1 Revision 1

- 2 Title: Synthesis and stability of feiite with implications for its formation conditions in nature
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- 13 Abstract

14 Feiite (Fe₃TiO₅) is a high-pressure Fe-Ti oxide mineral recently discovered in Martian 15 meteorite Shergotty. Feiite is isostructural with Fe₄O₅, a high-pressure iron oxide stable at 16 pressures greater than 10 GPa. The stability of feiite has yet to be studied, as it has not yet been 17 synthesized in the laboratory. To determine the minimum pressure at which feiite can be synthesized, we have conducted multi-anvil experiments at 1200°C and at pressures ranging 18 19 from 7 to 12 GPa. Major element compositions and XRD patterns indicate that we successfully 20 synthesized feite with an orthorhombic unit cell (*Cmcm* structure) in experiments conducted at 21 pressures 8 GPa or greater. Relative to A₂B₂O₅ phases with similar structure, feiite can be 22 synthesized at lower pressures. Coexistence of feiite and liuite (FeTiO₃-perovskite) in Shergotty 23 indicates that the upper pressure limit of feite stability is above 15 GPa. To investigate the effect

24 of oxygen fugacity on the composition and stability of feiite, we conducted an additional series of experiments at 1200°C and 10 GPa pressure in which we varied the Fe³⁺/Fe_{total} ratio of the 25 experimental starting materials. In doing so, we identified a minimum Fe³⁺ content necessary to 26 stabilize the feiite structure (Fe³⁺/Fe_{total} = 0.26 at 10 GPa and 1200°C). The importance of Fe³⁺ 27 for feiite stability suggests this phase would not form in lunar or HED meteorites, where iron-28 29 titanium oxides contain little to no ferric iron. Though our experimental results can only place a 30 lower limit on the shock pressures experienced in Shergotty, the determined pressure stability indicates feiite could also be present in diamond-bearing terrestrial rocks sourced from the upper 31 32 mantle or transition zone. Additionally, the presence of feiite would be an indicator of source Fe³⁺/ Fe_{total}. 33

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Introduction

36 Feiite (Fe₃TiO₅) is a high-pressure Fe-Ti oxide mineral recently discovered in a shock-37 induced melt pocket within the Martian meteorite Shergotty (Ma and Tschauner 2018; Ma et al. 38 2021). Feite is isostructural with Fe_4O_5 , a high-pressure iron oxide stable at pressures greater 39 than 8 GPa (Lavina et al. 2011), and other "CaFe₃O₅-type" oxides with *Cmcm* space group 40 symmetry. Additional high-pressure oxides with similar stoichiometry exist but have a modified 41 ludwigite-type structure with Pbam space group symmetry (e.g., Ishii et al. 2017). Together, these high-pressure oxide phases can be described by the general formula $A^{2+}_{2} B^{3+}_{2} O_5$ with A = 42 Fe^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , and $B = Fe^{3+}$, Cr^{3+} , Al^{3+} (e.g., Enomoto et al. 2009; Woodland et 43 al. 2013; Ishii et al. 2014; Boffa Ballaran et al. 2015; Ishii et al. 2015, 2017; Hong et al. 2016, 44 45 2018, 2022). Similar to magnetite, this oxide structure allows for a mix of iron oxidation states (Fe²⁺ and Fe³⁺), and thus could be important to interpreting the geophysical and magnetic 46 properties of planetary mantles (Fei et al. 1999). When identified in natural samples, the 47 Fe³⁺/Fe_{total} of A₂B₂O₅-type oxides may be indicative of source oxygen fugacity (Ishii et al. 2018, 48 Huang et al. 2021). 49

