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Iron-Manganese Phosphates with the Olivine – and Alluaudite-Type Structures: Crystal Chemistry and Applications

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1 Introduction

Iron-manganese phosphates are common accessory minerals occurring in granitic pegmatites, in metamorphic rocks, and in meteorites. In rare-elements pegmatites, primary phosphates of the triphylite-lithiophilite series $[\text{Li}(\text{Fe}^{2+}, \text{Mn}^{2+})(\text{PO}_4)\text{-Li}(\text{Mn}^{2+}, \text{Fe}^{2+})(\text{PO}_4)]$ form masses that can reach several meters in diameter, enclosed in silicates. During the oxidation processes affecting the pegmatites, these olivine-type phosphates progressively transform to ferrisicklerite-sicklerite $[\text{Li}_{1-x}(\text{Fe}^{3+}, \text{Mn}^{2+})(\text{PO}_4)\text{-Li}_{1-x}(\text{Mn}^{2+}, \text{Fe}^{3+})(\text{PO}_4)]$ and to heterosite-purpurite $[(\text{Fe}^{3+}, \text{Mn}^{3+})(\text{PO}_4)\text{-}(\text{Mn}^{3+}, \text{Fe}^{3+})(\text{PO}_4)]$, according to the substitution mechanism $\text{Li}^+ + \text{Fe}^{2+} \leftrightarrow \square + \text{Fe}^{3+}$. This oxidation sequence was first observed by Quensel (1937), and then confirmed by Mason (1941).

Minerals of the alluaudite group, with ideal chemical compositions ranging from $\text{Na}_2\text{Mn}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$ to $\square\text{NaMnFe}_2^{3+}(\text{PO}_4)_3$, are generally produced from primary triphylite-lithiophilite, by oxidation coupled with a $\text{Li} \leftrightarrow \text{Na}$ metasomatic exchange (Moore 1971). More recently, the existence of primary alluaudites was confirmed by Franolet et al. (1997, 1998, 2004), thus indicating that the metasomatic replacement process proposed by Moore (1971) cannot be generalized. As observed for phosphates of the triphylite-lithiophilite series, primary alluaudites, which are weakly oxidized, progressively transform into oxidized secondary alluaudites, according to the substitution mechanism $\text{Na}^+ + \text{Fe}^{2+} \leftrightarrow \square + \text{Fe}^{3+}$ (Mason 1941; Franolet et al. 1985, 1986, 2004). This mechanism explains the transformation of hagedorfite $[\text{Na}_2\text{MnFe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3]$ into alluaudite $[\square\text{NaMnFe}_2^{3+}(\text{PO}_4)_3]$, and of ferrohagedorfite $[\text{Na}_2\text{Fe}_2^{2+}\text{Fe}^{3+}(\text{PO}_4)_3]$ into ferroalluaudite $[\square\text{NaFe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3]$.

The past 20 years have seen an increasing number of publications devoted to olivine – and alluaudite-type phosphates. On the one hand, solid-state synthesis

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experiments, coupled with structural and spectroscopic investigations, have shown an unexpected flexibility for the alluaudite structure (Hatert et al. 2000; Hatert 2004, 2008), which can accommodate divalent and trivalent cations in its octahedral sites, as well as large monovalent cations in its channels parallel to the c axis. These properties will, no doubt, permit the use of alluaudite-type phosphates for practical applications, such as corrosion inhibition, passivation of metal surfaces, and catalysis (Korzanski et al. 1998; Kacimi et al. 2005). On the other hand, the exceptional performance of triphylite as cathode material for Li-ion batteries has initiated an increasing interest for these phosphates, which are now produced industrially and used in batteries for many applications such as electric cars, electric bicycles, or for the storage of green energy. This chapter will summarize the *crystal-chemical features of alluaudite- and olivine-type phosphates*, and will present their unusual properties and applications.

2 Olivine-Type Phosphates

The most common olivine-type phosphates, observed in granitic pegmatites, are triphylite and lithiophilite (triphylite: $a = 4.690$, $b = 10.286$, $c = 5.987$ Å, $Pbnm$). Their crystal structure has been investigated from synthetic samples (Geller and Durand 1960; Yakubovich et al. 1977) and natural minerals (Finger and Rapp 1969; Losey et al. 2004; Fehr et al. 2007), and is characterized by two chains of edge-sharing octahedra parallel to the c axis. The first chain is constituted by the $M(1)$ octahedra occupied by Li, while the second chain is formed by the $M(2)$ sites occupied by Fe and Mn (Fig. 1). The chains are connected in the b direction by sharing edges of their octahedral sites, and the resulting planes are connected in the a direction by the PO_4 tetrahedra. Natrophilite, $NaMnPO_4$, is another pegmatite

