High *P-T* phase relations of Al-bearing magnetite: Post-spinel phases as indicators for *P-T* conditions of formation of natural samples

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Abstract

The phase relations of Al-bearing magnetite were investigated between 6–22 GPa and 1000–1550 °C using a multi-anvil apparatus. This study demonstrates that the spinel-structured phase persists up to ~9–10 GPa at 1100–1400 °C irrespective of the amount of hercynite (FeAl₂O₄) component present (20, 40, or 60 mol%). At ~10 GPa, the assemblage Fe₂(Al,Fe)₂O₅ + (Al,Fe)₂O₃ forms and remains stable up to 16–20 GPa and 1200–1550 °C. Fe₂(Al,Fe)₂O₅ adopts the CaFe₃O₅-type structure with the *Cmcm* space group. At 18–22 GPa and T>1300 °C the assemblage Fe₃(Fe,Al)₄O₉ + (Al,Fe)₂O₃ becomes stable. Fe₃(Fe,Al)₄O₉ is isostructural with Fe₇O₉, having the monoclinic structure of the *C2/m* space group. At *T* <1300 °C, Fe₃(Fe,Al)₄O₉ + (Al,Fe)₂O₃ gives way to the assemblage of a hp-Fe(Fe,Al)₂O₄ + (Al,Fe)₂O₃. This hp-Fe(Fe,Al)₂O₄ phase is unquenchable; a defect-bearing spinel-structured phase was recovered instead, and it contained numerous lamellae parallel to {100} or {113} planes and notably less Al than the initial starting composition. While low-pressure spinel can have a complete solid solution between Fe³⁺-Al, the post-spinel phases have only very limited Al solubility, with a maximum of ~0.1 cpfu Al in hp-Fe(Fe,Al)₂O₄, ~0.3 cpfu in Fe₂(Fe,Al)₂O₅, and ~0.4 cpfu in Fe₃(Fe,Al)₄O₉, respectively. As a result, the phase relations of Fe(Fe_{0.8}Al_{0.2})₂O₄ can also be applied to bulk compositions richer in Al with the only difference being that larger amounts of an (Al,Fe)₂O₃ phase are present.

Coexisting rhombohedral-structured phases demonstrate that the binary miscibility gap established at low pressure between hematite and corundum is still valid up to 20 GPa. Since iron oxides (e.g., magnetite) with variable Al contents are found in extraterrestrial rocks or as inclusions in diamond, constraints on their high-*P*-*T*- f_{02} stability might help unravel their formation conditions.

Keywords: Magnetite, hercynite, iron oxides, Fe₄O₅, Fe₇O₉, Earth's mantle, phase relations, inclusion in diamond, shock metamorphism

INTRODUCTION

Along with iron, aluminum is another notable constituent of many oxides, hydroxides, as well as silicate phases. For example, spinel group minerals are well known as important carriers for Al, along with Fe. Such minerals occur widely in the Earth's mantle and crust and are also found as accessory phases in extraterrestrial rocks (e.g., Busche et al. 1971, 1972; Keil 2012; Krot 2019). In addition to end-member compositions spinel (MgAl₂O₄), hercynite (FeAl₂O₄), chromite (FeCr₂O₄), and magnetite (Fe²⁺Fe³⁺₂O₄), spinel-structured phases are known for their ability to form various solid solutions [e.g., MgFe₂O₄-Fe₃O₄ (Katayama and Iseda 2002); FeAl₂O₄-Fe₃O₄ (Turnock and Eugster 1962)]. Of all the possible major constituents, iron, as a multi-valent element, is sensitive to the prevailing redox conditions and thus can give insights into the local oxidation state within the Earth's interior. Although magnetite contains a significant amount of Fe³⁺ (Fe³⁺/Fe_{tot} = 2/3), the incorporation of other trivalent cations, such as Al or Cr can lower the Fe³⁺ content and thus stabilize

this phase over a larger range in oxidation states.

Previous experimental studies on the phase relations of spinel-structured oxides have demonstrated that their stability is often restricted to pressures corresponding to the upper mantle (e.g., Schollenbruch et al. 2010; Woodland et al. 2012; Uenver-Thiele et al. 2017a, 2017b; Ishii et al. 2014, 2015). At certain high-pressure (high-P) and high-temperature (high-T) conditions, the spinel-structured phase can: (1) break down into its constituent oxides [e.g., FeAl₂O₄ (Schollenbruch et al. 2010); MgAl₂O₄ (Akaogi et al. 1999)]; (2) transform into a high-P polymorph (hp-O₄) (e.g., Irifune et al. 1991, 2002; Funamori et al. 1998; Fei et al. 1999; Haavik et al. 2000; Levy et al. 2004; Chen et al. 2003a; Enomoto et al. 2009; Yong et al. 2012); or (3) produce an assemblage involving post-spinel phases with different stoichiometries [e.g., Fe4O5 (Lavina et al. 2011; Woodland et al. 2012); Fe₅O₆ (Lavina and Meng 2015; Woodland et al. 2015, 2023); Fe₇O₉ (Sinmyo et al. 2016); Mg₂Al₂O₅ (Enomoto et al. 2009); Mg₂Fe₂O₅ (Boffa Ballaran et al. 2015); (Mg,Fe)₂Fe₂O₅ and (Fe,Mg)₂Fe₄O₉ (Uenver-Thiele et al. 2017a, 2017b, 2018); Fe₉O₁₁ (Ishii et al. 2018)]. In this respect, knowing the phase relations for the chemically different post-spinel phases/assemblages can help constrain the formation conditions and evolution of certain

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high-P samples from the Earth's mantle, from shock-metamorphosed terrestrial rocks as well as from extraterrestrial samples, forming a kind of "oxide scale" as suggested by Zhang (2017). For instance, the experimentally determined stability fields of different post-spinel assemblages in the MgO-FeO-Fe2O3 system over a range in P and T allowed Uenver-Thiele et al. (2017b) to add constraints on the petrological history of diamonds with inclusions of magnesioferrite (MgFe2O4). Moreover, magnesioferrite exsolutions also have been found in several ferropericlase (Mg,Fe)O inclusions in diamond independent of the Fe content in the ferropericlase (e.g., McCammon et al. 1998; Harte et al. 1999; Wirth et al. 2014; Kaminsky et al. 2015; Palot et al. 2016; Anzolini et al. 2019; Sharygin et al. 2021; Lorenzon et al. 2023). Such exsolution from ferropericlase may occur during ascent from the upper or lower mantle, or it may result from a back-reaction from a high-P precursor phase (e.g., Wirth et al. 2014; Anzolini et al. 2020). Identifying a high-P precursor phase often requires detailed investigation of the micro-textures of the "magnesioferrite" crystals (e.g., Jacob et al. 2016; Anzolini et al. 2020), since Fe-Mg post-spinel oxide phases can suffer from retrograde reaction during exhumation and transform or break down into a spinel-structured phase.

