CRYSTAL CHEMISTRY AND STRUCTURE OF NON-METAMICT CHEVKINITE-(Ce)

FEDERICA LIZIERO

Dipartimento di Geoscienze, Università di Padova, Via Giotto 1, I-35137 Padova

Chevkinite-(Ce), a member of the chevkinite group of minerals, is a Ti- and rare earth element (REE)-rich silicate, with general formula $A_4BC_4O_8(Si_2O_7)_2$, in which A = REE, Ca, Th, Sr; B = Fe, Mn, Mg; and C = Ti, Fe, Nb, Mg, Al. The structure consists of two kinds of sheets, one made up of Si_2O_7 groups and B-octahedra, and one of C-octahedra, both parallel to the *ab* plane and alternating along the *c* axis. Rare earth ions lie between the sheets. Chevkinite is often metamict: alpha particles from radioactive decay of constantly present thorium cause damage to the structure, leading to partial or complete amorphization.

Accurate structural studies were carried out on non-metamict chevkinite from Pakistan and the Azores. One sample (Pakistan) was found in a high-temperature pneumatolithic vein from the Tangir valley and two others (AZ1, AZ4) in silica-saturated/over-saturated syenite clasts from São Miguel Island (Azores). Various methods were used to characterize them: single-crystal X-ray diffraction, electron microprobe analyses, Mössbauer spectroscopy, and transmission electron microscopy.

Quantitative chemical analyses gave different REE in A sites and (Zr+Nb) in octahedral sites in the samples from Pakistan and the Azores. The Fe^{3+}/Fe_{tot} ratio was also quite different, being higher in Pakistan (0.43 in average) and lower in the Azores (0.21 in AZ1 and 0.23 in AZ4).

Their average chemical formulae were:

Pakistan: $(Ce_{1.81}La_{0.81}Nd_{0.59}Pr_{0.18}Sm_{0.05}Gd_{0.01}Ca_{0.46}Th_{0.07}Sr_{0.03})_{\Sigma=4.01}$ $(Fe^{2+}_{0.80}Mg_{0.10}Mn_{0.10}Y_{0.01})_{\Sigma=1.01}$ $(Fe^{2+}_{0.35}Fe^{3+}_{0.87}Ti_{2.65}Nb_{0.04}Zr_{0.01}Al_{0.04})_{\Sigma=3.96}$ $Si_{4.02}$ O_{22};

Azores AZ1: $(Ce_{1.71}La_{1.05}Nd_{0.39}Pr_{0.14}Sm_{0.03}Gd_{0.01}Ca_{0.63}Th_{0.04})_{\Sigma=4.00}$ $(Fe^{2+}_{0.86}Mn_{0.09}Y_{0.02}Zr_{0.03})_{\Sigma=1.00}$ $(Fe^{2+}_{0.70}Mg_{0.01}Fe^{3+}_{0.40}Ti_{2.45}Nb_{0.36}Zr_{0.04}Al_{0.02})_{\Sigma=3.98}$ $Si_{4.00}$ O_{22};

Azores AZ4: $(Ce_{1.66}La_{1.00}Nd_{0.40}Pr_{0.13}Sm_{0.03}Gd_{0.02}Ca_{0.74}Th_{0.05})_{\Sigma=4.03}$ $(Fe^{2+}_{0.85}Mg_{0.04}Mn_{0.08}Y_{0.03})_{\Sigma=1.00}$ $(Fe^{2+}_{0.59}Fe^{3+}_{0.42}Ti_{2.55}Nb_{0.30}Zr_{0.10}Al_{0.04})_{\Sigma=4.00}$ $Si_{4.00}$ O_{22}.

Structural refinement was carried out against Fo^2_{hkl} in space group *C*2/*m*. The crystal structure was refined to conventional *R* ($I/\sigma(I) > 4$) of 2%. No chemical constraints were imposed on the refinement. The discrepancy between the electrons calculated from structure refinement and the analogous value calculated from the chemical composition was about 1% or less. The angle and *a* cell parameters were found to be positively correlated with (Ca + Sr) in the A sites.

Mössbauer analysis was carried out at 10 K on 50 mg of Pakistan crystal powder, to determine the oxidation state and coordination number of Fe. The best fit involved two Fe^{2+} and one Fe^{3+}, all in octahedral coordination. The Fe^{3+}/Fe_{tot} ratio was in good agreement with that of the mineral formula calculated from chemical analyses.

The cation distribution in the crystallographic sites of the two types of chevkinites was determined on the basis of the chemical and crystal structure results and also of the Fe^{3+}/Fe_{tot} ratio, if measured by Mössbauer spectroscopy. In order to allocate all the chemical species in sites A, B and C, minimization of an error function was performed. As a result, *i*) Ce and Ca were found to be fairly well distributed between A1 and A2; *ii*) the lightest REE, La, was found only in A2 site; *iii*) the heavier REE, *i.e.*, Pr, Nd,

Sm and Gd, were found together with Th in the same site, A1. In all samples, B site was dominantly occupied by Fe^{2+}. C sites were all disordered. At C1 site, dominant cations were Fe and Ti; in the Pakistan chevkinite Fe is only Fe^{3+}; and in the Azores chevkinites (where the Fe^{3+}/Fe_{tot} ratio was lower than in Pakistan) both Fe^{2+} and Fe^{3+} were present. At C2 sites, in all samples, Ti dominated over other cations with minor Fe^{2+}. The Azores chevkinites were also distinctive for their significant amounts of Zr and Nb: Zr was found ordered in C2A site; Nb mainly disordered between C2A and C2B sites. Distortions in B and C octahedra were examined in the light of cation distribution: B and C sites became less distorted as Fe^{2+} and Ti dominated, respectively, over the other cations.

Bond valence sums (BVS) were determined on the basis of Brown theory.

Good structural refinement results showed no clue to structural damage. Confirmation that the Pakistan and Azores chevkinites are non-metamict came from TEM investigations. Various types of information were obtained from TEM: low- and medium- magnification images, and Selected Area Electron Diffraction (SAED), to examine morphology and sizes and crystallinity degree and defects, to relate morphology with crystallographic directions, and to align crystals along the directions useful for obtaining structural images; and high-resolution TEM images (HRTEM) to evaluate structural characteristics and identify the kinds of local defects, if present. SAED showed the high crystallinity of the chevkinite grains in all samples, confirming that they are non-metamict, and confirmed the C lattice. HRTEM images also showed similar structural regularity. In addition, SAED observed along b axis, i.e., perpendicularly to the stacking direction of the structural layers, did not show streaked spots indicating the regularity of layer alternation.