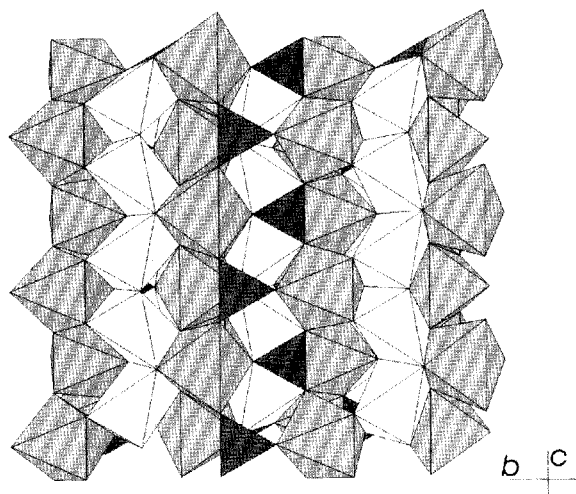


Fig. 1 The crystal structure of triphylite projected along the a axis. The $M(1)$ octahedra are *white*, the $M(2)$ octahedra are *light grey*, and the PO_4 tetrahedra are *dark grey*

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The crystal structure was confirmed by X-ray diffraction, who confirmed the olivine-type phosphate structure. Francou et al. (1976) confirmed the olivine-type phosphate structure, and established the crystal-chemical composition. The structure is characterized by two chains of octahedra along the c axis. The $M(1)$ and $M(2)$ sites are occupied by Li, Fe, and Mn, respectively. The $M(1)$ -O bonds are shorter than the $M(2)$ -O bonds, which demonstrates the different coordination environments of the $M(1)$ and $M(2)$ sites. The $M(1)$ site is occupied by Li, while the $M(2)$ site is occupied by Fe and Mn. The PO_4 tetrahedra are connected to the octahedra chains.

A detailed investigation was performed by Hatert et al. (2000, 2004, 2008) on the presence of Li in the $M(1)$ site. In the natural sample, the $M(1)$ site is occupied by Li, which induced a Jahn-Teller distortion of the $M(1)$ -O bonds (1.91 Å). This investigation confirmed the presence of any trace of Mn and Fe in the $M(1)$ site, respectively.

In order to investigate the oxidation state of the sample from lithiophilite, Hatert et al. (2004) performed a detailed investigation. Lithiophilite is colorless, while sicklerite is colorless, intermediate between sicklerite and triphylite. The crystal-chemical formula was determined by X-ray diffraction and electron microprobe analysis. The colors, were determined by X-ray diffraction and electron microprobe analysis. The unit-cell parameters were determined by X-ray diffraction (lithiophilite) and electron microprobe analysis. The structures were determined by X-ray diffraction. Li occurs in the $M(1)$ site, with a Li content of 0.75 Li per formula unit, as measured by electron microprobe analysis.

Hatert et al. (2004) investigated the structure, which shows the presence of lithiophilite.

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phosphate with the olivine structure, in which the *M*(1) site is occupied by Na while the *M*(2) site contains the smaller divalent cations (Moore 1972).

The crystal structure of natural triphylite was solved by Finger and Rapp (1969), who confirmed that the phosphate is isostructural with minerals of the olivine group. Fransolet et al. (1984) investigated twenty natural and five synthetic olivine-type phosphates of the triphylite-lithiophilite series by X-ray powder diffraction, and established correlations between the unit-cell parameters and the chemical composition. More recently, Losey et al. (2004) determined the structural variations along the triphylite-lithiophilite series, and showed that the bond lengths involving *M*(1) and *M*(2) decrease as the concentration of Fe increases, with the exception of the *M*(1)-O(3) bond. An examination of numerous olivine-type structures also demonstrates that if the size difference in the radius of the cations at the *M*(1) and *M*(2) sites is larger than 0.17 \AA , then the distortion is greater in the octahedron that is occupied by the larger cation (Losey et al. 2004).

A detailed mineralogical study of ferrisicklerite from Sidi Bou Othmane, Morocco, was performed by Fontan et al. (1976), who indicated a partial replacement of (PO_4) groups by (H_4O_4) groups. The crystal structure of the same sample showed the presence of Li and Na on the *M*(1) site, and of Mn^{2+} and Fe^{3+} on the *M*(2) site (Alberti 1976). In the crystal structure of heterosite, Eventoff and Martin (1972) noticed that the *M*(1) site was empty, and that the complete oxidation of iron and manganese induced a Jahn-Teller distortion of the *M*(2) O_6 octahedron, characterized by two short bonds ($1.912\text{--}1.914 \text{ \AA}$) and four long bonds ($2.030\text{--}2.163 \text{ \AA}$). Mössbauer spectral investigations of natural olivine-type phosphates show that triphylite does not contain any trace of Fe^{3+} , whereas ferrisicklerite and purpurite contain 17 and 6% Fe^{2+} , respectively (Li and Shinno 1997; Fehr et al. 2007).