To the best of our knowledge, the first report of naturally preserved hp-phases was by Chen et al. (2003a, 2003b), who identified two high-P polymorphs of chromite with the CaFe₂O₄-type [CF; named "Chenmingite", IMA 2017-036 (Ma and Tschauner 2017)] and CaTi₂O₄-type [CT; named "Xieite", IMA 2007-056 (Chen et al. 2008)] structures preserved in the shocked Suizhou meteorite. Chen et al. (2003a, 2003b) demonstrated that these two hp-polymorphs must have formed under shock conditions of ~20-23 GPa and 1800-2000 °C. The CF-FeCr₂O₄ (Chenmingite) was also reported in the highly shocked Tissint martian meteorite and was interpreted to have formed above 16-18 GPa and temperatures below ~1350 °C (Ma et al. 2019). In addition, occurrences of preserved post-spinel phases have been reported in terrestrial samples, including in a shocked gneiss from the Xiuyan impact crater [CF-type structured hp-MgFe₂O₄, named Maohokite, IMA 2017-047 (Chen et al. 2019)] or as inclusions in diamond from the Juina area, Mato Grosso State, Brazil [CaTi₂O₄-type structured Mg-Cr-Fe oxide and orthorhombic hp-CaCr₂O₄ (Kaminsky et al. 2015; Maohokite, Agrosì et al. 2019)]. Pressure-temperature conditions of the Xiuyan impact event were estimated to be 25-45 GPa and 800-900 °C (Chen et al. 2019), while the inclusions constrained diamond formation to have occurred in the deep transition zone or lower mantle (≥ 18 GPa; Kaminsky et al. 2015; Agrosì et al. 2019). Note that all these P-T constraints were based on experimental data.

Considering that high-*P* spinels occurring in both terrestrial and extraterrestrial rocks often contain significant amounts of magnetite and hercynite components (e.g., as inclusions in diamond: Newhouse and Glass 1936; Hayman et al. 2005; Stachel and Harris 2008; Kaminsky et al. 2009; Wirth et al. 2014; Palot et al. 2016; Smith et al. 2018; in extraterrestrial rocks: e.g., Keil 2012; Busche et al. 1972), knowledge about their high-*P* and high-*T* phase relations allows us to better constrain the physicochemical conditions of their formation, as well as that of their host material. However, to date only experimental data on the phase relations of the end-member FeAl₂O₄ and FeFe₂O₄ are available, and these relations are, in fact, quite contrasting (Schollenbruch et al. 2010; Woodland et al. 2012). Therefore, experimental investigations of solid solutions along the FeFe₂O₄-FeAl₂O₄ binary join are very important for understanding high-*P* phase stabilities in natural oxide samples containing both Fe³⁺ and Al. Here, we report the results of an experimental study on how the presence of Al affects the phase relations in Fe(Fe,Al)₂O₄. Since natural samples of high-*P* origin mostly have relatively low Al contents, we focused on a Fe³⁺-rich bulk composition (80 mol% Fe₃O₄ – 20 mol% FeAl₂O₄), although several reconnaissance experiments with higher Al-contents (i.e., 40 or 60 mol% FeAl₂O₄) or with a different stoichiometry of Fe³⁺₃Fe³⁺AlO₉ were also performed.

EXPERIMENTAL METHODS

Starting materials

Three different starting mixtures with compositions: (1) 80 mol% Fe₃O₄ -20 mol% FeAl2O4; (2) 60 mol% Fe3O4 - 40 mol% FeAl2O4; and (3) 40 mol% Fe3O4 60 mol% FeAl₂O₄ were employed in our high-P experiments. A further starting composition of $Fe_3^{2+}Fe_3^{2+}AlO_9$ stoichiometry was employed to directly test for the extent of Al solubility in the post-spinel phase Fe7O9. Magnetite (FeFe2O4) and hercynite (FeAl2O4) were both pre-synthesized in a CO-CO2 gas-mixing furnace at 1 atm under controlled f_{0_2} . Magnetite was produced by reducing hematite at 1300 °C and $\log f_{02} = -5.5$, which should yield an essentially stoichiometric composition (Dieckmann 1982). For the synthesis of hercynite, a stoichiometric mixture of Al₂O₃ and Fe2O3 was ground together, pressed into pellets, and equilibrated at 1300 °C. Initially, the oxygen fugacity was set at $\log f_{O_2} = -4$ to first produce a mixture of wüstite coexisting with a hercynite-magnetite solid solution. After 6 h, the sample was quenched in water, reground, and pressed into pellets for further sintering for 5 h under the same conditions. This procedure was repeated for an additional two cycles but with a stepwise shift to more reducing conditions ($\log f_{O_2} = -9$ for 4 h; $\log f_{O_2}$ =-11.4 for 1 h) to ensure all of the iron is Fe2+ in the final step. A direct synthesis at low f_{02} tends to produce a mixture of metallic Fe and corundum, which then does not react efficiently to hercynite. Several crystals of magnetite and hercynite were checked for homogeneity and chemical composition by electron microprobe (EPMA). Analysis of X-ray powder diffraction patterns gave a unit-cell parameter for magnetite and hercynite of $a_0 = 8.3966(6)$ or 8.1502(1) Å, respectively. The starting material of Fe3+Fe3+AlO9 was composed of a stoichiometric mixture of FeAl₂O₄, FeFe₂O₄, Fe₂O₃, and Fe⁰ in a 1:2:2:1 molar ratio. To prevent adsorption of moisture, the starting materials were stored in a desiccator.

Experimental procedure

High-P and high-T experiments were performed at the Goethe-Universität Frankfurt and the Bayerisches Geoinstitut in Bayreuth over a P-T range of 6-22 GPa and 1200-1550 °C (see Table 1). Experimental run conditions and run products are listed in Table 1. Experiments up to 14 GPa and some at 18 GPa were performed in Frankfurt using an 800t Walker-type multi-anvil apparatus (Walker et al. 1990). Experiments carried out at the Bayerisches Geoinstitut Bayreuth were conducted with 500 t, 1000 t, or 5000 t split-sphere Kawai-type multi-anvil presses (Kawai and Endo 1970). Mineral phase transitions (e.g., α-Mg₂SiO₄-β-Mg₂SiO₄, β-Mg₂SiO₄-γ-Mg₂SiO₄, coesite-stishovite, CaGeO₃ garnet-perovskite, MgSiO₃ ilmenite-perovskite) were used for pressure calibration with details described in Brey et al. (2008) and Keppler and Frost (2005). Different assembly sizes were used depending on the desired pressure. Up to 14 GPa, Cr2O3-doped MgO octahedra were employed along with tungsten carbide (WC) cubes having 8 mm truncation edges (so-called 14/8 assembly). Higher-pressure experiments were conducted using 10/4, 10/5, 18/8, or 18/11 assemblies/truncation lengths. The pressure cells in Frankfurt have a Re-foil heater, whereas LaCrO₂ was employed as a heater in the experiments at the Bayerisches Geoinstitut. The heater was placed inside either in a ZrO2 or a LaCrO3 (only for 10/4 experiments with Re-foil heater) sleeve, which acted as a thermal insulator. While the Re-foil had direct contact with the WC cubes, a molybdenum ring and disk were inserted at the top or the bottom of the LaCrO3 heater to ensure contact to the WC cubes. The sample capsule(s) and thermocouple were surrounded by MgO sleeves to avoid direct contact with the furnace. The starting material was usually loaded into Ag-foil capsules; however, several experiments employed Pt-foil when the desired temperature exceeded the

