

1 **Revision 1**

2 **The stability of Fe₅O₆ and Fe₄O₅ at high pressure and temperature**

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11 **ABSTRACT**

12 The oxygen fugacity in the interior of the Earth is largely controlled by iron-bearing minerals.

13 Recent studies have reported a variety of iron oxides with chemical compositions between FeO

14 and Fe₃O₄ above ~10 GPa. However, the stabilities of these high-pressure iron oxides remain

15 mostly uninvestigated. In this study, we performed in-situ X-ray diffraction (XRD)

16 measurements in a laser-heated diamond-anvil cell (DAC) to determine the phase relations in

17 both Fe₅O₆ and Fe₄O₅ bulk compositions to 61 GPa and to 2720 K. The results show that Fe₅O₆ is

18 a high-temperature phase stable above 1600 K and ~10 GPa, while FeO + Fe₄O₅ are formed at

19 relatively low temperatures. We observed the decomposition of Fe₅O₆ into 2FeO + Fe₃O₄ above

20 38 GPa and the decomposition of Fe₄O₅ into FeO + h-Fe₃O₄ at a similar pressure range. The

21 coexistence of FeO and Fe₃O₄ indicates that none of the recently discovered compounds between
22 FeO and Fe₃O₄ (i.e., Fe₅O₆, Fe₉O₁₁, Fe₄O₅, and Fe₇O₉) are formed beyond ~40 GPa at 1800 K,
23 corresponding to conditions in the shallow lower mantle. Additionally, as some superdeep
24 diamonds have genetic links with these high-pressure iron oxides, our results give constraints on
25 pressure and temperature conditions of their formation.

26 **Keywords:** Iron oxide, diamond-anvil cell, high pressure, Fe₄O₅, Fe₅O₆

27 INTRODUCTION

28 Since iron is the most abundant transition metal element, oxygen fugacity inside the Earth is
29 controlled by iron-bearing phases. According to recent analyses of natural samples, oxygen
30 fugacity varies widely in the mantle (Kaminsky et al. 2015; Smith et al. 2016). Oxidizing
31 materials include a fair amount of Fe³⁺, which may stabilize iron oxides as discrete minerals.
32 Recent high-pressure experimental studies have discovered a rich variety of iron oxides
33 intermediate in composition between FeO and Fe₃O₄, including Fe₅O₆ (Lavina and Meng 2015),
34 Fe₉O₁₁ (Ishii et al. 2018), Fe₄O₅ (Lavina et al. 2011), and Fe₇O₉ (Sinmyo et al. 2016). However,
35 the pressure-temperature (*P-T*) stability fields of these iron oxides are poorly known.

36 In order to understand the speciation of volatile elements in the mantle, mineral redox buffer
37 relations have been revised considering these new iron oxides; for example, Myhill et al. (2016)

38 showed that FeO-Fe₅O₆ line crosses the enstatite + magnesite = olivine + diamond (EMOD)
39 buffer line, suggesting Fe₅O₆ is stable at conditions where diamonds are formed. Therefore, a
40 better understanding of the thermodynamic stability of high-pressure, high-temperature iron
41 oxides might enable a more refined understanding of the redox of the Earth's lower mantle and
42 the origin of super-deep diamonds.

43 Here we examined the phase relations in Fe₅O₆ and Fe₄O₅ bulk compositions on the basis of
44 high *P-T* experiments up to 61 GPa and to 2720 K. Our results demonstrate that the stabilities of
45 Fe₅O₆ and Fe₄O₅ are limited to 35–40 GPa at 1800 K and both are decomposed into FeO wüstite
46 + h-Fe₃O₄ at higher pressures. Furthermore, our findings indicate that no intermediate compounds
47 between FeO and Fe₃O₄, including more recently discovered Fe₉O₁₁ and Fe₇O₉, are formed above
48 ~40 GPa.

