Unraveling the complexity of iron oxides at high pressure and temperature: Synthesis of Fe$_5$O$_6$

Barbara Lavina$^1$* and Yue Meng$^2$

The iron-oxygen system is the most important reference of rocks’ redox state. Even as minor components, iron oxides can play a critical role in redox equilibria, which affect the speciation of the fluid phases chemical differentiation, melting, and physical properties. Until our recent finding of Fe$_4$O$_5$, iron oxides were assumed to comprise only the polymorphs of FeO, Fe$_3$O$_4$, and Fe$_2$O$_3$. Combining synthesis at high pressure and temperature with microdiffraction mapping, we have identified yet another distinct iron oxide, Fe$_5$O$_6$. The new compound, which has an orthorhombic structure, was obtained in the pressure range from 10 to 20 GPa upon laser heating mixtures of iron and hematite at ~2000 K, and is recoverable to ambient conditions. The high-pressure orthorhombic iron oxides Fe$_3$O$_4$, Fe$_5$O$_6$, and h-Fe$_3$O$_4$ display similar iron coordination geometries and structural arrangements, and indeed exhibit coherent systematic behavior of crystallographic parameters and compressibility. Fe$_3$O$_4$, along with FeO and Fe$_2$O$_3$, is a candidate key minor phase of planetary interiors; as such, it is of major petrological and geochemical importance. We are revealing an unforeseen complexity in the Fe-O system with four different compounds—FeO, Fe$_2$O$_3$, Fe$_3$O$_4$, and h-Fe$_3$O$_4$—in a narrow compositional range (0.75 < Fe/O < 1.0). New, finely spaced oxygen buffers at conditions of the Earth’s mantle can be defined.

INTRODUCTION

Iron and oxygen are two of the most abundant elements of terrestrial planets. Participating in redox equilibria and carrying magnetism, the petrological and geochemical importance of iron oxides far exceeds their abundance (1). Extreme conditions control planetary interior processes and dynamics, as well as the outcome of large impacts on planets’ surfaces. Thus, it is fundamental to define structures, stability, properties, and crystal chemistry of iron oxides at high pressure and temperature.

The recent discovery of the high-pressure compound Fe$_4$O$_5$ (2) demonstrates that our understanding of one of the binary systems most important for the evolution of terrestrial planets is far too limited. The implied assumption that only the polymorphism of previously known iron oxides should be determined has been proven to limit our perspectives on planetary modeling. Fe$_3$O$_4$ has a layered structure stable at pressures greater than 10 GPa (2) and up to at least 40 GPa (3). Compositionally, its stability range extends toward high oxygen contents, because Fe$_3$O$_4$ was observed to break down into Fe$_2$O$_3$ and hematite at about 10 GPa (4). Furthermore, Fe$_3$O$_4$ has been found to accept large amounts of isomorphous substitutions (5). There is a clear parallelism between the structures of high-pressure orthorhombic iron oxides and those of calcium ferrites. Fe$_3$O$_4$ adopts the same structure of CaFe$_2$O$_5$ (2), whereas h-Fe$_3$O$_4$ assumes the arrangement of CaTi$_2$O$_5$, which is similar to the structure of CaFe$_2$O$_5$. On the basis of this systematics, we speculated that a new iron oxide might be stable at high pressure, a compound analogous to CaFe$_2$O$_5$ (6). We thereby investigated the FeO system at compositions close to Fe/O = 0.83 at high pressure and temperature, adopting advanced structural analysis techniques. Here, we report the discovery of a new compound, Fe$_5$O$_6$.

RESULTS

Mixtures of iron and hematite (Fe + 2Fe$_2$O$_3$ $\rightarrow$ Fe$_3$O$_4$) were pressurized to targeted pressure values (10 to 20 GPa) and subsequently heated up to ~2300 K using the online double-sided infrared (IR) laser heating technique (7). The samples, roughly 80 to 200 $\mu$m in diameter and 10 $\mu$m in thickness, were translated in front of the laser beams to convert most of the starting material into high-pressure products. The reaction progress was monitored by collecting diffraction patterns every ~30 s during the heating. The conversion of iron and hematite mixtures to high-pressure forms of oxides is prompt and complete upon achieving homogeneous heating. We heated some samples for up to 30 minutes and did not observe further phase changes. The high-pressure phases show unstrained diffraction peaks and grain size growth as shown by the spotty Debye rings in fig. S1. These observations suggest that the reactions proceeded toward definite lower energetic minima. There is no evidence of dissociation reactions or phase transitions upon temperature quenching (figs. S2 and S3).

