

Chevkinite-(Ce) from São Miguel, Azores Islands: monitoring the crystal structure from primary crystallization to late-stage hydrothermal events

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Chevkinite-(Ce), a REE-Ti-Fe silicate with general formula $X^{VIII}A_4^{VI}B^{VI}C_2^{VI}D_2Si_4O_{22}$, is an accessory phase in silica-saturated-oversaturated syenite clasts (weakly peralkaline) contained in the plinian pumice fall erupted at 5 ka from the Agua de Pau volcano (Fogo A deposit; São Miguel, Azores Islands) (Ridolfi et al. 2003). Ten crystals from 3 rock-samples were investigated by means of single-crystal X-ray structure refinement, combined with electron microprobe chemical analysis, in order to obtain accurate cation distribution. Previous extensive characterization by means of transmission electron microscopy (TEM) showed these minerals to exhibit high crystallinity and few defects, confirming that they are non-metamict. Azores chevkinite is characterized by significant quantities of HFSE besides the main constituent Ti, namely Nb (4 wt.% Nb₂O₅) and to a lesser extent Zr (1 wt.% ZrO₂). Substitution of REE³⁺ by Ca²⁺ in the A sites is accompanied by substitutions at the octahedral sites for charge compensation: the overall compositional variation is best represented by the relationship (Ca+Ti+Zr) ↔ (REE+Fe²⁺+Nb), thus Nb and Zr are inversely correlated with each other.

Structural refinements were carried out in space group *C2/m* without chemical constraints, taking care to properly select the scattering curves for site occupancy refinement in the A, B, C and D sites. Subsequently, both X-ray diffraction data and microprobe analyses were taken into account to achieve cation distribution by means of the minimization of an error function. The result is that Nb and Zr are found located in the D sites. Niobium site preference for the D sites is corroborated by an earlier prediction of Calvo and Faggiani (1974) who calculated that some pentavalent substitution in the D sites of chevkinite would enhance the chance for its appearance. Moreover, judging from Nb mineral/melt values, São Miguel chevkinite is particularly enriched in Nb relative to its host rock (Ridolfi et al. 2003) as was already noted by MacDonald et al. (2002) for two Kenyan samples. In addition, inspection of Nb content both in the bulk analysis and in chevkinite from the literature, allows us to speculate that chevkinite behaves as a “trash-bin” mineral for this element. With respect to the B site occupancy, Fe is dominant but in the most Ca-Ti-Zr-rich samples small quantities of Ca and Zr reside here. The C sites are mainly occupied by Ti and Fe. The 8- and 10-coordinated A sites, A1 and A2 respectively, are occupied dominantly by REE and Ca, and the cation distribution shows that they are unequally populated, mainly as a function of the ionic size.

In the studied chevkinites, the exchange reactions seem to be more complex than those suggested by Vlach and Gualda (2007 and references therein), i.e. (Ca+Sr)_A+(Ti+Zr)_C ↔ (REE,Y)_A+(M^{3+,2+})_C, which take into account only the A and C sites.

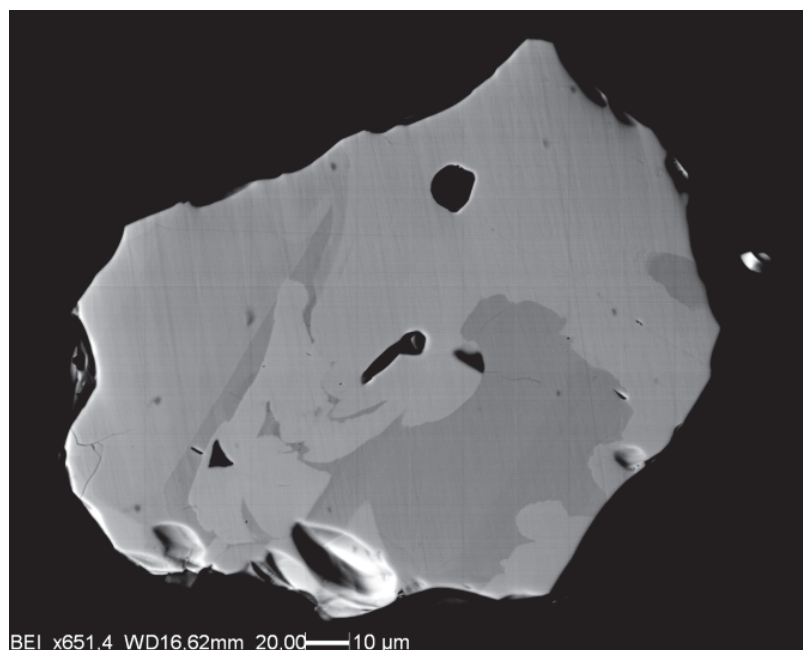


Fig. 1. Back-scattered electrons (BSE) image of one structurally refined zoned crystal; brighter areas are characterized by high REE, Nb and Fe abundances; darker zones are more enriched in Ca, Ti and Zr

In the ten crystals studied, 2 show complex, patchy zoning indicating resorption and recrystallization. Notably, one of them (Fig 1) shows the best structure refinement ($R=0.018$ for 1327 reflections) meaning that recrystallization did not affect its crystallinity. Primary crystallization occurred from peralkaline melts enriched in REE, Nb and Fe; subsequently chevkinite interacted with hydrothermal fluids more enriched in Ca, Ti and Zr. Areas enriched in Ca (and to a lesser extent Ti and Zr) display normal analytical totals from which good-quality mineral formulae can be derived. The charge balance relationship $(Ca+Ti+Zr) \leftrightarrow (REE+Fe^{2+}+Nb)$ is continuous with that of the other crystals studied. The total number of electrons determined from site occupancy refinement in the A, B, C and D sites is in good agreement with that derived from chemical composition averaged between the REE- and the Ca-rich areas. Chevkinite, that evolved in such a way from REE-rich to Ca-rich compositions, should have recorded a late stage deuteric alteration resulting from a closed-system, magmatic-hydrothermal stage of crystallization, rather than metasomatic contributions.

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References:

- Calvo C, Faggiani R (1974) A Re-investigation of the Crystal Structures of Chevkinite and Perrierite. *Am Mineral* 59:1277-1285
- Macdonald R, Marshall AS, Dawson JB, Hinton RW, Hill PG (2002) Chevkinite-group minerals from salic volcanic rocks of the East African Rift. *Miner Mag* 66(2):287-299
- Ridolfi F, Renzulli A, Santi P, Upton BGJ (2003) Evolutionary stages of crystallization of weakly peralkaline syenites: evidence from ejecta in the plinian deposits of Agua de Pau volcano (São Miguel, Azores Islands). *Miner Mag* 67(4):749-767
- Vlach SRF, Gualda GAR (2007) Allanite and chevkinite in A-type granites and syenites of the Graciosa Province, Southern Brazil. *Lithos* 97:98-121