

## Thermoelasticity, cation exchange, and deprotonation in Fe-rich holmquistite: Toward a crystal-chemical model for the high-temperature behavior of orthorhombic amphiboles

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### ABSTRACT

The thermoelastic behavior of a crystal of Fe-rich holmquistite with crystal-chemical formula  ${}^A(\text{K}_{0.01}\text{Na}_{0.01}){}^B(\text{Li}_{1.88}\text{Mg}_{0.10}\text{Na}_{0.02}){}^C(\text{Mg}_{1.68}\text{Fe}_{1.42}\text{Mn}_{0.02}^{2+}\text{Al}_{1.88}){}^T\text{Si}_{8.00}\text{O}_{22}{}^W[(\text{OH})_{1.97}\text{F}_{0.03}]$  was studied by single-crystal X-ray diffraction at temperatures up to 1023 K, where isothermal annealing in air for 160 h yielded the loss of 0.85 H apfu coupled with oxidation of  ${}^M\text{Fe}$ . A complex pattern of cation exchanges was deciphered by comparing structure refinements done before and after annealing. Li migration from the *M4* to *M3* site is responsible for nonlinearity of the *c* parameter around 600 K during the first annealing. Cooling of the partially deprotonated crystal to room temperature (RT) showed discontinuities in trends of the *b* and *c* parameters around 820–800 K, which cannot be ascribed to a phase transition and can be explained by a rearrangement of the structural units affecting the geometry of the *M4* polyhedron. Such discontinuities have never been observed in amphiboles before and must be related to dimensional constraints deriving from the peculiar composition of this amphibole, which contains the smallest possible homovalent constituents, i.e.,  ${}^B\text{Li}$ ,  ${}^C\text{Al}$ , and  ${}^T\text{Si}$ . The calculated thermoelastic parameters are: Fe-rich holmquistite:  $\alpha_a = 1.36(2) \times 10^{-5}$ ;  $\alpha_b = 0.55(1) \times 10^{-5}$ ;  $\alpha_c = 1.5(1) \times 10^{-5} - 6.7(9) \times 10^{-9}$ ;  $\alpha_V = 3.5(3) \times 10^{-5} - 0.8(3) \times 10^{-8}$  (polynomial);  $2.58(6) \times 10^{-5}$  (linear); partially deprotonated Fe-rich holmquistite:  $\alpha_a = 1.324(9) \times 10^{-5}$  (RT–1023 K);  $\alpha_b = 0.60(1) \times 10^{-5}$  (RT–773 K);  $\alpha_c = 0.68(2) \times 10^{-5}$  (RT–773 K);  $\alpha_V = 2.59(2) \times 10^{-5}$  (RT–773 K). Fe-rich holmquistite is much stiffer than all the previously studied orthorhombic *Pnma* and *Pnmm* amphiboles. The results of this work allow progress toward a general model that may explain how the amphibole structure responds to non-ambient conditions, and allows the release of water in diverse geological environments.

**Keywords:** Amphibole, holmquistite, HT behavior, thermoelasticity, deprotonation, structure refinement