Crystal chemistry of the divalent cation in the alluaudite structure, Frédéric Hatert and Mélanie Rondeux, *Laboratory of Mineralogy B.18, University of Liège, B-4000 Liège, Belgium*. E-mail: fhatert@ulg.ac.be

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Alluaudite is a Na-, Mn-, Fe-bearing phosphate mineral, which is known to occur in granitic pegmatites. Moore [1] determined the crystal structure of alluaudite in the *C*2/*c* space group and derived the general structural formula, $X(2)X(1)M(1)M(2)_2(PO_4)_3$, with $Z = 4$. Recently, Hatert *et al*. [2] proposed a new structural formula for alluaudite, which takes into account the presence of new crystallographic sites in the channels of the structure: $[A(2)A(2)'][A(1)A(1)'A(1)''_2]M(1)M(2)_2(PO_4)_3$.

In natural alluaudites, divalent cations are localized in the A(1) (Mn, Ca), M(1) (Mn, Fe^{2+}), and M(2) (Fe^{2+}, Mn, Mg) crystallographic sites [3]. The exotic cations Cd and Co^{2+} have also been inserted experimentally in the alluaudite-type compounds $Na_2Cd_2M^{3+}(PO_4)_3$ (M^{3+} = Fe^{3+}, Ga, Cr) [4] and $M^+Co^{2+}_3(PO_4)(HPO_4)_2$ (M^+ = Ag, Na) [5] [6].

Since alluaudite is a key mineral in the genetic evolution affecting the Fe-Mn-bearing phosphates, it is of interest to investigate the crystal chemistry of the divalent cation in the alluaudite structure. With this goal in mind, we decided to study the $Na_{1.5}(Mn_{1-x}M^{2+}_x)_{1.5}Fe^{3+}_{1.5}(PO_4)_3$ (M^{2+} = Cd, Zn) and $Na_2(Mn_{1-x}M^{2+}_x)Fe^{2+}Fe^{3+}(PO_4)_3$ (M^{2+} = Ca, Cd, Ni, Zn, Mg) solid solutions of alluaudite-type compounds.

The phosphates of the $Na_{1.5}(Mn_{1-x}M^{2+}_x)_{1.5}Fe^{3+}_{1.5}(PO_4)_3$ solid solutions were synthesized by solid state reactions in air, between 800 and 900°C. The X-ray powder diffraction patterns confirm the presence of pure alluaudite-type compounds for x = 0 to 1. The phosphates of $Na_2(Mn_{1-x}M^{2+}_x)Fe^{2+}Fe^{3+}(PO_4)_3$ solid solutions were synthesized hydrothermally between 400 and 600°C at 1 kbar, using horizontally arranged Tuttle-type cold-seal bombs. For x = 1, the X-ray powder diffraction patterns indicate that the Cd-bearing sample is constituted by pure alluaudite, whereas the Ca-, Ni-, Zn-, and Mg-bearing compounds contain small amounts of impurities.

The Rietveld refinements of the X-ray powder diffraction patterns of $Na_{1.5}(Mn_{1-x}M^{2+}_x)_{1.5}Fe^{3+}_{1.5}(PO_4)_3$ show that Zn is localized in the M(1) and M(2) sites, whereas Cd occurs in the A(1), M(1) and M(2) sites. This feature probably results from the large ionic radius of Cd^{2+} (0.95 Å), compared to that of Zn^{2+} (0.740 Å) [7]. Several correlations have also been established between the variations of unit-cell parameters and the variations of bond distances.

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