After the synthesis, samples typically display heterogeneity with respect to phase and grain size distributions. Heterogeneities are a consequence of thermally induced chemical gradients and the narrow compositional differences between high-pressure orthorhombic iron oxides. Diffraction data were collected in fine two-dimensional grids before and after laser heating at high pressure for proper characterization of synthesis products. The microdiffraction mapping (8) allowed us to identify all phases, find the locations most suitable for the crystallographic analysis of each phase, and map the phase distribution. In most patterns, we observed diffraction peaks that could not be attributed to any of the known iron oxides. Considering that the interpretation of multiphase powder diffraction data is often non-unique, particularly when coexisting phases have relatively large and comparable unit cell parameters, we performed multiple syntheses and purposely searched for micrometer-sized crystal grains. Therefore, our structural determination is based on the larger grains for which the diffraction effects could be isolated in the three dimensions of the reciprocal space.
The structure of the unknown phase was determined from the diffraction effects of a few selected grains isolated in multiphase diffraction images, an example of which is shown in Fig. 1A. This approach ensures unique index assignment (Fig. 1B). The peaks were indexed with an orthorhombic unit cell, with parameters $a = 2.815(10)$ Å, $b = 9.795(3)$ Å, and $c = 15.011(4)$ Å at 11.4 GPa, 300 K. The cell parameters $a$ and $b$ are comparable to those of Fe₂O₄ and h-Fe₃O₄. The length of $c$ is about 3 Å greater than that of Fe₄O₅, roughly the same difference observed between Fe₂O₃ and h-Fe₃O₄ (fig. S4). It follows that the unit cell volume of the new phase is ~150 Å³ larger than that of Fe₄O₅, a difference similar to that observed between Fe₂O₃ and h-Fe₃O₄ (fig. S5). The unit cell comparison provided the first evidence that the stoichiometry of the phase could indeed be that of the new compound Fe₅O₆. We therefore proceeded with the analysis of observed structure factors and obtained the space group Cmcm as the most plausible symmetry. Refinements with the structural model of CaFe₂O₆ resulted in substantial agreement between the observed and calculated structure factors of multiple grains from different samples. An example of a structural refinement obtained for a grain synthesized at 11.4 GPa is shown in Table 1.

Table 1. Structural data of Fe₅O₆ at 11.4 GPa. The least-squares refinement of the unit cell parameters was performed against 200 reflections. The refinement of 10 atomic fractional coordinates and the scale factor was performed against 81 Fe₂O₃² (after averaging symmetry equivalents), and converged with satisfactory statistical parameters ($R_{wp} = 10\%, R_{all} = 11\%$).

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>11.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (K)</td>
<td>300</td>
</tr>
<tr>
<td>$K_0$ (GPa)</td>
<td>173(2)</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>2.815(10)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>9.795(3)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>15.011(4)</td>
</tr>
<tr>
<td>$V$ (Å³)</td>
<td>414(2)</td>
</tr>
<tr>
<td>$&lt;$Fe₄c&gt;O&gt; (Å)</td>
<td>2.076</td>
</tr>
<tr>
<td>$&lt;$Fe₄r&gt;O&gt; (Å)</td>
<td>2.058</td>
</tr>
<tr>
<td>$&lt;$Fe₅r&gt;O&gt; (Å)</td>
<td>2.075</td>
</tr>
<tr>
<td>$x$, $y$, $z$ (Fe₄c)</td>
<td>0, 0.6379(5), $\frac{1}{4}$</td>
</tr>
<tr>
<td>$x$, $y$, $z$ (Fe₄r)</td>
<td>0, 0.1341(3), 0.4527(3)</td>
</tr>
<tr>
<td>$x$, $y$, $z$ (Fe₅r)</td>
<td>0, 0.3959(4), 0.3568(4)</td>
</tr>
<tr>
<td>$x$, $y$, $z$ (O1)</td>
<td>0, 0.290(2), $\frac{1}{4}$</td>
</tr>
<tr>
<td>$x$, $y$, $z$ (O2)</td>
<td>0, 0.782(2), 0.421(2)</td>
</tr>
<tr>
<td>$x$, $y$, $z$ (O3)</td>
<td>0, 0.043(2), 0.332(2)</td>
</tr>
<tr>
<td>$x$, $y$, $z$ (O4)</td>
<td>0, $\frac{1}{2}$, 0</td>
</tr>
</tbody>
</table>