49 **METHODS**

50 We used Fe₅O₆ and Fe₄O₅ as starting materials, both of which were synthesized from mixtures
51 of reagent grade Fe metal and Fe₂O₃ hematite powders at 10 GPa/1700 K and 15 GPa/1700 K,
52 respectively, in a Kawai-type multi-anvil press at the Bayerisches Geoinstitut (Ishii et al. 2016).
53 The Raman spectra of the Fe₅O₆ sample were collected at 1 bar and at high pressures to 27 GPa
54 in a diamond-anvil cell (DAC) without any pressure medium by using a micro-confocal laser

55 Raman system (*JASCO* NRS-3100) (Fig. S1 in the supplemental information).

56 Laser-heated DAC experiments were performed using diamond anvils with 300 μm culets.
57 The Fe_5O_6 and Fe_4O_5 samples were pressed into ~ 10 μm thick plates and loaded into 100 μm
58 sample chambers at the centers of preindented rhenium gaskets. NaCl or KCl, dried in an oven
59 until just prior to the loading, was used as both a pressure medium and a pressure standard. After
60 compression, the sample was heated from both sides using 100 W single-mode Yb fiber lasers
61 with beam-shaping optics, which converts a Gaussian beam to one with a flat energy distribution.
62 Using this flat-top laser heating system, the resultant laser-heated spots had reduced radial
63 temperature gradients and were approximately 30 μm in diameter. We measured temperature
64 using spectroradiometry (Ozawa et al. 2016). Sample pressures were calculated from the unit-cell
65 volume of NaCl-B1 (Brown 1999), NaCl-B2 (Ueda et al. 2008), or KCl (Dewaele et al. 2012) at
66 high P - T obtained by X-ray diffraction (XRD) measurements. The temperatures of NaCl and KCl
67 were estimated from measured sample temperature (T_{meas}) (Pigott et al. 2015) as;

68
$$T_{\text{NaCl,KCl}} = \frac{3T_{\text{meas}}+300}{4} \pm \frac{T_{\text{meas}}-300}{4} \quad (1)$$

69 In-situ XRD measurements were conducted at the BL10XU, SPring-8. An incident X-ray
70 beam with a wavelength of 0.4127–0.4158 \AA was focused using compound refractive lenses and
71 collimated so that the full width at half maximum was 6 μm . XRD patterns were collected on a

72 flat panel detector (*Perkin Elmer*) with an exposure time of 1 sec during heating and 20–30 sec at
73 300 K. We employed the IPAnalyzer software package to integrate the 2D diffraction patterns
74 into 1D patterns and the PDIndexer to analyze the pattern.

75 RESULTS

76 Stability fields of Fe_5O_6 and Fe_4O_5

77 A total of nine separate high P - T runs were used to determine the phase relations in the Fe_5O_6
78 bulk composition ([Fig. 1a](#)). Since the Fe_5O_6 starting material consisted of a small number of
79 grains and was under large deviatoric stress upon compression at room temperature, it exhibited
80 broad and limited XRD peaks at high pressure before heating. [Figures 2a](#) and [2b](#) show the
81 changes in integrated XRD patterns for run #8 (see [Fig. S2](#) in the supplemental information for
82 the raw 2D XRD images). All peaks from the sample were indexed to Fe_5O_6 before heating at 36
83 GPa. Upon heating to 1930 K, the peaks from Fe_5O_6 mostly disappeared, and new FeO wüstite
84 and Fe_4O_5 peaks were observed. With further heating to 2350 K at 34 GPa, the peaks of Fe_5O_6
85 emerged once again in < 1 min. This sample was compressed further to 59 GPa. At this point, the
86 area outside the laser-heated spot had decomposed into FeO + Fe_4O_5 due to the temperature
87 gradient. Soon after we started heating a new spot consisting of FeO + Fe_4O_5 , the XRD pattern
88 drastically changed, showing the presence of FeO wüstite + h- Fe_3O_4 . While the crystal structure

89 of h-Fe₃O₄ remains controversial, we assume its space group to be *Cmcm* based on Ricolleau and
90 Fei (2016). On the basis of these experiments using Fe₅O₆ as the starting material, we found that
91 the stability of Fe₅O₆ is limited to temperatures above 1500 K and a pressure range of 10 to 36
92 GPa (Fig. 1a). Furthermore, the boundary between Fe₅O₆ and FeO + Fe₄O₅ has a small positive
93 Clapeyron slope. In the other runs, we heated a previously unheated portion of a sample at each
94 heating cycle. The stabilities of Fe₅O₆, FeO + Fe₄O₅, and FeO + h-Fe₃O₄ in the Fe₅O₆ bulk
95 composition were determined on the basis of the appearance of new diffraction peaks and their
96 growth (Fig. 1a). The peaks from preexisting, unstable phase(s) decreased in intensity but did not
97 fully disappear due to sluggish kinetics of phase transitions between these phases.