TABLE 1. Experimental conditions and run products

Experiment	Р	Т	Duration	Phase assemblage
	(GPa)	(°C)	(h)	_
Fe(Al _{0.2} Fe _{0.8}) ₂ O ₄				
M798ª	6	1200	3	O ₄
M808	8	1300	2.5	O ₄
M830	9	1400	1	O ₄
M840	9	1100	3	O ₄
M804 ^a	11	1300	2	$O_5 + cor_{ss} + w\ddot{u}$
M789	12	1300	1.5	$O_5 + hem_{ss} + cor_{ss}$
M788	14	1200	2.5	$O_5 + hem_{ss} + cor_{ss}$
M790	14	1400	1.5	$O_5 + hem_{ss} + cor_{ss}$
Z2039uª	15	1200	3	$O_5 + cor_{ss} + (sid)$
Z20310 ^a	16	1200	3	$O_5 + cor_{ss} + (hem_{ss}) + (sid)$
Z20300 ^a	16	1500	1	$O_5 + cor_{ss} + (sid)$
M823 ^a	18	1200	2.5	[hp-O ₄] + cor _{ss}
M825ª	18	1300	2	$O_5 + cor_{ss}$
M841	18	1300	2	$O_9 + [hp - O_4] + cor_{ss}$
Z2040u ^a	18	1400	1	$O_9 + hem_{ss} + cor_{ss}$
Z1953o	20	1300	1	[hp-O ₄] + cor _{ss} + UQ
S7317	20	1550	1.5	$O_5 + cor_{ss}$
H5668	20	1400	1.5	$O_9 + cor_{ss}$
S7316	22	1300	1.5	$[hp-O_4] + cor_{ss}$
H5745	22	1450	1 min	$O_9 + cor_{ss}$
Fe(Al _{0.4} Fe _{0.6}) ₂ O ₄				
M815 ^a	14	1400	1.5	$O_{5} + cor_{ss} + (O_{6})$
M822	18	~1250	2	$O_9 + cor_{ss} + (sid)$
$Fe(AI_{0.6}Fe_{0.4})_2O_4$				
M842	10	1200		$O_4 + (O_5) + (hem_{ss})_+ (cor_{ss})$
M826	13	1200	3	$O_5 + cor_{ss}$
M843	14	1400	1.5	$O_5 + cor_{ss}$
Fe ₃ Fe ₃ AlO ₉				
M844	18	1400	1.5	$O_5 + cor_{ss} + (sid)$
M784	18	1500	1	$O_5 + cor_{ss} + (sid)$

Notes: $O_4 = \text{cubic Fe}(AI, Fe)_2O_4$; $O_5 = \text{orthorhombic Fe}_2(AI, Fe)_2O_5$ phase; $O_9 = \text{monoclinic Fe}_3(AI, Fe)_4O_9$ phase; wü = wüstite. UQ = unquenchable phase that dissociated into Fe}³⁺-bearing corundum + nearly pure magnetite; sid = siderite; hematite-corundum solid solutions are referred to as cor_{st} or hem_{st}; phase in parentheses = only present in traces; phase in brackets = assumed high-pressure polymorph that reacted back to defect-magnetite during quenching. ^a Experiment performed with a Pt-capsule.

melting point of Ag. Capsule dimensions depended on the particular assembly employed with 1.2 to 2 mm diameter and 1.2 to 1.7 mm length. Either a $W_{s/}$ Re₉₅– W_{26}/Re_{74} thermocouple (800t multi-anvil press) or a W_3/Re_{97} – W_{25}/Re_{75} thermocouple (1000 t, 5000 t multi-anvil press) was inserted axially from the top of the octahedron to monitor the temperature, with the electromotive force uncorrected for pressure. Further details of the experimental setup have been described in Brey et al. (2008) and Keppler and Frost (2005). Uncertainties in pressure and temperature are ±0.5 GPa and ±30–50 °C, respectively (Keppler and Frost 2005). The experiments were conducted first by cold pressurization, followed by heating to the desired temperature at a rate of 50 °C/min. The experiment was terminated by turning off the power while maintaining the pressure. Depending on the experimental *P-T* conditions, the duration varied from 1 to 3 h (see Table 1). After quenching, decompression was immediately initiated.

Analytical methods

The recovered samples were analyzed with electron microprobe (EPMA), powder X-ray diffraction, and/or transmission electron microscope (TEM). For chemical analyses, several fragments of the recovered sample were mounted in epoxy, polished, and carbon-coated. Measurements were carried out with a fivespectrometer JEOL JXA-8530F plus Hyperprobe at the University of Frankfurt operating in the wavelength-dispersive mode with an acceleration voltage of 15 kV, a probe current of 20 nA, and a spot size of 1 μ m. Pure Fe₂O₃, Al₂O₃, and Pt metal were employed as primary standards. Integration times for Al were 20 s on the peak and 10 s on the background, while 40 s on the peak and 20 s on the background were adjusted for Fe and Pt. A CITZAF algorithm was employed for the matrix correction (Armstrong 1993). For investigating microtextures and verifying the homogeneity of the mineral grains, backscatter electron images were taken (e.g., Figs. 1a–1d).

Further phase identification by X-ray diffraction was performed using an STOE Stadi P diffractometer equipped with a linear PSD or a Mythen detector and a Ge(111) monochromator at the University of Frankfurt operating at 45 kV and 35 mA and using MoKa (λ = 0.70926 Å) radiation. Recovered sample material

and small amounts of silicon which served as internal standard were ground together and mounted in a 0.5 mm diameter glass capillary. Measurements were performed in Debye-Scherrer mode in transmission geometry between 1–100° 20. Determination of the unit-cell parameters was obtained by full-pattern refinement using the General Structure Analysis System (GSAS) (Larson and Von Dreele 1994) software package and the EXPGUI interface of Toby (2001).