In the structure of Fe₅O₆, iron is located in three non-equivalent crystallographic sites with point group symmetries 4c, 8f₁, and 8f₂ (Fig. 2). Like the other high-pressure orthorhombic iron oxides, Fe₂O₆ has a layered structure where edge-sharing FeO₆ octahedra alternate with FeO₆ trigonal prisms perpendicularly to the $c$ axis. The layers of octahedra are two, three, and four atoms thick for h-Fe₃O₄, Fe₂O₅, and Fe₅O₆, respectively. The relation in structural arrangements in the series of high-pressure iron oxides is consistent with the aforementioned trends in unit cell parameter lengths (fig. S4). The $a$ unit cell parameters of Fe₂O₅ and Fe₅O₆ are similar in the investigated pressure range, whereas the $b$ parameters differ by roughly 0.15 Å (fig. S4). Considering that the shortest Fe-Fe distances ($=a$) occur between equivalent iron atoms in the direction parallel to the $a$ axis, the $a$ cell parameter might be controlled by the Fe-Fe repulsion and therefore the charge distribution between iron sites. The $b$ axis length is, in the first approximation, controlled by the size of the octahedra. The average charge of iron in Fe₅O₆ is lower than that in Fe₂O₅, which translates to a greater mean octahedral size, and may explain the difference in $b$ axis lengths of the two phases (fig. S4). The largest average Fe–O bonds were observed for iron in the trigonal prismatic coordination, similar to what has been observed in Fe₄O₅ (2). The two octahedra appear to differ significantly in size and degree of distortion (Table 1). The Fe₁ octahedron (dark blue in Fig. 2) is smaller and less distorted than the Fe₂ octahedron (light blue in Fig. 2).

The phase maps in Fig. 3 illustrate an example of the spatial distribution of the synthesis products. Fe₅O₆ is abundant in the space separating regions high in wüstite and in Fe₄O₅, corroborating the composition proposed for the new compound, which is intermediate between the two known phases. Although we do not exclude the existence of iron in the trigonal prismatic coordination, similarly to what has been observed in Fe₄O₅ (2).
of even more complex iron oxides (with formula Fe$_5$O$_6 + n$FeO), we do not have clear evidence of other phases compositionally intermediate between Fe$_5$O$_6$ and wüstite within the investigated pressure and temperature ranges.

We found that Fe$_5$O$_6$, like Fe$_4$O$_5$, is recoverable, whereas h-Fe$_3$O$_4$ reverts to magnetite at pressures lower than 5 GPa (9). The bulk compressibility of Fe$_5$O$_6$ is shown in Fig. 4; our measured ambient condition volume is $440.6 (5) \, \text{Å}^3$. The bulk modulus of Fe$_5$O$_6$, estimated by fitting the data to the second-order Birch-Murnaghan equation of state, is 173 (2) GPa. Fe$_5$O$_6$ is, expectedly, more compressible than Fe$_4$O$_5$ [$K_0 = 185.7 \, \text{GPa}$ (2)] and h-Fe$_3$O$_4$ [$K_0 = 198 \, \text{GPa}$ (10)]. The bulk moduli of the three orthorhombic iron oxides follow a Vegard’s trend (Fig. 4, inset), further supporting the inferred composition.

**DISCUSSION**

The oxygen fugacity of the Earth’s mantle varies in three dimensions as a result of the crystal chemical control of major phases, the raise of reduced material from the bottom regions of the mantle, and the incorporation of oxidized materials from subduction [for example, (11–13)]. Redox equilibria influence phase stability and properties, differentiation and melting, and ultimately have a strong role in the whole planetary chemical and physical dynamics. All phases containing elements with multiple valence states participate in redox equilibria, chiefly the most abundant iron-bearing silicates and magnesiowüstite [for example, (13–15)]. Nonetheless, minor iron-bearing phases, such as iron oxides, can play a critical role in mantle redox equilibria (16), particularly in locally iron-rich environments.

