

SYNTHESIS AND STABILITY OF FEIITE WITH IMPLICATIONS FOR ITS FORMATION CONDITIONS IN NATURE. K. B. Prissel^{1,2}, Y. Fei², T. A. Strobel². ¹Jacobs, NASA Johnson Space Center, Houston, TX. ²Earth and Planets Laboratory, Carnegie Institution for Science, 5241 Broad Branch Road NW, Washington D.C. 20015. (kelsey.prissel@nasa.gov)

Introduction: Feiite is a high-pressure Fe-Ti oxide mineral recently discovered in a shock-induced melt pocket within the Martian meteorite Shergotty [1, 2], but it has not been synthesized in the laboratory. Feiite (Fe_3TiO_5) is isostructural with Fe_4O_5 , a high-pressure iron oxide synthesized at pressures greater than 10 GPa [3]. Another synthetic mineral with similar structure, $\text{Mg}_2\text{Fe}_2\text{O}_5$, is stable at pressures greater than 11 GPa [4]. Though the high-pressure phase transitions in Fe_2TiO_4 are known [5], the stability of Fe_3TiO_5 has yet to be studied. We have conducted the first feiite synthesis experiments and defined the minimum pressure and composition range required for synthesis of the new mineral. Comparing our synthetic Fe_3TiO_5 to studies of Fe_4O_5 and $\text{Mg}_2\text{Fe}_2\text{O}_5$ elucidates the effects of Ti and oxygen fugacity on the stability, structure, and chemistry of $\text{A}_2\text{B}_2\text{O}_5$ -type oxides.

Methods: We conducted synthesis experiments using the multi-anvil presses at Carnegie Earth and Planets Laboratory. Starting materials were made from mixtures of FeO , Fe_2O_3 , and TiO_2 powders that targeted intermediate compositions between Fe_3TiO_5 and Fe_4O_5 . Experiments were conducted at pressures ranging from 7 GPa to 12 GPa using a 14/8 assembly with a Re heater and ZrO_2 insulator. Pressure was calibrated using the CaGeO_3 garnet-perovskite transition at 6 GPa and coesite-stishovite transition at 9 GPa. Sample mixes were held within a welded Au capsule approximately 3 mm in height, and the Au capsule was contained within an Al_2O_3 sleeve. Each experiment was conducted at 1200°C and monitored with a Type C thermocouple.

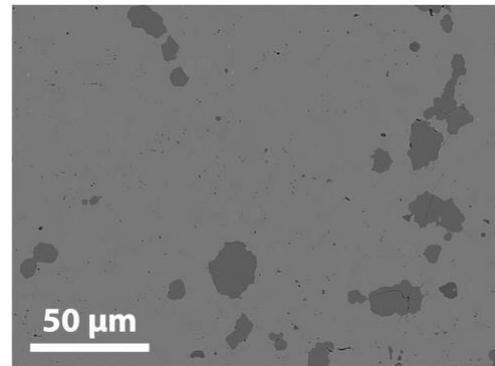


Figure 1. Backscattered electron image of feiite-bearing experiment LO1723. The light gray matrix is feiite and the dark gray grains are ilmenite.

Run durations ranged from 12 to 36 hours. Experiments were quenched by turning off the power to the assembly.

After recovery, sample capsules were cut in half, mounted in epoxy, and polished for analysis. Samples were analyzed for major element chemistry using the JEOL JXA-8530F electron microprobe at Carnegie Earth and Planets Laboratory, and the data were processed using Probe for EPMA software. For each sample, phase identification was confirmed by XRD patterns acquired using the Bruker D8 X-ray diffractometer 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.

Table 1. Experiment run conditions and run products. “Mix” column indicates the Fe_3TiO_5 : Fe_4O_5 ratio in the starting material for each experiment. Feiite is stable at pressures above 8 GPa.

Experiment	Mix	P (GPa)	T (°C)	Time (hr)	Phases
LO1723	60:40	12	1200	12.7	feiite + ilmenite
LO1724	50:50	12	1200	36.0	feiite + ilmenite
PL1498	50:50	10	1200	12.0	feiite + ilmenite
PL1504B	60:40	10	1200	12.0	feiite + ilmenite
PL1504T	80:20	10	1200	12.0	feiite + ilmenite + wüstite
PL1503	50:50	9	1200	12.0	feiite + ilmenite
PL1501	50:50	8	1200	12.0	ilmenite + wüstite
PL1496	50:50	7	1200	12.1	ilmenite + wüstite

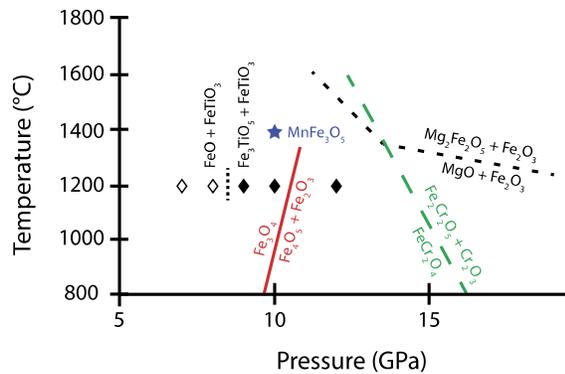


Figure 2. Pressure-temperature phase relationships for Fe_3TiO_5 relative to other high-pressure $\text{A}_2\text{B}_2\text{O}_5$ oxide phases. Figure adapted from [4] to include the lower pressure limit of feiite stability at 1200°C (this study) and synthesis conditions of MnFe_3O_5 in [6]. Our experiment conditions are plotted as diamonds, with filled markers for feiite-bearing experiments and open markers for experiments without feiite.