Two samples (S7316; Z1953o) had: (1) not enough sample material for powder X-ray diffraction and/or (2) included phases with breakdown textures so that TEM analyses were necessary. Those run products were investigated using a FEI Titan G2 80-200 S/TEM equipped with 4 SDD energy-dispersive X-ray spectrometers (EDS) and a Philips CM20FEG with a pure Ge EDS, operating at 200 kV at the Bayerisches Geoinstitut Bayreuth (Germany). Some of the recovered sample material was und polished to make a thin section. The thin section was placed on a 3 mm sized Mo grid and thinned to electron transparency by Ar-ion milling at an accelerating voltages of 3.5 kV and an angle of incident of 8° using a precision ion polishing system (Gatan, model 691). The sample foil was carbon-coated to reduce charging and then investigated by imaging microtextures, selected area electron diffraction (SAED) and energy-dispersive X-ray (EDX) analyses. In addition, a part of the recovered material of sample Z1953o was polished on the surface and thinned to the electron transparency using a focused Ga ion beam (FIB) milling machine (FEI, Scios Dual Beam system) at the Bayerisches Geoinstitut Bayreuth (Germany).

RESULTS AND DISCUSSION

Experimental run products

The resulting phase assemblages, as well as chemical compositions and lattice parameters of the individual phases, are summarized in Tables 1, 2, and 3. A total of 20 experiments with the Fe²⁺(Fe³⁺_{0.8}Al_{0.2})₂O₄ starting composition were performed over a *P*-*T* range of 6–22 GPa and 1100–1550 °C. A limited number of experiments were performed with higher Al contents corresponding to stoichiometries of Fe²⁺(Fe³⁺_{0.6}Al_{0.4})₂O₄ and Fe²⁺(Fe³⁺_{0.4}Al_{0.6})₂O₄ (Table 1). These experiments were performed to clarify the extent of Al solubility in the high-*P* post-spinel phases. Following the identification of a phase with (Fe²⁺)₃(Fe³⁺,Al)₄O₉ stoichiometry (O₉-phase; see text below), two further experiments with a starting composition of Fe²⁺₂Fe³⁺₂AlO₉ were specifically performed to investigate the maximum amount of Al that can be incorporated into this phase.

Backscattered electron (BSE) imaging of the run products confirms noticeable grain growth (2–60 μ m in size) with complete recrystallization into chemically homogenous grains. Straight grain boundaries and triple junctions, often with grain boundary angles of ~120° in the polycrystalline samples, indicate that an "equilibrium-fabric" was reached during the experiments (Figs. 1a–1d) (Passchier and Trouw 2005). The apparent even distribution of the newly formed phases (Fig. 1) indicates that the starting material was well homogenized. One exception is sample Z19530, which includes an additional phase that exhibits internal textures of very fine-grained crystals (Fig. 1d), indicating that this phase dissociated during quench (unquenchable phase; named hereafter UQ-phase). The Fe²⁺-bearing oxide phases always form the largest grains, while interstitial corundum-hematite solid solutions are much smaller in size.

Phase relations of Fe²⁺(Fe³⁺_{0.8}Al_{0.2})₂O₄

Breakdown into Fe₂(Fe,Al)₂O₅ + (Al,Fe)₂O₃. Low-pressure experiments demonstrate that the stability of the spinel-structured phase persists up to about 9–10 GPa at temperatures of 1200–1400 °C (Fig. 2). In most cases, this phase has a composition similar to that of the initial starting mixture (see Table 2). At higher pressure, the spinel-structured phase breaks down to a



FIGURE 1. Backscatter electron images of the experimental run products showing: (**a**) the assemblage of well crystallized $cor_{ss} + hem_{ss} + Fe_2(Fe,Al)_2O_5$; (**b**) coexistence of large crystals of $Fe_3(Fe,Al)_4O_9$ with interstitial $cor_{ss} + hem_{ss}$; (**c**) crystals of cor_{ss} and a striated high-pressure post-spinel phase, presumably hp-O₄, that have transformed during quenching into defect magnetite (dmt; see text for details); (**d**) run products of Z19530 with an UQ-phase coexisting with the same dmt as in **c**. The dmt has slightly variable contrast due to effects of composition as well as orientation, and is full of striations, comparable to those observed in **c**. Note that the UQ-phase differs from dmt by its texture (see text below for details). Abbreviations: hematite-corundum solid solutions are referred to as cor_{ss} or hem_{ss}; UQ-phase = unquenchable phase; [hp-O₄] = spinel phase with a high-magnetite component formed presumably by retrograde reaction from a high-*P* polymorph during quench.

multi-phase assemblage as indicated by BSE imaging and X-ray powder diffraction. Analysis of diffraction patterns (Online Materials¹ Fig. OM1) reveals an $A_2B_2O_5$ phase with a CaFe₃O₅-type structure (space group Cmcm) (Lavina et al. 2011; Boffa Ballaran et al. 2015) coexisting with one or two corundum-type structured phases (space group $R\overline{3}c$) having (Fe,Al)₂O₃ stoichiometry. The $O_5\mbox{-}structured$ phase is equivalent to those found in the $Fe^{2+}\mbox{-}Fe^{3+}$ and Mg-Fe³⁺ end-member systems (e.g., Woodland et al. 2012; Uenver-Thiele et al. 2017a, 2017b). Siderite appeared in some experiments in trace amounts, barely detectable in most powder diffraction patterns. We attribute its presence to the reaction of adsorbed CO₂ with the fine-grained starting material powders, which implies minor reduction of Fe3+ to Fe2+ during the experiment. In experiment M815, tiny amounts of a Fe₅O₆ structured phase (Lavina and Meng 2015; Woodland et al. 2015, 2023) were identified in the powder XRD pattern. Its presence might also be attributed to a small degree of reduction during the experiment.

In terms of composition, the O_5 -phase contains relatively low amounts of Al, with only up to 0.3 cpfu present, corresponding to 15 mol% Fe₂Al₂O₅ component (Table 2). Thus, this phase incorporated proportionally less Al than present in the starting material [i.e., Al/(Al+Fe³⁺) = 0.15 compared to 0.2 in the starting composition]. The Al poorer and Fe²⁺ richer stoichiometry of the O₅-phase compared to the starting bulk composition causes an excess of trivalent cations (Al and Fe³⁺) that stabilizes the coexisting corundum-hematite solid solutions (hereafter referred to as cor_{ss} or hem_{ss} depending on the Al/Fe ratio, Table 1). In many experiments, two separate phases were present, indicating that the large miscibility gap along the Al₂O₃-Fe₂O₃ binary documented by Feenstra et al. (2005) at <4.0 GPa and 1300 °C persists to at least 18 GPa (Table 1). For instance, this is manifested in the coexistence of hematite with up to 23.5 mol% Al₂O₃ (hem_{ss}) and corundum with up to 10.5 mol% Fe₂O₃ (cor_{ss}) in many of our experiments (see Tables 1 and 3).