Natural feiite was found to contain 66% feiite endmember (Fe₃TiO₅), 20% Fe₄O₅, 10% 50 51 (Fe,Mg,Mn,Ca)₂(Al,Cr,V)₂O₅, and 4% Fe₃SiO₅ (Ma et al. 2021). The chemistry of the natural 52 occurrence suggests that a solid solution exists between feiite and the other A₂B₂O₅-type oxides, notably Fe₄O₅. Solid solution between $(Fe^{2+})_2(Fe^{2+}Ti^{4+})O_5$ and $(Fe^{2+})_2(Fe^{3+})_2O_5$ would require 53 the coupled substitution $Fe^{2+}Ti^{4+} = 2Fe^{3+}$ to maintain charge balance. This coupled substitution is 54 commonly observed in Fe-Ti oxide mineral solid solutions, such as that between ülvospinel 55 $(Fe^{2+}_{2}Ti^{4+}O_{4})$ and magnetite $(Fe^{2+}Fe^{3+}_{2}O_{4})$, as well as that between ilmenite $(Fe^{2+}Ti^{4+}O_{3})$ and 56 hematite ($Fe^{3+}_{2}O_{3}$). Importantly, the coupled substitution of Fe^{2+} and Ti^{4+} for $2Fe^{3+}$ is highly 57

sensitive to temperature and oxygen fugacity, and thus, the Ti content of coexisting Fe-Ti oxides is often used as a geothermometer and oxybarometer (Buddington and Lindsley 1964). In this way, feiite may be calibrated as an indicator for the oxygen fugacity of martian magmas. This oxybarometer would be applicable to other planetary bodies should feiite be discovered in additional meteorite or terrestrial samples.

63 Feilte likely formed from shock metamorphism of an Fe-Ti oxide precursor during an 64 impact event on Mars. Though the high-pressure phase transitions in Fe_2TiO_4 are known (Akaogi 65 et al. 2019), the stability of Fe₃TiO₅ has yet to be studied as it has not yet been synthesized in the 66 laboratory. Recoverable Fe_4O_5 has been synthesized at pressures greater than 8 GPa, and the 67 minimum pressure of stability increases with increasing oxygen fugacity (Lavina et al. 2011; 68 Woodland et al. 2012, 2013; Myhill et al. 2016). Another synthetic A₂B₂O₅-type oxide, 69 $Mg_2Fe_2O_5$, has been synthesized at pressures greater than 11 GPa (Uenver-Thiele et al. 2017). 70 We have conducted the first feiite synthesis experiments and defined the minimum pressure and 71 composition range required for synthesis of the new mineral. Comparing our synthetic Fe_3TiO_5 72 to studies of Fe_4O_5 and $Mg_2Fe_2O_5$ elucidates the effects of Ti and oxygen fugacity on the 73 stability, structure, and chemistry of A₂B₂O₅-type oxides.

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Experimental and Analytical Methods

76 Multi-anvil experiments

We conducted synthesis experiments using the split-cylinder (Walker 1991) type multi-anvil
presses at Carnegie Earth and Planets Laboratory. Starting materials were made from mixtures of
FeO (Alfa Aesar 99.5%), Fe₂O₃ (Alfa Aesar 99.995%), and FeTiO₃ (Alfa Aesar 99.8+%)
powders that targeted intermediate compositions between Fe₃TiO₅ and Fe₄O₅. Mixes were made

81	with Fe ₃ TiO ₅ :Fe ₄ O ₅ molar ratios equal to 50:50, 60:40, and 80:20. Multi-anvil experiments were
82	conducted at pressures ranging from 7 GPa to 12 GPa (Table 1) using a 14/8 assembly with a Re
83	heater and ZrO ₂ insulator (Figure 1). Pressure was calibrated using the CaGeO ₃ garnet-perovskite
84	transition at 1140°C and 6 GPa, the coesite-stishovite transition at 1500°C and 10 GPa, and the
85	olivine-wadsleyite transition at 1627°C and 14.4 GPa (Bertka and Fei 1997; Bennett et al. 2016).
86	Sample mixes were held within a welded Au capsule approximately 3 mm in height, and the Au
87	capsule was contained within an Al ₂ O ₃ sleeve (Figure 1). Each experiment was pressurized to the
88	target pressure, then heated to 1200°C as monitored with a Type C thermocouple. Run durations
89	ranged from 12 to 36 hours (Table 1). Experiments were quenched by turning off the power to
90	the assembly. To investigate two compositions at the same pressure and temperature condition,
91	experiment PL1504 consisted of two welded Au sample capsules stacked vertically and
92	contained within a 4-mm length Al ₂ O ₃ sleeve. The two samples from this assembly are
93	designated with a "T" and "B", with sample "T" having been located closer to the thermocouple.
94	After recovery, sample capsules were cut in half, mounted in epoxy, and polished for analysis.