In order to shed some light on the structural modifications induced by the oxidation processes affecting lithiophilite, Hatert (2010) investigated a natural sample from the Altai Mountains, China, in which a progressive transition from lithiophilite to sicklerite is observed. Under the polarizing microscope, lithiophilite is colorless, whereas sicklerite shows a deep orange color. Several grains also show intermediate colors, suggesting a progressive transition from lithiophilite to sicklerite. This progressive transition is confirmed by SIMS (Secondary Ion Mass Spectrometry) analyses, which indicate Li values from 0.96 to 0.69 Li atoms per formula unit (*p.f.u.*). Five single-crystals, corresponding to zones with different colors, were extracted from the sample and investigated by single-crystal X-ray diffraction techniques. The samples are orthorhombic, space group *Phnm*, with unit-cell parameters ranging from $a = 4.736(1)$, $b = 10.432(2)$, $c = 6.088(1) \text{ \AA}$ (lithiophilite) to $a = 4.765(1)$, $b = 10.338(2)$, $c = 6.060(1) \text{ \AA}$ (sicklerite). The structures were refined to R_1 values ranging from 2.19% to 2.94%, and show that Li occurs on the *M*(1) site, with occupancy factors from 0.99 Li *p.f.u.* (lithiophilite) to 0.75 Li *p.f.u.* (sicklerite). These values are in good agreement with the values measured by SIMS.

Hatert et al. (2009) reported SIMS analyses of six natural triphylite samples, which show lithium contents from 9.51 to 9.88 wt.% Li_2O , while the analyses of four lithiophilites show higher Li_2O contents ranging from 10.23 to 11.15 wt.% (Fig. 2).

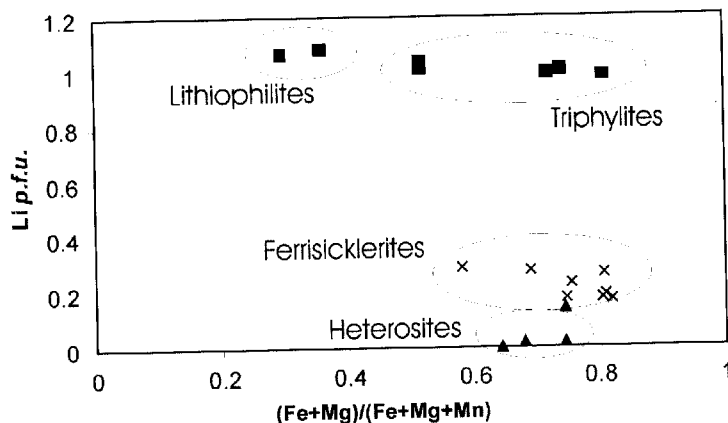


Fig. 2 Diagram showing the chemical composition of natural olivine-type phosphates

These compositions correspond to 0.99–1.04 Li *a.p.f.u.* in triphylites, and 1.07–1.15 Li *a.p.f.u.* in lithiophilites. The significant Li enrichment of lithiophilites indicates that Li can also occur in the *M*(2) site of the olivine structure. Eleven ferrisicklerite samples show Li₂O-contents from 1.65 to 2.84 wt.% (= 0.17–0.29 *a.p.f.u.*), and three heterosite samples contain 0.16–0.21 wt.% Li₂O (= 0.02 *a.p.f.u.*) (Hatert et al. 2009). The presence of significant amounts of Li in heterosites was unexpected, and the low Li content of ferrisicklerites indicates that trivalent manganese also occurs in this mineral. The formula of Li-poor ferrisicklerite corresponds to Li_{0.17}(Fe³⁺_{0.75} Mn³⁺_{0.10} Mn²⁺_{0.08} Mg_{0.06})(PO₄).

In the literature are present many synthetic phosphates with the olivine structure, among which LiCo(PO₄) (Kubel 1994; Bramnik et al. 2004; Penazzi et al. 2004), LiNi(PO₄) (Warda and Lee 1998; Abrahams and Easson 1993), LiMg(PO₄) (Hanic et al. 1982), and NaCd(PO₄) (Ivanov et al. 1974). More recently, Hatert et al. (2010) investigated the alluaudite + triphylite assemblage by hydrothermal technique, and observed a significant amount of Na in triphylite. This amount evolves from 0.04 to 0.08 wt.% Na₂O at 400°C, to 1.25–1.58 wt.% Na₂O at 800°C, according to the substitution mechanism Na → Li. This first experimental evidence of Na incorporation into triphylite is not really surprising, since the *M*(1) site of the olivine structure can be completely filled by Na in natrophilite (Moore 1972).

