

Site distribution of Fe²⁺ and Fe³⁺ in the axinite mineral group: New crystal-chemical formula

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ABSTRACT

A set of nine samples of axinite, selected from 60 specimens from worldwide localities, were investigated by single-crystal X-ray diffraction, electron and ion microprobe, and ⁵⁷Fe Mössbauer spectroscopy. The selected samples cover the compositional join from almost pure ferroaxinite (80%) to pure manganaxinite (95%). A new crystal-chemical formula for the axinite mineral group is proposed: $^{VI}[X1 X2 Y Z1 Z2]_2^{IV}[T1 T2 T3 T4 T5]_2O_{30}(O_wOH_{1-w})_2$, where VI and IV are coordination numbers; X1 = Ca and very minor Na; X2 = Ca (in axinites) or Mn (in tinzenite); Y = Mn (in manganaxinite and tinzenite), Fe²⁺ (in ferroaxinite) or Mg (in magnesioaxinite), with minor Al and Fe³⁺; Z1 = Al and Fe³⁺; Z2 = Al; T1, T2, and T3 = Si; T4 = Si (and presumably very minor B); T5 = B and minor Si. Charge unbalance (*w*), due to heterovalent substitutions, is compensated for by O²⁻ → OH⁻ substitution.

From ferroaxinite to manganaxinite, cell volume increases linearly from 568.70 to 573.60 Å³. This is mainly due to an increase in the <Y-O> mean distance from 2.220 to 2.255 Å, which is directly related to the Mn population (up to 1.89 apfu). Fe³⁺ concentrations, as determined by ⁵⁷Fe Mössbauer spectra at 80 K, sub-regularly increase up to 0.27 apfu, and three cases are evidenced: (1) Fe³⁺ << Fe²⁺ (or no Fe³⁺), in ferroaxinite; (2) Fe³⁺ < Fe²⁺, in intermediate compositions, and (3) Fe³⁺ > Fe²⁺ (or only Fe³⁺), in manganaxinite.

Chemical and structural data were co-processed via a computer minimization program to obtain the cation distribution scheme. Adopting the Hard-Sphere Model, empirical cation-oxygen distances were refined for every cation in the axinite structure. The results revealed that Fe²⁺ is ordered at the octahedral Y site (up to 1.61 apfu), whereas Fe³⁺ is ordered at the octahedral Z1 site (up to 0.26 apfu) and is almost absent in the smallest Z2 site, which is fully populated by Al. The observed Fe³⁺ partitioning is in agreement with the structural results, which show that the Z1 octahedron is always larger than Z2. Moreover, no Fe³⁺ is found at the tetrahedral sites, but Si → B substitution occurs at T5. The continuous Y dimensional increase from ferroaxinite to manganaxinite involves progressive enlargement of the edge-sharing Z1 octahedron. As a consequence, the ^{Z1}Fe³⁺ → ^{Z1}Al³⁺ substitution is structurally favored toward manganaxinite and points to a new end-member with the suggested name “ferri-manganaxinite.”