Stability of Fe $_{3}^{2+}$ (**Fe** $_{3}^{3+}$,**Al**)₄**O**₉ + (**Al**,**Fe**)₂**O**₃. In the *P*-*T* range of 16–20 GPa and 1200–1550 °C, the maximum stability of the O₅-phase is reached, and above such pressures, another phase assemblage becomes stable (Figs. 1 and 2). The XRD patterns

Experiment	nAl			Lattice parameters		
experiment	(cpfu)	<i>a</i> (Å)	b (Å)	c (Å)	V (ų)	β (°)
		Fe(Fe,AI) ₂ C) ₄			
M798	0.38(1)	8.3464(1)			581.423(14)	
M830	0.39(3)	8.3387(1)			579.822(10)	
M840	0.41(1)	8.3379(1)			579.66(2)	
M808	0.44(2)	8.3421(1)			580.54(2)	
M842	0.85(1)	8.2901(1)			569.75(3)	
		defect-Fe(Fe,A	I) ₂ O ₄ ^a			
Z1953o	0.10(1)	8.3783(1)			588.11(2)	
S7316	0.11(1)	-			-	
M823	0.11(1)	8.3830(1)			589.11(2)	
M841	0.14(1)	8.3697(4)			586.31(9)	
		Fe ₂ (Fe,Al) ₂ (D₅			
M788	0.07(1)	2.8928(1)	9.7820(3)	12.5678(4)	355.632(12)	
M789	0.09(1)	2.8945(1)	9.7750(2)	12.5671(2)	355.572(8)	
M790	0.11(1)	2.8938(1)	9.7676(2)	12.5633(2)	355.109(8)	
M825	0.12(1)	2.8946(1)	9.7632(2)	12.5593(2)	354.934(8)	
Z2039u	0.12(1)	2.8933(1)	9.7634(3)	12.5557(3)	354.683(10)	
M843	0.12(1)	2.8937(1)	9.7725(2)	12.5640(2)	355.289(7)	
M826	0.13(1)	2.8939(1)	9.7654(2)	12.5580(2)	354.900(7)	
M844	0.14(1)	2.8942(1)	9.7582(3)	12.5582(3)	354.670(11)	
M784	0.17(1)	2.8941(1)	9.7545(2)	12.5491(2)	354.270(6)	
M804	0.17(1)	2.8933(1)	9.7588(5)	12.5558(5)	354.51(2)	
M815	0.20(1)	2.8929(1)	9.7495(3)	12.5484(4)	353.923(14)	
Z2030o	0.23(1)	2.8934(1)	9.7449(2)	12.5435(2)	353.667(7)	
Z2031o	0.23(1)	2.8937(1)	9.7699(3)	12.5647(3)	355.223(10)	
S7317	0.30(1)	2.8924(1)	9.7316(5)	12.5334(5)	352.780(18)	
		Fe ₃ (Fe,Al) ₂ 0	D ₆			
M815	-	2.8936(3)	9.8707(12)	15.3316(14)	437.89(5)	
		Fe ₃ (Fe,Al) ₄ 0	D,			
Fe ₇ O ₉ ^b	0.00	9.696(2)	2.8947(6)	11.428(3)	314.10(12)	101.69(2)
M841	0.22(1)	9.6784(3)	2.8991(1)	11.4112(4)	313.545(14)	101.685(3)
Z2040u	0.23(1)	9.6717(4)	2.8961(1)	11.4222(4)	313.248(14)	101.741(3)
H5668	0.28(1)	9.6732(2)	2.8960(1)	11.4127(3)	313.042(9)	101.726(2)
M822	0.33(1)	9.6683(3)	2.8930(7)	11.3925(3)	312.00(1)	101.729(2)
H5745	0.42(2)	9.6604(9)	2.8919(2)	11.3965(9)	311.74(3)	101.725(6)
^a Defect-magnetite	phase with relict features of an n	resumably hn-nolymorph and an	Al-noor composition	n		

TABLE 2. Unit-cell parameters of Fe(Fe,AI) $_2O_4$, Fe $_2$ (Fe,AI) $_2O_5$, and Fe $_3$ (Fe,AI) $_4O_9$

^b End-member data from Sinmyo et al. (2016).

of run products from four experiments (Z2040u, M841, H5668, H5745) indicate the presence of a Fe₇O₉-structured phase (Sinmyo et al. 2016) (see Fig. 1b, Online Materials¹ Fig. OM2, and Table 1). In experiment Z2040u and H5668, $Fe_3(Al,Fe)_4O_9$ represents the majority phase together with hem_{ss} and/or cor_{ss}

(Fig. 1b). The sample is well crystallized with no apparent reaction zones (Fig. 1b). Coexisting cor_{ss}, also occurring as inclusions in the O₉-phase indicate that the O₉-phase was saturated in Al. Thus, under the conditions of our experiments, it appears that only up to 10.5 mol % of a Fe₃Al₄O₉ component can be incor-

TABLE 3. Unit-cell parameters of corundum-hematite solid solutions

Experiment	Corundum				Hematite			
	(Fe ³⁺ /Fe ³⁺ +AI)	a (Å)	<i>c</i> (Å)	V _{mol} (cm³/mol)	(Fe ³⁺ /Fe ³⁺ +AI)	a (Å)	<i>c</i> (Å)	V _{mol} (cm³/mol)
M842	0.040	-	-	-	0.985	-	-	-
M804 ^a	0.045	4.7694(3)	13.014(1)	256.37(3)				
M815	0.045	4.7711(3)	13.018(2)	256.64(4)				
M826	0.045	4.7672(1)	13.0084(5)	256.030(9)				
Z2030o	0.045	4.7733(7)	13.012(3)	256.75(7)				
M825	0.055	4.7698(1)	13.0141(5)	256.42(1)				
Z2031o	0.065	4.7676(5)	13.018(2)	256.25(4)	0.970	-	-	-
M784	-	4.7749(2)	13.0310(8)	257.30(2)				
M823	0.065	4.7768(2)	13.0333(8)	257.55(2)				
M841	0.070	4.7800(3)	13.0428(11)	258.08(2)				
S7316	0.075	-		-				
M788	-	4.7820(3)	13.0407(2)	258.25(3)	0.850	4.9985(1)	13.6336(5)	295.000(11)
Z2039u	0.080	4.7698(2)	13.0148(10)	256.43(2)				
Z1953o	-	4.7845(4)	13.0290(10)	258.29(3)				
M843	0.090	4.7854(1)	13.0501(4)	258.810(8)				
M844	0.090	4.7797(3)	13.0439(12)	258.08(3)				
M822	0.095	4.7896(1)	13.0656(5)	259.570(9)				
H5668	0.100	4.7897(2)	13.0612(10)	259.50(2)				
M789	0.105	4.7900(2)	13.0564(10)	259.43(2)	0.815	4.9892(1)	13.6056(7)	293.30(2)
S7317	0.110	4.7858(8)	13.057(4)	258.99(7)				
H5745	0.115	4.7901(4)	13.0725(2)	259.76(3)				
Z2040u	0.120	4.7976(4)	13.0845(12)	260.82(3)	0.820	4.9714(3)	13.604(3)	291.18(6)
M790	0.145	4.7996(2)	13.0825(8)	260.99(2)	0.765	4.9741(2)	13.5698(9)	290.76(2)
^a Wüstite has b	een detected with	lattice parame	ters of <i>a</i> = 4.271	8(2) Å and V _{mol} = 77.953(1	2) cm ³ /mol.			



