High-pressure phase transitions in FeTiO$_3$, Fe$_2$TiO$_4$ and FeTi$_2$O$_5$

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Introduction
Iron titanium oxides are of considerable importance in earth science as magnetic minerals and indicators of oxidation state. FeTiO$_3$, Fe$_2$TiO$_4$ and FeTi$_2$O$_5$ are Fe-Ti endmembers of natural ilmenite, spinel and pseudobrookite, respectively. Although several high-pressure investigations on the Fe-Ti oxides have been made with a diamond anvil cell, the results are still controversial, particularly at pressure above 20 GPa.

Experimental methods
We have examined detailed phase relations in FeTiO$_3$, Fe$_2$TiO$_4$ and FeTi$_2$O$_5$ up to 35 GPa and 1600 °C, using multianvil apparatus with tungsten carbide anvils. The quenched samples were examined by microfocus and powder X-ray diffractometers, and composition analysis was made using SEM-EDS. In-situ X-ray diffraction experiments on FeTi$_2$O$_5$ were performed with a laser-heated DAC at SPring-8.

Results and discussion
FeTiO$_3$ ilmenite (Ilm) transforms at 14 GPa and 1200 °C to perovskite (Pv) which changes to LiNbO$_3$-type phase on release of pressure [1]. In contrast to Pv-postPv transition in MgSiO$_3$, FeTiO$_3$ Pv dissociates at 27 GPa into two phases: calcium titanate (CT) type Fe$_2$TiO$_4$ + O1-type TiO$_2$ below 1100 °C and Fe$_2$TiO$_4$ CT + a new FeTi$_2$O$_5$ phase above 1100 °C. The in-situ X-ray studies at 35 GPa showed that the new FeTi$_2$O$_5$ phase has orthorhombic symmetry and is 7 % denser than the low-pressure assemblage of FeTiO$_3$ Pv + TiO$_2$ O1. Fe$_2$TiO$_4$ ulvospinel dissociates into FeTiO$_3$ Ilm + wustite at 4 GPa, which changes into Pv + wustite at 14 GPa, and further they combine into Fe$_2$TiO$_3$ CT at 17 GPa. These results indicate that Fe$_2$TiO$_4$ CT, TiO$_2$ O1 and the new orthorhombic FeTi$_2$O$_5$ phase are stable phases in the FeO-TiO$_2$ system in the upper part of lower mantle. A LiNbO$_3$-type FeTiO$_3$ phase recently discovered in shocked gneiss in the Ries Crater, Germany, was interpreted to be the retrograde transformation product of FeTiO$_3$ Pv [2]. Based on the phase relations in this study, we estimate that the phase occurred at shock pressure between 14 and 27 GPa.