



A new nomenclature scheme for the alluaudite supergroup

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Abstract: The alluaudite supergroup contains sixteen Na–Mn–Fe-bearing phosphates occurring in granitic pegmatites, as well as nineteen Na-bearing arsenates found in various geological environments; these minerals are characterized by a monoclinic symmetry (generally $C2/c$ or $P2_1/n$ space-group types), and by unit-cell parameters generally around $a \sim 12$, $b \sim 12.5$, $c \sim 6.5$ Å, $\beta \sim 115^\circ$. The simplified structural formula of alluaudite-type minerals is $A(2)'A(1)M(1)M(2)_2(\text{TO}_4)_3$, and the new nomenclature scheme proposed herein is mainly based on the contents of the $M(1)$ and $M(2)$ octahedral sites. For phosphates, the root name is defined on the basis of the $M(2)$ content, allowing a valency-imposed double-site occupancy for that site: $M^2(\text{Fe}^{3+}\text{Fe}^{3+}) = \text{alluaudites } s.l.$, $M^2(\text{Fe}^{2+}\text{Fe}^{3+}) = \text{hagendorfites } s.l.$, and $M^2(\text{Mn}^{2+}\text{Fe}^{3+}) = \text{varulites } s.l.$ The root-name is used without prefix if the $M(1)$ site is occupied by Mn, but the prefix “ferro-” is added when $M(1)$ is predominantly occupied by Fe^{2+} . For arsenates, the nomenclature is more complex, and numerous root-names are already defined in the literature. We consequently recommend preferentially adding prefixes to these root-names, in order to differentiate arsenates with identical $M(2)$ contents, but with different $M(1)$ contents. Charge-balanced end-member formulae are given for all minerals of the supergroup, and a method to calculate formulae from the electron-microprobe analyses is given as appendix.

Key-words: alluaudite; phosphate; arsenate; wylleite; nomenclature.

1. Introduction

The name alluaudite was given by Damour (1847, 1848) for a Na–Mn–Fe-bearing phosphate mineral found in the Chan-teloube pegmatite, Limousin, France. The mineral was named after the French naturalist François II Alluaud (1778–1866), Mayor of Limoges and director of a ceramics factory. Fisher (1957) demonstrated that two other species, varulite from the Varuträsk pegmatite, Sweden (Quensel, 1937, 1940), and hühnerkobelite from the Hühnerkobel pegmatite, Bavaria (Mason, 1942), also belong to the alluaudite group.

Alluaudite samples from the Buranga pegmatite were investigated by Thoreau (1954), and then by Moore (1971) who described the crystal structure of the mineral. Alluaudite is monoclinic, space group $C2/c$, $a = 12.004$ (2), $b = 12.533$ (4), $c = 6.404$ (1) Å, $\beta = 114.4$ (1)°, with the structural formula $X(2)X(1)M(1)M(2)_2(\text{PO}_4)_3$. Recently, Hatert *et al.* (2000) and Krivovichev *et al.* (2013) proposed the formula $[A(2)A(2)'A(2)']_2[A(1)A(1)'A(1)']_2M(1)M(2)_2(\text{PO}_4)_3$, which takes into account the distinct crystallographic positions observed in the channels of the structure.

The alluaudite structure consists of kinked chains of edge-sharing $M(1)$ and $M(2)$ octahedra, stacked parallel to the $\{101\}$ plane. These chains are connected by the $\text{P}(1)\text{O}_4$ and $\text{P}(2)\text{O}_4$ tetrahedra, to form layers perpendicular to the crystallographic \mathbf{b} axis (Fig. 1). Between these layers occur

two types of channels running along the \mathbf{c} axis: channel 1 which contains the $A(1)$, $A(1)'$, and $A(1)''$ sites, and channel 2 which contains the $A(2)$, $A(2)'$, and $A(2)''$ sites (Fig. 1). Generally, only $A(1)$ and $A(2)'$ are significantly occupied.

Moore & Ito (1973) described the new phosphate wylleite in the Victory mine pegmatite, South Dakota, and found unit-cell parameters $a = 11.862$ (2), $b = 12.382$ (1), $c = 6.354$ (9) Å, $\beta = 114.52$ (8)°, space group $P2_1/n$. The unit-cell parameters of this phosphate are very close to those of alluaudite, and a single-crystal investigation by Moore & Molin-Case (1974) indicates a crystal structure topologically identical to the alluaudite structure. The only difference between these two groups of phosphates is the presence of significant Al in wylleite, thus implying the splitting of the $M(2)$ and $X(1)$ sites of alluaudite into $M(2a)$ – $M(2b)$ and $X(1a)$ – $X(1b)$ in wylleite, as well as a change of space group. The structural formula of wylleite-type phosphates corresponds to $X(2)X(1a)_{0.5}X(1b)_{0.5}M(1)M(2a)M(2b)(\text{PO}_4)_3$. More recently, Ercit *et al.* (1986a, b) described bobfergusonite, $\square\text{Na}_2\text{Mn}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$, in the crystal structure of which the adjacent octahedral chains show an ordering, thus implying a doubling of the c unit-cell parameter of wylleites: $P2_1/n$, $a = 12.773$ (2), $b = 12.486$ (2), $c = 11.038$ (2) Å, $\beta = 97.15^\circ$.

Numerous arsenates also show the alluaudite structure. Caryinite, $(\text{Na,Pb})(\text{Ca,Na})\text{Ca}(\text{Mn,Mg})_2(\text{AsO}_4)_3$, was described by Lundström (1874) in the Långban pegmatite,

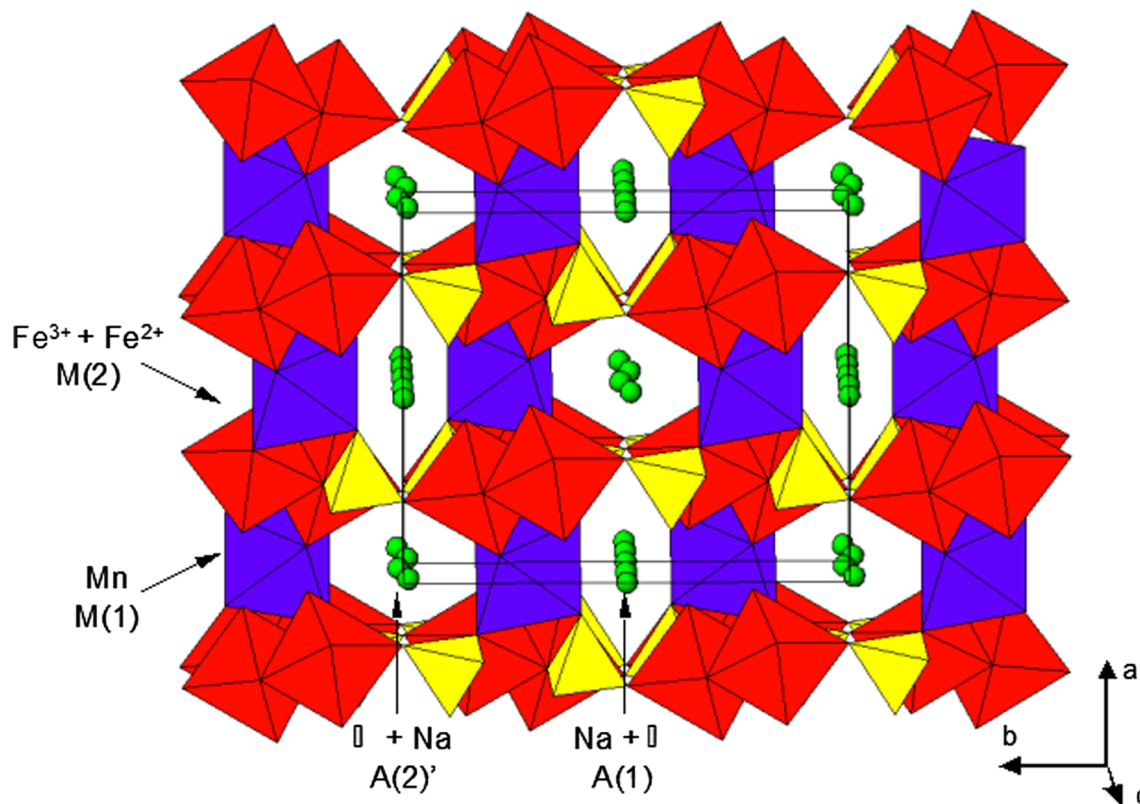


Fig. 1. The alluaudite structure. $M(2)$ octahedra are red, $M(1)$ octahedra are blue, and PO_4 tetrahedra are yellow. Green circles represent Na atoms in the channels of the structure.

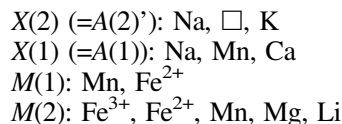
Sweden, and was later shown by [Strunz \(1960\)](#) to be isostructural with alluaudite. The other arsenates arsenioleite, badalovite, bradaczekite, calciojohillerite, camanchaite, canutite, erikapohlite, hatertite, johillerite, keyite, khrenovite, magnesiocanutite, magnesiohatertite, nickenichite, odanielite, paraberzeliite, yazganite, and zinco-bradaczekite also belong to the alluaudite group ([Keller et al., 1981, 1982](#); [Dunn & Peacor, 1987](#); [Auernhammer et al., 1993](#); [Cooper & Hawthorne, 1996](#); [Krivovichev et al., 2001, 2013](#); [Sarp & Černý, 2005](#); [Schlüter et al., 2013](#); [Kampf et al., 2014, 2017, 2018](#); [Pekov et al., 2016a, b, c, d, 2018a, b](#)).

According to the IMA-CNMNC recommendations for classification ([Mills et al., 2009](#)), mineral groups are defined on the basis of their crystal structure. Consequently, alluaudite-type arsenates and phosphates belong to the same group, which is named “alluaudite group” since alluaudite is the first described mineral ([Damour, 1847, 1848](#)). Wyllieite- and bobfergusonite-type phosphates show topologically similar structures, but with different space-groups and/or unit-cell parameters, thus implying the definition of the distinct “wylieite” and “bobfergusonite” groups. The alluaudite supergroup consequently contains phosphates and arsenates topologically related to the alluaudite structure; these minerals are alluaudite-type phosphates and arsenates (alluaudite group: 6 phosphates and 19 arsenates), wylieite-type phosphates (wylieite group: 6 phosphates), bobfergusonite-type phosphates (bobfergusonite group: 3 phosphates), and manitobaite ([Ercit et al., 2010](#)).

The goal of this paper is to revise the classification of the alluaudite supergroup, in order to homogenize the nomenclature of these phosphates and arsenates; this new nomenclature scheme has been accepted by the IMA-CNMNC.