FIGURE 2. Phase stabilities for the bulk composition $Fe^{2+}(Fe^{3+}_{0.8}Al_{0.2})_2O_4$. The boundaries of the assemblage stability fields are delineated by solid lines. The dashed black line indicates the breakdown reaction for magnetite which was observed in situ by Schollenbruch et al. (2010) and later identified by Woodland et al. (2012). Also shown is the position of the breakdown reaction for hercynite (dotted line) from Schollenbruch et al. (2010). The errors in *P* and *T* are approximately equal to the size of the symbol. Note: Experiment Z19530 at 20 GPa and 1300 °C contains an additional UQ-phase (see also Fig. 1d).

porated into Fe7O9.

The appearance of $Fe_3(Fe,Al)_4O_9$ is notable since no O_9 -phase has been observed in the phase relations of either the Fe₃O₄ or FeAl₂O₄ end-members (e.g., Woodland et al. 2012; Schollenbruch et al. 2010). However, it is likely that further new studies of different spinel compositions will also reveal the stability of an O₉-phase. For example, Uenver-Thiele et al. (2017b) reported the existence of Mg₃Fe₄O₉ and Mg_{1.5}Fe_{1.5}Fe₄O₉ in the MgFe₂O₄ and Mg_{0.5}Fe²⁺_{0.5}Fe₂O₄ systems, respectively. More recently, Ishii et al. (2020) also studied the high-T and high-P phase relations of MgFe₂O₄. Their study confirmed the existence of an O₉-phase + hem assemblage, but over a somewhat different P-T range (Ishii et al. 2020) than reported earlier. In any case, both studies of Mg-bearing compositions indicate that an O₉-structured phase becomes stable at pressures beyond the stability of an M_4O_5 + hem assemblage and its stability appears to be limited to a narrow range in P-T space. Here, in Al-bearing compositions, we also find that the stability of Fe₃(Fe,Al)₄O₉ is limited to a narrow range in P and T beginning at ~18 GPa (at 1300-1400 °C) and widens

to higher P and T (at 20 GPa >1300 °C but <1550 °C; see Fig. 2).

Appearance of a hp-polymorph. As previously described, Fe₃(Fe,Al)₄O₉ becomes stable at $P \ge 18$ GPa and $T \ge 1300$ °C. At 18 GPa and 1300 °C (M841) run products include an O₂-phase together with cor_{ss} as well as an additional phase. At lower T, the O₉-phase completely disappears. Analysis of the XRD patterns suggests that a spinel-structured phase with a lattice parameter of a = 8.3696(4) - 8.3830(1) Å is present. However, low-pressure experiments indicate that the spinel-structured Fe²⁺(Fe³⁺_{0.8}Al_{0.2})₂O₄ phase has its maximum pressure stability at 9-11 GPa with a lattice parameter of a = 8.3379(1) Å (e.g., sample M840; Table 1; Fig. 2). Chemical analyses by EPMA and TEM (see Table 2) reveal that this phase (at ≥ 18 GPa) has an extremely low Al content, approaching an almost pure magnetite composition $[Fe^{2+}(Fe^{3+}_{0.05}Al_{0.05})_2O_4]$, which is consistent with the observed lattice parameter. However, since experimental studies have demonstrated that magnetite is also only stable up to 9-10 GPa (e.g., Woodland et al. 2012, Fig. 2), this phase in experiments at ≥18 GPa must be a product of a retrograde back-reaction from a high-P phase during quenching. To clarify the presence or even the nature of the precursor phase of the magnetite, sample S7316 and Z19530 were investigated by TEM, with sample Z19530 being discussed in more detail since it contains not only a spinel-structured phase but also an UQ-phase (see Figs. 1d and 3a). Striations within this magnetite-rich spinel observed by BSE imaging were investigated in detail and proved to be numerous lamellae (Fig. 3). Some of these lamellae have an orientation corresponding to the {113} plane in the magnetite (Fig. 3c), which is consistent with the orientation of {113} twins. The twinning along {113} usually reflects a back-transformation from a galenalike archetype structure belonging to the lillianite homologies series (Makovicky 1977) and as such may result from the backreaction of a hp-phase like Fe_4O_5 or Fe_5O_6 (Schollenbruch et al. 2010; Woodland et al. 2012, 2023; Myhill et al. 2016). Since the lamellae within the magnetite of sample Z1953o are not only on the {113} plane but also on the {100} plane and $Fe_3(Fe,Al)_4O_9$ is quenchable without any retrograde microtextures, we interpreted this defect magnetite (dmt) phase to be indicative of a previous high-P orthorhombic O₄-polymorph (e.g., Haavik et al. 2000). However, although the {100} and {113} lamellae seem to have twin-like features, their twin law remains to be determined and statistically proven, and the stability of this hp-polymorph at *P* and *T* needs to be verified by in situ high-*P*-*T* experiments.

Detailed TEM observations of the UQ-phase confirm that it results from the dissociation into two phases (Fig. 4) during quench. The new nanometer-sized crystals are vermicularly intergrown, a texture that is commonly known for exsolution processes within minerals (e.g., feldspar). Moreover, TEM observations indicate that the crystals are in an epitaxial relation with the larger surrounding crystals, which is not expected if they crystallize from a melt. As can be seen from EDS chemical map illustrated in Figure 4b, the dissociation products are either Alor Fe-rich. The electron diffraction patterns of the Al-dominant phase are consistent with a corundum structure (Fig. 4c), while those of the Fe-dominant phase corresponds to a spinel structure (i.e., magnetite) (Fig. 4d). It is noteworthy that this magnetite within the UQ-domain differs from the dmt described above. For instance, the magnetite within the UQ-phase does not have the a)

American Mineralogist, vol. 109, 2024

◄ FIGURE 3. (a) Bright-field (BF) TEM image of sample Z19530 illustrating the assemblage of dmt + UQ-phase. (b) BF-TEM image of the dmt phase (right grain in the BF-TEM in a) with numerous lamellae normal to the projection of the {100} plane. The inset shows the corresponding precession selected area electron diffraction (SAED) pattern (circle), indicating a superimposition of the <011> and the <121> zone axes of magnetite. The two zone axes have a common direction along <011> (the diagonal direction from the lower left to upper right in the electron diffraction pattern). Note that the indexing is with the <011> zone axis of magnetite. (c) Dark-field TEM image (with g-vectors of 400 from the matrix and twins) of the lamella-bearing dmt phase (the center one in image a) displaying {113} twin lamellae. The inset shows a SAED pattern indicating the twin relation.

characteristic relict features expected for transformation from a previous hp-polymorph. This phase is also richer in Al-content than the dmt phase.

