TITANIUM-BEARING PHASES IN THE $MgO–SiO_2–TiO_2±Al_2O_3$ SYSTEM AT 10–24 GPa AND 1600°C): PHASE RELATIONS, STRUCTURAL FEATURES AND SOLID SOLUTIONS.

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The influence of minor 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); however, Ti-rich lithologies may occur in the mantle as a result of oceanic crust subduction. Thus, the titanium content is ~2 wt% TiO_2, in MORB (Wilson, 1989). Accumulation of titanium in the Earth's mantle proceeds through crust-mantle interaction during the subduction of crustal material to different depths of the mantle.

Our experiments were aimed to the study of phase relations, achieve synthesis of Ti-bearing phases (rutile, weberite, geikielite, bridgmanite etc.) and their solid solutions in the $MgSiO_3$–$MgTiO_3$ system and to study of the conditions of formation, structural peculiarities, and compositional changes of Ti-rich phases. At 10–24 GPa and 1600°C, we studied the full range of the starting compositions 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 analysed using SEM-EDS.

The main phases obtained in experiments were rutile, wadsleyite, $MgSiO_3$-enstatite, $MgTiO_3$-ilmenite, $MgTiSi_2O_7$ with the weberite structure type (*Web*), $Mg(Si,Ti)O_3$ and $MgSiO_3$ with perovskite-type structure. At a pressure of ~13 GPa, an association of *En+Wad+Rt* is replaced by the paragenesis of *Web*+*Wad*+*Rt*, for Ti-poor bulk compositions, With increasing Glk content, *Gkl+Wad+Rt* association is formed. It was found, that the solubility of titanium into synthesized phases is different. Our data indicate an immiscibility with an $MgTiO_3$-rich bridgmanite. Thus, in our experiments at 24 GPa we have two different phases with perovskite-type structure such as $Mg(Si,Ti)O_3$-bridgmanite with up to 60 mol% $MgTiO_3$ and $MgSiO_3$-bridgmanite with a relatively modest solubility of $MgTiO_3$-component (~15 mol%). We observed an increase in MgTiO3 solubility with pressure in bridgmanite.

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 new Ti-bearing bridgmanite-like phase and $MgTiSi_2O_7$ with the weberite structure type 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.

The Al-Ti-bridgmanite was found to be orthorhombic, space group *Pnma*, with lattice parameters a = 14.767(3), b = 6.958(1), c = 4.812(1) Å, V = 494.4(2) Å3, which represents a 3**a** × **b** × **c** superstructure of the typical *Pnma* perovskite structure. The superstructure mainly arises from the ordering of titanium in one of the octahedral positions. Crystal-chemical details of the different polyhedra in the superstructure are discussed in comparison to pure $MgSiO_3$. This is the first documented superstructure of a bridgmanite phase. The study also shows that large amounts of Ti can stabilize bridgmanite-like compounds at considerably lower pressure than lower mantle conditions (Bindi et al., 2017).

$MgTiSi_2O_7$ was found to crystallize with the weberite-3T structure type, space group $P3_121$, with lattice parameters a = 6.3351(7), c = 16.325(2) Å, V = 567.4(1) $Å^3$. The successful synthesis of this phase demonstrates that titanium can stabilize heretofore unknown Mg-Si-oxides, The major Earth and rocky planet-forming materials, and can provide new constraints on thermobarometry of wadsleyite / Ringwoodite, and garnet-bearing assemblages (Bindi et al., 2017).

This study was supported by the Foundation of the President of the Russian Federation (projects no. MK 1277.2017.5 and МД 3464.2017.5 to ES) and by the Russian Foundation for Basic Research (project no. 17-55-50062 to. ES and AB).

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