2. Crystal chemistry and current nomenclature of alluaudite-type phosphates

The nomenclature of alluaudite- and wylieite-type phosphates has been established by [Moore & Ito \(1979\)](#), from the examination of chemical analyses of natural samples. These analyses were interpreted taking into account the structural formula of alluaudite proposed by [Moore \(1971\)](#): $X(2)X(1)M(1)M(2)_2(\text{PO}_4)_3$. In natural samples, cations are distributed over the different crystallographic sites according to their ionic radii, with the smaller cations on $M(2)$ and the largest cations on $X(2)$:



According to [Moore & Ito \(1979\)](#), alluaudite-type phosphates are defined on the basis of the dominant cation on the $M(2)$ site: Fe^{3+} in alluaudites, Mn in varulites, and Fe^{2+} in hagendorfites (this mineral was described by [Strunz \(1954\)](#) in the Hagendorf pegmatite, Bavaria). The $M(1)$ site

is generally occupied by Mn, but prefixes “ferro-” or “mag-” may be added to the root-name when Fe^{2+} or Mg are dominant on $M(1)$, respectively.

Five alluaudite-type phosphates currently occur in the IMA-CNMNC mineral list, which follow this nomenclature scheme: alluaudite, $\text{NaMnFe}_2^{3+}(\text{PO}_4)_3$, hagendorfite, $\text{NaCaMnFe}_2^{2+}(\text{PO}_4)_3$, varulite, $\text{NaCaMnMn}_2^{2+}(\text{PO}_4)_3$, ferroalluaudite, $\text{NaFe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3$, and maghagendorfite, $\text{NaMnMgFe}_2^{2+}(\text{PO}_4)_3$. Groatite, $\square\text{NaCaMn}_2(\text{PO}_4)(\text{HPO}_4)_2$, is a protonated alluaudite-type phosphate which does not follow the current nomenclature scheme (Cooper *et al.*, 2009).

3. Problems to apply this nomenclature scheme

Mineralogists involved in the study of pegmatite phosphates know, by experience, that the nomenclature scheme suggested by Moore & Ito (1979) does not work properly. In order to demonstrate this feature, we decided to examine all chemical analyses of alluaudite-type phosphates occurring in the literature. A total of 64 analyses were selected and recalculated in order to uniformize the data, on the basis of 3 P atoms per formula unit (*apfu*). Then, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio was calculated to maintain charge balance. In some extremely oxidized samples, it was also necessary to oxidize some Mn^{2+} into Mn^{3+} to reach the 9 positive charges in the cationic groups of the formula unit. Protonated alluaudite-type phosphates were not considered in these calculations, since they contain only 7 positive charges in the cationic groups of the formula unit. Their nomenclature will be briefly discussed below.

A procedure to calculate electron-microprobe analyses of alluaudite-type phosphates is given in the Appendix, and the complete list of analyses is freely available as Supplementary Material linked to this article at <https://pubs.geoscience-world.org/eurjmin/>.

Starting from these recalculated analyses, we distributed the cations on the different crystallographic sites of the structure, following the known crystal-chemical constraints mainly established from synthetic compounds (Hatert *et al.*, 2000, 2003, 2005a; Hatert, 2008; Rondeux & Hatert, 2010). According to these constraints, cations with small effective ionic radii (Shannon, 1976) were assigned to the $M(2)$ site (Fe^{3+} , Mn^{3+} , Al, Mg, Zn). When necessary, this site was filled by Fe^{2+} and then by Mn^{2+} . The $M(1)$ site was mainly filled by divalent cations Fe^{2+} , Mn^{2+} , and Ca, but it may also contain small amounts of Fe^{3+} and Na. The $A(1)$ position is mainly occupied by Na, Ca, Mn^{2+} and sometimes vacancies, while the large $A(2)$ site contains large monovalent cations Na, Li and K, as well as significant vacancies.

Figure 2 shows a ternary diagram where the cationic contents of the $M(2)$ site have been plotted. From this diagram, it is clear that the majority of analyses fall in the Fe^{3+} -dominant field, corresponding to alluaudites *sensu stricto*. The analyses of type varulites are far away from the Mn-dominant pole: they are located on the Fe^{3+} -Mn side of the diagram, not far from the $\text{Fe}_{0.5}^{3+}\text{Mn}_{0.5}$ boundary. Analyses of

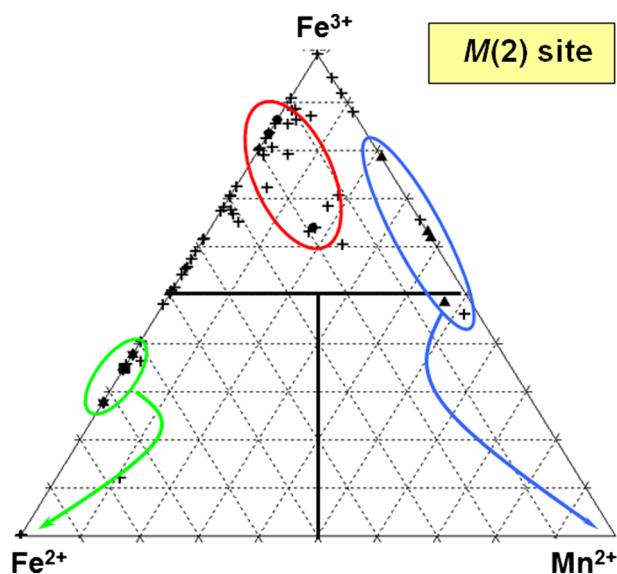


Fig. 2. Cationic distribution on the $M(2)$ site of alluaudite-type phosphates. Black circles = type alluaudites (Damour, 1847, 1848), stars = type hagendorfites (Strunz, 1954), triangles = type varulites (Quensel, 1937, 1940).

type hagendorfites are also far from the Fe^{2+} -dominant end-member; they are closer to the $\text{Fe}_{0.5}^{3+}\text{Fe}_{0.5}^{2+}$ boundary.

From this diagram, it is obvious that the nomenclature scheme of Moore & Ito (1979), which considers the cation dominance on the $M(2)$ site as the main criteria to define the root name of alluaudite-type phosphates, is in contradiction with the analyses of type varulites and hagendorfites. A careful examination of the cationic distribution on the different crystallographic sites of these phosphates (Table 1) indicates $M(2)$ occupancies close to $\text{Fe}_{0.5}^{3+}\text{Mn}_{0.5}$ for type varulite (Quensel, 1937), and close to $\text{Fe}_{0.5}^{3+}\text{Fe}_{0.5}^{2+}$ for type hagendorfite (Strunz, 1954), thus showing the necessity to redefine the ideal formulae of these minerals.

In the IMA-CNMNC list of minerals, hagendorfite is defined as $\text{NaCaMnFe}_2^{2+}(\text{PO}_4)_3$, and varulite as $\text{NaCaMnMn}_2(\text{PO}_4)_3$. These formulae were established by considering Ca as dominant on the $A(1)$ site, in order to achieve charge balance. However, as shown on Fig. 3 in which the cationic contents on the $A(1)$ site of alluaudite-type phosphates were plotted, Ca does not play a significant role, since $A(1)$ is mainly occupied by Na in the majority of samples. This confirms again that the current nomenclature scheme is inappropriate.

Table 1 shows the cationic distributions in several alluaudite-type phosphates, taking into account the nomenclature scheme of Moore & Ito (1979). As shown on this table, trying to derive end-member formulae by simply considering the site dominant cation would lead to unbalanced formulae in several cases (identified by double quotes), *e.g.* the compositions of type varulite, type hagendorfite, as well as for two compositions reported by Moore & Ito (1979). If we consider the 64 analyses from the literature, it appears that 44% of these analyses do not allow the straightforward derivation of a charge-balanced formula, thus explaining the difficulties of some authors to identify phosphates of

Table 1. Cationic distributions in minerals of the alluaudite group, according to the nomenclature scheme of Moore & Ito (1979). The site dominant species is shown in bold.

Ref.	Sample	A(2)'	A(1)	M(1)	M(2)	Ideal cationic charges*	Tentative end-member formula
1	Alluaudite (TYPE)	0.316 Na + 0.684 □	0.595 Na + 0.405 Mn	1.000 Mn	1.280 Fe³⁺ + 0.376 Fe ²⁺ + 0.344 Mn	9	□NaMnFe ₂ ³⁺ (PO ₄) ₃
2	Varulite (TYPE)	0.424 Na + 0.293 Li + 0.013 K + 0.270 □	0.595 Na + 0.405 Mn	0.851 Mn + 0.149 Ca	0.953 Fe³⁺ + 0.924 Mn + 0.088 Fe ²⁺ + 0.035 Al	10	–
3	Hühnerkobelite (TYPE)	0.493 Na + 0.130 Li + 0.006 K + 0.371 □	0.843 Ca + 0.157 Na	0.491 Mn + 0.417 Fe ²⁺ + 0.092 Ca	1.380 Fe²⁺ + 0.529 Fe ³⁺ + 0.091 Mg	9	NaCaMnFe ₂ ²⁺ (PO ₄) ₃
4	Hagendorfite (TYPE)	0.847 Na + 0.018 K + 0.135 □	0.531 Na + 0.318 Mn + 0.151 Ca	0.995 Mn + 0.005 Fe ²⁺	1.251 Fe²⁺ + 0.666 Fe ³⁺ + 0.083 Mg	8	–
5	Alluaudite (Buranga)	1.000 □	0.636 Na + 0.199 Mn + 0.126 Ca + 0.031 Li + 0.008 □	0.893 Mn + 0.107 Fe ²⁺	1.628 Fe³⁺ + 0.257 Fe ²⁺ + 0.056 Mn ³⁺ + 0.059 Mg	9	□NaMnFe ₂ ³⁺ (PO ₄) ₃
6	(North Groton)	0.978 Na + 0.022 □	0.530 Na + 0.273 Mn + 0.197 Ca	0.845 Mn + 0.155 Fe ²⁺	1.050 Fe²⁺ + 0.552 Fe ³⁺ + 0.398 Mg	8	–
6	(Dyke Lode)	0.080 Na + 0.018 Li + 0.902 □	0.843 Na + 0.085 Mn + 0.072 Ca	0.657 Mn + 0.343 Fe ³⁺	0.802 Fe³⁺ + 0.600 Mn ³⁺ + 0.598 Mg	9	□NaMnFe ₂ ³⁺ (PO ₄) ₃
6	(Townsite)	0.563 Na + 0.437 □	0.900 Na + 0.098 Ca + 0.002 Mn	1.000 Mn	1.338 Fe³⁺ + 0.340 Mn + 0.275 Fe ²⁺ + 0.047 Mg	10	–
6	(Pleasant Valley)	0.763 □ + 0.225 Na + 0.012 Li	0.843 Na + 0.135 Ca + 0.022 Mn	0.533 Fe²⁺ + 0.467 Mn	1.605 Fe³⁺ + 0.235 Mg + 0.160 Fe ²⁺	9	□NaFe ²⁺ Fe ₂ ³⁺ (PO ₄) ₃
6	(Tsaobismund)	0.753 □ + 0.247 Na	0.713 Na + 0.190 Ca + 0.097 Mn	0.765 Mn + 0.235 Fe ²⁺	1.465 Fe³⁺ + 0.310 Fe ²⁺ + 0.225 Mg	9	□NaMnFe ₂ ³⁺ (PO ₄) ₃

1. Damour (1848); 2. Quensel (1937); 3. Mason (1942); 4. Strunz (1954); 5. Thoreau (1954); 6. Moore & Ito (1979).

*In bold when the end-member formula tentatively derived by mere consideration of the dominant species in the cationic sites were unbalanced.

the alluaudite group. Among these analyses, 48% are alluaudites, 3% are hagendorfites, 3% are ferroalluaudites, and 2% are unknown end-members, while varulites are absent.

