Mineral and crystal chemical study of pseudo-C2/m non-metamict chevkinite-(Ce): An investigation into the intracrystalline distribution of LREE, HREE, and octahedral cations in samples from the Azores and Pakistan

Susanna Carbonin1,*, Filippo Ridolfi2, Alberto Renzulli3, Elena Belluso4, Luca Nodari5, Federica Liziero1, and Silvana Capella4

1Dipartimento di Geoscienze, University of Padova, Via Gradenigo 6, I-35131 Padova, Italy
2Institut für Mineralogie, Leibniz Universität, Callinstr. 3, D-30167 Hannover, Germany
3Dipartimento di Scienze Pure e Applicate (DiSPeA), University of Urbino, Via Ca’ Le Suore 2-4, I-61029 Urbino, Italy
4Dipartimento di Scienze della Terra, University of Torino, Via Valperga Caluso 35, I-10125 Torino, Italy
5Istituto di Chimica della Materia Condensata e di Tecnologie per l’Energia, Consiglio Nazionale delle Ricerche, (ICMATE-CNR), Corso Stati Uniti 4, I-35127 Padova, Italy

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 A₄BC₂D₂O₇(SiO₄)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 Azores Islands, and three are euclidean chevkinite crystals of a quartz-bearing pegmatite from Tangir Valley, northwestern Pakistan. The real space group for these samples is P2₁/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 \( f_{\text{SQ}} \) 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 Fe²⁺ component was identified, which occupies the C sites. Among the two ferrous doublets, the component with the highest isomeric shift value is Fe²⁺ entering the most distorted crystallographic site B, while the other, representative of a less distorted octahedral site, corresponds to Fe²⁺ entering the D sites.

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

INTRODUCTION

Chevkinite-(Ce), a rare earth elements (REE)-Ti-Fe-rich sorosilicate, is a member of the chevkinite group of minerals (CGM) (Macdonald et al. 2002) with the general formula A₄BC₂D₂O₇(SiO₄)₂, where A = REE, Ca, Th, Sr; B = Fe, Mn, Mg; C = Fe, Ti, Nb, Zr, Mg, Al; and D = Ti. While the A sites, hosting relatively large cations (i.e., REE, Ca, Sr), are at least 7-coordinated by O atoms, the remaining B, C, and D sites all have distorted octahedral coordination, hosting smaller cations. Chevkinite-(Ce) belongs to the chevkinite subgroup, with the other subgroup represented by perrierite with the same general formula but a different structure (Sokolova et al. 2004; Sokolova and Hawthorne 2004; Macdonald et al. 2019).

Macdonald et al. (2019) extensively reviewed the CGM and highlighted their compositional diversity and occurrence in a wide range of crustal, and some extraterrestrial, environments. CGM, when found, inter alia, i.e., as single crystals or as inclusions in early formed minerals of plutonic or subvolcanic