Crystal-chemical behavior of high-P phases

Influence of Al on the stability of hp-phases. A few experiments were performed with magnetite solid solutions having higher Al contents. Experiments with starting compositions of $Fe(Fe_{0.6}Al_{0.4})_2O_4$ or $Fe(Fe_{0.4}Al_{0.6})_2O_4$ produced post-spinel assemblages similar to those obtained with lower bulk Al contents, such as $Fe_2(Fe,Al)_2O_5 + (Fe,Al)_2O_3$ or $Fe_3(Fe,Al)_4O_9 + (Fe,Al)_2O_3$ (Table 1). The appearance of these assemblages occurred in about the same *P*-*T* range as for the $Fe(Fe_{0.8}Al_{0.2})_2O_4$ bulk composition. This is due to the limited incorporation of Al in the O_5 and O_9 phases, and their compositions do not differ significantly from those synthesized with a $Fe(Fe_{0.8}Al_{0.2})_2O_4$ bulk composition. Thus, phase relations of $Fe(Fe_{0.8}Al_{0.2})_2O_4$ (shown in Fig. 2) are also valid at higher bulk Al contents, the only difference being a higher proportion of cor_{ss} and hem_{ss} in the assemblage.

Fe₄O₅-Fe₂Al₂O₅ solid solutions. The molar volume of the Fe4O5 phase decreases strongly and linearly with increasing Al content (Fig. 5a). This behavior can be explained by the substitution of the smaller Al^{3+} cation for Fe^{3+} (ionic radius = 53.5 vs. 64.5 pm, respectively) (Shannon 1976). The decrease in molar volume is mostly due to changes in the b- and c-parameters (Figs. 5c-5d). The *a*-lattice parameter does not significantly change with composition (Fig. 5b). This implies that little to no Al substitution occurs on the prismatic M3 site and is consistent with the observation of Boffa Ballaran et al. (2015) that this site is dominated by divalent cations. As already indicated, Al3+ substitution for Fe³⁺ in the O₅-phase is quite limited. The reason for this may be that the observed large changes in unit-cell parameters with Al incorporation act to destabilize the crystal structure. This contrasts with the successful synthesis of a Fe2Cr2O5 end-member (Ishii et al. 2014), probably because Cr³⁺ has an ionic radius much more similar to that of Fe^{3+} (61.5 pm) (Shannon 1976).

Al-substitution in Fe₇O₉. The crystal structure of Fe₇O₉ is monoclinic and comprises four different crystallographic sites for cations (Fe1, Fe2, Fe3, Fe4); Fe1, Fe2, and Fe3 are edgesharing octahedra and the Fe4 site is trigonal prismatic (Sinmyo et al. 2016). Sinmyo et al. (2016) indicate that the Fe4 site is almost fully occupied by Fe²⁺. Therefore, we consider that in our Fe₃(Al,Fe)₄O₉ phase, Al will substitute for Fe³⁺ at the Fe1, Fe2, and Fe3 octahedral sites, whereas the Fe4 site will be occupied by Fe²⁺. This distribution is consistent with our limited lattice



FIGURE 4. (a) High-angle annular dark-field (HAADF) STEM image illustrating the dmt phase (left-hand side) next to the fine-grained unquenchable domains (right-hand side) and (b) EDS chemical map of the UQ-domain indicating Al-dominant and Fe-dominant dissociation products. (c) BF-TEM images of the Al-dominant phase indexed with a corundum structure (Crn) shown in the lower right inset. (d) BF-TEM images of the Fe-dominant phase. A selected area electron diffraction (SAED) pattern was taken in the area indicated by the white circle that is consistent with magnetite. Notably, this magnetite does not have the features of a defect magnetite structure. (Color online.)

parameter data for Al-bearing Fe₇O₉. The *b*-parameter, which is mostly controlled by the height of the trigonal prism, does not vary significantly with Al content. On the other hand, we find that even small amounts of Al (e.g., 0.22-0.33 cpfu; see Table 2) substitution can lead to a significant shortening in the *a*- and cparameters. The *a*-parameter is the direction of the edge-sharing octahedral strips containing the Fe1, Fe2, and Fe3 sites in the structure, and the stacking direction of these strips is along the *c*-axis (Sinmyo et al. 2016). Based upon the coexistence with a corundum solid solution in our experiments, it appears that the



FIGURE 5. Lattice parameters of $Fe_2Fe_2O_3$ - $Fe_2Al_2O_3$ solid solutions as a function of Al content (cpfu). These solid solutions adopt the same $CaFe_3O_3$ -type structure (*Cmcm* space group) as $Mg_2Fe_2O_3$ reported by Boffa Ballaran et al. (2015). Variation in (**a**) molar volume, (**b**) *a*-parameter, (**c**) *b*-parameter, and (**d**) *c*-parameter with the amount of Al in the crystal structure. For comparison, lattice parameters of the end-member Fe_4O_3 from the study by Woodland et al. (2023) are also shown. Error bars are within the size of the symbols.



FIGURE 6. Plot of the Fe³⁺/(Fe³⁺+Al) of Al-bearing hematite and Febearing corundum as a function of synthesis temperature. Experimental results obtained in the studies by Feenstra et al. (2005) at 1–40 kbar, Turnock and Eugster (1962) at 2–4 kbar and Atlas and Sumida (1958) at 1 bar are also shown for comparison.

maximum Al content that the O_9 -phase can accommodate is even more limited than observed for the O_5 -phase.

Fe₂O₃-Al₂O₃ solid solutions. In most experiments, Fe³⁺-bearing corundum coexists with other high-P Fe-Al-oxides (Table 1). In five experiments, both Fe-bearing corundum and Al-bearing hematite are present (Table 1). The chemical compositions and lattice parameters for these two phases are given in Table 3. It is notable that the chemical compositions of coexisting hem_{ss} and cor_{ss} from our experiments are faithfully consistent with the binary miscibility gap observed at much lower pressures of ≤4 GPa (Fig. 6) (Feenstra et al. 2005; Turnock and Eugster 1962; Atlas and Sumida 1958). In addition, our unit-cell-composition systematics agree very well with those reported by Feenstra et al. (2005) (Fig. 7). This implies that the mixing behavior along the hematite-corundum binary described by Feenstra et al. (2005) is still valid for pressures up to 20 GPa. In some experiments, the cor_{ss} does not coexist with a hem_{ss} and is, therefore, not necessarily Fe3+ saturated.