As shown on Fig. 3, we attempted to correlate the unit-cell parameters of Li-bearing, vacancy-free olivine-type phosphates, with the mean ionic radius of the cations occurring on the *M*(2) site. The correlations are excellent and generally follow Vegard's law, except for the *a* parameter which has been fitted with a second order polynomial curve. These correlations can be used to predict the unit-cell parameters of olivine-type phosphates, but also to estimate the Fe/(Fe + Mn) ratio within the triphylite-lithiophilite solid solution. Starting from the unit-cell parameters published by Fransolet et al. (1984) and by Losey et al. (2004) on natural minerals of the triphylite group, we estimated the Fe/(Fe + Mn) ratio according to

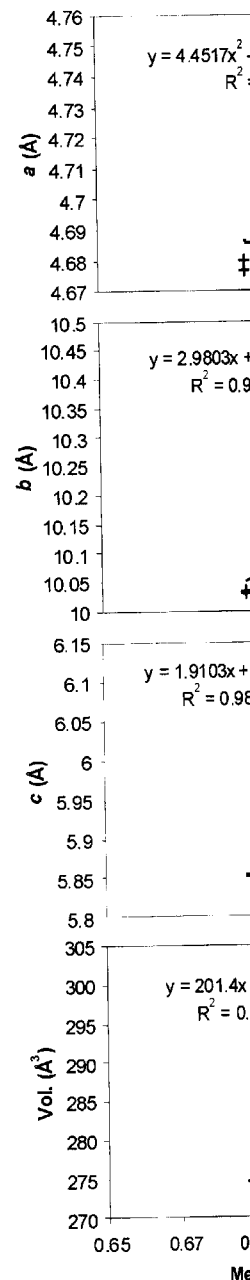


Fig. 3 Variations of the unit-cell parameters

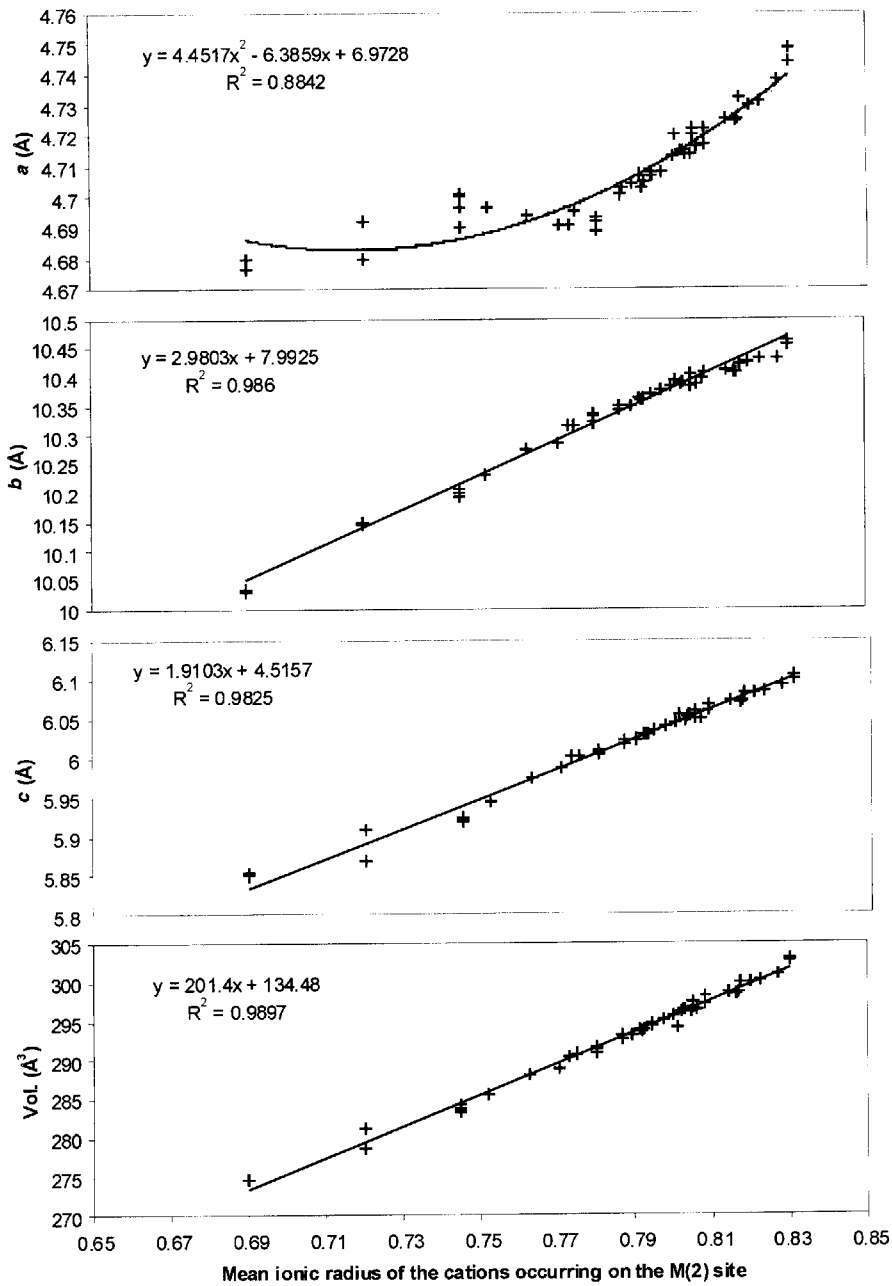


Fig. 3 Variations of the unit-cell parameters in natural and synthetic olivine-type phosphates

the equations of Fig. 3 for b , c , and V . The results are satisfactory when the Mg content of the phosphates is lower than 0.016 *a.p.f.u.*, as shown by a $Fe/(Fe + Mn)$ ratio estimated with an accuracy of $\pm 7\%$. However, an increase of the Mg content induces a significant overestimation of the $Fe/(Fe + Mn)$ ratio, which is characterized by an error reaching 35% for a Mg content of 0.23 *a.p.f.u.*

Since Padhi et al. (1997) reported the reversible electrochemical extraction of lithium from $LiFePO_4$, the olivine-type phosphates $LiMPO_4$ ($M = Fe, Mn, Co, Ni$) have received a strong attention as candidates for lithium batteries (e.g. Andersson et al. 2000; Okada et al. 2001; Ravet et al. 2003; Prosini et al. 2002; Song et al. 2002; Takahashi et al. 2002; Yang et al. 2003; Bramnik et al. 2004; Deniard et al. 2004; Fehr et al. 2007). The