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96 Analysis of recovered samples

97 Quenched samples were analyzed for major element chemistry (Ti, Fe, Mg, and O) using the 98 JEOL JXA-8530F electron microprobe at Carnegie Earth and Planets Laboratory. Analyses were 99 acquired with a 15 kV accelerating voltage, 25 nA current, and 1 µm beam diameter. A 100 conventional, linear peak-to-background correction was applied, and the chosen analytical 101 standards were Zagi Mountain ilmenite (Ti), ZCA Mine magnetite (Fe), San Carlos olivine (Mg), 102 and Alfa Aesar synthetic spinel (O). Data were processed using Probe for EPMA software

103 (<u>http://www.probesoftware.com/</u>). Figure 2 presents representative back-scattered electron
104 images of run products that were used to identify phases and evaluate texture.

- For each sample, phase identification was confirmed by powder XRD patterns acquired using the Bruker D8 X-ray diffractometer equipped with an Incoatec $Cu_{K\alpha}$ microfocus source and Lynxeye detector at Carnegie Earth and Planets Laboratory. For LO1723, we extracted the sample from the Au capsule and crushed the material to a powder in order to improve powder averaging statistics, though some preferred orientation of grains was still observed. All other samples were analyzed in the sample capsule, and thus some XRD patterns exhibit preferred orientation of grains and/or diffraction associated with the Au sample capsule.
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Results and Discussion

114 **Pressure dependence of Fe₃TiO₅ stability**

We have determined that the lower-pressure stability limit of feiite lies between 7 and 8 GPa at 115 116 1200°C. The experimental series we used to define the minimum pressure for feite synthesis 117 was performed on the starting composition with 50 mol% Fe₃TiO₅ 50 mol% Fe₄O₅. Major 118 element compositions and XRD patterns indicate that we successfully synthesized feiite with an 119 orthorhombic unit cell (*Cmcm* structure) in experiments conducted from 8 to 12 GPa (Table 2, 120 Figure 3). For the 50 mol% Fe_3TiO_5 50 mol% Fe_4O_5 starting material, the compositions of feite 121 synthesized at 12 GPa (LO1724), 10 GPa (PL1498), and 9 GPa (PL1503) are the same within the 122 measured analytical uncertainty. Further, the similarity in feite compositions between the 12-123 hour syntheses and the 36-hour run duration experiment (LO1724) indicate that a 12-hour run 124 time was sufficient for equilibration at the experimental temperature of 1200°C. For each

125	experiment, phase proportions (wt%) were calculated from a linear least squares solution using
126	the average phase compositions and the bulk composition of the starting material (Table 1). For
127	the compositions used in this study, the synthesized feiite always coexists with ilmenite.
128	Experiments conducted at 7 and 8 GPa also produced wüstite. Inspection of the Au capsule by
129	EDS indicated that little to no Fe diffused into the Au capsule during the experiment.
130	We confirmed the presence or absence of the Fe ₄ O ₅ -type structure in our experiments
131	using XRD analysis (Figure 3). Only the experiment conducted at 7 GPa (PL1496) lacked the
132	structural features characteristic of feiite. Full-profile refinement of the powder XRD pattern

