

The thermal breakdown of Fe_4O_5 at ambient pressure

D. M. Trots (1), A. Kurnosov (1), A. B. Woodland (2), and D. J. Frost (1)

(1) Bayerisches Geoinstitut, University of Bayreuth, Germany (dmytro.trots@uni-bayreuth.de), (2) Universität Frankfurt, Institut für Geowissenschaften, Frankfurt, Germany (woodland@em.uni-frankfurt.de)

Fe_4O_5 is a recently discovered Fe-oxide that is stable at pressures of ~ 10 GPa (Lavina et al. 2011) and magnetite is now known to break down to an assemblage of $\text{Fe}_4\text{O}_5 + \text{Fe}_2\text{O}_3$ under such conditions (Woodland et al. 2012). Thus it is important to determine the properties of Fe_4O_5 as it apparently plays an important role in the simple Fe-O system at high pressures and temperatures. To this end we set out to measure accurate molar volumes of this phase as a function of temperature at ambient pressure conditions to measure its thermal expansion. This goal was compromised by its low thermal stability at 1 bar, which revealed a series of different transformations.

Fe_4O_5 was synthesised from a mixture of magnetite and Fe at 11 GPa and 1000°C in a multi-anvil press. Ambient P and T lattice parameters are $a=2.89339(6)$ Å, $b=9.8067(3)$ Å, $c=12.5834(3)$ Å and a volume of $357.05(2)$ Å³. Subsequently, a powder was sealed in a glass capillary and run at the high-resolution beamline B2 at HASYLAB/DESY. X-ray powder diffraction measurements were performed as a function of temperature up to 900°C.

Already at 150°C, new diffraction peaks appeared, indicating that Fe_4O_5 was decomposing to a mixture of Fe_3O_4 and Fe_xO . The unit-cell of Fe_xO reveals a composition of $x=\sim 0.8$. Diffraction peaks from Fe_4O_5 virtually disappeared by 200°C. Between 200 and 250°C, metallic Fe and an additional Fe_yO phase appeared that had a unit-cell more like “typical” wüstite ($y=\sim 0.96$), revealing a further reaction where Fe^{3+} -rich Fe_xO breaks down to a mixture of $\text{Fe}_3\text{O}_4 + \text{Fe}^{3+}$ -poor $\text{Fe}_y\text{O} +$ metallic Fe. With increasing T, both Fe_xO and Fe_yO progressively undergo a disproportionation reaction producing metallic Fe and Fe_3O_4 . Above 470°C, Fe_yO disappears and a small amount of metastable Fe_xO coexists with the stable assemblage of metallic Fe + Fe_3O_4 . At 600°C, the true wüstite stability field is reached and metallic Fe reacts with magnetite to produce Fe_zO , where $z=0.93(1)$. No further changes are observed up to 900°C. Calculated phase proportions at 900°C are 0.37 Fe_zO and 0.63 Fe_3O_4 , which correspond very closely to the initial Fe_4O_5 composition, indicating that this series of reactions was not driven by oxidation or reduction, but occurred at nearly constant oxygen content. The metastable appearance of Fe_xO at low T must be related to the fact that the Fe_4O_5 crystal structure contains wüstite-like octahedral layers that alternate with Ca-ferrite slabs. Initial breakdown favors the formation Fe^{3+} -rich Fe_xO , which may be an indicator of the cation distribution in the original Fe_4O_5 phase.

Lavina et al. (2011) PNAS, 108, 17281-17285.

Woodland et al. (2012) abstract emc2012-317, this meeting