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Mineral and crystal chemical study of pseudo-*C*2/*m* non-metamict chevkinite-(Ce): An investigation into the intracrystalline distribution of LREE, HREE, and octahedral cations in samples from the Azores and Pakistan

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ABSTRACT

The cation distribution among the A, B, C, and D sites of 13 crystals of chevkinite-(Ce) by X-ray single-crystal diffraction and electron microprobe analyses is reported in this article. The general formula of chevkinite-(Ce) is $A_4BC_2D_2O_8(Si_2O_7)_2$, where A = REE, Ca, Th, Sr; B = Fe, Mn, Mg; C = Fe, Ti, Nb, Zr, Mg, Al; and D = Ti. Ten crystals come from quartz-bearing syenite samples of Agua de Pau (Azores Islands), and three are euhedral chevkinite crystals of a quartz-bearing pegmatite from Tangir Valley, northwestern Pakistan. The real space group for these samples is $P2_1/a$, but the average structure in space group $C2/m$ was used for structural refinement and further interpretation. Cation distribution was determined by minimization of the function $f_{\Sigma N_\sigma^2}$ that represents the sum of the squared numbers of standard deviation by which each expected quantity differs from the calculated one. Both X-ray diffraction and electron microprobe data were considered in minimization. Our results show that the two non-equivalent A sites are occupied dominantly by REE and Ca, distributed mainly as a function of their ionic size. Lanthanum enters only the 10-coordinated A2 site, whereas heavier and smaller REE enter only the 8-coordinated A1. Furthermore, comparison between bond valence sum and formal charge revealed highly stretched bonds for the A1 polyhedron, suggesting that bond lengths are too long for HREE. These findings can help better characterize the well-known ability of chevkinite to fractionate LREE from HREE. The Azores chevkinite is particularly enriched in Nb relative to its host rock. Our results show that Ti occupancy in the D sites can be as low as ca. 50% due to the presence of significant amounts of Nb, besides Fe and Zr. For two Azores crystals showing patchy zoning, a complex history of late-stage crystallization is inferred, with multiple events of Ca and REE enrichments. One of these crystals showed the best structure refinement, implying that late-magmatic to deuteric alteration stages did not affect its crystallinity. The CaO content of Azores chevkinites practically spans the entire chevkinite field in the chevkinite/perrierite CaO vs. FeO discrimination diagram. In addition, we identified possible structural stability limits that can be linked to the occupancy of the B site at high CaO, and of the C sites at high-FeO contents. The Pakistan chevkinites were also analyzed by Mössbauer spectroscopy. Only one Fe^{3+} component was identified, which occupies the C sites. Among the two ferrous doublets, the component with the highest isomeric shift value is Fe^{2+} entering the most distorted crystallographic site B, while the other, representative of a less distorted octahedral site, corresponds to Fe^{2+} entering the D sites.

Keywords: Chevkinite, crystal structure, non-metamict, deuteric alteration, Mössbauer spectroscopy