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Titanium-bearing phases in the Earth's mantle (evidence from experiments in the $MgO–SiO_2–TiO_2$ $\pm Al2O_3$ system at 10–24 GPa)

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Introduction
Despite significant interest of experimentalists to the study of geophysically important phase equilibria in the Earth's mantle and a huge experimental database on a number of the model and multicomponent systems, incorporation of minor elements in mantle phases was mostly studied on a qualitative level. The influence of such elements on structural peculiarities of high-pressure phases is poorly investigated, although incorporation of even small portions of them may have a certain impact on the PT-parameters of phase transformations. Titanium is one of such elements with the low bulk concentrations in the Earth's mantle (0.2 wt % TiO_2) [1]; however, Ti-rich lithologies may occur in the mantle as a result of oceanic crust subduction. Thus, the titanium content is 0.6 wt% in Global Oceanic Subducted Sediments (GLOSS) [2], and ~1.5 wt% TiO_2, in MORB [3]. In this regard, accumulation of titanium in the Earth's mantle is related to crust-mantle interaction during the subduction of crustal material at different depths of the mantle.
Experimental methods
At 10–24 GPa and 1600°C, we studied the full range of the starting materials in the $MgSiO_3$ (En) – $MgTiO_3$ (Gkl) system in increments of 10–20 mol% Gkl and 1–3 GPa, which allowed us to plot the phase PX diagram for the system $MgSiO_3$–$MgTiO_3$ and synthesize titanium-bearing phases with a wide compositional range. The experiments were performed using a 2000-t Kawai-type multi-anvil high-pressure apparatus at the Geodynamics Research Center, Ehime University (Japan). The quenched samples were examined by single-crystal X-ray diffractometer, and the composition of phases was analyzed using SEM-EDS.
Results
The main phases obtained in experiments were rutile, wadsleyite, $MgSiO_3$-enstatite, $MgTiO_3$-ilmenite, MgTiSi2O7 with the weberite structure type (Web), $Mg(Si,Ti)O_3$ and $MgSiO_3$ with perovskite-type structure. At a pressure of ~13 GPa for Ti-poor bulk compositions, an association of En+Wad+Rt is replaced by the paragenesis of Web+Wad+Rt. With increasing Glk content in the starting composition, Gkl+Wad+Rt association is formed. At a pressure of >17 GPa, an association of two phases with Prv-type structure is stable within a narrow range of starting compositions.
Addition of Al to the starting material allows us to simulate the composition of natural bridgmanites, since lower mantle bridgmanites are characterized by significant Al contents. In addition, this study shows that, in contrast to Al, the high contents of Ti can stabilize bridgmanite-like compounds at considerably lower pressure (18 GPa) in comparison with pure $MgSiO_3$ bridgmanite.
Small crystals of titanium-rich phases, including Ti-Al–Brd and Web were examined by single-crystal X-ray diffractometer, which allowed us to study the influence of Ti on crystallochemical peculiarities of the mantle phases and on the phase transformations.
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