

CHEMICAL CHARACTERISATION AND XRD STUDY OF ZIRCONOLITE FROM HÅKESTAD ALKALINE PEGMATITE, LARVIK PLUTONIC COMPLEX, SOUTH NORWAY

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Zirconolite, ideally $\text{CaZrTi}_2\text{O}_7$, is a mineral that has been in focus in the past several decades due to its property to incorporate large amounts of actinides and lanthanides into its structure and due to its long-term chemical durability in the geological environment. Because of these properties, the doped synthetic phase analogous to zirconolite is one of the ingredients of SYNROC ceramics designed for the immobilization of the components of high-level nuclear waste. Depending on the content of radioactive elements and the geological age, zirconolite often undergo metamictization, transition from crystalline to partially or completely amorphous state. In the previous works, minerals with composition close to $\text{CaZrTi}_2\text{O}_7$ were called zirconolite, polymignite or zirkelite. Currently such polytypoids with fluorite type structure should be called zirconolite-2M, -3T or -3O depending on their symmetry. Zirkelite should be the cubic mineral with formula $(\text{Ti,Ca,Zr})\text{O}_{2-x}$. However, the relationship between zirconolite polytypoids and zirkelite is not well understood yet.

We examined zirconolite from alkaline pegmatite in Håkestad quarry, Larvik plutonic complex in Norway. Zirconolite there forms euhedral black lathy crystals about 3 cm long with striated prismatic and pinacoidal faces. Associating minerals are mainly albite, K-feldspar, biotite, magnetite, britholite, zircon, pyrochlore, and nepheline. EPMA analysis gives analytical totals of 95.2 to 96.35 wt% for fresh parts. Mineral formula and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was calculated on the basis of 4 cations and 7 anions, so in result near all the Fe seems to be in the ferrous form (about 7.3–7.8 wt% FeO against 0–0.9 wt% Fe_2O_3). The zirconolite is enriched in Y+REE, Nb, Ta and Fe and the resulting formula is as follows: $(\text{Ca}_{0.53-0.55}\text{REE}^{3+}_{0.33-0.35}\text{Th}_{0.07-0.08}\text{U}_{0.02-0.03})(\text{Zr}_{0.93-0.98})(\text{Ti}_{1.06-1.13}\text{Nb}_{0.35-0.40}\text{Ta}_{0.02}\text{Me}^{2+}_{0.47-0.52}\text{Me}^{3+}_{0.01-0.07})(\text{O}_{6.94-6.95}\text{F}_{0.05-0.13})$, where REE^{3+} includes Ce, Nd, Y, La dominating over Pr, Sm, Gd, Dy, Er, Yb; Me^{2+} includes most of Fe dominating over Mn, Mg and Me^{3+} includes small amounts of Fe^{3+} and Al. The reliable determination of the substitution vectors is complicated by very homogenous chemical composition, but the positive correlation of the Me^{2+} vs. Me^{3+} , Me^{2+} vs. REE^{3+} and Me^{3+} vs. REE could indicate substitution involving $\text{REEZrMe}^{5+}\text{Me}^{2+}\text{O}_7$ end-member. Zirconolite significantly enriched in $\text{REEZrMe}^{5+}\text{Me}^{2+}\text{O}_7$ molecule is described by DELLA VENTURA *et al.* (2000).

Some narrow zones along the rim or the cracks within the crystal were altered by penetrating

hydrothermal fluid that significantly affected the chemical composition of these zones. The most distinct changes are the enrichment of SiO_2 (from nearly Si-free fresh parts increased to about 5–6 wt% SiO_2 in altered region), Al_2O_3 (increased from 0.14 to 0.27 wt%), WO_3 (increased from nearly W-free to 0.3–0.4 wt%), F (increased from 0.3 to 0.5 wt%) and the content of actinides and lanthanides is also relatively slightly higher in altered parts. The hydration of the mineral is also probable. On the other hand there is a great loss of Fe (decreased from about 7.6 wt% FeO to about 1 wt%), quite distinct loss of Ca (decreased from 7 to 4 wt% CaO), Ti (decreased from 20.5 to 18 wt% TiO_2), Zr (decreased from 28 to 26.5 wt% ZrO_2), and lower disparities in Pb, Mg and Mn content. This behaviour during alteration is in agreement with published data (BULAKH *et al.*, 1998). The content of U, Th and Y+REE seems not to be significantly affected by the alteration.

The radiation dose the mineral have suffered calculated from the contents of ThO_2 and UO_2 assuming the geological age to be 295 Ma is about 2.0 to $2.8 \cdot 10^{16}$ α decays per mg, which is one order more than the transition from crystalline to metamict zirconolite is usually occurred (LUMPKIN *et al.*, 1997, 1998). XRD study confirms its metamict state. The annealing of the zirconolite powder under an inert atmosphere to 800°C caused recrystallization to a phase with the cubic space group $Fm\bar{3}m$ and with the cell parameter $a_0 = 5.104(3)$ Å that is close to the cubic ZrO_2 , tazheranite, $(\text{CaTiZr}_2\text{O}_8)$ or zirkelite. This result is very similar to that which was gained by BULAKH *et al.* (1998), but their specimen was described as zirkelite because of its cubic morphology. During heating to 900°C another unidentified phase appeared.

References

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