Cation ordering, valence states, and symmetry breaking in the crystal-chemically complex mineral chevkinite-(Ce): X-ray diffraction and photoelectron spectroscopy studies and mechanisms of Nb enrichment

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ABSTRACT

The crystal structures of natural Nb-rich chevkinite-(Ce) from the Biraya rare-metal deposit, Russia, crystallizing in space groups C2/m and P21/a, were solved and refined to Rl = 0.03 and R1 = 0.07, respectively, from data collected with a single-crystal diffractometer. X-ray photoelectron spectroscopy was used to determine the oxidation states of the following ions: Ce3+, Fe2+, Fe3+, Ti4+, and Ti3+. Typically, Nb-rich chevkinite-(Ce) has space group C2/m, but specimens with space group P21/a were also identified. While XPS shows that both C2/m and P21/a crystal structures contain Ti4+ and Ti3+, it also indicates that Ti2+ may occur in the P21/a phases. The general formula for the Nb-rich chevkinite-(Ce) having space group C2/m is (Ce3+,La3+,Nd3+,Pr3+,Ca2+,Na+)×Fe2+(Fe2+,Mg2+,Al3+)×2(Ti4+,Ti3+,Nb5+,Mg2+)×2(Si2O7)×2O8 and with P21/a is (Ce3+,La3+,Nd3+,Pr3+,Ca2+,Na+)×(Fe2+,Mg2+,Ti3+)×1(Ti4+,Ti3+,Nb5+,Al3+)×2(Si2O7)×2O8.

It is proposed that, in addition to the substitution 3Fe3+ + 3Ti4+ ↔ 3Fe2+ + 3Nb5+, niobium can also be incorporated into chevkinite-(Ce) by the substitution 2Ti4+ ↔ Nb5+, Ti3+, leading to substantial Nb-enrichment. The study has revealed that the distribution of cations between the various structural sites is considerably more complex than that envisaged in standard models of the chevkinite group, and that cations such as Ti can have more than one valency in the structure. Lighter elements with larger ionic radii (Mg2+) tend to occupy the D site in the C2/m crystal structure, whereas in the P21/a structure these elements (Mg2+, Ti3+) tend to enter the B site. Niobium is distributed between the C and D sites. The techniques employed provide a comprehensive representation of the distribution of cations and can be used to examine similar complexity in other mineral groups. The present study has shown that Nb can also be fractionated from residual melts.

Keywords: Chevkinite-(Ce), niobium, crystal structure, EPMA, X-ray photoelectron spectroscopy, chevkinite-group minerals, the Biraya deposit, Russia

INTRODUCTION

Chevkinite-group minerals (CGM), comprising 12 species, are accessory phases in a wide range of igneous and metamorphic rocks (Macdonald and Belkin 2002; Vlach and Gualda 2007; Carlier and Lorand 2008; Belkin et al. 2009; Macdonald et al. 2009, 2012). They are challenging to characterize structurally and compositionally, as they display extensive compositional zonation and considerable metamictization (due to Th4+), the latter phenomenon usually involving hydration. In only a few CGM with relatively simple compositions and largely unzoned crystals has it been possible to assign cations to particular sites with some certainty (Popov et al. 2001; Sokolova et al. 2004; Holtstam et al. 2017).

Zoning and metamictization can lead to considerable difficulties in reconciling compositions derived by electron microprobe analysis (EPMA) with those obtained by refinement of site occupancies from single-crystal X-ray diffraction (XRD). This significant problem was discussed in detail by Sokolova et al. (2004) in their study of radiation-damaged chevkinite-(Ce). These authors also showed that thermal annealing of partially metamict chevkinite-(Ce) in air at 1100 °C for 3 h resulted in a considerable improvement in the refined site-scattering values (ssv = electrons per site) that allowed a more meaningful assignment of site occupancies.

In this paper we report the structural characterization of natural Nb-rich chevkinite-(Ce) having space groups C2/m and P21/a from the same hand specimen, with a view to understanding the origin of the C → P structural transition. Both crystals studied are compositionally zoned and partially metamict. Given the reported difficulty in correlating electron microprobe analyses with site-scattering values for such crystals (Sokolova et al. 2004), which was also observed in our study, our main aim was to identify the possible coupled substitution mechanisms responsible for the substantial Nb enrichment of these samples of chevkinite-(Ce).