Finally, it is surprising to see that the analysis of “hühnerkobelite”, described by Mason (1942) and later discredited by Moore & Ito (1973), leads to the charge-balanced end-member formula NaCaMnFe₂²⁺(PO₄)₃ (Table 1), which is now attributed to hagendorfite. As shown above, however, type hagendorfite does not contain high amounts of Ca (Strunz, 1954).

4. A new nomenclature scheme for alluaudite-type phosphates

To solve this issue, we suggest to start from alluaudite, which is the only near-end-member frequently observed in

Nature. Alluaudite occurs in many pegmatites, and is frequently of secondary origin. As observed by Fransolet *et al.* (2004) in the Kibingo pegmatite, Rwanda, a primary weakly-oxidized hagendorfite may be oxidized into secondary alluaudite, from the substitution mechanism: Na⁺ + Fe²⁺ = □ + Fe³⁺. This oxidation is clearly visible in thin sections, where green hagendorfite is oxidized, along fractures, into yellow alluaudite (Fig. 4). During this oxidation mechanism, phosphates show chemical compositions plotted on Fig. 5, which clearly indicates positive correlations between the Fe³⁺ contents and the number of vacancies per formula unit. The slopes of these correlations are close to 1.0, thus confirming the substitution mechanism defined above.

Starting from the end-member formula of alluaudite, □NaMnFe₂³⁺(PO₄)₃, and applying the oxidation mechanism Na⁺ + Fe²⁺ = □ + Fe³⁺, it is then possible to redefine

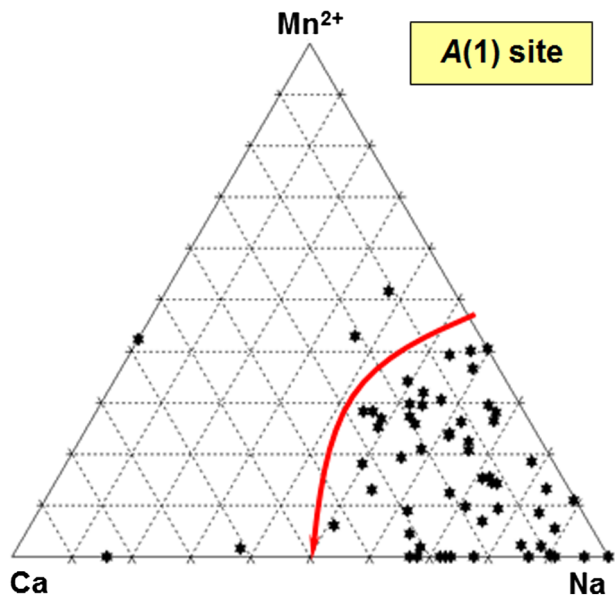


Fig. 3. Cationic distribution on the A(1) site of alluaudite-type phosphates.

the end-member composition of primary hagendorfite as $\text{NaNaMn}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$. This formula seems to contradict the dominant-constituent rule, since a mixed occupancy of the $M(2)$ site by 50% Fe^{2+} and 50% Fe^{3+} is considered here. However, as recommended by Hatert & Burke (2008), valency-imposed double site-occupancy may be required to establish charge-balanced end-member formulae. We consequently suggest to apply, for the nomenclature of alluaudite-type phosphates and arsenates, a nomenclature that takes into account this double site occupancy.

It is important to underline that such a nomenclature scheme is consistent with the nomenclature of the wylleite group, in which the $M(2)$ site is split into two crystallographically independent positions, $M(2a)$ and $M(2b)$. But unlike the wylleite group, the two $M(2)$ sites are not symmetrically distinct in the alluaudite group, even if the “ $M(2a)$ ” and “ $M(2b)$ ” sites names are also used in this proposal. This “artificial splitting” is only applied, here, for nomenclature purposes.

As mentioned above, the end-member formula of varulite, accepted by the CNMNC-IMA, is $\text{NaCaMn}(\text{MnMn})(\text{PO}_4)_3$, which does not correspond to the observed chemical compositions. If we allow a valency-imposed double site occupancy on $M(2)$, and if we take into account the measured composition of type varulite (Table 2; Figs. 2, 3), we can redefine the end-member formula of varulite as $\text{NaNaMn}(\text{MnFe}^{3+})(\text{PO}_4)_3$.

Table 2 shows the cationic distributions in selected analyses from the literature, considering this new nomenclature scheme. This table shows that the majority of tentative end-member formulae are now charge-balanced, except the formulae of type alluaudite, type hühnerkobelite, and of the sample from Dyke Lode (Moore & Ito, 1973). This is due to the fact that some heterovalent substitutions occur

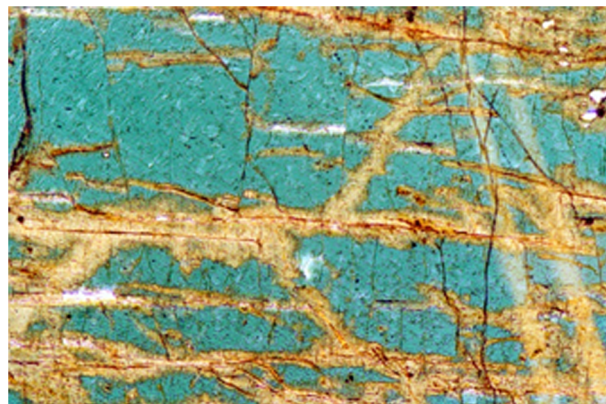


Fig. 4. The oxidation of green hagendorfite to yellow alluaudite. Kibingo pegmatite, Rwanda. The length of the picture represents 3 mm.

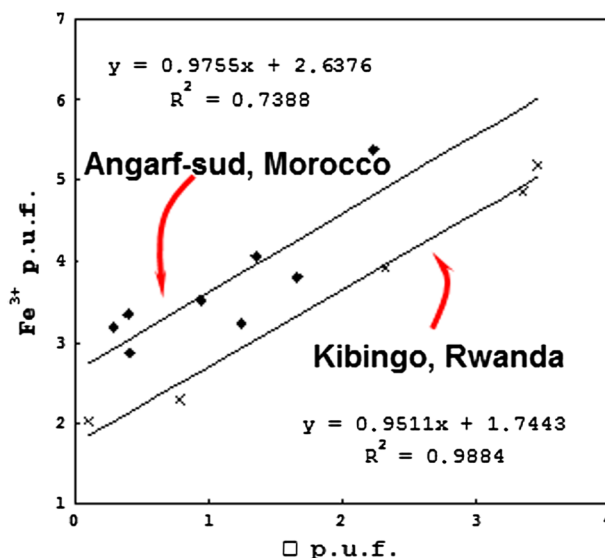


Fig. 5. Correlation between Fe^{3+} and vacancies in alluaudite-type phosphates from Kibingo, Rwanda (Fransolet *et al.*, 2004), and Angarf Sud, Morocco (Fransolet *et al.*, 1985).

in these samples, which modify their compositions. In type alluaudite and in type hühnerkobelite, the substitution mechanism $\text{Na}^+ + \text{Fe}^{2+} = \square + \text{Fe}^{3+}$ occurs, responsible for the presence of significant Na on $A(2)'$ and Fe^{2+} on $M(2a)$ in type alluaudite, and of significant vacancies on $A(2)'$ and Fe^{3+} on $M(2b)$ in type varulite (Table 2).

Even if the end-member formulae of these type samples are not straightforwardly derived in the new nomenclature scheme, we recommend keeping the end-member formula of alluaudite as $\square\text{NaMn}(\text{Fe}^{3+}\text{Fe}^{3+})(\text{PO}_4)_3$, since this composition is extremely common in pegmatites and corresponds to the ideal composition of alluaudite from the Buranga pegmatite, which was investigated in detail (Table 2).

Consequently, we recommend modifying the end-member formulae of alluaudite-type phosphates as reported in Table 3. In this new nomenclature, the root-name is defined

by the $M(2)$ content, and a prefix is added depending on the $M(1)$ content. Three situations occur:

1. $0.5 < {}^{M(2)}M^{2+} < 1.5$ (M^{2+} mainly Fe^{2+}): hagendorfites,
2. $0.5 < {}^{M(2)}M^{2+} < 1.5$ (M^{2+} mainly Mn^{2+}): varulites,
3. ${}^{M(2)}M^{2+} < 0.5$ (M^{3+} mainly Fe^{3+}): alluaudites.

The application of the new nomenclature scheme to all chemical analyses from the literature shows that it allows one to derive straightforwardly a charge-balanced end-member formula for 72% of the samples, which constitutes a significant improvement compared to the previous nomenclature. For the other samples, it is necessary to identify the substitution mechanisms, in order to find the end-member composition. From a general point of view, four different types of substitution mechanisms occur in alluaudite-type phosphates:

1. S1: $\text{Na}^+ + M^{2+} = \square + \text{Fe}^{3+}$ (oxidation),
2. S2: $\square + 2\text{Fe}^{3+} = M^{2+} + 2 M^{2+}$ (Na constant),
3. S3: $\text{Na}^+ + \text{Na}^+ = \square + \text{Mn}^{2+}$ (Fe constant),
4. S4: $\text{Na}^+ + \text{Fe}^{3+} = M^{2+} + M^{2+}$ (\square constant).

The oxidation mechanism S1 was demonstrated above (Fig. 5), and Fig. 6 shows a negative correlation between $\text{Fe}^{3+} + \square$ and the M^{2+} content, thus confirming substitution mechanism S2.

A careful examination of the chemical analyses shows that when a tentative end-member formula (derived by mere consideration of the site-dominant constituent) is not charge-balanced, this is due to the influence of one of these supplementary substitution mechanisms. The most common mechanism is S3, which explains how the number of Na atoms may decrease on the A sites, where they are replaced by Mn and vacancies. Several examples of this type are shown in Table 2:

1. The alluaudite type sample (Damour, 1848) corresponds to hagendorfite, since 0.720 M^{2+} (dominantly Fe^{2+}) occur on $M(2)$. However, the substitution mechanism S3 renders vacancies dominant on $A(2)'$, which, upon mere consideration of the site-dominant constituent, would lead to the unbalanced tentative end-member formula " $\square\text{NaMnFe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ ". This mineral has to be considered as a Na-poor hagendorfite.
2. The sample from the Buranga pegmatite, investigated by Hérens (1989), is an alluaudite, since it contains less than 0.298 M^{2+} cations on $M(2)$, where Fe^{3+} is dominant. However, the $A(1)$ site is dominantly occupied by Mn, due to substitution mechanism S3, which again offers the pitfall of an unbalanced tentative formula, " $\square\text{MnMnFe}_2^{3+}(\text{PO}_4)_3$ ". This sample has to be considered as a Mn-rich alluaudite.
3. A sample from La Fregeneda pegmatite, Spain (Roda et al., 1996), contains 0.586 Fe^{2+} on $M(2)$, and therefore corresponds to a hagendorfite. The $M(1)$ site is predominantly occupied by Fe^{2+} , so it is a "ferrohagendorfite" (not IMA-CNMNC approved). However, vacancies are dominant on $A(2)'$ due to the

substitution mechanism S3, thus leading to the unbalanced tentative formula " $\square\text{NaFe}^{2+}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$ ". This sample has to be considered as a Na-poor "ferrohagendorfite".

