$Ti_{10}(Si,P)_{6\text{-}7}$ and $Ti_{11}(Si,P)_{10}$, new phases from the Luobusa ophiolite, China: Implications for crystallization of Ti-Si-P melts

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Corundum extracted from chromitite body Cr-11 in the Luobusa ophiolite near Kangjinla (Tibet, China) contains inclusions of super-reduced phases in the Ti-Si-P system, four of which are found in a spheroid 20 μm across, one half of which is composed of $TiSi_2$ enclosing globules of TiP, the other half comprises two ternary phases for which chemical analysis (EDX) yielded compositions $Ti_{10}(Si_{5.4}P_{1.4})$ and $Ti_{11}(Si_{7.5}P_{2.5})$. 3-dimensional electron diffraction collected on the same crystals allowed structure solution and refinement (dynamical) in the hexagonal space group $P6_3/mcm$ with a = 7.30(14) Å c = 5.09(10) Å (Z = 1) and tetragonal $I4/mmm$ with a = 9.4(2) Å, c = 13.5(3) Å (Z = 4), respectively. The hexagonal phase belongs to the same structural type as mavlyanovite (Mn_5Si_3) and the synthetic end-members Ti_5Si_3 and $Ti_5P_{3.15}$, but is unique in being a ternary Ti-Si-P solid solution. Cell parameters, symmetry and structure of the tetragonal phase closely resemble binary and ternary synthetic G-phases, *e.g.*, Grytsiv *et al.*, 2006 [1], although no natural or synthetic G-phase has been reported in the Ti-Si-P system. The spheroid could have been a melt droplet that crystallized with decreasing temperature suggested by liquidi for the Ti-P [2] and Ti-Si [3] binary systems: $Ti_{10}(Si,P)_{6\text{-}7} \rightarrow Ti_{11}(Si,P)_{10} \rightarrow TiSi_2 + TiP$. Such melt droplets were products of the interaction of mantle $CH_4 \pm H_2$ fluids with basaltic magmas in the shallow lithosphere (~30–100 km) [4, 5].

[1] Grytsiv, A. *et al.* (2003) *Intermetallics*, **11**, 351–359. [2] Okamoto, H. (2007) *J. Phase Equilibria Diffusion*, **28**, 587. [3] Fiore, M. *et al.* (2016) *Materials Research*, **19**, 942-953. [4] Griffin *et al.* (2016) *J. Petrology*, **57**, 655–684. [5] Q. Xiong *et al.* (2017) *Eur. J. Mineral*, **29**, 557-570.