IMPLICATIONS

Recent experimental syntheses of new high-pressure postspinel phases with stoichiometries of M_4O_5 , M_5O_6 , M_7O_9 , and M_9O_{11} give rise to the question if these phases might occur in natural samples. Since they are all stable over certain ranges in *P* and *T*, they could serve as "index phases" indicative of the conditions the host sample experienced (e.g., deep mantle or shock-metamorphosed samples). For instance, diamonds and their inclusions provide a unique opportunity to directly study pristine material from great depths in the Earth's mantle. Several studies report exotic non-ultramafic (non-silicate) inclusions from uncertain or controversial depths (e.g., Hayman et al. 2005). In some cases, magnetite has been identified either as discrete grains or associated with other phases such as wüstite, metallic alloy, hematite or pyrrhotite (e.g., Anzolini et al. 2019, 2020; Shirey et al. 2019; Jacob et al. 2011, 2016; Wirth et al.



FIGURE 7. Lattice parameters *a* (**a**) and *c* (**b**) as well as volume (**c**) plotted vs. chemical composition of corundum-hematite solid solutions. Insets show enlargements. Dashed lines show linear mixing between synthetic Al_2O_3 and Fe_2O_3 (Finger and Hazen 1980; Newnham and de Haan 1962).

2014; Hayman et al. 2005; Stachel et al. 1998; Hutchison 1997). Since end-member magnetite is stable only up to ~10 GPa, the logical interpretation is that such inclusions formed in the upper mantle. However, the occurrence of particular microstructures in magnetite can be an indicator that it formed as a breakdown product from a precursor phase (e.g., Jacob et al. 2016; Anzolini et al. 2020). For example, Jacob et al. (2016) reported framesitic diamond with inclusions of pyrrhotite that had a partially developed nanocrystalline reaction rim of magnetite. Based on the epitaxial growth of pyrrhotite, magnetite and diamond, Jacob et al. (2016) concluded that magnetite formed at the expense of pyrrhotite directly, followed by the precipitation of diamond on this magnetite corona. In performing Transmission Kikuchi Diffraction (TKD) analyses, they identified twinning on the {311} planes [note, the {311} plane is equivalent to the {113} plane (Fig. 3c) in the cubic system], a textural feature shown to occur as a consequence of a breakdown of $Fe_4O_5 + Fe_2O_3$ or $Fe_4O_5 + O_2$ (Woodland et al. 2012; Myhill et al. 2016). Thus, Uenver-Thiele et al. (2017b) interpreted this twinning in the natural magnetite to be the first evidence for the natural occurrence of an O₅-phase in a mantle sample. Since magnetite both with and without {311} twinning was present in the diamond, Uenver-Thiele et al. (2017b) considered the origin of these inclusions to lie in the upper mantle between 8-10 GPa, conditions at which Fe₄O₅ and magnetite can coexist (Myhill et al. 2016; Schollenbruch et al. 2010; Woodland et al. 2012). Nevertheless, twinning on the {311} planes in magnetite can also result from the retrograde reaction of other iron oxide phases such as Fe₅O₆ (Woodland et al. 2023). On the other hand, the $\{100\}$ and $\{113\}$ lamellae in our recovered defect magnetite, which we interpret to have formed from a hp- O_4 phase at P and T (see above), can also help distinguish one precursor candidate from another. This means that detailed documentation of twinning features and lamellae textures is important in future studies of experimental and natural samples.

The results of this work also demonstrate that the composition of phases in the Fe2+-Fe3+-Al-oxide system can help discriminate whether a spinel-structured phase formed from a precursor phase or not. In contrast to spinel-structured phases, the high-P postspinel phases in this study are found to incorporate only minor amounts of Al (~0.1 cpfu Al in a hp-O₄ polymorph, ~0.3 cpfu Al in $A_2B_2O_5$ or ~0.4 cpfu in $A_4B_3O_9$). This implies that any spinel that formed from a higher-P precursor phase must also have a low-Al content. In fact, spinels occurring as inclusions in diamond generally have low-Al contents (Hayman et al. 2005; Wirth et al. 2014; Palot et al. 2016; Anzolini et al. 2020), but this may also be due to formation in a low-Al environment. For such compositions, our current results indicate that the phase relations of Mg_{0.5}Fe_{0.5}Fe₂O₄ presented by Uenver-Thiele et al. (2017b) are still applicable. On the other hand, Wirth et al. (2014) reported Al-rich spinels with compositions ~(Mg_{0.73}Fe_{0.25}Mn_{0.02}) (Fe_{0.44}Al_{1.17}Cr_{0.39})O₄ occurring together with magnetite-magnesioferrite solid solutions within a magnesiowüstite (MW) inclusion in a diamond from Brazil. Since the Al-rich spinels were found to be in epitaxial relationships with the host MW and the nearly Al-free magnesioferrite/magnetite, Wirth et al. (2014) considered that their exsolution from the MW host must have taken place under the same P-T conditions predicted for the magnesioferrite/ magnetite. Our current study indicates that this Al-rich spinel could not have initially formed as a post-spinel phase. However, the high-Mg content reported by Wirth et al. (2014) may also suggest that in this case the spinel structure was stabilized to higher pressures, up to $\sim 15-16$ GPa at $\sim 1200-1600$ °C (Akaogi et al. 1999). The effect of Mg on phase relations is the subject of an ongoing study (Uenver-Thiele et al. in prep). In any case, in Al-rich bulk compositions at *P*-*T* conditions above spinel stability, an additional Al-rich phase like corundum or garnet would be expected to coexist with low-Al oxide phases, like those described here.

ACKNOWLEDGMENTS AND FUNDING

We are grateful to Thomas Kautz, Nicki Siersch, Svyatoslav Shcheka, Caterina Melai, and Tony Withers for their technical advice and assistance with the multianvil experiments at the University of Frankfurt and the Bayerisches Geoinstitut Bayreuth. Thanks to Nils Pravitz, Raphael Njul, and Dorothea Wiesner for sample preparation and preparation of a FIB lamella, respectively. Lea Ruckes is thanked for technical support with the electron microprobe. We also acknowledge two anonymous reviewers for their valuable feedback, which helped to significantly improve this manuscript. We acknowledge the DFG for funding the FIB facility (grant INST 91/315-1 FUGG) and the TEM facility (grant INST 91/251-1 FUGG). This study was supported by the Deutsche Forschungsgemeinschaft (DFG) to A.B.W. (Wo 652/20-2) and T.B.B. (Bo 2550/7-2).

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MANUSCRIPT RECEIVED JANUARY 20, 2023

MANUSCRIPT ACCEPTED AUGUST 6, 2023

Accepted manuscript online August 18, 2023

MANUSCRIPT HANDLED BY RYOSUKE SINMYO

Endnote:

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