

## Crystal chemistry of the axinite-group minerals: A multi-analytical approach

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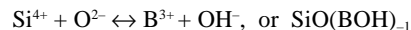
### ABSTRACT

Sixty axinite samples from 24 localities worldwide were characterized by electron microprobe analysis (EMPA) to define the limits of compositional variation. Three samples are very close to the Mn, Fe, and Mg end-members. Ternary (Mn,Fe<sup>2+</sup>,Mg)-compositions occur mostly in the ferroaxinite and manganaxinite fields, and are constrained by the relation  $Mg \leq Fe$ . Core-rim chemical zoning was observed in 20 samples, with systematic enrichment of Fe in the core and Mn in the rim, independent of sample provenance.

The chemical composition (including B, H, and Fe<sup>2+</sup>/Fe<sup>3+</sup>) of 17 homogeneous samples was investigated using electron-microprobe analysis, thermo-gravimetry (TG), ion microprobe (SIMS), crystal-structure refinement (SREF), and Mössbauer spectroscopy (MS). For all samples except pure manganaxinite, most of the iron is Fe<sup>2+</sup>. The content of Fe<sup>3+</sup> and the Fe<sup>3+</sup>/ΣFe ratio increase with Mn content up to 0.31 atoms per formula unit (apfu) and 0.80, respectively. Fe<sup>3+</sup> may substitute for Al or also for divalent cations balanced by the OH deficiency:

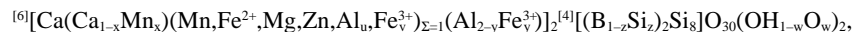


Boron content ranges from 1.88 to 2.07 apfu ( $\pm 2.5\%$  relative) and shows an inverse relation with Si content. Direct measurement of the B-tetrahedron size provides structural confirmation of the Si  $\leftrightarrow$  B exchange. Hydroxyl deficiency accompanies this substitution and the following coupled mechanism is proposed:



Hydrogen content ranges from 1.7 to 2.1 apfu ( $\pm 5\%$  relative). The deficiency of OH from the stoichiometric value of 2.0 per formula unit is related directly to the number of trivalent and tetravalent cations, as OH content plays a crucial role in charge-balance relations.

A revised *chemical* formula for the axinite-group minerals is proposed:



where  $x \leq 1$ ,  $u < 1$ ,  $v < 1$ ,  $y < 1$ ,  $z \ll 1$ , and  $w = (u + v + z)$ .