Fe$_5$O$_6$ is a new high-pressure iron oxide that was characterized by high-pressure microdiffraction analysis and is supported by the consistent behavior of structural parameters and compressibility in the series of orthorhombic high-pressure iron oxides. The synthesis is rapid and repeatable, with no evidence of further structural transitions upon temperature quenching and pressure release. The spatial distribution of coexisting iron oxides in several samples synthesized at high pressure and temperature supports the composition inferred for the new compound. The samples did not reach chemical homogeneity; we found that wüstite, Fe$_5$O$_6$, and Fe$_4$O$_5$ are stable at the same pressure and temperature, and their distribution follows...
we have found that the iron-oxygen system is surprisingly complex, oxidation state is indeed typically defined relative to redox exchanges and magnetite-hematite (MH); for example, (18)) and are indeed the reference of oxygen fugacity of rocks. Phase stability with respect to oxidation state is indeed typically defined relative to redox exchanges with iron oxides [for example, (19–27)]. At pressure greater than 10 GPa, we have found that the iron-oxygen system is surprisingly complex, Fe$_5$O$_6$ being the fourth compound described in a narrow compositional range, between 0.75 and 1.0 Fe/O, in addition to FeO, Fe$_4$O$_5$, and Fe$_3$O$_4$. With the discovery of Fe$_5$O$_6$ and Fe$_4$O$_5$, we can define new, finely spaced oxygen fugacity buffers that apply to pressures greater than ~10 GPa. These are given by the reactions 5FeO + 1/2 O$_2$ = Fe$_5$O$_6$, 4FeO + 1/2 O$_2$ = Fe$_4$O$_5$, and 3FeO + 1/2 O$_2$ = 4 Fe$_3$O$_4$. Fe$_5$O$_6$ and Fe$_4$O$_5$ are plausible new players in the Earth’s mantle redox equilibria. Assessing the degree of the influence of these phases on planetary interior processes is a challenging task that requires the petrological analysis of complex systems of realistic compositions.

High-resolution structural studies at extreme conditions allow unraveling the complexity of matter at high pressure, as we have shown here for the binary system of the Earth’s two most abundant elements. Concurrently, enhanced resolution of seismic profiles reveals the marked heterogeneities in the Earth’s mantle. Parallel paradigm shifts that span from mantle lateral heterogeneity to the Fe-O system high-pressure behavior might be related by an unforeseen complexity of redox equilibria.

**MATERIALS AND METHODS**

Iron and hematite fine powders were mixed in appropriate proportions (Fe + 2Fe$_2$O$_3$ = Fe$_5$O$_6$) and loaded at pressures ranging from ~10 to ~20 GPa in diamond anvil cells. Neon was used as pressure medium and thermal insulator for laser heating under high pressures, whereas gold and ruby were used as pressure standards. The samples, pressurized between 10 and 20 GPa, were heated to temperatures of about 2000 K using a double-sided IR laser heating system (7) installed in the 16IDB experimental station of the High Pressure Collaborative Access Team (HPCAT), Advanced Photon Source (APS), Argonne National Laboratory. We used a relatively large heating spot size, about 30 μm in flat top area and 60 μm in full width at half maximum (FWHM), at the same time, moving the sample position relative to the heating laser to ensure the conversion of the whole sample into the high-pressure phases of iron oxides. Although the synthesis is fast, we heated the samples for ~15 min, moving the cells and adjusting the laser power to complete the reaction of the whole sample. Monochromatic hard x-ray beams of energy ranging between 30 and 37 keV focused to 6 × 5–μm FWHM were used for the structural characterization. Even with such a small beam, only a few diffraction images were collected being single-phase Fe$_5$O$_6$, and they were typically neither ideal powder nor single-crystal patterns. The grain size of the samples appears to be fairly coarse and highly variable. The finer-textured diffraction patterns were processed with powder diffraction methods and used for lattice parameter determination (table S1). None of these powder patterns were suitable for a reliable structure analysis of Fe$_5$O$_6$ atomic parameters. Diffraction intensities were nonetheless used for the rough determination of phase abundances. A few locations, identified while microdiffraction mapping the samples, showed relatively large grains of Fe$_5$O$_6$ with low strain in multiphase diffraction images. The diffraction peaks of these grains, isolated in the reciprocal space, provide conclusive determination of the structure of Fe$_5$O$_6$. Pressure-dependent data were collected in decompression, assuring a quasi-hydrostatic stress field. The softwares GSE_ADA, RSV (28), SHELXL (29), FIT2D (30), and Jade were used for reduction and refinement of diffraction data. VESTA (31) was used for the representation of the structure. The nominal composition of these phases is deduced from the structural analysis of single crystal grains; minor differences in stoichiometry cannot be discriminated with this approach.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/1/5/e1400260/DC1

Fig. S1. Diffraction image (A) and integrated pattern (B) collected during synthesis (~15 GPa, ~2000 K).

Fig. S2. Diffraction image (A) and integrated pattern (B) collected at 10.7 GPa where Fe$_5$O$_6$, wüstite, neon, and gold were the phases identified.

Fig. S3. Diffraction image (A) and integrated pattern (B) collected at ~11 GPa where Fe$_5$O$_6$, Fe$_4$O$_5$, and neon were the phases identified.

Fig. S4. Comparison of the axial compressibility of Fe$_5$O$_6$ and Fe$_4$O$_5$.

Fig. S5. Volume (A) and relative compressibility (B) of the orthorhombic iron oxides.

Table S1. Example of cell parameter fitting results from powder diffraction analysis.

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