

Crystal chemistry and paragenesis of compositionally unique (Al-, Fe-, Nb-, and Zr-rich) titanite from Afrikanda, Russia

ANTON R. CHAKHMOURADIAN*

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

ABSTRACT

Titanite is a common accessory mineral in silicocarbonatite from the Afrikanda alkaline-ultramafic complex, Kola Peninsula, Russia. In addition to large crystals (described elsewhere), this rock contains microscopic crystals and aggregates of titanite intimately associated with, or mantling, primary Ti minerals (perovskite, ilmenite, magnetite, and garnets). The microcrystals commonly exhibit complex zoning patterns that represent a combination of oscillatory, core-rim, and/or sectorial zoning. Eight varieties of microcrystic titanite, differing in chemical composition, mode of occurrence, and style of zoning, can be distinguished. Most of the compositions have >20% of the Ti site occupied by Al, Fe, Nb, Zr, or a combination thereof, whereas substitutions at the Ca site are limited to <2%. Analysis of element correlations and Raman spectra suggests that the compositional diversity of the titanite arises from the following substitutions: $(\text{Al,Fe}^{3+})(\text{OH})\text{Ti}_{1-x}\text{O}_{3-x}$, $(\text{Al,Fe}^{3+})\text{NbTi}_{1-x}$, $\text{Al}(\text{OH})\text{Zr}_{1-x}\text{O}_{3-x}$, and ZrTi_{1-x} . Using the end-member notation, different varieties of the microcrystals contain up to 20 mol% $\text{CaFeSiO}_4(\text{OH})$, 37 mol% $\text{CaAlSiO}_4(\text{OH})$, 35 mol% $\text{Ca}(\text{Al}_{0.5}\text{Nb}_{0.5})\text{SiO}_5$, and 26 mol% CaZrSiO_5 . This compositional diversity is unparalleled by titanite from any other locality or rock type, including material from three other Kola carbonatites examined in the present work (Kovdor, Turiy Mys, and Seblyavr). All compositional varieties of the microcrystic titanite crystallized at late evolutionary stages as products of reaction between the primary Ti minerals and a deuteric aqueous fluid at temperatures near 200 °C, weakly acidic pH, and $a(\text{H}_4\text{SiO}_4) > 10^{-4}$. Under these conditions, the earlier-formed Zr minerals zirconolite and zircon were unstable and underwent extensive re-equilibration with the fluid, involving partial removal of Zr. Implications of these data for the safe disposal of nuclear waste are discussed. The structure of zirconian titanite was examined using a synthetic sample of analogous composition (25 mol% CaZrSiO_5). Its structure was refined by the Rietveld method from X-ray powder diffraction data in space group $A2/a$ [a 7.1119(7), b 8.7724(8), and c 6.6007(6) Å, β 113.569(4)°]. Reflections violating A centering and/or indicative of Ti-Zr ordering were not observed, and attempts to refine the structure in two alternative space groups ($P2_1/a$ and $P2_1$) were unsuccessful.