4. Another sample from La Fregeneda contains 0.703 divalent cations on $M(2)$, among which Mn^{2+} is clearly dominant: it is a varulite. However, the S3 substitution mechanism provokes the dominance of vacancies on $A(2)'$, leading to an unbalanced tentative formula, " $\square\text{NaMn}(\text{MnFe}^{3+})(\text{PO}_4)_3$ ". This sample has to be considered as a Na-poor varulite.
5. The sample from Skruppetorp is characterized by a very high Mn^{3+} content, reaching 0.484 Mn^{3+} on $M(2)$. In that case, a cationic distribution considering a splitting of the $M(2)$ site seems to indicate a formula $\square\text{NaMn}(\text{Mn}^{3+}\text{Fe}^{3+})(\text{PO}_4)_3$. However, two cations of the same valence state occur on the same site, and this cannot be considered as a valency-imposed double site-occupancy. The "artificial splitting" of $M(2)$ cannot be applied here, and since M^{3+} cations reach 1.667 *apfu* on $M(2)$, with Fe^{3+} dominant, we have simply a Mn^{3+} -rich alluaudite.

These examples illustrate how to use the new nomenclature scheme to determine an alluaudite-type phosphate. Taking into account the multiple substitution mechanisms, it is now possible to identify all samples. Starting from the 64 analyses from the literature, we found 33% hagendorfites, 31% alluaudites, 11% varulites, 1% ferroalluaudites, and 24% of new species that will be described below. Maghagendorfite is absent from the samples, since the cationic distribution used here considers a preference of Mg for the $M(2)$ site, not for $M(1)$, as experimentally demonstrated by Rondeux & Hatert (2010). Since the cationic distribution of maghagendorfite is unlikely, we recommend considering this species as "Questionable".

5. Definition of new end-members

In order to define new possible end-member compositions, we decided to establish theoretically all possible formula types for alluaudite-type phosphates. Starting from the formula of alluaudite, $\text{NaMnFe}_2^{3+}(\text{PO}_4)_3$, we defined formulae of type 1, $\text{NaM}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3$ (Fig. 7). We consider here Fe^{3+} as the main trivalent cation occurring on $M(2)$; however, some analyses from the literature show that Mn^{3+} may play a significant role on that site (Table 2). In wylleites, Al also occurs on one of the two $M(2)$ positions; this will be discussed in detail below. From type formula 1, it is then possible to define the formulae $\text{NaM}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_3 =$ alluaudites, and $\text{NaM}^{2+}\text{Mn}_2^{3+}(\text{PO}_4)_3 =$ a new root-name called ROOT1 (Fig. 8).

Starting from alluaudites, and applying the oxidation mechanism S1, we obtain type 2 with the theoretical formula $\text{Na}_2\text{M}_2^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ (Fig. 7). From this general formula we deduce three root-names: hagendorfites = $\text{Na}_2\text{M}^{2+}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$, varulites = $\text{Na}_2\text{M}^{2+}(\text{Mn}^{2+}\text{Fe}^{3+})$

Table 2. Cationic distributions in minerals of the alluaudite group, considering the new nomenclature scheme. Site dominant species is shown in bold.

Ref.	Sample	A(2)'	A(1)	M(1)	M(2a)	M(2b)	Ideal cationic charges*	Tentative end-member formula* (name)
1	Alluaudite (TYPE)	0.316 Na + 0.684 □	0.595 Na + 0.405 Mn	1.000 Mn	0.376 Fe²⁺ + 0.344 Mn + 0.280 Fe ³⁺	1.000 Fe³⁺	8	“□NaMn(Fe ²⁺ Fe ³⁺)(PO ₄) ₃ ” (Na-poor hagendorfite)
2	Varulite (TYPE)	0.424 Na + 0.293 Li + 0.013 K + 0.270 □	0.595 Na + 0.405 Mn	0.851 Mn + 0.149 Ca	0.924 Mn + 0.076 Fe ²⁺	0.953 Fe³⁺ + 0.035 Al + 0.012 Fe ²⁺	9	NaNaMn(MnFe ³⁺)(PO ₄) ₃ (Varulite)
3	Hühnerkobelite (TYPE)	0.493 Na + 0.130 Li + 0.006 K + 0.371 □	0.843 Ca + 0.157 Na	0.491 Mn + 0.417 Fe ²⁺ + 0.092 Ca	1.000 Fe²⁺	0.529 Fe³⁺ + 0.380 Fe ²⁺ + 0.091 Mg	10	“NaCaMn(Fe ²⁺ Fe ³⁺)(PO ₄) ₃ ” (Na-rich hagendorfite-Ca)
4	Hagendorfite (TYPE)	0.847 Na + 0.018 K + 0.135 □	0.531 Na + 0.318 Mn + 0.151 Ca	0.995 Mn + 0.005 Fe ²⁺	1.000 Fe²⁺	0.666 Fe³⁺ + 0.251 Fe ²⁺ + 0.083 Mg	9	NaNaMn(Fe ²⁺ Fe ³⁺)(PO ₄) ₃ (Hagendorfite)
5	Alluaudite (Buranga)	1.000 □	0.636 Na + 0.199 Mn + 0.126 Ca + 0.031 Li + 0.008 □	0.893 Mn + 0.107 Fe ²⁺	0.628 Fe³⁺ + 0.257 Fe ²⁺ + 0.056 Mn ³⁺ + 0.059 Mg	1.000 Fe³⁺	9	NaMnFe ₂ ³⁺ (PO ₄) ₃ (Alluaudite)
6	(North Groton)	0.978 Na + 0.022 □	0.530 Na + 0.273 Mn + 0.197 Ca	0.845 Mn + 0.155 Fe ²⁺	1.000 Fe²⁺	0.552 Fe³⁺ + 0.398 Mg + 0.050 Fe ²⁺	9	NaNaMn(Fe ²⁺ Fe ³⁺)(PO ₄) ₃ (Hagendorfite)
6	(Dyke Lode)	0.080 Na + 0.018 Li + 0.902 □	0.843 Na + 0.085 Mn + 0.072 Ca	0.657 Mn + 0.343 Fe ³⁺	0.598 Mg + 0.402 Mn ³⁺	0.802 Fe³⁺ + 0.198 Mn ³⁺	8	“□NaMn(MgFe ³⁺)(PO ₄) ₃ ” (Na-poor ROOT2)
6	(Townsite)	0.563 Na + 0.437 □	0.900 Na + 0.098 Ca + 0.002 Mn	1.000 Mn	0.340 Mn + 0.338 Fe ³⁺ + 0.275 Fe ²⁺ + 0.047 Mg	1.000 Fe³⁺	9	NaNaMn(MnFe ³⁺)(PO ₄) ₃ (Varulite)
6	(Pleasant Valley)	0.763 □ + 0.225 Na + 0.012 Li	0.843 Na + 0.135 Ca + 0.022 Mn	0.533 Fe²⁺ + 0.467 Mn	0.605 Fe³⁺ + 0.235 Mg + 0.160 Fe ²⁺	1.000 Fe³⁺	9	NaFe ²⁺ Fe ₂ ³⁺ (PO ₄) ₃ (Ferroalluaudite)
6	(Tsaobismund)	0.753 □ + 0.247 Na	0.713 Na + 0.190 Ca + 0.097 Mn	0.765 Mn + 0.235 Fe ²⁺	0.465 Fe³⁺ + 0.310 Fe ²⁺ + 0.225 Mg	1.000 Fe³⁺	9	NaMnFe ₂ ³⁺ (PO ₄) ₃ (Alluaudite)
7	(Skruppetorp)	0.585 □ + 0.415 Na	1.000 Na	0.611 Mn + 0.607 Ca + 0.082 Na	0.484 Mn³⁺ + 0.322 Mn ²⁺ + 0.183 Fe ³⁺ + 0.011 Mg	1.000 Fe³⁺	9	NaMnFe ₂ ³⁺ (PO ₄) ₃ (Mn ³⁺ -rich alluaudite)
8	Alluaudite calcifère (Sidi Bou Othmane)	0.719 □ + 0.276 Na + 0.0005 K	0.611 Ca + 0.374 Na + 0.015 Mn	0.975 Mn + 0.025 Fe ²⁺	0.881 Fe²⁺ + 0.119 Fe ³⁺	0.974 Fe³⁺ + 0.026 Mg	9	□CaMn(Fe ²⁺ Fe ³⁺)(PO ₄) ₃ (Hagendorfite-Ca)
9	(Angarf Sud)	0.514 Na + 0.483 □ + 0.003 Li	0.510 Na + 0.429 Ca + 0.061 Mn	0.715 Fe²⁺ + 0.285 Mn	0.615 Fe²⁺ + 0.385 Mg	0.980 Fe³⁺ + 0.012 Al + 0.008 Mg	9	NaNaFe ²⁺ (Fe ²⁺ Fe ³⁺)(PO ₄) ₃ (Hagendorfite)
9	(Angarf Sud)	0.660 Na + 0.340 □	0.675 Na + 0.308 Ca + 0.017 Mn	0.618 Fe²⁺ + 0.382 Mn	0.515 Mg + 0.470 Fe ²⁺ + 0.015 Fe ³⁺	1.000 Fe³⁺	9	NaNaFe ²⁺ (MgFe ³⁺)(PO ₄) ₃ (FerroROOT2)
10	(Buranga)	1.000 □	0.341 Mn + 0.286 Na + 0.166 Ca + 0.207 □	1.000 Mn	0.702 Fe³⁺ + 0.147 Fe ²⁺ + 0.102 Mn + 0.041 Mg + 0.008 Zn	1.000 Fe³⁺	10	“□MnMnFe ₂ ³⁺ (PO ₄) ₃ ” (Mn-rich alluaudite)
11	(Fregeneda)	0.763 □ + 0.237 Na	0.651 Na + 0.296 Mn + 0.053 Ca	0.651 Fe²⁺ + 0.349 Mn	0.586 Fe²⁺ + 0.414 Fe ³⁺	0.997 Fe³⁺ + 0.003 Al	8	“□NaFe ²⁺ (Fe ²⁺ Fe ³⁺)(PO ₄) ₃ ” (Na-poor “ferrohagendorfite”)
11	(Fregeneda)	0.517 □ + 0.473 Na + 0.010 K	0.780 Na + 0.185 Mn + 0.035 Ca	1.000 Mn	0.575 Mn²⁺ + 0.191 Mn ³⁺ + 0.128 Mg + 0.106 Fe ³⁺	0.995 Fe³⁺ + 0.005 Al	8	“□NaMn(MnFe ³⁺)(PO ₄) ₃ ” (Na-poor varulite)
11	(Fregeneda)	0.680 Na + 0.245 □ + 0.075 Ca	0.576 Ca + 0.424 Mn	1.000 Mn	0.785 Fe²⁺ + 0.215 Mn	0.755 Fe²⁺ + 0.238 Fe ³⁺ + 0.007 Al	9	NaCaMnFe ₂ ²⁺ (PO ₄) ₃ (ROOT3)

1. Damour (1848); 2. Quensel (1937); 3. Mason (1942); 4. Strunz (1954); 5. Thoreau (1954); 6. Moore & Ito (1979); 7. Mason (1940); 8. Huvelin *et al.* (1972); 9. Fransolet *et al.* (1985); 10. Hérens (1989); 11. Roda *et al.* (1996).