number of publications devoted to these compounds increases linearly since 2001, and has reached 300 publications per year in 2010. Recently, Kang and Ceder (2009) showed that $LiFePO_4$ -based batteries can achieve ultrafast charging and discharging in 10–20 s, thus reaching the performance of supercapacitors.

The principle of a $LiFePO_4$ -based battery is shown on Fig. 4. During the charging process (Fig. 4a), electrons are removed from the triphylite electrode, and Li^+ is consequently extracted from this electrode to maintain charge balance. Li^+ then migrates through an electrolyte to reach a metallic Li electrode. It is noteworthy that this Li^+ extraction process provokes a progressive oxidation of triphylite into heterosite during the charge. During discharge (Fig. 4b), the process is inverted, and electrons are extracted from the metallic Li electrode. Li^+ then migrates to the heterosite electrode, which progressively transforms again into triphylite.

The performance of these $LiFePO_4$ -based batteries is exceptional, with a potential of 3.4 V, a very high capacity around 160–170 mAh/g, and a good resistance to cycling. Moreover, this electrode material can be manufactured at low cost from abundant chemicals, and is characterized by a very low toxicity. These features make of $LiFePO_4$ the best candidate for producing batteries for many applications, such as electric bicycles, electric boats, electric cars, or for the storage of green energy. These recent technological advances, which will significantly contribute to improve our future, are one of the best examples of how mineralogical sciences can stimulate the development of new advanced materials.

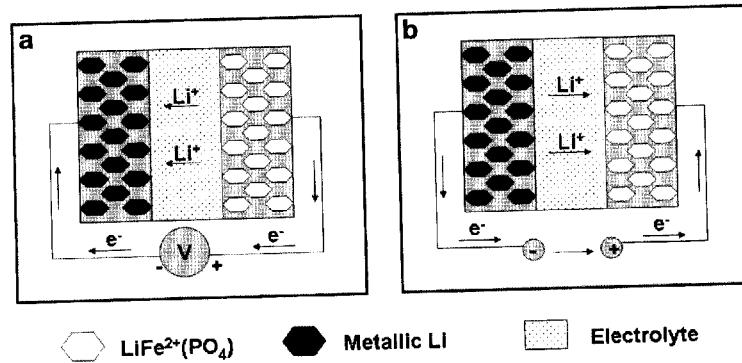


Fig. 4 Principle of a $LiFePO_4$ -based battery during charge (a) and discharge (b)

