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The breakdown of Fe_3O_4 to Fe_4O_5 + Fe_2O_3 at high pressure and temperature

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It has been recognised that magnetite (Fe_3O_4) breaks down at pressures above 10 GPa (Schollenbruch et al. 2011). However, the exact structure of the high-pressure phase has remained elusive in part due the fact that it is unquenchable. Recent multianvil experiments coupled with energy dispersive X-ray diffraction collected up to 1873 K and 10-13 GPa revealed a set of reflections that were inconsistent with either of the previously proposed orthorhombic $CaMn_2O_4$ or $CaTi_2O_4$-type structures (Schollenbruch et al. 2011). However, the resolution of the diffraction patterns was too poor unambiguously determine structure of the high-pressure phase. To resolve this problem, new high quality angle dispersive X-ray diffraction patterns were collected using a Paris-Edinburgh apparatus at pressures of up to ~12 GPa and 1300 K. This apparatus is of sufficient volume to allow a clean diffraction pattern of the high-P phase of Fe_3O_4 to be collected without interferences from pressure calibrants and capsule materials.

Diffraction pattern refinement reveals that magnetite does not transform isochemically, but rather undergoes a disporportionation reaction, producing the assemblage Fe_4O_5 + Fe_2O_3. At 947 K and 11.4 GPa, the Fe_4O_5 phase has the following lattice parameters: a= 2.87366(8)Å, b=9.6940(3)Å, c=12.4116(4)Å and a volume of 345.753(18) Å^3. This is comparable with values obtained by Lavina et al. (2011). Although the Fe_4O_5 phase appears to be quenchable by itself, in the presence of hematite it rapidly recombines back to magnetite upon decompression. At yet higher pressures, the assemblage Fe_4O_5 + Fe_2O_3 is expected to recombine to produce a h-Fe_3O_4 phase with $CaMn_2O_4$ or $CaTi_2O_4$-type structures.

Schollenbruch et al. (2011) Am. Min., 96, 820-827.

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