*End-member formula tentatively derived by mere consideration of the dominant species in the cationic sites, which in some instances may lead to an unbalanced formula (in double quotes), *i.e.* a charge number differing from 9 in the cationic groups (then noted in bold-face type).

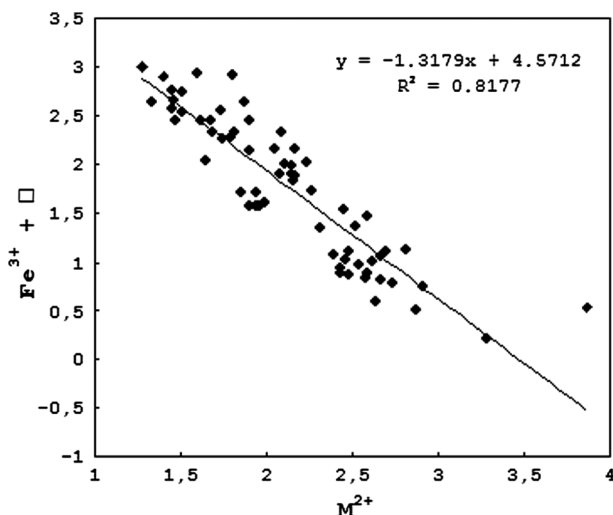


Fig. 6. Correlation between $\text{Fe}^{3+} + \square$ and M^{2+} in alluaudite-type phosphates from the literature.

$(\text{PO}_4)_3$, and a new root-name called ROOT2 = $\text{Na}_2M^{2+}(\text{MgFe}^{3+})(\text{PO}_4)_3$ (Fig. 8).

Starting from alluaudites and applying substitution mechanism S2, or starting from formula type 2 and applying substitution mechanism S4, we obtain formula type 3, $\text{NaM}_4^{2+}(\text{PO}_4)_3$ (Fig. 7). Taking into account the crystal-chemical constraints existing in alluaudite-type phosphates, it is possible to define three root-names from this formula type: $\text{NaCaM}^{2+}\text{Fe}_2^{2+}(\text{PO}_4)_3 = \text{ROOT3}$, $\text{NaCaM}^{2+}\text{Mg}_2(\text{PO}_4)_3 = \text{ROOT4}$, and $\text{NaCaM}^{2+}\text{Mn}_2^{2+}(\text{PO}_4)_3 = \text{ROOT5}$ (Fig. 8).

Finally, starting from formula type 3 and applying the substitution mechanism S1, or starting from formula type 2 and applying the substitution mechanism S3, we obtain formula type 4, $M_3^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ (Fig. 7). The possible root-names are $\square\text{CaM}^{2+}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3 = \text{hagendorfites-Ca}$, $\square\text{CaM}^{2+}(\text{Mn}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3 = \text{varulites-Ca}$, and $\square\text{CaM}^{2+}(\text{MgFe}^{3+})(\text{PO}_4)_3 = \text{ROOT2-Ca}$ (Fig. 8). Note that in those cases, the $M(2)$ contents are identical to those of formulae type 2, but the two Na cations on the A sites are replaced by Ca^{2+} and a vacancy. Therefore, the names of type 2 phosphates are used with the addition of a chemical suffix to designate that Ca is dominant on A(1). This suffix is written without parentheses since A cations in the alluaudite structure occur in channels, and can therefore be considered as extra-framework cations (Hatert *et al.*, 2013).

6. The nomenclature of alluaudite-type arsenates

Nineteen arsenates belong to the alluaudite group; they are listed in Table 4. Among these species, four show a double occupancy of the $M(2)$ site: caryinite, hatertite, badalovite and magnesiocanutite, thus implying the use of the new nomenclature scheme. Alluaudite-type arsenates are found

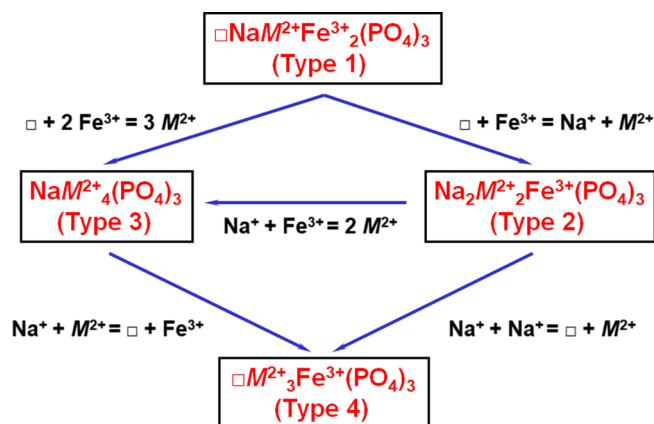


Fig. 7. The different types of end-member formulae existing in the alluaudite group.

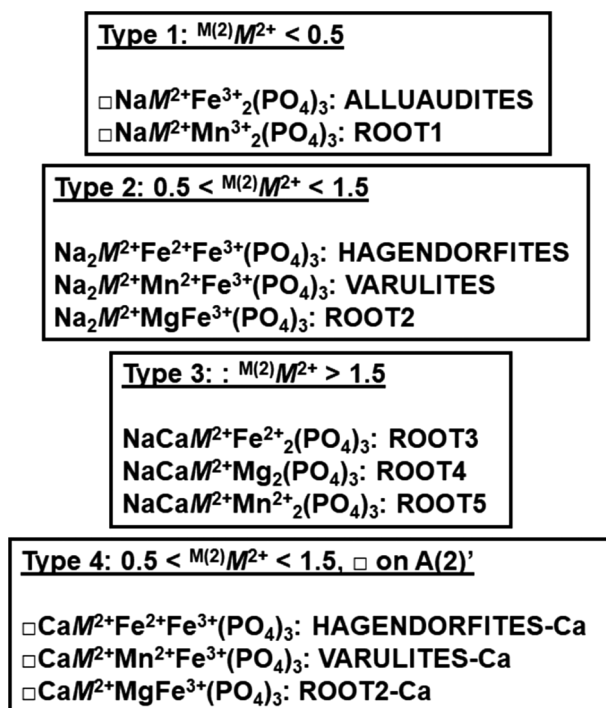


Fig. 8. Hypothetical root-names in the alluaudite group.

in exotic geochemical environments, such as volcanic fumaroles or Pb–Zn deposits. For this reason, their crystal chemistry is very different from that of alluaudite-type phosphates, with divalent cations Zn, Cd, and Cu^{2+} playing significant roles.

The formulae of alluaudite-type arsenates are most frequently of type 3, $\text{NaM}_4^{2+}(\text{AsO}_4)_3$, but significant amounts of hydrogen, of water molecules, or of vacancies may occur in these minerals (Table 4). Three different mechanisms can be identified, to explain the presence of vacancies: (i) an oxidation mechanism producing Fe^{3+} on $M(2)$ and vacancies on the A sites, as observed in yazganite; (ii) the replacement of Na^+ by $(0.5 \text{ Cu}^{2+} + 0.5 \square)$, as observed in keyite and

Table 3. Formulae modifications in the alluaudite group of phosphates.

Mineral name	Old CNMNC formula	New ideal formula
Alluaudite	(Na,Ca)(Mn,Mg,Fe ²⁺)(Fe ³⁺ ,Mn ²⁺) ₂ (PO ₄) ₃	□NaMnFe ₂ ³⁺ (PO ₄) ₃
Ferroalluaudite	NaFe ²⁺ Fe ₂ ³⁺ (PO ₄) ₃	□NaFe ²⁺ Fe ₂ ³⁺ (PO ₄) ₃
Hagendorffite	NaCaMn ²⁺ Fe ₂ ²⁺ (PO ₄) ₃	Na ₂ MnFe ²⁺ Fe ³⁺ (PO ₄) ₃
Maghagendorffite	(Na,□)MgMn ²⁺ (Fe ²⁺ ,Fe ³⁺) ₂ (PO ₄) ₃	Na ₂ MgFe ²⁺ Fe ³⁺ (PO ₄) ₃
Varulite	NaCaMn ₃ ²⁺ (PO ₄) ₃	Na ₂ Mn ₂ Fe ³⁺ (PO ₄) ₃

erikapohlite; (iii) the presence of H atoms in the channels, producing the protonated arsenates o'danielite, canutite, magnesiocanutite and camanchacaite. Hatertite and badalovite are characterized by formulae of type 2, Na₂M₂²⁺Fe³⁺(AsO₄)₃, while khrenovite has the ideal formula Na₃Fe₂³⁺(PO₄)₃ (Table 4).

In these minerals, cationic distributions in the channels are governed by the presence of water molecules and hydrogen atoms, as underlined by Krivovichev *et al.* (2013) and Kampf *et al.* (2014). In unprotonated alluaudite-type arsenates, the A(1) and A(2)' sites are generally occupied but, if vacancies occur, they are preferentially located on A(2)', as observed in yazganite, keyite and erikapohlite (Table 4). The resulting free space is filled by water molecules in channel 2 of these minerals; it seems that half occupancy of A(2)' is enough to accommodate one water molecule. In protonated arsenates, channel 1 is occupied by the H atoms of the [AsO₃(OH)] and [AsO₂(OH)₂] groups, thus explaining the presence of vacancies on the A(1) sites of o'danielite, canutite, magnesiocanutite and camanchacaite (Table 4).

No nomenclature guidelines actually exist for alluaudite-type arsenates; for this reason, new names were given for each species. According to the CNMNC guidelines (Hatert *et al.*, 2013), we recommend preserving the existing historical names, reported in Table 4. These names must be considered as root-names; they are defined from their contents on both M(1) and M(2) sites. If new arsenates would be found, belonging to the alluaudite group, they could receive a new root-name if their occupancies on M(1) and M(2) are different from those of known species (Table 4). However, as has recently been done for magnesiocanutite, zinco-bradaczekite and magnesiohatertite, a prefix may also be used to designate the cationic content on the M(1) or M(2) sites. If the M(1) and M(2) occupancies are identical, but if the cations occurring in the channels are different, we recommend keeping the existing root-name, and to add a chemical suffix without parentheses, to describe the cationic content of the A(1) and A(2)' extra-framework sites. A maximal number of two suffixes would be sufficient.

