

NATURAL AND SYNTHETIC ALLUAUDITE-TYPE PHOSPHATES: CRYSTAL CHEMISTRY AND APPLICATIONS

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The name alluaudite designates a Na-Mn-Fe-bearing phosphate mineral which is known to occur in the beryl-columbite-phosphate subtype of the rare-element pegmatites, according to the classification of Černý (1991). The crystal structure of a natural alluaudite sample from Buranga, Rwanda, was reported by Moore (1971) who found that the mineral was monoclinic with the $C2/c$ space group and the structural formula, $X(2)X(1)M(1)M(2)_2(PO_4)_3$, with four formula units per unit cell.

Over the past twenty years a variety of synthetic alluaudite-like compounds have been reported; see Hatert *et al.* (2000) for a brief summary of this work. The study of these new alluaudite-like structures reveal more structural complexity than that reported by Moore (1971), a complexity which results from cationic sites not reported earlier. This complexity is best represented as $[A(2)A(2)'] [A(1)A(1)'A(1)''_2] M(1)M(2)_2(PO_4)_3$, a formulation in which the crystallographic A sites may be either empty or partially filled and the M sites must be filled. Thus, in $NaCdIn_2(PO_4)_3$ the $A(1)$ site is filled with Na^+ and the remaining A sites are empty (Antenucci *et al.* 1993) whereas in $NaMnFe^{3+}_2(PO_4)_3$ both the $A(1)$ and $A(2)'$ sites contain Na^+ (Hatert *et al.* 2000).

The structure consists of kinked chains of edge-sharing octahedra stacked parallel to $\{101\}$. These chains are formed by a succession of $M(2)$ octahedral pairs linked by highly distorted $M(1)$ octahedral. Equivalent chains are connected in the b direction by the $P(1)$ and $P(2)$ phosphate tetrahedra to form sheets oriented perpendicular to $[010]$. These interconnected sheets produce channels parallel to the c axis, channels which contain the A sites (Figure 1).

In granitic pegmatites, alluaudite exhibits chemical compositions ranging from $Na_2Mn(Fe^{2+}Fe^{3+})(PO_4)_3$ to $NaMnFe^{3+}_2(PO_4)_3$, with Mn^{2+} or some Ca^{2+} replacing Na^+ on the $A(1)$ site, Fe^{2+} replacing Mn^{2+} on the $M(1)$ site, and some Mg^{2+} or Mn^{2+} replacing iron on the $M(2)$ site, where \square represents a lattice vacancy on the $A(2)'$ site. The transition between these two end-member compositions corresponds to the substitution mechanism, $Na^+ + Fe^{2+} \rightarrow \square + Fe^{3+}$ (Fransolet *et al.* 1986), and occurs during the oxidation processes affecting the complex phosphate associations within the granitic pegmatites.

The family of phosphates exhibiting an alluaudite-like structure has been considerably extended during the past twenty years. By solid-state reactions, exotic cations have been inserted into the alluaudite framework. Antenucci (1992), Antenucci *et al.* (1993, 1995), Hatert (2002), Hatert *et al.* (2003) and Rondeux (2004) have shown that the $M(2)$ site can accept In^{3+} , Ga^{3+} , Cr^{3+} , Cd^{2+} , Zn^{2+} , Mg^{2+} and that the $M(1)$ site can accept Ca^{2+} , Cd^{2+} , Ni^{2+} , Mg^{2+} , Zn^{2+} and In^{3+} . New mixed-valence compounds have also been prepared, such as Cu^+ and Cu^{2+} in $Cu_{1.35}Fe_3(PO_4)_3$ or $Cu_2Mg_3(PO_4)_3$ (Warner *et al.* 1993), Fe^{2+} and Fe^{3+} in $Na_2Fe^{2+}_2Fe^{3+}(PO_4)_3$ (Yakubovich *et al.* 1977), in $NaFe_{3.67}(PO_4)_3$ (Korzenski *et al.* 1998), and more recently in the $Na_2(Mn_{1-x}Fe^{2+x})_2Fe^{3+}(PO_4)_3$ solid solution (Hatert *et al.* 2004). In contrast with these hydrogen-free compounds, new protonated groups of alluaudite-like phosphates have also been reported (Lii & Shih 1994; Leroux *et al.* 1995a, b; Guesmi & Driss 2002).

Because the geochemical role of lithium is essential in rare-element granitic pegmatites, in which the formation of alluaudite takes place, Hatert *et al.* (2000, 2002) and Hatert (2004) decided to investigate the crystallochemical role of lithium in the alluaudite structure. These authors synthesized the solid solutions (Na_{1-x}

$_{x}\text{Li}_x\text{MnFe}^{3+}_2(\text{PO}_4)_3$, $(\text{Na}_{1-x}\text{Li}_x)\text{CdIn}_2(\text{PO}_4)_3$ and $(\text{Na}_{1-x}\text{Li}_x)_{1.5}\text{Mn}_{1.5}\text{Fe}^{3+}_{1.5}(\text{PO}_4)_3$, respectively, and demonstrated that Li occurs on the large A(1) crystallographic site.

