NEW STRUCTUTRAL DATA ON BELGIAN ARDENNITES

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Ardennite is a Mn-rich silicate mineral which contains arsenate and/or vanadate groups. This mineral was first discovered in a quartz vein in Salmchâteau (Ardennes, Belgium), in association with apatite and albite. The two mineral species, ardennite-(As) and ardennite-(V), are occurring in highly oxidized and manganiferous metasediments that were affected by low- to high-grade metamorphism (1).

The general formula of ardennite may be written as $A_4M_6T_6O_{22}(OH)_6$. The large *A* sites mainly contain Mn^{2+} and smaller amount of Ca^{2+} and Mg^{2+}, the octahedral *M* sites can host Al^{3+}, Fe^{3+}, Mn^{3+}, Mg^{2+} and other minor six-fold coordinated cations, and the tetrahedral *T* sites can host S^{i4+}, As^{5+}, V^{5+}, and P^{5+} (1). The mineral is orthorhombic, with space group *Pnnm*, and $a \approx 8.8$ Å, $b \approx 5.8$ Å, $c \approx 18.6$ Å (2).

Single-crystal X-ray diffraction measurements were performed on three new occurrences of Belgian ardennites, from Bihain, Thier del Preu, and Regné, respectively. Structure refinements were performed to R_1 = 2.16-5.1%, in the *Pmmn* space group, with a = 5.7981(0)-5.8035 Å, b = 18.4670(7)-18.4792(2) Å, c = 8.6888(3)-8.6959(5) Å, V = 930.58(6)- 932.59(11) Å^3, Z = 2. The crystal structure of ardennite is formed by chains of edge-sharing [MO_6] octahedra running along the *a* axis and connected by [TO_4] and [T_3O_{10}] groups. The large *A* cations occur in the cavities of the structure in six- and seven-fold coordination polyhedra. In the asymmetric unit of the ardennite structure, occur four independent *T* sites, three *M* sites and two larger *A* sites. *T*1, *T*2 and *T*3 are occupied by Si^{4+} while the *T*4 site hosts As^{5+}. Samples from Bihain and Regné present lower refined occupancies in this site (0.81, 0.85), thus indicating a substitution towards ardennite-(V). The *A* sites are occupied by Mn^{2+}, the charge balance is then compensated by a coupled substitution ($T^{4+} + M^{3+} \leftrightarrow T^{5+} + M^{2+}$) in the *M*3 site, which mainly contains Mg^{2+}. The knowledge of the cation distributions in these three new occurrences, combined with chemical data, will help us to better understand the crystal chemistry of the complex ardennite group.

References:

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