133 from 12 GPa experiment LO1723 yielded unit-cell parameters for feiite a = 2.9245(2) Å, b = 9.8328(7) Å, c = 12.6094(8) Å, and ilmenite9

238	feiite stability requires Fe ³⁺ , this phase would not form in more reducing environments, such as
239	those in lunar or HED meteorites (Sato et al. 1973, Stolper 1977).
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241	Implications
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243	Here we have presented the first experimental synthesis of feiite and identified compositional
244	and pressure limitations on its stability. Though our experimental results can only place a lower
245	limit on the shock pressures experienced in Shergotty, the determined pressure stability and

oxygen fugacity of Earth indicate feiite could also be present in terrestrial diamond-bearing

rocks. For instance, feiite may be found in rocks with diamonds that have majoritic garnet

inclusions from the deep upper mantle or transition zone (Stachel et al. 2005; Collerson et al.

sourced from the lower mantle (Walter et al. 2011; Akaogi et al. 2019). It would be interesting to

re-examine some of the Fe-Ti oxide inlcusions in light of our new understanding of high-

pressure A₂B₂O₅-type oxides. For example, one Fe-Ti oxide inclusion (Ju5-47) from the Juina-5

kimberlite in Brazil (Walter et al. 2011) identified as ülvospinel by Raman spectroscopy is

particularly intriguing because the major element analysis of the "ülvospinel" has a reported

stochiometry of 4 cations to 5 oxygens, which is consistent with A₂B₂O₅ instead of spinel

 (AB_2O_4) . If this phase is indeed an $A_2B_2O_5$ -type oxide, the chemistry is approximately 80%

Fe₃TiO₅, 10% Fe₄O₅, and 10% (Fe₃Mg)₂Al₂O₅. Assuming stoichiometric components and

valence states Ti^{4+} , Al^{3+} , and Mg^{2+} , the estimated Fe^{3+}/Fe_{total} is 0.09 for this grain. This

Inclusions of Fe-Ti oxide have been found in "ultradeep" diamonds in kimberlites

2010). Additionally, the presence of feiite would be an indicator for source Fe^{3+}/Fe_{total} .

260 calculation assumes that the chemical composition reported in Walter et al. (2011) is

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representative of one mineral, however the composition may instead represent a mixture of ulvöspinel and another oxide phase. Given that feiite was only recently discovered in martian meteorite Shergotty, future structural characterization of Fe-Ti oxide inclusions in deep diamonds might lead to discovery of feiite with a terrestrial origin.

265 Feilte has the potential to be calibrated as an oxybarometer in planetary materials. Solid solution between feiite and Fe_4O_5 contains both Fe^{2+} and Fe^{3+} , and the titanium content of feiite 266 267 is a function of oxygen fugacity. Oxygen fugacity can also be estimated from the iron and 268 magnesium compositions of Fe₄O₅ solid solutions (Myhill et al. 2016; Huang et al. 2021). With 269 additional experimental data, the partitioning of iron and titanium between feiite and coexisting 270 Fe-Ti oxide minerals, such as ilmenite or liuite, could be calibrated as an oxybarometer 271 analogous to that for magnetite and ilmenite solid solutions (Buddington and Lindsley 1964). In 272 this case, the relevant reactions for Fe-Ti exchange between ilmenite and feiite and the 273 dependence of mineral stability on oxygen fugacity would be as follows:

$$FeTiO_3 + Fe_4O_5 \rightarrow Fe_2O_3 + Fe_3TiO_5$$

- $Fe_4O_5 + \frac{1}{2}O_2 \rightarrow 2 Fe_2O_3$
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Knowledge of the feiite stability field in pressure and compositional space combined with
measurements of the ferric iron content in feiite could provide a tight constraint on its origin
environment.