Results: We have determined that the lower-pressure stability limit of feiite lies between 8 and 9 GPa. Major element compositions and XRD patterns indicate that we successfully synthesized feiite with an orthorhombic unit cell ($Cmcm$ structure) in experiments conducted between 9 and 12 GPa (Table 1). Relative to $\text{A}_2\text{B}_2\text{O}_5$ phases with similar structure, feiite is synthesized at lower pressures (Figure 2).

Feiite chemistry. The composition of the synthetic feiite did not vary significantly with pressure (Figure 3). Starting compositions with higher proportions of Fe_4O_5 resulted in feiite and ilmenite compositions with higher Fe^{3+} contents, as estimated from mineral stoichiometry. In pure feiite, all of the Fe is Fe^{2+} , whereas in Fe_4O_5 the iron exists as a mixture of Fe^{2+} and Fe^{3+} . Synthetic Fe_4O_5 does not exist at $\log f_{\text{O}_2} < -4$, and with increasing oxygen fugacity, requires higher pressures to stabilize [7]. We were not able to synthesize the feiite endmember, $\text{Fe}_2(\text{FeTi})\text{O}_5$, from a pure Fe_3TiO_5 starting material, indicating that feiite forms limited Ti substitution in the Fe_4O_5 structure by the coupled substitution $\text{Fe}^{2+}\text{Ti}^{4+} = 2\text{Fe}^{3+}$ (Figure 3). Thus, it appears that Fe^{3+} is required to stabilize the Fe_4O_5 -type structure. This result explains the observed composition of the natural feiite discovered in Shergotty that contains 66% feiite endmember and 20% Fe_4O_5 component [2]. Experiment PL1504T with a higher Fe_3TiO_5 : Fe_4O_5 ratio resulted in the formation of wüstite coexisting with feiite and ilmenite, indicating a minimum $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio to stabilize feiite.

Implications: The shock pressure for Shergotty is estimated to be approximately 30 GPa [8]. Natural feiite is hypothesized to form from an ulvöspinel precursor and coexists with liuite (FeTiO_3 -perovskite) [1, 2]. Feiite is present in our experiments with ilmenite \pm wüstite, not liuite, because FeTiO_3 -perovskite is only stable above 15 GPa [9]. Coexistence of feiite and liuite in Shergotty indicates that the upper pressure limit of feiite stability is above 15 GPa. The importance of Fe^{3+} for feiite stability suggests this phase would not form in lunar or HED meteorites, where iron-titanium oxides contain little to no ferric iron. Though our experimental results can only place a lower limit on the shock pressures experienced in Shergotty, the determined pressure stability indicates feiite could also be present in terrestrial rocks that contain diamonds with majoritic garnet inclusions from the mantle [10]. Additionally, the presence of feiite would be an indicator for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of the source.

References: [1] Ma C. and Tschauner O. (2018) *Eur. J. Mineral.*, 39, 1189. [2] Ma C. et al. (2021) *LPSC* 52, Abstract #1681. [3] Lavina et al. (2011) *PNAS*, 108 (42), 17281-17285. [4] Uenver-Thiele et al. (2017) *Am. Min.* 102, 632-642. [5] Akaogi et al. (2019) *Minerals* 9, 614. [6] Hong et al. (2016) *Z. Anorg. Allg. Chem.* 642 (23), 1355-1358. [7] Myhill et al. (2016) *Cont. Min. Pet.* 171:51. [8] Fritz et al. (2005) *MaPS* 40, 1393-1411. [9] Akaogi et al. (2017) *Phys. Chem. Minerals* 44, 63-73. [10] Stachel et al. (2005) *Elements* 1, 73-78.

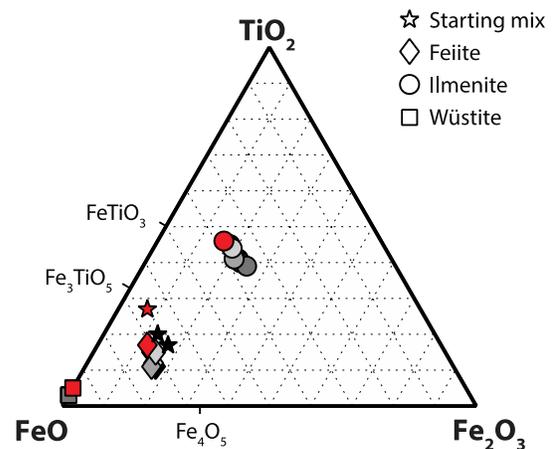


Figure 3. Compositions of experimental phases and starting materials. Marker colors reflect experiment pressure, with darker gray for higher pressures and lighter gray for lower pressures. Red markers note the compositions from experiment PL1504T, in which feiite, ilmenite, and wüstite co-exist.