A careful examination of the site populations for alluaudite-type arsenates, given in Table 4, shows that some end-member formulae have to be significantly modified, compared to those occurring in the IMA-CNMNC mineral list. The main modifications are given in Table 5, but all CNMNC formulae have to be modified according to Table 4.

The double site-occupancy is applied for mineral with a mixed valence on M(2); however, no artificial splitting is

used when M²⁺ cations are dominant on this site. The valency-imposed double site-occupancy is therefore only applicable for hatertite, badalovite, and magnesiohatertite (Table 3). In arsenioleite, the A(1) site is mainly occupied by Ca, not by Na (Table 3).

The most problematic issue in alluaudite-type arsenates concerns the recently described calciojohillerite (Pekov *et al.*, 2016c), which shows a M(2)–M(1) distribution similar to that of nickenichite, but with slightly different cationic distributions between the sites occurring in channel 1. Indeed, nickenichite is the only alluaudite-type arsenate in which both A(1) and A(1)' sites are significantly occupied. The resulting ideal formula of nickenichite becomes Na(Ca_{0.5}Cu_{0.5})MgMg₂(AsO₄)₃, while calciojohillerite corresponds to NaCaMgMg₂(AsO₄)₃. In this special case, we recommend keeping both mineral species, but in the future, we suggest to avoid defining alluaudite-type minerals from slight modifications of the cationic distributions among the different crystallographic positions located in the channels. We recommend considering, for nomenclature purpose, the cations A(1) + A(1)' + A(1)'' (channel 1) as a whole, as well as the cations A(2) + A(2)' + A(2)'' (channel 2).

Table 6 gives a summary of the classification of alluaudite-type arsenates, distributed according to their M(2) contents.

7. The wyllieite group, the bobfergusonite group, and manitobaite

Phosphates of the wyllieite group also occur in granitic pegmatites, but they generally crystallize as primary phases (Vignola, 2018), or under high-temperature hydrothermal conditions, by reaction between Fe–Mn–phosphates and albite (Fig. 9). For this reason, these phosphates contain significant amounts of aluminium. The presence of this element induces a splitting of the M(2) and X(1) sites of alluaudite into M(2a)–M(2b) and X(1a)–X(1b), and provokes a change of space group. For this reason, wyllieite-type phosphates form their own mineral group within the alluaudite supergroup.

Wyllieite is the first species described in the group (Moore & Ito, 1973); however, its name was changed to ferrowyllieite by Moore & Ito (1979) who established nomenclature guidelines for the group. According to this nomenclature scheme, and to recent crystal-chemical investigations (Hatert *et al.*, 2005b, 2006, 2010, 2016), the M(2a) site of the structure is systematically occupied by Al; the root-name consequently depends on the M(2b) content:

Table 4. The nomenclature and composition of alluaudite-type arsenates (site-dominant cation in bold).

Ref.	Mineral	A(2) ⁺	A(1)	M(1)	M(2a)	M(2b)	Ideal cationic charges	End-member formula
1	O'danielite	Na	□	Zn	Zn	Zn	7	Na ₃ □Zn ₃ [AsO ₄] ₂ [AsO ₄ (OH)] ₂
2	Johillerite	0.77 Na + 0.01 Pb + 0.01 Ca + 0.03 K	1.00 Cu ²⁺	0.79 Mg + 0.21 Cu ²⁺	0.39 Cu ²⁺ + 0.30 Mg + 0.25 Fe ³⁺ + 0.06 Al	1.00 Mg	9	NaCaMgMg ₂ (AsO ₄) ₃
3	Caryinite	0.62 Na + 0.38 Na	□	0.67 Ca + 0.33 Mn ²⁺	1.00 Mn ²⁺	0.56 Mg + 0.44 Mn ²⁺	9	Na ₃ CaMn ₂ (AsO ₄) ₃
4	Nickenicite	0.76 Na + 0.24 □	0.41 Ca + 0.39 Cu ²⁺ + 0.20 □	0.89 Mg + 0.11 Fe ³⁺	1.00 Mg	0.56 Mg + 0.44 Fe ³⁺	9	Na(Ca _{0.5} Cu _{0.5})MgMg ₂ (AsO ₄) ₃
5	Arsenopleite	0.93 Na + 0.06 Pb + 0.01 Ba	0.68 Ca + 0.32 Na	1.00 Mn	1.00 Mn	0.52 Mg + 0.27 Fe ³⁺ + 0.21 Mn	9	NaCaMnMn ₂ (AsO ₄) ₃
6	Bradaczekite	1.00 Na	0.84 Cu ²⁺ + 0.16 Na	1.00 Cu ²⁺	0.93 Cu ²⁺ + 0.07 Zn	0.97 Cu ²⁺ + 0.03 Fe ³⁺	9	NaCuCuCu ₂ (AsO ₄) ₃
7	Keyite	0.52 □ + 0.48 Cu ²⁺	0.93 Cu ²⁺ + 0.05 Pb + 0.02 Ca	0.85 Cd + 0.10 Mn + 0.05 Ca	0.84 Zn + 0.16 Cu ²⁺	1.00 Zn	9	(□ _{0.2} Cu _{0.3} Cu _{0.5})Cu ₂ Zn ₂ (AsO ₄) ₃ ·H ₂ O
8	Yazganite	1.00 □	0.97 Na + 0.03 □	0.43 Mg + 0.26 Mn + 0.20 Fe ²⁺ + 0.07 Zn + 0.02 Fe ³⁺	1.00 Fe ³⁺	1.00 Fe ³⁺	9	NaMgFe ³⁺ (AsO ₄) ₃ · H ₂ O
9	Erikapohlite	0.60 Cu ²⁺ + 0.40 □	1.00 Cu ²⁺	1.00 Ca	0.63 Zn + 0.37 Cu ²⁺	0.61 Zn + 0.39 Mg	9	(□ _{0.2} Cu _{0.3} Cu _{0.5})Cu ₂ Cu ₂ (ZnZn)(AsO ₄) ₃ ·H ₂ O
10	Hatertite	0.55 Na + 0.30 K + 0.15 □	0.87 Na + 0.13 Ca	0.60 Ca + 0.27 Na + 0.13 Mn	0.40 Cu ²⁺ + 0.32 Zn + 0.28 Al	0.90 Fe ³⁺ + 0.10 Al	9	Na ₃ NaCaCu ²⁺ Fe ³⁺ (AsO ₄) ₃
11	Canutite	0.85 Na + 0.15 Mn	0.80 □ + 0.20 Na	1.00 Mn	0.83 Mn + 0.14 Cu ²⁺ + 0.03 Co	0.66 Mn + 0.34 Mg	7	Na□MnMn ₂ [AsO ₄] ₂ [AsO ₄ (OH)] ₂
12	Zincobradaczekite	0.90 Na + 0.08 K	1.00 Cu ²⁺	0.70 Cu ²⁺ + 0.12 Mg + 0.08 Fe ³⁺ + 0.03 Zn	1.00 Zn	1.00 Zn	9	NaCuCuZn ₂ (AsO ₄) ₃
13	Badalovite	0.90 Na + 0.10 □	0.85 Na + 0.15 Ca	0.90 Mg + 0.10 Ca	1.00 Mg	0.95 Fe ³⁺ + 0.05 Mg	9	NaNaMg(MgFe ³⁺)(AsO ₄) ₃
14	Magnesiocanutite	0.92 Na + 0.03 Cs + 0.05 Mn	0.90 □ + 0.10 Na	0.78 Mn + 0.22 Mg	0.70 Mn + 0.16 Cu + 0.11 Co + 0.03 Mg	1.00 Mg	7	Na□MnMg ₂ [AsO ₄] ₂ [AsO ₄ (OH)] ₂
15	Calciojohillerite	0.99 Na + 0.01 K	0.70 Ca + 0.25 Na + 0.05 □	0.95 Mg + 0.05 Mn ²⁺	1.00 Mg	0.70 Mg + 0.25 Fe ³⁺ + 0.05 Al	9	NaCaMgMg ₂ (AsO ₄) ₃
16	Magnesiobadaczekite	0.88 Na + 0.12 K	0.52 Na + 0.30 Ca + 0.18 Cu	0.93 Ca + 0.07 Mn ²⁺	0.88 Mg + 0.12 Cu ²⁺	0.52 Fe ³⁺ + 0.24 Cu ²⁺ + 0.24 Zn	9	NaNaCaMgFe ³⁺ (AsO ₄) ₃
17	Khrenovite	0.74 Na + 0.19 □ + 0.07 K	0.91 Na + 0.09 Mn	0.60 Na + 0.16 Zn + 0.14 Cu + 0.10 Mn	0.67 Fe ³⁺ + 0.19 Cu + 0.14 Mn	1.00 Fe ³⁺	9	Na ₃ Fe ³⁺ (AsO ₄) ₃
18	Paraberzefite	0.80 Na + 0.15 Ca	0.60 Ca + 0.40 Na	0.95 Ca + 0.05 Mn ²⁺	0.70 Mg + 0.20 Fe ²⁺ + 0.10 Mn ²⁺	1.00 Mg	9	NaCaCaMg ₂ (AsO ₄) ₃
19	Camanchacite	0.99 Na + 0.01 □	1.00 □	0.84 Ca + 0.11 Mg + 0.02 Mn	1.00 Mg	1.00 Mg	7	Na□CaMg ₂ [AsO ₄] ₂ [AsO ₄ (OH)] ₂

1. Keller & Hess (1988); 2. Tait & Hawthorne (2004); 3. Ercit (1993); 4. Auenhammer *et al.* (1993); 5. Tait & Hawthorne (2003); 6. Filatov *et al.* (2001); 7. Cooper & Hawthorne (1996), Malcherek & Schillter (2005); 8. Sarp and Černý (2005); 9. Schillter *et al.* (2013); 10. Krivovichev *et al.* (2013); 11. Kampf *et al.* (2014); 12. Pekov *et al.* (2016a); 13. Pekov *et al.* (2016b); 14. Kampf *et al.* (2016a); 15. Pekov *et al.* (2017); 16. Pekov *et al.* (2016c); 17. Pekov *et al.* (2018a); 18. Pekov *et al.* (2018b); 19. Kampf *et al.* (2018).

Table 5. Main formulae modifications for alluaudite-type arsenates.

