s5.m15.o3 **Crystal Chemistry of The Divalent Cation in the Alluaudite Structure.** Frédéric Hatert and Mélanie Rondeux, *Laboratory of Mineralogy B.18, University of Liege, B-4000 Liege, Belgium. E-mail: fhatert@ulg.ac.be*

Keywords: alluaudite; phosphate; divalent cation

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 $C2/c$ 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$.
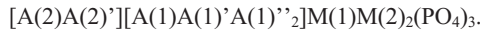
In natural alluaudites, divalent cations are localized in the A(1) (Mn, Ca), M(1) (Mn, Fe^{2+}), and M(2) ($Fe2+$, Mn, Mg) crystallographic sites [3]. The exotic cations Cd and Co^{2+} have also been inserted experimentally in the alluaudite-type compounds $Na_2Cd_2M^{3+}(PO_4)_3$ (M^{3+} = Fe^{3+}, 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 $Na_2(Mn_{1-x}M^{2+}x)Fe^{2+}Fe3+(PO_4)_3$ (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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s5.m15.o4 **Anti-Loewenstein Behaviour in the Melilite and Sodalite Structure Types.** Depmeier, W. & Peters, L., *Institut für Geowissenschaften, Universität Kiel, Germany. E-mail: wd@min.uni-kiel.de*

Keywords: Loewenstein's Rule; Gehlenite; Sodalite

As Loewenstein [1] stated, "one of the most important features of the modern theory of silicates is the double rôle of aluminium, which can substitute for silicon in tetrahedra […]". Loewenstein based his rule, which is also known as aluminium-avoidance-Rule, on the observation that "in all known cases […] the maximum substitution is 50%". This led him to conclude that "no two aluminium ions can occupy the centers of tetrahedra linked by one oxygen". $Ca_2Al[AlSiO_7]$, gehlenite, crystallizes in space group $P\bar{4}2_1m$ in the melilite structure type. It contains two topologically different tetrahedral positions, one of which is fully occupied by $Al3+$, whereas the second one contains Al^{3+} and Si^{4+}. Normally the Al^{3+} molar fraction in the second tetrahedral position does not exceed x_{Al} = 0.5, in accordance with Loewenstein's Rule. In this contribution we show that it is possible to substitute much more Al^{3+} for Si^{4+} than is allowed by Loewenstein's Rule. This happens via a coupled substitution of ($Re^{3+}+Al^{3+}$) for ($Ca^{2+}+Si^{4+}$). Compounds of the composition $Eu_xCa_{2-x}Al[Al_{1+x}Si_{1-x}O_7]$ and $La_xCa_{2-x}Al[Al_{1+x}Si_{1-x}O_7]$ with $0 < x < 1$ were synthesized at 1773 K, atmospheric pressure. Rietveld-refinements of powder diffraction patterns show that the single phased products crystallize in space group $P\bar{4}2_1m$, without changing the Wyckoff-positions of the ions in the melilite structure. Substitutions of a similar type were shown to be possible in the sodalite structure, starting from the mineral bicchulite, $Ca_8[Al_8Si_4O_{24}](OH)_8$. Note that the sodalite structure type contains only one topologically independent tetrahedral position. Solid solutions in the com-positional range $Ca_8[Al_8Si_4O_{24}](OH)_8$ – $Eu_4Ca_4[Al_{12}O_{24}](OH)_8$ have been synthesized hydrothermally at 800-900 K, 0.1 GPa, starting from the melilite-type compounds. Up to date it has not been possible to synthesize the corresponding La homologues, presumably because of the significantly bigger ionic radius of La^{3+} compared with those of Ca^{2+} and Eu^{3+}. Up until now we have no answer to the question whether violations of Loewenstein's rule are restricted to particular structure types only, and if so, what makes the particularities of these structure types.

[1]   Loewenstein, W. (1954): *Amer. Min*., **39**, 92-96