The existence of channels in the alluaudite structure makes possible its use as ionic or electric conductor. The Li-bearing alluaudites are therefore of interest as candidates for lithium battery cathodes, and Richardson (2003) investigated the ionic conductivity properties of $\text{LiMnFe}^{3+}_2(\text{PO}_4)_3$. However, the efficiency of this compound was rather poor. Warner *et al.* (1993) synthesized $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$ and $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$, which contain mixed valences of Cu and Fe. Warner *et al.* (1994) showed that the electric properties of $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$ were similar to those of nasicon-type compounds, whereas Daidouh *et al.* (2002) evidenced the ionic character of the electrical conductivity of $(\text{Ag}_{1-x}\text{Na}_x)_2\text{Mn}_2\text{Fe}(\text{PO}_4)_3$.

Finally, the alluaudite structure shares similarities with garnet, langbeinite, nasicon, and $\text{Sc}_2(\text{WO}_4)_3$ structures and might display analogous catalytic behavior. The investigation by Kacimi *et al.* (2004) concerns the catalytic activity of some compounds belonging to the alluaudite structure-type, such as $\text{AgCaCdMg}_2(\text{PO}_4)_3$ and $\text{AgCd}_2\text{Mg}_2(\text{PO}_4)_3$. Their catalytic performances have been studied and compared to that of other phosphates, using butan-2ol as the probe reaction. The results are satisfactory and show a better efficiency for $\text{AgCaCdMg}_2(\text{PO}_4)_3$ than for $\text{AgCd}_2\text{Mg}_2(\text{PO}_4)_3$.

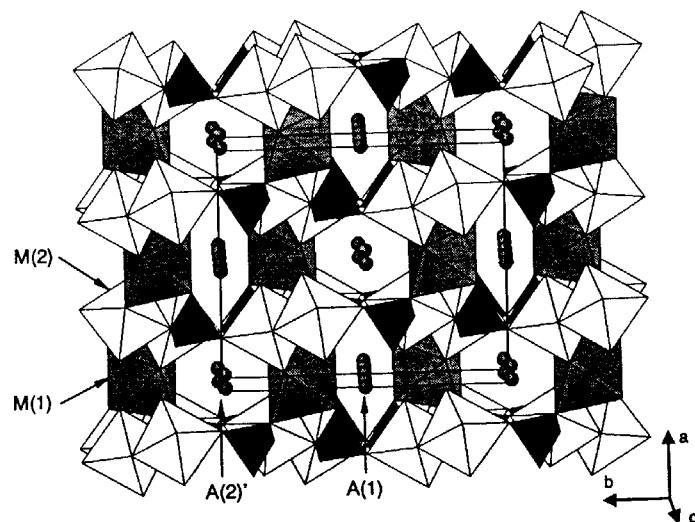


Figure 1. Projection of the alluaudite structure.