Mineral name	Old CNMNC formula	New ideal formula
Nickenichite	(Na,Ca,Cu) _{1,6} (Mg,Fe ³⁺ ,Al) ₃ (AsO ₄) ₃	Na(Ca _{0,5} Cu _{0,5})MgMg ₂ (AsO ₄) ₃
Arseniopleite	(Na,Ca)NaMn ²⁺ (Mn ²⁺ ,Mg,Fe ²⁺) ₂ (AsO ₄) ₃	NaCaMnMn ₂ (AsO ₄) ₃
Keyite	Cu ₃ ²⁺ Zn ₄ Cd ₂ (AsO ₄) ₆ ·2H ₂ O	(□ _{0,5} Cu _{0,5})CuCdZn ₂ (AsO ₄) ₃ ·H ₂ O
Erikapohlite	Cu ₃ ²⁺ (Zn,Cu,Mg) ₄ Ca ₂ (AsO ₄) ₆ ·2H ₂ O	(□ _{0,5} Cu _{0,5})CuCaZn ₂ (AsO ₄) ₃ ·H ₂ O
Hatertite	Na ₂ (Ca,Na)(Fe ³⁺ ,Cu) ₂ (AsO ₄) ₃	NaNaCa(Cu ²⁺ Fe ³⁺)(AsO ₄) ₃
Magnesiohatertite	(Na,Ca) ₂ Ca(Mg,Fe ³⁺) ₂ (AsO ₄) ₃	NaNaCa(MgFe ³⁺)(AsO ₄) ₃

Table 6. Classification of alluaudite-type arsenates, according to their *M*(2) contents.

<i>M</i> (2)	<i>A</i> (2)' <i>A</i> (1) <i>M</i> (1)	Name
(ZnZn)	□NaZn	O'danielite
	NaCuCu	Zincobradaczekite
	(□ _{0,5} Cu _{0,5})CuCd	Keyite
	(□ _{0,5} Cu _{0,5})CuCa	Erikapohlite
(MgMg)	Na(Ca _{0,5} Cu _{0,5})Mg	Nickenichite
	NaCaMg	Calciojohillerite
	NaCuMg	Johillerite
	NaCaCa	Paraberezeliite
	□NaMn	Magnesiocanutite
	□NaCa	Camanchacaite
(MnMn)	□NaMn	Canutite
	NaCaMn	Arseniopleite
	NaCaCa	Caryinite
(CuCu)	NaCuCu	Bradaczekite
(Fe ³⁺ Fe ³⁺)	□NaMg	Yazganite
	NaNaNa	Khrenovite
(CuFe ³⁺)	NaNaCa	Hatertite
(MgFe ³⁺)	NaNaMg	Badalovite
	NaNaCa	Magnesiohatertite

Fe²⁺ in wyllieites, Fe³⁺ in rosemaryites, and Mg in qingheite. The *M*(1) site is dominantly occupied by Mn or Fe²⁺; in the latter case, the prefix “ferro-” is added to the mineral name. The six valid mineral species in the wyllieite group, as well as their end-member formulae, are reported in Table 7.

Cation occupancies, established from X-ray crystal-structure determinations, indicate that the *X*(1a) site is generally occupied by Mn, while the *X*(1b) site contains Na. If we consider both sites together, for nomenclature purposes, we realize that *X*(1a+b) systematically contains significant amounts of Mn, in contradiction with the ideal end-member formulae which consider this site as predominantly occupied by Na. In rosemaryite and ferrosemaryite, the presence of significant amounts of vacancies on the *X*(1a+b) sites indicates the occurrence of the substitution mechanism Na⁺ + Na⁺ = □ + Mn²⁺, previously observed in alluaudites.

This feature is also due to the detailed cationic distributions established from structural data: different cation grouping would generally provoke a dominant occupancy of Na on the *X*(1a+b) sites. Cationic distributions established from chemical data, by grouping cations according to their ionic radii, are also shown on Table 7; they better fit with the end-member formulae. The significant amounts of vacancies

on the *X*(2) site of qingheite-(Fe²⁺) are due to the presence of Fe³⁺ on the *M*(2b) site of the structure, according to the substitution mechanism: $X^2Na^+ + M^{2b}Mg^{2+} = X^2□ + M^{2b}Fe^{3+}$. And the significant amounts of Mn on the *X*(1a + b) sites of qingheite are due to the presence of significant amounts of Fe²⁺ on the *M*(2a) site, according to the substitution mechanism: $X^{1(a+b)}Na^+ + M^{2a}(Al,Fe)^{3+} = X^{1(a+b)}Mn^{2+} + M^{2a}Fe^{2+}$ (Table 7). These small differences between the ideal end-member formulae and the observed occupancies are not significant for nomenclature purpose, since the nomenclature of the wyllieite group is based on the contents of the *M*(2a), *M*(2b), and *M*(1) sites.

We recommend keeping the current nomenclature scheme for wyllieite-type phosphates, with three root-names wyllieite, rosemaryite, and qingheite. In order to uniformize the nomenclature of the group, we suggest to re-name “qingheite-(Fe²⁺)” in “ferroqingheite”. If new species would be found in the group, with different *M*(1) occupancies, a prefix would be added to the corresponding root-name. New occupancies of the *X* sites would necessitate the addition of chemical suffixes without parentheses, as recommended for alluaudite-type phosphates and arsenates (see above).

An important remark concerns the distinction between alluaudite- and wyllieite-type phosphates. Indeed, both structure types are topologically identical, the only difference being the space-group types. But the accurate determination of space group in these minerals is tricky. To demonstrate this feature, we collected X-ray diffraction data on a single crystal of alluaudite from the Buranga pegmatite, Rwanda (sample RGM-9156, Rigaku Xcalibur four-circle diffractometer, EOS detector, MoK α radiation). A reciprocal-space image of the *hk0** plane (Fig. 10) clearly shows weak 120-type diffraction spots, forbidden in the alluaudite *C2/c* space group. Moreover, both structure refinements in the *C2/c* or *P2₁/n* space groups give excellent structural models, with *R*₁ factors of 2.34% in *C2/c* and 2.64% in *P2₁/n*. This very difficult space-group choice forces us to redefine the wyllieite group as phosphates with an alluaudite topology, containing between 0.5 and 1.5 Al per formula unit on the *M*(2a+b) sites, and/or unambiguously with space-group type *P2₁/n*. An Al-free phosphate with the alluaudite topology, impossible to refine satisfactorily in *C2/c*, but refining well in *P2₁/n*, would then belong to the wyllieite group.

Recently, the new mineral species fupingquite, (Na, Mn²⁺)₂Mn₂Fe³⁺(PO₄)₃, was described by Yang *et al.* (2017) as a wyllieite-type phosphate, since its

Table 7. The nomenclature and composition of wyllieite-type phosphates (site-dominant species in bold).

Ref.	Mineral	X(2)	X(a) + X(b)	M(1)	M(2b)	M(2a)	End-member formula
Results of chemical analyses							
1	Wyllieite	0.79 Na + 0.21 □	0.73 Na + 0.23 Mn + 0.04 Ca	1.00 Mn	0.80 Fe ²⁺ + 0.14 Fe ³⁺ + 0.06 Mn	0.73 Al + 0.20 Mg + 0.07 Fe ³⁺	NaNaMn(Fe ²⁺ Al)(PO ₄) ₃
2	Ferrowyllieite	0.78 Na + 0.22 □	0.48 Na + 0.30 Mn + 0.22 Ca	1.00 Fe ²⁺	0.96 Fe ²⁺ + 0.03 Li + 0.01 Mg	0.75 Al + 0.23 Mg + 0.02 Fe ³⁺	NaNaFe ²⁺ (Fe ²⁺ Al)(PO ₄) ₃
3	Rosemaryite	0.88 □ + 0.12 Na	0.47 Na + 0.43 Mn + 0.10 Ca	0.94 Mn + 0.06 Fe ²⁺	0.83 Fe ³⁺ + 0.09 Fe ²⁺ + 0.08 Mg	0.79 Al + 0.21 Fe ³⁺	□NaMn(Fe ³⁺ Al)(PO ₄) ₃
4	Ferrosermaryite	1.00 □	0.42 Na + 0.28 Mn + 0.04 Ca + 0.26 □	0.71 Fe ²⁺ + 0.24 Mn + 0.05 Fe ³⁺	1.00 Fe ³⁺	0.82 Al + 0.16 Fe ³⁺ + 0.02 Mg	□NaFe ³⁺ (Fe ³⁺ Al)(PO ₄) ₃
1	Qingheite	1.07 Na	0.54 Mn + 0.41 Na + 0.05 Ca	0.91 Mn + 0.09 Fe ²⁺	0.96 Mg + 0.04 Al	0.44 Al + 0.24 Fe ³⁺ + 0.32 Fe ²⁺	NaNaMn(MgAl)(PO ₄) ₃
5	Qingheite-(Fe ²⁺)	0.65 □ + 0.35 Na	0.58 Na + 0.40 Mg + 0.02 Ca	0.68 Fe ²⁺ + 0.32 Mn	0.72 Mg + 0.23 Fe ³⁺ + 0.05 Fe ²⁺	0.62 Al + 0.38 Fe ³⁺	NaNaFe ²⁺ (MgAl)(PO ₄) ₃
Results of structure refinements							
1	Wyllieite	1.00 Na	0.50 Na + 0.50 Mn	0.75 Mn + 0.20 Na + 0.05 Ca	0.55 Fe ²⁺ + 0.20 Fe ³⁺ + 0.20 Mg + 0.05 Al	0.70 Al + 0.25 Fe ²⁺ + 0.05 Mn	NaNaMn(Fe ²⁺ Al)(PO ₄) ₃
2	Ferrowyllieite	0.70 Na + 0.30 □	0.46 Na + 0.25 Ca + 0.25 Mn + 0.04 □	0.75 Fe ²⁺ + 0.25 Mg	1.00 Fe ²⁺	0.75 Al + 0.25 Fe ²⁺	NaNaFe ²⁺ (Fe ²⁺ Al)(PO ₄) ₃
3	Rosemaryite	0.56 □ + 0.44 Na	0.52 Mn + 0.15 Na + 0.33 □	0.75 Mn + 0.10 Ca + 0.08 Mg + 0.07 Fe ²⁺	0.80 Fe ³⁺ + 0.10 Al + 0.10 Mn	0.69 Al + 0.24 Fe ³⁺ + 0.08 Fe ²⁺	□NaMn(Fe ³⁺ Al)(PO ₄) ₃
4	Ferrosermaryite	1.00 □	0.47 Mn + 0.24 Na + 0.04 Ca + 0.25 □	0.57 Fe ²⁺ + 0.20 Fe ³⁺ + 0.18 Na + 0.05 Mn	0.88 Fe ³⁺ + 0.10 Al + 0.02 Mg	0.72 Al + 0.14 Fe ²⁺ + 0.14 Fe ³⁺	□NaFe ²⁺ (Fe ³⁺ Al)(PO ₄) ₃
1	Qingheite	0.95 Na + 0.05 Ca	0.50 Na + 0.50 Mn	0.93 Mn + 0.07 Fe ³⁺	0.60 Mg + 0.40 Fe ²⁺	0.47 Al + 0.34 Mg + 0.18 Fe ³⁺	NaNaMn(MgAl)(PO ₄) ₃
5	Qingheite-(Fe ²⁺)	0.65 □ + 0.18 Na + 0.15 Mn + 0.02 Ca	0.50 Na + 0.50 Mn	0.52 Fe ²⁺ + 0.25 Na + 0.16 Fe ³⁺ + 0.07 Mn	0.44 Mg + 0.35 Fe ³⁺ + 0.21 Fe ²⁺	0.62 Al + 0.28 Mg + 0.10 Fe ³⁺	NaNaFe ²⁺ (MgAl)(PO ₄) ₃

1. Hatert *et al.* (2016); 2. Moore & Molin-Case (1974); 3. Hatert *et al.* (2006); 4. Hatert *et al.* (2005b); 5. Hatert *et al.* (2010).

