

Zirconolite from Larvik Plutonic Complex, Norway, its relationship to stefanweissite and nöggerathite, and contribution to the improvement of zirconolite end-member systematics

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ABSTRACT

The very first description of zirconolite, originally called polymignyte, discovered in alkaline pegmatites within the Larvik Plutonic Complex (LPC), Norway, was published almost 200 yr ago. We studied zirconolite from three occurrences located in this region using modern techniques—X-ray powder diffraction (XRPD) upon thermal annealing of initially radiation-damaged mineral, electron probe microanalysis, and Mössbauer spectroscopy. The initial XRPD pattern lacked any sharp diffraction maxima, as the accumulated radiation dose exceeded a critical value of ca. 10^{16} α -decays/mg. Annealing at 400–800 °C induced recrystallization to a transitional, cubic phase interpreted to have a disordered, defect fluorite structure [space group $Fm\bar{3}m$; unit-cell parameters: $a = 5.1047(4)$ Å, $V = 133.02(2)$ Å³], with its XRPD pattern being very similar to that of cubic ZrO₂. Rietveld analysis of the XRPD pattern obtained after a phase transition at 900 °C shows a mixture of -3O [wt. fraction of ca. 60%, space group $Cmca$, unit-cell parameters: $a = 7.2664(8)$ Å, $b = 14.1877(15)$ Å, $c = 10.1472(12)$ Å, $V = 1046.1(2)$ Å³], and -3T [wt. fraction of ca. 40%, space group $P3_121$, unit-cell parameters: $a = 7.2766(6)$ Å, $c = 17.0627(15)$ Å, $V = 752.42(11)$ Å³] zirconolite polytypes. However, the crystal habits of zirconolite from the LPC show a distinct orthorhombic symmetry. Although their chemical compositions are far from the ideal zirconolite composition and a large number of elements are involved in high concentrations [up to ca. 17 wt% REE₂O₃, ≤ 7 wt% ACTO₂, ≤ 18 wt% Me⁵⁺O₅, ≤ 9 wt% Me²⁺O + Me₂³⁺O₃, Fe³⁺/(Fe³⁺+Fe²⁺) ≈ 0.2 , where ACT = Th + U, Me⁵⁺ = Nb \pm Ta, Me²⁺ = Fe²⁺ \pm Mg, Me³⁺ \approx Fe³⁺], the compositional variability is relatively limited. To quantitatively describe the two distinct compositional trends observed, we introduced a concept called “edgemembers,” so that mixing is approximated to occur between two terminal compositions situated at two edges of the zirconolite composition space. These marginal compositions were determined from observed compositional trends, i.e., heterovalent substitution of Me⁵⁺ for Ti in octahedral sites and ACT enrichment associated with increasing Ti/Me⁵⁺ ratio. This approach provides general substitution vectors for both, Håkestad-type mode (ACT + 3 Ti + Me³⁺ = Ca + 3 Me⁵⁺ + Me²⁺), and Ståmaker-type mode (0.7 ACT + 0.5 REE + 0.9 Ti + 0.7 Me³⁺ + 0.05 Zr = 1.2 Ca + 1.3 Me⁵⁺ + 0.3 Me²⁺ + 0.05 Mn). In terms of chemical composition, the studied zirconolite corresponds to recently approved zirconolite-related minerals stefanweissite (for Ca > REE) and nöggerathite (for REE > Ca). Based on a careful analysis of zirconolite composition space, we show that our observed Håkestad-type compositional trend, as well as a high number of published zirconolite compositions worldwide (with Me²⁺ + Me³⁺ sum of ca. 1 atom per 14 O), can be well approximated by a modified end-member set comprising Ca₂Zr₂Me₂⁵⁺TiMe²⁺O₁₄, REE₂Zr₂Ti₃Me²⁺O₁₄, CaACTZr₂Ti₃Me²⁺O₁₄, CaREEZr₂Ti₃Me³⁺O₁₄, and Ca₂Zr₂Ti₂Me⁵⁺Me³⁺O₁₄ without a need to involve the ideal zirconolite formula Ca₂Zr₂Ti₄O₁₄. The redefined composition space constrained by end-members from this set, together with ideal zirconolite, may be representative of the vast majority of more than 450 published zirconolite compositions worldwide with Me²⁺ + Me³⁺ totaling ≤ 1 atom per 14 O. The equation $X_{Me^{3+}} = 2 - 2X_{REE^*} - 3X_{Me^{5+}}$ provides an independent calculation of iron oxidation state or $X_{Me^{3+}} = Me^{3+}/(Me^{2+} + Me^{3+})$ for this remarkable group of zirconolites, where X_{REE^*} is derived from $X_{REE} = REE/(REE + Ca)$ and $X_{Me^{5+}}$ from $X_{Me^{5+}} = Me^{5+}/(Me^{5+} + Ti)$. Understanding the oxidation state of iron in zirconolite may be helpful to characterize redox conditions during its crystallization.

Keywords: Zirconolite, stefanweissite, nöggerathite, polymignyte, Larvik Plutonic Complex, metamict, end-member, composition space, substitution, Rietveld refinement