3 Alluaudite-

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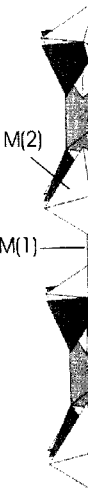


Fig. 5 The alluaudite $M(1)$ octahedra are

3 Alluaudite-Type Phosphates

Phosphates of the alluaudite group occur as accessory minerals in granitic pegmatites, particularly in the beryl-columbite-phosphate subtype of the rare-element pegmatites. By using a single-crystal from the Buranga pegmatite, Rwanda, Moore (1971) determined the crystal structure of alluaudite in the monoclinic $C2/c$ space group ($a = 12.004(2)$, $b = 12.533(4)$, $c = 6.404(1)$ Å, $\beta = 114.4(1)^\circ$), and proposed the general structural formula $X(2)X(1)M(1)M(2)_2(PO_4)_3$, with $Z = 4$. 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 $M(1)$ octahedra. 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 distorted cubic $X(1)$ site and the four-coordinated $X(2)$ site (Fig. 5).

According to Moore (1971), the cations are distributed among the different crystallographic sites as a function of their ionic radii. Accordingly, the large $X(2)$ site contains Na, K and vacancies; $X(1)$ contains Na, Mn and Ca; $M(1)$ contains Mn and Fe^{2+} ; and the small $M(2)$ site contains Fe^{3+} , Fe^{2+} , Mn, Mg and Li. Because Mn dominates on the $M(1)$ site, and Fe^{2+} and Fe^{3+} dominate on the $M(2)$ site, Moore (1971) proposed the ideal formula $Na_2MnFe^{2+}Fe^{3+}(PO_4)_3$, from which the majority of natural alluaudites can be derived.

Moore and Ito (1979) investigated the crystal chemistry of several natural alluaudite samples, and also proposed a systematic nomenclature for the alluaudite group, which is based on the cation distribution among the different crystallographic sites.

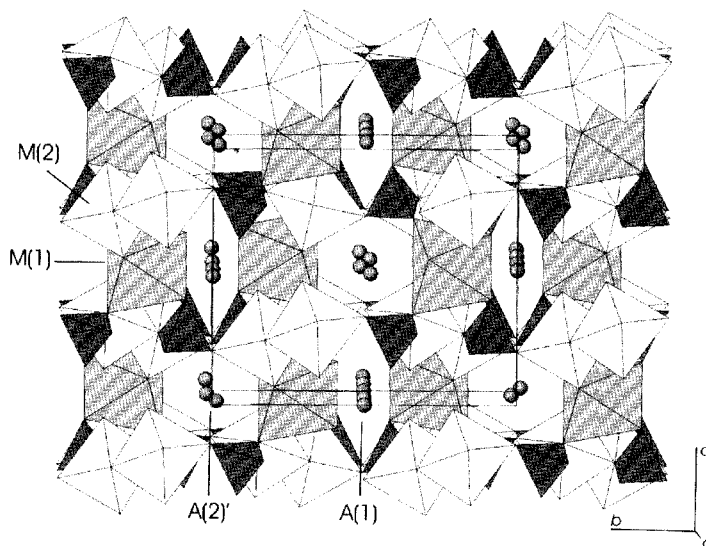


Fig. 5 The alluaudite structure, projected along the c axis. The $M(2)$ octahedra are white, the $M(1)$ octahedra are light grey, and the PO_4 tetrahedra are dark grey

The mineral is given a generic name, that depends on the predominant $M(2)$ content (Mn = varulite, Fe^{2+} = hagendorfite, Fe^{3+} = alluaudite), and characterized by a prefix reflecting the $M(1)$ content (Fe^{2+} = ferro-, and Mg = mag-). For example, the compositions $\text{Na}_2\text{Fe}_2^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$, $\text{Na}_2\text{MnFe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$, and $\text{Na}_2\text{Mn}_2\text{Fe}^{3+}(\text{PO}_4)_3$ correspond to the minerals ferrohagendorfite, hagendorfite, and varulite, respectively, whereas the more oxidized compositions $\square\text{NaFe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3$ and $\square\text{NaMnFe}_2^{3+}(\text{PO}_4)_3$ correspond to ferroalluaudite and alluaudite, respectively.

Over the past 20 years, many phosphates, arsenates, molybdates, vanadates, and tungstates with the alluaudite structure have been synthesized (e.g. Auernhammer et al. 1993; Khorari 1997; Solodovnikov et al. 1998; Hatert et al. 2000; Tsyrenova et al. 2000; Hatert 2004, 2008, Redhammer et al. 2005). The structural investigation of these synthetic compounds showed the existence of new crystallographic sites localized in the channels of the structure, on positions which are different from those of $X(1)$ and $X(2)$. In order to take these new crystallographic sites into account, Hatert et al. (2000) proposed the new general formula $[A(2)A(2)'] [A(1)A(1)']_2 [M(1)M(2)]_2 [\text{PO}_4]_3$ for alluaudite-type compounds. In this formula, $A(1)$ and $A(2)'$ correspond to $X(1)$ and $X(2)$, respectively (Fig. 5).

