

## 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  $P2_1/a$ , were solved and refined to  $R_1 = 0.03$  and  $R_1 = 0.07$ , respectively, from data collected with a single-crystal diffractometer. X-ray photoelectron spectroscopy was used to determine the oxidation states of the following ions:  $Ce^{3+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Ti^{4+}$ , and  $Ti^{3+}$ . Typically, Nb-rich chevkinite-(Ce) has space group  $C2/m$ , but specimens with space group  $P2_1/a$  were also identified. While XPS shows that both  $C2/m$  and  $P2_1/a$  crystal structures contain  $Ti^{4+}$  and  $Ti^{3+}$ , it also indicates that  $Ti^{2+}$  may occur in the  $P2_1/a$  phases. The general formula for the Nb-rich chevkinite-(Ce) having space group  $C2/m$  is  $(Ce^{3+}, La^{3+}, Nd^{3+}, Pr^{3+}, Ca^{2+}, Na^+)_{\Sigma 4} Fe^{2+}(Fe^{3+}, Nb^{5+}, Al^{3+})_{\Sigma 2} (Ti^{4+}, Ti^{3+}, Nb^{5+}, Mg^{2+})_{\Sigma 2} (Si_2O_7)_2 O_8$  and with  $P2_1/a$  is  $(Ce^{3+}, La^{3+}, Nd^{3+}, Pr^{3+}, Ca^{2+}, Na^+)_{\Sigma 4} (Fe^{2+}, Mg^{2+}, Ti^{2+})_{\Sigma 1} (Fe^{3+}, Nb^{5+}, Al^{3+})_{\Sigma 2} (Ti^{4+}, Ti^{3+}, Nb^{5+})_{\Sigma 2} (Si_2O_7)_2 O_8$ .

It is proposed that, in addition to the substitution  ${}^CFe^{3+} + {}^DTi^{4+} \leftrightarrow {}^CFe^{2+} + {}^DNb^{5+}$ , niobium can also be incorporated into chevkinite-(Ce) by the substitution  $2{}^DTi^{4+} \leftrightarrow {}^DNb^{5+} + {}^DTi^{3+}$ , 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 ( $Mg^{2+}$ ) tend to occupy the *D* site in the  $C2/m$  crystal structure, whereas in the  $P2_1/a$  structure these elements ( $Mg^{2+}$ ,  $Ti^{2+}$ ) 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