98 We have also conducted an additional experiment using Fe₄O₅ as a starting material (run #12).
99 Broad XRD peaks from Fe₄O₅ were present at 39 GPa and 300 K. They became sharp during
100 heating up to 1620 K. With further heating to 1860 K and above, we observed the dissociation of
101 Fe₄O₅ into FeO wüstite + h-Fe₃O₄ (Fig. 2c). The *P-T* stability of Fe₄O₅, in experiments using
102 starting compositions of bulk Fe₄O₅ and Fe₅O₆ (through the decomposition of Fe₅O₆ at high
103 temperatures), are shown in Figure 1b. Fe₄O₅ is stable as a single phase up to 38 GPa at 1950 K
104 and ~60 GPa at 1200 K. The boundary between Fe₄O₅ and FeO + h-Fe₃O₄ exhibits a negative
105 Clapeyron slope although the slope is not tightly constrained from the present experiments.

106 **Compression curve of Fe₄O₅**

107 We obtained the volume of Fe₄O₅ at 300 K in a wide pressure range from 8 to 61 GPa (Table
108 S1 and Fig. S3 in the supplemental information). A large volume reduction (~3%) was observed
109 at 50 GPa (Fig. 3). Since the volumes of Fe₄O₅ above 50 GPa are too small to be fitted by a single
110 compression curve together with the lower pressure data, we fit a third-order Birch-Murnaghan
111 equation of state (EoS) to these pressure-volume data up to 47 GPa, which gives bulk modulus at
112 1 bar of $K_0 = 201(7)$ GPa and its pressure derivative, $K' = 3.1(5)$ using $V_0 = 357.1 \text{ \AA}^3$ at 1 bar
113 from Lavina et al. (2011). When we instead fit a second-order BM EoS, we obtained $K_0 = 188(2)$
114 GPa, consistent with the $K_0 = 185.7$ GPa reported by Lavina et al. (2011) based on their data up
115 to 28 GPa.

116

DISCUSSION

117 While only three iron oxides, FeO wüstite, Fe₃O₄ magnetite, and Fe₂O₃ hematite, are found at
118 1 bar, recent high-pressure experiments report a rich variety of intermediate compounds between
119 FeO and Fe₃O₄ above ~10 GPa. They include not only Fe₄O₅ and Fe₅O₆, which were directly
120 examined in this study, but also Fe₉O₁₁ (Ishii et al. 2018) and Fe₇O₉ (Sinmyo et al. 2016). In the
121 Earth's interior, these iron oxides may be formed in Fe³⁺-bearing oxidizing materials such as
122 subducted banded iron formations (BIFs) and play important roles in oxidation/reduction

123 reactions in the presence of fluids. This study demonstrates that FeO coexists with Fe₃O₄ above
124 38 GPa and 1950 K, which is the invariant triple point where FeO, Fe₅O₆, Fe₄O₅, and h-Fe₃O₄
125 coexist in the two-component system (Fig. 1). These findings indicate that any intermediate
126 compounds between FeO and Fe₃O₄ cannot form beyond that point. Therefore, the roles of Fe₅O₆,
127 Fe₉O₁₁, Fe₄O₅, and Fe₇O₉ in oxidation/reduction reactions are limited to *P-T* conditions of the
128 deep upper mantle to the shallow lower mantle.

129 Our experiments show that Fe₄O₅ undergoes a distinct volume contraction at around 50 GPa
130 (Fig. 3). This mirrors the significant volume reduction that was previously reported to occur in
131 h-Fe₃O₄ at ~50 GPa (Ricolleau and Fei 2016), which is caused by the high-spin to low-spin
132 transition of octahedral Fe³⁺ (Greenberg et al. 2017). The structural similarity between Fe₄O₅ and
133 h-Fe₃O₄ suggests that the observed volume change in Fe₄O₅ might also be attributed to the spin
134 transition of Fe³⁺.

