

## Crystal chemistry of Belgian ardennites

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*Ardennite* is a rare Mn-rich aluminium silicate originally found in Salmchâteau, Stavelot Massif, Belgium, during the second half of the 19<sup>th</sup> Century. Samples were simultaneously investigated by A. von Lasaulx and F. Pisani leading to some controversies between the two scientists as they initially considered the mineral as vanadium-bearing [1-3], and then as arsenic-rich [4]. Nowadays, two distinct species were defined: ardennite-(As) with the ideal formula  $Mn^{2+}_4Al_4(AlMg)(AsO_4)(SiO_4)_2(Si_3O_{10})(OH)_6$  and with type-locality Salmchâteau (Belgium), and ardennite-(V) with the ideal formula  $Mn^{2+}_4Al_4(AlMg)(VO_4)(SiO_4)_2(Si_3O_{10})(OH)_6$  and with type-locality Sparone (Piedmont, Italy [5]). During the past years, new occurrences of *ardennite* were discovered in the southern part of the Stavelot Massif, initiating the crystal-chemical investigation of eleven Belgian *ardennite* samples originated from various localities or mineralogical and petrographic associations.

Chemical compositions obtained from electron-microprobe analyses are in good agreement with single-crystal structure refinements. The  $As^{5+} \leftrightarrow V^{5+}$  homovalent substitution on the *T4* tetrahedral site explains the existence of a complete solid solution between ardennite-(As) and ardennite-(V), while the incorporation of  $Si^{4+}$  and  $P^{5+}$  seems to be more restricted. Solid solutions towards the potential new species "ardennite-(P)" and "ardennite-(Si)" therefore appear to be relatively limited although some samples show significant enrichments, with up to 0.28  $P^{5+}$  atoms per formula unit (apfu) and 0.74  $Si^{4+}$  apfu. An heterovalent substitution mechanism involving the *T4* and *M3* sites,  $T^4Si^{4+} + M^3(Al, Fe)^{3+} \leftrightarrow T^4(As, V, P)^{5+} + M^3Mg^{2+}$ , also clearly occurs. Due to the various multiplicities of the *M3* and *T4* sites, 4 and 2 respectively, a valency-imposed double-site occupancy on *M3* is necessary to preserve charge-balance [6] in the ideal end-member formulae of ardennite-group minerals. Only a few satisfactory trends were observed between the chemical composition and the structural parameters of ardennites, probably due to an overall adjustment of the unit-cell. The unit-cell parameters tend to increase with the (Ca + Mg + Fe) contents of ardennites and a negative correlation has been observed between the bond length distortion coefficients on the *M3* and *T4* sites, that seems to be controlled by the position of the oxygen shared by both sites. Discussions concerning the nomenclature of the ardennite group are also presented.

### References:

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