References

- Antenucci, D. (1992): *Synthèse et cristallographie de composés à structure alluaudite. Incidences dans les processus d'altération des phosphates Fe-Mn des pegmatites granitiques. Thèse de Doctorat, Université de Liège, 259 p.*
- Antenucci, D., Miehe, G., Tarte, P., Schmahl, W.W., Fransolet, A.-M. (1993): Combined X-ray Rietveld, infrared and Raman study of a new synthetic variety of alluaudite, $\text{NaCdIn}_2(\text{PO}_4)_3$. *European Journal of Mineralogy*, **5**, 207-213.
- Antenucci, D., Fransolet, A.-M., Miehe, G., Tarte, P. (1995): Synthèse et cristallographie de $\text{NaCaCdMg}_2(\text{PO}_4)_3$, phosphate nouveau à structure alluaudite sans cation trivalent. *European Journal of Mineralogy*, **7**, 175-181.
- Černý, P. (1991): Rare-element granitic pegmatites. Part I: Anatomy and internal evolution of pegmatite deposits. *Geoscience Canada*, **18(2)**, 49-67.
- Daidouh, A., Durio, C., Pico, C., Veiga, M.L., Chouaibi, N. & Ouassini, A. (2002): Structural and electrical study of the alluaudites $(\text{Ag}_{1-x}\text{Na}_x)_2\text{FeMn}_2(\text{PO}_4)_3$ ($x = 0, 0.5$ and 1). *Solid State Sciences*, **4**, 541-548.
- Fransolet, A.-M., Keller, P., Fontan, F. (1986): The phosphate mineral associations of the Tsaobismund pegmatite, Namibia. *Contributions to Mineralogy and Petrology*, **92**, 502-517.
- Guesmi, A. & Driss, A. (2002): $\text{AgCo}_3\text{PO}_4(\text{HPO}_4)_2$. *Acta Crystallographica*, **C58**, i16-i17.
- Hatert, F. (2002): Cristallographie et synthèse hydrothermale d'alluaudites dans le système Na-Mn-Fe-P-O: contribution au problème de la genèse de ces phosphates dans les pegmatites granitiques. Ph. D. Thesis, University of Liège, 247 p.
- Hatert, F. (2004): The crystal chemistry of lithium in the alluaudite structure: a study of the $(\text{Na}_{1-x}\text{Li}_x)_{1.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ solid solution ($x = 0$ to 1). *Mineralogy and Petrology*, **81**, 205-217.
- Hatert, F., Keller, P., Lissner, F., Antenucci, D., Fransolet, A.-M. (2000): First experimental evidence of alluaudite-like phosphates with high Li-content: the $(\text{Na}_{1-x}\text{Li}_x)\text{MnFe}_2(\text{PO}_4)_3$ series ($x = 0$ to 1). *European Journal of Mineralogy*, **12**, 847-857.
- Hatert, F., Antenucci, D., Fransolet, A.-M., Liégeois-Duyckaerts, M. (2002): The crystal chemistry of lithium in the alluaudite structure: a study of the $(\text{Na}_{1-x}\text{Li}_x)\text{CdIn}_2(\text{PO}_4)_3$ solid solution ($x = 0$ to 1). *Journal of Solid State Chemistry*, **163**, 194-201.
- Hatert, F., Hermann, R.P., Long, G.J., Fransolet, A.-M., Grandjean, F. (2003): An X-ray Rietveld, infrared, and Mössbauer spectral study of the $\text{NaMn}(\text{Fe}_{1-x}\text{In}_x)_2(\text{PO}_4)_3$ alluaudite-like solid solution. *American Mineralogist*, **88**, 211-222.
- Hatert, F., Rebbouh, L., Hermann, R., Fransolet, A.-M., Long, G.J. & Grandjean, F. (2004): Crystal chemistry of the hydrothermally synthesized $\text{Na}_2(\text{Mn}_{1-x}\text{Fe}^{2+}_x)_2\text{Fe}^{3+}(\text{PO}_4)_3$ alluaudite-type solid solution. *American Mineralogist*, accepted in June 2004.
- Kacimi, M., Ziyad, M. & Hatert, F. (2004): Structural features of $\text{AgCaCdMg}_2(\text{PO}_4)_3$ and $\text{AgCd}_2\text{Mg}_2(\text{PO}_4)_3$, two new compounds with the alluaudite-type structure, and their catalytic activity in butan-2-ol conversion. *Materials Research Bulletin*, submitted in May 2004.
- Korzenski, M.B., Schimek, G.L., Kolis, J.W., Long, G.J. (1998): Hydrothermal synthesis, structure, and characterization of a mixed-valent iron (II/III) phosphate, $\text{NaFe}_{3.67}(\text{PO}_4)_3$: a new variation of the alluaudite structure type. *Journal of Solid State Chemistry*, **139**, 152-160.
- Leroux, F., Mar, A., Payen, C., Guyomard, D., Verbaere, A., Piffard, Y. (1995a): Synthesis and structure of $\text{NaMn}_3(\text{PO}_4)(\text{HPO}_4)_2$, an unoxidized variant of the alluaudite structure type. *Journal of Solid State Chemistry*, **115**, 240-246.
- Leroux, F., Mar, A., Guyomard, D., Piffard, Y. (1995b): Cation substitution in the alluaudite structure type: synthesis and structure of $\text{AgMn}_3(\text{PO}_4)(\text{HPO}_4)_2$. *Journal of Solid State Chemistry*, **117**, 206-212.
- Lii, K.-H. & Shih, P.-F. (1994): Hydrothermal synthesis and crystal structures of $\text{NaCo}_3(\text{PO}_4)(\text{HPO}_4)_2$ and $\text{NaCo}_3(\text{AsO}_4)(\text{HAsO}_4)_2$: synthetic modifications of the mineral alluaudite. *Inorganic Chemistry*, **33**, 3028-3031.
- Moore, P.B. (1971): Crystal chemistry of the alluaudite structure type: Contribution to the paragenesis of pegmatite phosphate giant crystals. *American Mineralogist*, **56**, 1955-1975.
- Richardson, T.J. (2003): Phosphate-stabilized lithium intercalation compounds. *Journal of Power Sources*, **119-121**, 262-265.
- Rondeux, M. (2004): Cristallographie du cation bivalent dans les composés $\text{Na}_2M^{2+}\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ ($M^{2+} = \text{Ca}, \text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$) à structure alluaudite. Diploma thesis, University of Liège, 53 p.

Warner, T.E., Milius, W., Maier, J. (1993): Synthesis and structure of $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$ and $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$: new mixed valence compounds of the alluaudite structure type. *Journal of Solid State Chemistry*, **106**, 301-309.

Warner, T.E., Milius, W., Maier, J. (1994): New copper phosphates with the NASICON or alluaudite-type structures as ionic or mixed conductors. *Solid State Ionics*, **74**, 119-123.

Yakubovich, O.V., Simonov, M.A., Egorov-Tismenko, Y.K., Belov, N.V. (1977): The crystal structure of a synthetic variety of alluaudite, $\text{Na}_2(\text{Fe}^{3+}_{0.5}\text{Fe}^{2+}_{0.5})_2\text{Fe}^{2+}[\text{PO}_4]_3$. *Soviet Physics Doklady*, **22(10)**, 550-552.