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Clintonite-1*M*: Crystal chemistry and its relationships to closely associated Al-rich phlogopite

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Abstract

Crystal-structure refinements were performed on clintonite-1*M* crystals [ideal composition $^{[6]}Ca^{[6]}(Mg_2Al)^{[4]}(SiAl_3)O_{10}(OH)_2$] from skarns of the Predazzo-Monzoni area and Adamello Massif (northern Italy) with the aim of characterizing some aspects of their crystal chemistry and their relationships with closely associated phlogopite-1*M*. In the clintonite samples examined, the tetrahedral composition ranges from $Si_{1.19}Al_{2.78}Fe_{0.03}$ to $Si_{1.28}Al_{2.70}Fe_{0.02}$, indicating that the extent of the exchange vector $^{[4]}Al_{-1}{}^{[6]}Mg_{-2}{}^{[4]}Si^{[6]}(Al,\square)$, which links trioctahedral with dioctahedral Ca-bearing brittle micas, was very limited. Single-crystal X-ray diffraction data were collected and structure refinements completed in space group *C2/m* converging to R_{obs} from 0.027 to 0.037 for six samples. The $^{[4]}Al^{3+}$ for $^{[4]}Si^{4+}$ substitution, which is close to 70%, produces more regular and flatter tetrahedra than in the case of phlogopite, together with an increase in the thickness and in the lateral dimensions of the sheet; the presence of Al^{3+} in octahedral coordination, on the other hand, reduces the dimensions of both M1 and M2 sites with a consequent decrease in the thickness of the sheet. The volume, the flattening angle Ψ, and the central cation off-center shift (BLD) of the trans M1 octahedral site are greater than those of the cis M2 site, thus indicating a normal octahedral ordering. The high misfit value (from 1.187 to 1.326 Å) between tetrahedral and octahedral sheets is mostly compensated by the distortion of the tetrahedral ring (tetrahedral rotation angle α: $23.1 \leq \alpha \leq 24.9°$). Relative to phlogopite, the interlayer separation in clintonite is reduced by about 0.6 Å.