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The crystal-chemistry of holmquistites: Ferroholmquistite from Greenbushes (Western Australia) and hints for compositional constraints in ^{B}Li amphiboles

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ABSTRACT

A systematic crystal-chemical investigation of orthorhombic holmquistites has been done to determine the reasons for their limited compositional variations. Structural constraints to the relative stability of ^{B}Li amphiboles are also suggested by the occurrence of ferro- and ferri-ferroclinoholmquistites, and the lack of clinoholmquistite. Detailed crystal-chemical analysis shows: (1) a remarkable constancy in composition, both in terms of charge arrangement and of limited homovalent $^{M1,3}(Mg_{-1}Fe^{2+})$, $^{M2}(Al_{-1}Fe^{3+})$, and $^{O3}(OH_{-1}F)$ exchanges, (2) a remarkable constancy in the unit-cell dimensions, with the Fe^{3+} content at the M2 site being the only factor affecting the *b* edge; (3) complete ordering of Li at the M4 site, in contrast with the common partitioning between the M4 and M3 sites in clinoamphiboles, which however couples with partial A-site occupancy; (4) complete ordering of trivalent cations at the M2 site; (5) an inverse relationship between the Fe^{2+} and the Fe^{3+} contents, which is interpreted as a way to keep the size of the octahedral strip constant; (6) a strong distortion of the octahedral sites, both in terms of angular variance and quadratic elongation.

$^{A}\square^{B}Li_2{}^{C}(Mg_3Al_2)^{T}Si_8O_{22}(OH)_2$ is the amphibole composition composed of the smallest possible structural moduli. Crystallization in *Pnma* symmetry, where the two double-chains of tetrahedra can assume different conformations, is probably required by the need to obtain a more suitable [5 + 1]-coordination for ^{B}Li, and to shrink the cation-cation distances. This arrangement does not allow for extensive incorporation of larger homovalent substituents, which are hosted via mechanisms implying distortion of the octahedral sites.

During this work, a sample with Fe^{2+} slightly but significantly higher than Mg was characterized, and then recognized as a mineral species by the IMA-CNMMN (2004-030). Holotype ferroholmquistite has $a = 18.287$ (1), $b = 17.680$ (1), and $c = 5.278$ (1) Å, and $V = 1706.6(1)$ Å^3. Its crystal-chemical formula is $^{A}K_{0.01}Na_{0.01}{}^{B}(Li_{1.88}Mg_{0.08}Na_{0.03}Fe^{2+}_{0.01})^{C}(Al_{1.89}Fe^{2+}_{1.70}Mg_{1.39}Mn^{2+}_{0.02})^{T}Si_{8.00}O_{22}(OH_{1.97}F_{0.03})$. Ferroholmquistite occurs as elongated black to bluish-violet prismatic crystals; it is biaxial negative, with $\alpha = 1.628$, $\beta = 1.646$, and $\gamma = 1.651$ ($\lambda = 589$ nm), $2V_x$ (calc.) = 55.1°. It is weakly pleochroic, with α = colorless, β = pale violet-blue, and γ = blue to deep violet; the calculated density is 3.145 g/cm^3. The holotype specimen belongs to the mineral collection of Renato and Adriana Pagano (Italy), and comes from the Greenbushes pegmatite (Western Australia). The analyzed sample has been deposited at the Museum of the Dipartimento di Scienze della Terra, Università di Pavia (Italy) under the code 2004-01.