Structure and titanium distribution of feiite characterized using synchrotron single-crystal X-ray diffraction techniques

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ABSTRACT

A solid solution of the mineral feiite (Fe3TiO5) was recently discovered in a shock-induced melt pocket of the Shergotty martian shergottite. It is particularly interesting for its potential as an indicator of pressure-temperature (P-T) and oxygen fugacity in martian crust and mantle material. To date, complete crystallographic analysis of feiite has not been conducted, as the mineral was previously analyzed by electron backscatter diffraction on micrometer-size grains (Ma et al. 2021). Here we report a convergent crystal-structure model for feiite based on synchrotron single-crystal X-ray diffraction data collected on three grains of feiite synthesized at 12 GPa and 1200 °C. Feiite adopts the CaFe2O4 structure type (Cmcm, Z = 4), which is composed of two octahedral M1 and M2 sites and one trigonal prismatic M3 site (M = metal) in a ratio of 1:2:1. The three feiite grains with composition Ti0.46–0.60Fe3.54–3.40O5 were best modeled by substituting Ti4+ into only the octahedral M2 site, accounting for 30% of this site. Comparisons of the measured average bond lengths in the coordination polyhedra with the optimized Ti4+-O, Fe3+-O, and Fe2+-O bond lengths suggest that ferrous iron occupies the trigonal M3 site, while iron is mixed valence in the octahedral M1 and M2 sites. The Ti4+ and Fe3+ content constrained by our crystal-chemical analyses suggests that at least ~30% of the available iron must be ferric (i.e., Fe3+/Fe(total) = 0.3) for the sample synthesized at 12 GPa and 1200 °C and higher P-T conditions may be needed to form the end-member feiite (Fe3+TiO5).

Keywords: Feiite, crystal structure, iron oxides, Shergotty, mixed valence, titanium oxide

INTRODUCTION

The compositions of coexisting iron-titanium-oxides found in terrestrial and extraterrestrial rocks have been established as important indicators of oxygen fugacity in processes including melt crystallization and high P-T impact (e.g., Buddington and Lindsley 1964; Tophis and Carol 1995; Herd et al. 2001). Previous studies have predominantly explored the geochemical and thermodynamic properties of the hematite-ilmenite and magnetite-ulvöspinel (Fe2TiO4) series (e.g., Buddington and Lindsley 1964; Ghiorsos and Sack 1991; Brown et al. 1993; Ghiorsos and Evans 2008; Pearce et al. 2010; Lilova et al. 2012); however, a new (Fe,Ti)-oxide solid solution between feiite (Fe3TiO5) and Fe2O3 was recently discovered in a shock-induced melt pocket of the Shergotty martian shergottite coexisting with FeTiO3 (Ma et al. 2021), adding new complexities to these geochemical tracers in relation to shocked processes. Experimentally, feiite solid solutions with compositions Fe1.7TiO2.2 have been synthesized between 7 and 12 GPa at 1200 °C (Prissel et al. 2022a, 2022b), supporting that feiite is a high-pressure and high-temperature (P-T) product of martian impact processes. Examination of