In general, the cation distribution in synthetic alluaudite-type phosphates is controlled by the ionic radii of the cations, as suggested by Moore (1971) and Moore and Ito (1979) (Table 1). However, Li is surprisingly not localized on the small $M(2)$ crystallographic site, but rather on the large $A(1)$ site (Hatert et al. 2000, 2002; Hatert 2004), and a partially disordered distribution of cations with similar

Table 1 Cation distribution in alluaudite-type phosphates

Cation	Ionic radii (Å)		Crystallographic site			
	[VI]	[VIII]	$A(2)'$	$A(1)$	$M(1)$	$M(2)$
Ag^+	1.15	1.28	X	X		
Na^+	1.02	1.18	X	X	X	
Cu^+	0.77	–	P	P		
Li^+	0.76	0.92	P	P		
Ca^{2+}	1.00	1.12	P	P	P	
Cd^{2+}	0.95	1.10		P	X	P
Mn^{2+}	0.830	0.96	P	P	X	X
Fe^{2+}	0.780	0.92			X	X
Co^{2+}	0.745	0.90			X	X
Zn^{2+}	0.740	0.90			X	P
Cu^{2+}	0.73	–		P		
Mg^{2+}	0.720	0.89			X	X
Ni^{2+}	0.690	–			X	X
In^{3+}	0.800	0.92			P	X
Fe^{3+}	0.645	0.78		P		X
Ga^{3+}	0.620	–				P
Cr^{3+}	0.615	–				P
Al^{3+}	0.535	–				P

X: Complete occupancy of the site, P: Partial occupancy of the site

ionic radii has been observed (Antenucci 1992), $\text{NaMn}(\text{Fe}^{2+}\text{Fe}^{3+})_2(\text{PO}_4)_3$ (Hatert et al. 2000) (Hatert 2008), and $\text{Na}_2(\text{Mn}_2\text{Fe}^{3+})_2(\text{PO}_4)_3$ (Hatert 2010). Extensive M(1) occupancy has been observed (Hermann et al. 2002; Hatert 2004), and the existence of next-nearest neighbor sites in the M sites.

The alluaudite structure is oriented along the c axis, in which octahedra, such as Na, Li, Cu, and Mn, host significant amounts of intercalated phosphates $M\text{Co}_3(\text{PO}_4)[\text{PO}_4]$ (Lii and Shih 1994; Leroux et al. 2000). The mineral groatite, $\text{NaCaMn}_2(\text{Fe}^{2+}\text{Fe}^{3+})_2(\text{PO}_4)_3$ of the alluaudite structure shows a large diameter of pores and is used in alluaudite-type phosphates as corrosion inhibition, passivation (Korzenski et al. 1998).

Many papers were published on the properties (Warner et al. 1999; Hatert 2001; Durio et al. 2002; Hatert 2004) and properties (Warner et al. 1999; Hatert 2001; Durio et al. 2002; Hatert 2004) of alluaudite-type phosphates of interest as candidates for cathodes with electronic conductivity, the intercalation reaction. Richardson (2003) compared $\text{Na}_2\text{Mn}_2\text{Fe}(\text{PO}_4)_3$, and $\text{LiNi}(\text{PO}_4)_2$ performance as intercalation electrodes. Hatert et al. (2010) tested the intercalation as positive electrode in lithium-ion batteries with significant polarization, with a low rate. However, the diffusion character in alluaudite-type phosphates is not as good as in those of the diffusion character in alluaudite-type phosphates. To improve the performance of alluaudite-type phosphates, thus certainly required (Trasatti et al. 2004).

The catalytic activity of alluaudite-type phosphates measured by Kacimi et al. (2004) for the oxidation of butan-2-ol in methyl ethyl ketone was higher than those of well-known nasicon-type phosphates. The alluaudite-type phosphates of alluaudites certainly constitute promising materials.