135 **IMPLICATIONS**

136 The origins of superdeep diamonds may be related to carbonaceous melts, C-H-O fluids, or
137 Fe-rich metallic melts in a deep mantle (Shirey 2013; Smith et al. 2016). Magnesiowüstite
138 (Mg,Fe)O found as inclusions in such superdeep diamonds is associated with Fe³⁺-rich phases as
139 exsolution lamella or clusters (Kaminsky et al. 2015). Their bulk composition suggests that these

140 inclusions (magnesiowüstite + Fe³⁺-rich phases) are relics of high-pressure iron oxides such as
141 Fe₄O₅ and Fe₅O₆. Myhill et al. (2016) reported that the EMOD buffer line is in the Fe₅O₆ stability
142 field and thus Fe₅O₆ can coexist with diamond, while Fe₄O₅ can co-occur only with carbonate.
143 Accordingly, such diamond inclusions (magnesiowüstite + Fe³⁺-rich phases) could be relics of the
144 decomposition of Fe₅O₆ which, as shown by this study, has a stability field limited to high *P-T*
145 conditions (> 10 GPa and > 1500 K) (Fig. 1a). This stability field is close to the conditions along
146 normal mantle geotherm and the solidus of carbonated mantle rocks (Dasgupta 2013). The host
147 diamonds may therefore have a genetic link with CO₂-rich partial melts in the deep upper mantle
148 and below.

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219 **FIGURE 1.** Phase relations in (a) Fe_5O_6 and (b) Fe_4O_5 bulk compositions. In (a), blue diamonds
220 = Fe_5O_6 ; orange squares = $\text{FeO} + \text{Fe}_4\text{O}_5$; green triangles = $\text{FeO} + \text{h-Fe}_3\text{O}_4$; purple circle =
221 condition for synthesizing the Fe_5O_6 starting material. White squares and triangles are from (b).
222 In (b), yellow squares = Fe_4O_5 ; light blue triangles = $\text{FeO} + \text{h-Fe}_3\text{O}_4$; red circle = condition for
223 synthesizing the Fe_4O_5 starting material. Open symbols are the data from (a). The $\text{Fe}_5\text{O}_6 +$
224 $\text{h-Fe}_3\text{O}_4$ region is supposed to exist although not observed in this study. The dark gray area is the
225 region where Woodland et al. (2012) reported the breakdown of Fe_3O_4 into $\text{Fe}_2\text{O}_3 + \text{Fe}_4\text{O}_5$. The
226 light gray area indicates the conditions at which Fe_4O_5 was synthesized by Lavina et al. (2011).
227 The dashed line is based on Myhill et al. (2016). The chain curve shows the melting curve of FeO
228 (Fisher and Campbell 2010), which can be a guide for melting temperatures of Fe_5O_6 and Fe_4O_5 .
229 Error bars are smaller than symbols where they are not shown.

230

231 **FIGURE 2.** Changes in XRD patterns (a, b) in run #8 and (c) in run #12, using the Fe_5O_6 and
232 Fe_4O_5 starting materials, respectively. The wavelength of the incident X-ray beam was 0.4141 \AA
233 for the former and 0.4150 \AA for the latter. The color of labels: black = Fe_5O_6 , red = Fe_4O_5 , blue =
234 $\text{h-Fe}_3\text{O}_4$, and green = FeO . Peak positions moved to some extent upon heating because of the
235 release of large deviatoric stress at 300 K. See text for further details.

236

237 **FIGURE 3.** Compression curve of Fe_4O_5 . The volume at 1 bar is from Lavina et al. (2011). Error
238 bars are smaller than symbols where they are not shown. The solid gray curve is the fit by
239 third-order Birch-Murnaghan equation of state based on data up to 47 GPa which yields $K_0 =$
240 201(7) GPa and $K' = 3.1(5)$. A ~3% volume reduction is found above 50 GPa.

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