The stability of Fe$_5$O$_6$ and Fe$_4$O$_5$ at high pressure and temperature

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ABSTRACT

The oxygen fugacity in the interior of the Earth is largely controlled by iron-bearing minerals. Recent studies have reported various iron oxides with chemical compositions between FeO and Fe$_3$O$_4$ above ~10 GPa. However, the stabilities of these high-pressure iron oxides remain mostly uninvestigated. In this study, we performed in situ X-ray diffraction (XRD) measurements in a laser-heated diamond-anvil cell (DAC) to determine the phase relations in both FeO and Fe$_3$O$_4$ bulk compositions to 61 GPa and to 2720 K. The results show that Fe$_5$O$_6$ is a high-temperature phase stable above 1600 K and ~10 GPa, while FeO + Fe$_3$O$_4$ are formed at relatively low temperatures. We observed the decomposition of Fe$_5$O$_6$ into 2FeO + Fe$_3$O$_4$ above 38 GPa and the decomposition of Fe$_3$O$_5$ into FeO + h-Fe$_3$O$_4$ at a similar pressure range. The coexistence of FeO and Fe$_3$O$_4$ indicates that none of the recently discovered compounds, corresponding to conditions in the shallow lower mantle. Additionally, as some superdeep diamonds have genetic links with these high-pressure iron oxides, our results give constraints on pressure and temperature conditions of their formation.

Keywords: Iron oxide, diamond-anvil cell, high pressure, Fe$_5$O$_6$, Fe$_4$O$_5$, Volatile Elements in Differentiated Planetary Interiors

INTRODUCTION

Since iron is the most abundant transition metal element, oxygen fugacity inside the Earth is controlled by iron-bearing phases. According to recent analyses of natural samples, oxygen fugacity varies widely in the mantle (Kaminsky et al. 2015; Smith et al. 2016). Oxidizing materials include a fair amount of Fe$^{3+}$, which may stabilize iron oxides as discrete minerals. Recent high-pressure experimental studies have discovered a rich variety of iron oxides intermediate in composition between FeO and Fe$_3$O$_4$, including Fe$_5$O$_6$ (Lavina and Meng 2015), Fe$_9$O$_{11}$ (Ishii et al. 2018), Fe$_4$O$_5$ (Lavina et al. 2011), and Fe$_7$O$_9$ (Simnyo et al. 2016). However, the pressure-temperature (P-T) stability fields of these iron oxides are poorly known.

To understand the speciation of volatile elements in the mantle, mineral redox buffer relations have been revised considering these new iron oxides; for example, Myhill et al. (2016) showed that FeO-Fe$_5$O$_6$ line crosses the enstatite + magnesite = olivine + diamond (EMOD) buffer line, suggesting Fe$_5$O$_6$ is stable at conditions where diamonds are formed. Therefore, a better understanding of the thermodynamic stability of high-pressure, high-temperature iron oxides might enable a more refined understanding of the redox of the Earth’s lower mantle and the origin of super-deep diamonds.

Here we examined the phase relations in Fe$_5$O$_6$ and Fe$_4$O$_5$ bulk compositions on the basis of high P-T experiments up to 61 GPa and to 2720 K. Our results demonstrate that the stabilities of Fe$_5$O$_6$ and Fe$_4$O$_5$ are limited to ~40 GPa at 1800 K and both are decomposed into FeO wüstite + h-Fe$_3$O$_4$ at higher pressures. Furthermore, our findings indicate that no intermediate compounds between FeO and Fe$_3$O$_4$ (i.e., Fe$_{6-9}$O$_{8-11}$, Fe$_{5-7}$O$_{6-9}$, and Fe$_{9}$O$_{11}$) are formed beyond 40 GPa at 1800 K.

METHODS

We used Fe$_5$O$_6$ and Fe$_4$O$_5$ as starting materials, both of which were synthesized from mixtures of reagent-grade Fe metal and Fe$_2$O$_3$ hematite powders at 10 GPa/1700 K and 15 GPa/1700 K, respectively, in a Kawai-type multi-anvil press at the Bayerisches Geoinstitut (Ishii et al. 2016). The Raman spectra of the Fe$_5$O$_6$ sample were collected at 1 K and at high pressures to 27 GPa in a diamond-anvil cell (DAC) without any pressure medium by using a micro-confocal laser Raman system (JASCO NRS-3100) (Supplemental Fig. S1).

Laser-heated DAC experiments were performed using diamond anvils with 300 μm culets. The Fe$_5$O$_6$ and Fe$_4$O$_5$ samples were pressed into ~10 μm thick plates and loaded into 100 μm sample chambers at the centers of pre-indented rhenium gaskets. NaCl or KCl, dried in an oven until just prior to the loading, was used as both a pressure medium and a pressure standard. After compression, the sample was heated from both sides using 100 W single-mode Yb fiber lasers with beam-shaping optics, which converts a Gaussian beam to one with a flat energy distribution. Using this flat-top laser heating system, the resultant laser-heated spots had radial temperature gradients and were approximately 30 μm in diameter. We measured temperature using spectroradiometry (Ozawa et al. 2016). Sample pressures were calculated from the unit-cell volume of NaCl-B11 (Brown 1999), NaCl-B2 (Ueda et al. 2008), or KCl (Dewaele et al. 2012) at high P-T obtained by X-ray diffraction (XRD) measurements. The temperatures of NaCl and KCl were estimated from measured sample temperature (T$_{sample}$) (Pigott et al. 2015) as;