Acknowledgments Many thanks to the "Chercheur Qualifié".

minant $M(2)$ content characterized by a prefix. For example, the $\text{Na}_2\text{Mn}_2\text{Fe}^{3+}(\text{PO}_4)_3$ (Hatert 2008), and $\text{Na}_2(\text{Mn}_{1-x}\text{M}^{2+}_x)\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ ($M^{2+} = \text{Cd, Mg}$) (Rondeux and Hatert 2010).

tes, vanadates, and e.g. Auernhammer et al. 2000; Tsyrenova et al. 2000; structural investigations show crystallographic sites are different from sites into $[A(2)A(2)']A(1)A(1)$ this formula, $A(1)$

type phosphates is Moore (1971) and localized on the Hatert et al. 2000, cations with similar

$M(1)$	$M(2)$
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X	X
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	P
	P
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ionic radii has been observed in the compounds $\text{Na}_2\text{Cd}_2M^{3+}(\text{PO}_4)_3$ ($M^{3+} = \text{Ga, Fe}^{3+}, \text{Cr}$) (Antenucci 1992), $\text{NaMn}(\text{Fe}^{3+}_{1-x}\text{In}_x)_2(\text{PO}_4)_3$ (Hatert et al. 2003), $\text{Na}_2(\text{Mn}_{1-x}\text{Fe}^{2+}_x)_2\text{Fe}^{3+}(\text{PO}_4)_3$ (Hatert et al. 2005), $\text{Na}_{1.5}(\text{Mn}_{1-x}M^{2+}_x)_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ ($M^{2+} = \text{Cd, Zn}$) (Hatert 2008), and $\text{Na}_2(\text{Mn}_{1-x}M^{2+}_x)\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ ($M^{2+} = \text{Cd, Mg}$) (Rondeux and Hatert 2010). Extensive Mössbauer spectral investigations have also been realized (Hermann et al. 2002; Hatert et al. 2003, 2004, 2005; Redhammer et al. 2005), showing the existence of next-nearest neighbour interactions affecting the iron atoms localized in the M sites.

The alluaudite structure is characterized by the existence of two channels parallel to the c axis, in which occur the A crystallographic sites containing monovalent cations, such as Na, Li, Cu, and Ag (Fig. 5, Table 1). Moreover, these channels can host significant amounts of hydrogen, as for example in the synthetic alluaudite-type phosphates $M\text{Co}_3(\text{PO}_4)[\text{PO}_3(\text{OH})]_2$ and $M\text{Mn}_3(\text{PO}_4)[\text{PO}_3(\text{OH})]_2$ ($M = \text{Na, Ag}$) (Lii and Shih 1994; Leroux et al. 1995a, b; Guesmi and Driss 2002), as well as in mineral groatite, $\text{NaCaMn}_2^{2+}(\text{PO}_4)[\text{PO}_3(\text{OH})]_2$ (Cooper et al. 2009). The channels of the alluaudite structure show a diameter from 2.5 to 4.0 Å (Fig. 5), corresponding to the diameter of pores observed in microporous phases. As a consequence, alluaudite-type phosphates are potential materials for practical applications, such as corrosion inhibition, passivation of metal surfaces, catalysis, and energy storage (Korzenski et al. 1998).

Many papers were published on the magnetic (Warner et al. 1993; Chouaibi et al. 2001; Durio et al. 2002; Hatert et al. 2004; Hidouri et al. 2004) and electrochemical properties (Warner et al. 1994; Daidouh et al. 2002; Durio et al. 2002; Richardson 2003; Trad et al. 2010) of alluaudite-type phosphates. Indeed, these compounds are of interest as candidates for lithium battery cathodes because of their expected high electronic conductivity, their high intercalation mobility, and their ease of preparation. Richardson (2003) consequently investigated the $\text{Li}_{0.75}\text{Na}_{0.25}\text{MnFe}_2(\text{PO}_4)_3$, $\text{Na}_2\text{Mn}_2\text{Fe}(\text{PO}_4)_3$, and $\text{LiNaMn}_2\text{Fe}(\text{PO}_4)_3$ compounds, which showed poor performance as intercalation electrodes in non-aqueous lithium cells. More recently, Trad et al. (2010) tested the intercalation/deintercalation properties of $\text{NaMnFe}_2(\text{PO}_4)_3$ as positive electrode in lithium and sodium batteries. The cycling curves exhibit a significant polarization, with 1.5 Li^+ ions and electrons intercalated in the structure at low rate. However, the very difficult electronic transfer, as well as the 1D diffusion character in alluaudites, tends to make difficult the alkaline metal diffusion. To improve the performance of alluaudite-type compounds, nanomaterials are thus certainly required (Trad et al. 2010).

The catalytic activity of $\text{AgCaCdMg}_2(\text{PO}_4)_3$ and $\text{AgCd}_2\text{Mg}_2(\text{PO}_4)_3$ was measured by Kacimi et al. (2005), by using as probe reaction the conversion of butan-2-ol in methyl ethyl ketone. These promising catalytic results are similar to those of well-known nasicon-type phosphates, thus confirming that the large family of alluaudites certainly constitutes a rich source for the engineering of new challenging materials.

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