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444	List of Figure Captions
445	Figure 1. Schematic diagram of the 14/8 sample assembly used in feiite synthesis experiments.
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447	Figure 2. Back-scattered electron images of run products from experiment series conducted at 10
448	GPa and 1200°C with three different starting compositions: (a) 80 mol% Fe ₃ TiO ₅ , PL1504T (b)

449	60 mol% Fe ₃ TiO ₅ , PL1504B (c) 50 mol% Fe ₃ TiO ₅ , PL1498. Feiite is the medium gray phase and
450	ilmenite is the darkest gray phase. Wüstite is only present in (a) and is the lightest gray phase.
451	
452	Figure 3. X-ray diffraction pattern for each experiment. Feiite is present in every experiment
453	except for PL1496 conducted at 7 GPa. The hkl reflections for feiite and ilmenite at 10 GPa are
454	plotted for reference. Peaks associated with wüstite (Wüs) and the Au sample capsule (Au) are

456

455

457 Figure 4. Results of the Rietveld refinement for the powder X-ray diffraction pattern measured

labeled with the phase abbreviation and *hkl* value.

458 on the feiite-ilmenite mixture in experiment LO1723 (feiite Bragg-R = 1.72%, ilmenite Bragg-R
459 = 2.09%).

460

Figure 5. Pressure-temperature diagram adapted from Uenver-Thiele et al. (2017) and Ishii et al. (2020) to include the lower pressure limit of feiite stability at 1200°C (this study, diamonds) and synthesis conditions of $MnFe_3O_5$ in Hong et al. (2016). Relative to $A_2B_2O_5$ phases with similar structure, feiite is synthesized at lower pressures.

465

Figure 6. Compositions of experimental phases and starting materials depicted in FeO-Fe₂O₃-TiO₂ ternary space. Marker color corresponds to starting material composition (gray = 50 mol% Fe₃TiO₅, red = 60 mol% Fe₃TiO₅, yellow = 80 mol% Fe₃TiO₅). For experiments on the 50 mol% Fe₃TiO₅ starting material, gray marker shading reflects experiment pressure (darker gray = higher pressure). Yellow markers note compositions from wüstite-bearing experiment PL1504T and define the minimum Fe³⁺/Fe_{total} to stabilize feiite at 10 GPa.

473	Figure 7. (a) Titanium compositions of coexisting feiite and ilmenite. With increasing Fe_4O_5 in
474	the starting material, Ti concentrations in both feiite and ilmenite decrease. Ilmenite is always
475	more enriched in Ti than feiite. (b) Partitioning of Ti between ilmenite and feiite expressed as
476	molar ratio (D_{Ti} = mol Ti ilmenite / mol Ti feiite). $D_{Ti}^{ilmenite-feiite}$ is always greater than 1.
477	
478	Figure 8. Ilmenite compositions from lunar samples, lunar meteorites, HED meteorites, and
479	martian meteorites. The dashed line denotes molar Fe/Ti = 1 for an ideal ilmenite stoichiometry
480	(Fe ²⁺ TiO ₃). Molar Fe/Ti ratios greater than one indicate an increasing Fe ³⁺ ₂ O ₃ component in the
481	ilmenite solid solution, and thus a more oxidized environment. Ilmenite data accessed May 2022
482	from AstroDB (https://search.astromat.org/filter).
483	
484	
485	Tables
486	(Provided in Excel spreadsheet)
487	Table 1. Experimental run details.
488	Table 2. Major element compositions.

Table 2. Major element compositions of experimental phases as determined by electr

Experiment	Phase	n	Ti (wt%)	stdev Ti	Fe (wt%)
LO1723	feiite	26	8.20	0.19	65.44
	ilmenite	17	23.65	0.19	45.04
LO1724	feiite	31	6.25	0.09	67.81
	ilmenite	21	20.94	0.17	48.03
PL1498	feiite	31	6.35	0.12	67.26
	ilmenite	24	21.10	0.19	47.46
PL1504B	feiite	30	8.42	0.17	65.05
	ilmenite	20	23.20	0.12	45.32
PL1504T	feiite	28	9.76	0.06	63.51
	wüstite	19	3.21	0.20	71.46
	ilmenite	29	24.66	0.06	43.68
PL1503	feiite	37	6.29	0.11	67.50
	ilmenite	29	20.97	0.19	47.86
PL1501	feiite	6	4.99	0.58	69.18
	wüstite	20	1.74	0.11	73.62
	ilmenite	27	19.21	0.16	49.64
PL1496	wüstite	20	1.68	0.07	73.94
	ilmenite	21	19.94	0.12	48.98

on microprobe analysis.

