, compressed to 92 GPa. The sample peaks remain and shift to higher Q. d, After laser-heating and quenching to ambient temperature, the pressure dropped to 87 GPa, and the goethite peaks disappeared. The new pattern consists of peaks of the P-phase, Ne and minor amounts of ϵ -FeOOH (red stars).



Extended Data Figure 5 | **Phonon dispersion relations of FeO₂ P-phase. a**, At 0 GPa; **b**, At 300 GPa. The P-phase is mechanically stable at 0 GPa and 300 GPa.

Extended Data Table 1 | Additional multigrain XRD data was obtained at 13BM-C ${\bf a}$

h	k	l	2 0 (°)	ω (°)	η (°)	dobs (Å)	d _{cal} (Å)	∆ d/d
0	-2	0	11.43	-11.1	30.5	2.181	2.181	0.000
0	2	0	11.44	11.3	210.4	2.181	2.181	0.000
0	-2	1	12.79	6.9	5.9	1.952	1.951	0.001
-1	-1	-3	19.03	-7.5	103.5	1.314	1.315	0.000
1	1	3	19.02	12.0	283.5	1.315	1.315	0.000

b

h	k	1	20 (°)	(°)	η (°)	dobs (Å)	d _{cal} (Å)	∆ d∕d
-1	1	1	9.88	4.9	281.5	2.522	2.520	0.001
1	-1	-1	9.89	-5.2	101.3	2.520	2.520	0.000
0	-2	0	11.42	-5.9	46.3	2.183	2.183	0.000
0	2	0	11.42	9.8	226.3	2.183	2.183	0.000
-2	0	2	16.18	10.0	317.2	1.541	1.543	-0.001

с

h	k	l	2θ (°)	ω	η (°)	dobs (Å)	$d_{\rm cal}({\rm \AA})$	$\Delta d/d$
-1	-1	1	9.89	-8.6	82.5	2.520	2.520	0.000
1	1	-1	9.88	1.4	262.7	2.521	2.520	0.001
-1	-2	0	12.78	-0.5	120.8	1.952	1.952	0.000
2	2	-2	19.85	6.4	262.5	1.260	1.260	0.000

d

h	k	l	2 θ (°)	@ (°)	η (°)	$d_{\rm obs}$ (Å)	$d_{\rm cal}({\rm \AA})$	$\Delta d/d$
-1	1	-1	9.89	0.0	225.1	2.520	2.519	0.000
0	-2	1	12.78	-4.9	83.7	1.952	1.951	0.001
0	2	-1	12.79	8.0	263.7	1.950	1.951	0.000
-1	-3	1	19.01	-5.2	103.0	1.315	1.315	0.000

e

h	k	l	2 0 (°)	ω	η (°)	dobs (Å)	d_{cal} (Å)	∆ d/d
1	-1	-1	9.9	3.4	143.0	2.517	2.518	0.000
-1	-2	0	12.79	-7.5	68.5	1.950	1.950	0.000
1	2	0	12.8	6.5	248.6	1.949	1.950	-0.001
-1	3	1	19	6.0	296.5	1.316	1.315	0.001

a, Single-crystal XRD peaks for a selected P-phase crystalline with unit-cell parameter a = 4.3618(6) Å at 76 GPa (space group $Pa\overline{3}$, incident beam wavelength $\lambda = 0.4344$ Å). The Bragg angle 2θ , rotation angle ω and azimuthal angle η are calculated from the orientation matrix. b-e, XRD indexing for the second, third, fourth and fifth P-phase crystalline, with unit-cell parameters a = 4.3664(8) Å, 4.3640(8) Å, a = 4.3625(7) Å, a = 4.3616(8) Å, respectively. The d-spacings are as follows: d_{obs} are the observed peak positions, d_{cal} are calculated from lattice parameters, $\Delta d = d_{obs} - d_{cal}$. The estimated standard deviations are included in parentheses.

	a (Å)	Volume (Å ³)
Grain1	4.3618(6)	82.98(4)
Grain2	4.3649(8)	83.16(6)
Grain3	4.3640(8)	83.11(5)
Grain4	4.3625(7)	83.03(4)
Grain5	4.3616(8)	82.97(6)
Powder	4.3628(1)	83.04(1)
Simulation	4.331	81.23

Extended Data Table 2 | The lattice parameters and atomic positions of pyrite-type FeO₂ at 76 GPa

Lattice parameters are calculated from five selected grains with X-ray wavelength 0.4344 Å. Diffraction pattern is treated and averaged as powder rings for Rietveld refinements. The Fe atoms are in 4a Wyckoff positions with fractional coordinates (0.0, 0.0, 0.0) (1/2, 0, 1/2) (0, 1/2, 1/2) (1/2, 1/2, 0) and oxygen in 8c positions (u, u, u), (-u + 1/2, -u, u + 1/2), (-u, u + 1/2, -u + 1/2), (u + 1/2, -u + 1/2, -u, -u, -u), (u + 1/2, u - u, 1/2, u, u + 1/2), (-u + 1/2, u + 1/2, u + 1/2, (u - u + 1/2, u - u + 1/2), (u + 1/2, u + 1/2, (u - u + 1/2, u - u + 1/2), (u + 1/2, u + 1/2, (u + 1/2, u - u + 1/2), (u + 1/2, u + 1/2

Extended Data Table 3 \mid Bonding lengths and angles in pyrite-type FeO_2 at 76 GPa

	Experiment	Simulation
Pressure (GPa)	76	76
Temperature (K)	297	0
<fe-o> (Å)</fe-o>	1.792(5)	1.781
<o-o>(Å)</o-o>	1.937(11)	2.077
Bond angle: O-Fe-O (°)	95.6(1)	96.52
Bond angle: Fe-O-O (°)	99.1(3)	96.82

Both experimental and computational bonding information is summarized. Uncertainties are calculated from structural refinement.