stdev Fe	Mg (wt%)	stdev Mg	O (wt%)	stdev O	Total	stdev Total
0.23	0.01	0.00	26.89	0.11	100.55	0.21
0.19	0.01	0.00	31.88	0.17	100.59	0.33
0.21	0.01	0.00	26.71	0.13	100.79	0.25
0.19	0.01	0.00	31.50	0.12	100.48	0.22
0.25	0.02	0.00	26.51	0.17	100.14	0.23
0.24	0.01	0.01	31.23	0.25	99.81	0.47
0.28	0.013	0.002	27.00	0.12	100.49	0.28
0.20	0.012	0.003	31.75	0.14	100.28	0.21
0.22	0.053	0.053	27.08	0.10	100.41	0.23
0.48	0.057	0.057	24.95	0.16	99.68	0.32
0.13	0.038	0.019	31.86	0.09	100.23	0.16
0.21	0.014	0.003	26.49	0.12	100.29	0.20
0.19	0.010	0.010	31.26	0.21	100.11	0.33
0.71	0.01	0.00	26.33	0.228	100.52	0.37
0.21	0.02	0.01	24.86	0.14	100.25	0.24
0.15	0.02	0.01	31.15	0.18	100.01	0.26
0.20	0.07	0.01	24.72	0.13	100.42	0.25
0.12	0.04	0.01	31.22	0.15	100.17	0.29

O formula	Ti formula	stdev Ti	Fe formula	stdev Fe
5	0.51	0.01	3.49	0.02
3	0.74	0.01	1.21	0.01
5	0.39	0.01	3.64	0.02
3	0.67	0.00	1.31	0.01
5	0.40	0.01	3.63	0.03
3	0.68	0.01	1.31	0.01
5	0.52	0.01	3.45	0.02
3	0.73	0.00	1.23	0.01
5	0.60	0.00	3.36	0.02
1	0.04	0.00	0.82	0.01
3	0.78	0.00	1.18	0.00
5	0.40	0.01	3.65	0.02
3	0.67	0.00	1.32	0.01
5	0.32	0.04	3.76	0.06
1	0.02	0.00	0.85	0.01
3	0.62	0.00	1.37	0.01
1	0.02	0.00	0.86	0.01
3	0.64	0.00	1.35	0.01

Mg formula	stdev Mg	cation sum	stdev cation sum	avg Fe valence
0.0017	0.0004	4.00	0.01	2.28
0.0007	0.0002	1.96	0.01	2.49
0.0017	0.0004	4.03	0.02	2.32
0.0008	0.0001	1.98	0.01	2.55
0.0021	0.0006	4.04	0.03	2.31
0.0009	0.0004	1.98	0.01	2.52
0.0016	0.0003	3.97	0.02	2.29
0.0008	0.0002	1.96	0.01	2.50
0.006	0.006	3.97	0.01	2.26
0.001	0.001	0.87	0.01	
0.002	0.001	1.96	0.01	2.46
0.0017	0.0004	4.05	0.02	2.31
0.0009	0.0004	1.99	0.01	2.52
0.0020	0.0003	4.08	0.03	2.32
0.0007	0.0002	0.87	0.00	
0.0010	0.0008	1.99	0.01	2.58
0.0019	0.0002	0.88	0.00	
0.0024	0.0004	1.99	0.01	2.55

Figure 1









Figure 3













Figure 7