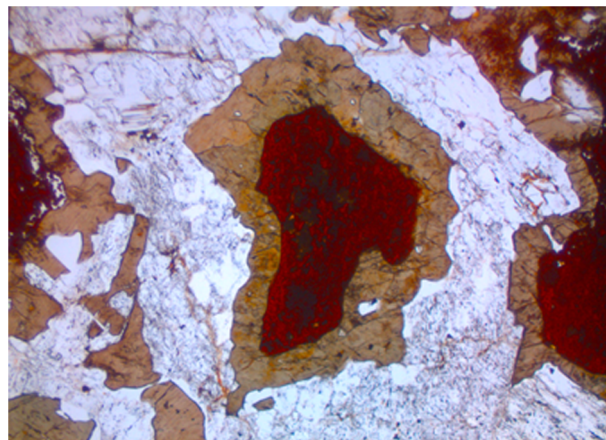


Fig. 9. Ferroqingheite (= “qingheite-(Fe²⁺)”) from the Sebastião Cristino pegmatite, Minas Gerais, Brazil, forming a reaction rim between frondelite (red) and albite (white). Plane-polarized light, length of the photomicrograph = 5 mm.

space-group type was $P2_1/n$. However, the authors did not provide the results of the structure refinement in $C2/c$, thus preventing an unambiguous space-group determination. Moreover, the composition of this species corresponds to the ideal composition of redefined varulite; consequently, varulite and fupingquiite are topologically similar polymorphs, and cannot be considered as separate mineral species (Nickel & Grice, 1998). We recommend consequently discrediting fupingquiite.

Finally, the bobfergusonite group contains three mineral species: bobfergusonite, $\square\text{Na}_2\text{Mn}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$ (Ercit *et al.*, 1986a, b), ferrobobfergusonite, $\text{Na}_2\text{Fe}_5^{2+}\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$ (Yong *et al.*, 2017), and zhanghuifenite, $\text{Na}_3\text{Mn}_4\text{Mg}_2\text{Al}(\text{PO}_4)_6$ (Yang *et al.*, 2016). Their crystal structures are based on the alluaudite topology, but an ordering of the adjacent octahedral chains provokes a doubling of the c unit-cell parameter, compared to wyllieites: space-group $P2_1/n$, $a = 12.773(2)$, $b = 12.486(2)$, $c = 11.038(2)$ Å, $\beta = 97.15^\circ$ (for bobfergusonite). Manitobaite, $\text{Na}_{16}\text{Mn}_{25}^{2+}\text{Al}_8(\text{PO}_4)_{30}$, is a separate species with an even larger unit-cell: $a = 13.452(2)$, $b = 12.515(2)$, $c = 26.661(3)$ Å, $\beta = 101.58(1)^\circ$ (space group Pc ; Ercit *et al.*, 2010). Nomenclature guidelines for the bobfergusonite group cannot be defined here, due to the few mineral species of this group known to date. However, some of these species may appear as topologically similar polymorphs of alluaudite- or wyllieite-type phosphates.

8. Conclusions

Due to the different geochemical environments in which minerals of the alluaudite supergroup occur, and to their complex crystal chemistry, it is very difficult to establish a unique nomenclature for the whole supergroup. However, the use of a nomenclature based on a double occupancy of the $M(2)$ site is necessary, for alluaudite-type phosphates and arsenates, in order to better describe their chemical complexity. This new nomenclature scheme is consistent with

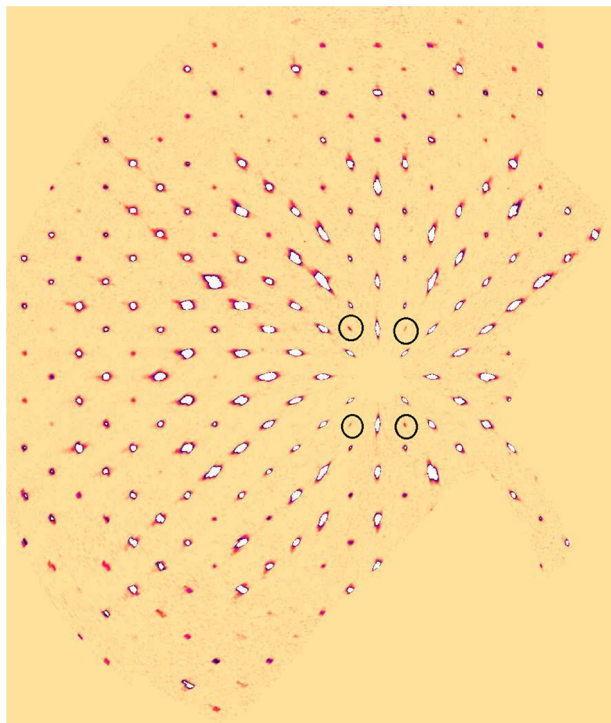


Fig. 10. Reciprocal-space image of the $hk0^*$ plane in alluaudite from Buranga, Rwanda (sample RGM-9156). The circles indicate 120-type reflections, incompatible with the $C2/c$ alluaudite space-group type.

the nomenclature of wyllieites, and allows one to easily establish charge-balanced end-member formulae for these phosphates.

A summary of the IMA-CNMNC-approved formulae of alluaudite-supergroup minerals is given in Table 8.

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Table 8. IMA-CNMNC-approved end-member formulae of alluaudite-supergroup minerals.

Alluaudite group – phosphates	
Alluaudite	$\text{NaMnFe}^{3+}_3(\text{PO}_4)_3$
Ferroalluaudite	$\text{NaFe}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_3$
Hagendorfite	$\text{Na}_2\text{Mn}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$
Maghagendorfite*	$\text{Na}_2\text{Mg}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$
Varulite	$\text{Na}_2\text{Mn}(\text{MnFe}^{3+})(\text{PO}_4)_3$
Groatite	$\square\text{NaCaMn}_2(\text{PO}_4)(\text{HPO}_4)_2$
Alluaudite group – arsenates	
O'danielite	$\text{Na}\square\text{ZnZn}_2[\text{AsO}_4][\text{AsO}_3(\text{OH})]_2$
Johillerite	$\text{NaCuMgMg}_2(\text{AsO}_4)_3$
Caryinite	$\text{NaCaCaMn}_2(\text{AsO}_4)_3$
Nickenichite	$\text{Na}(\text{Ca}_{0.5}\text{Cu}_{0.5})\text{MgMg}_2(\text{AsO}_4)_3$
Arseniopleite	$\text{NaCaMnMn}_2(\text{AsO}_4)_3$
Bradaczekite	$\text{NaCuCuCu}_2(\text{AsO}_4)_3$
Keyite	$(\square_{0.5}\text{Cu}_{0.5})\text{CuCdZn}_2(\text{AsO}_4)_3\cdot\text{H}_2\text{O}$
Yazganite	$\text{NaMgFe}^{3+}_2(\text{AsO}_4)_3\cdot\text{H}_2\text{O}$
Erikapohlite	$(\square_{0.5}\text{Cu}_{0.5})\text{CuCaZn}_2(\text{AsO}_4)_3\cdot\text{H}_2\text{O}$
Hatertite	$\text{NaNaCa}(\text{Cu}^{2+}\text{Fe}^{3+})(\text{AsO}_4)_3$
Canutite	$\text{Na}\square\text{MnMn}_2[\text{AsO}_4][\text{AsO}_3(\text{OH})]_2$
Zincobradaczekite	$\text{NaCuCuZn}_2(\text{AsO}_4)_3$
Badalovite	$\text{NaNaMg}(\text{MgFe}^{3+})(\text{AsO}_4)_3$
Magnesiocanutite	$\text{Na}\square\text{MnMg}_2[\text{AsO}_4]_2[\text{AsO}_2(\text{OH})]_2$
Calciojohillerite	$\text{NaCaMgMg}_2(\text{AsO}_4)_3$
Magnesiobatertite	$\text{NaNaCa}(\text{MgFe}^{3+})(\text{AsO}_4)_3$
Khrenovite	$\text{Na}_3\text{Fe}^{3+}_3(\text{AsO}_4)_3$
Paraberkzeliite	$\text{NaCaCaMg}_2(\text{AsO}_4)_3$
Camanchacaite	$\text{Na}\square\text{CaMg}_2[\text{AsO}_4]_2[\text{AsO}_2(\text{OH})]_2$
Wyllieite group	
Wyllieite	$\text{NaNaMn}(\text{Fe}^{2+}\text{Al})(\text{PO}_4)_3$
Ferrowyllieite	$\text{NaNaFe}^{2+}(\text{Fe}^{2+}\text{Al})(\text{PO}_4)_3$
Rosemaryite	$\square\text{NaMn}(\text{Fe}^{3+}\text{Al})(\text{PO}_4)_3$
Ferrorosemaryite	$\square\text{NaFe}^{2+}(\text{Fe}^{3+}\text{Al})(\text{PO}_4)_3$
Qingheite	$\text{NaNaMn}(\text{MgAl})(\text{PO}_4)_3$
Ferroqingheite	$\text{NaNaFe}^{2+}(\text{MgAl})(\text{PO}_4)_3$
Bobfergusonite group	
Bobfergusonite	$\square\text{Na}_2\text{Mn}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$
Ferrobobfergusonite	$\text{Na}_2\text{Fe}^{2+}_5\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6$
Zhanghuifenite	$\text{Na}_3\text{Mn}_4\text{Mg}_2\text{Al}(\text{PO}_4)_6$
Manitobaite	
Manitobaite	$\text{Na}_{16}\text{Mn}^{2+}_{25}\text{Al}_8(\text{PO}_4)_{30}$

*Questionable species.

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APPENDIX

Calculation of electron-microprobe analyses for H-free alluaudite-type phosphates

Alluaudite-type phosphates generally contain Fe^{2+} and Fe^{3+} , and it is necessary to recalculate the contents of these cations in the analyses.

Calculation basis is 3 P atoms per formula unit (*apfu*). Then, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is calculated to reach nine positive charges in the cationic groups of the formula unit, maintaining charge balance. If a significant deficit of positive charges is still observed when all Fe is considered as Fe^{3+} , it means that we have an extremely oxidized alluaudite. In that case, it is recommended considering all iron as Fe^{3+} , and to calculate the $\text{Mn}^{2+}/\text{Mn}^{3+}$ ratio to reach nine positive charges in the cationic groups.

Cations are then distributed among the crystallographic sites, according to their ionic radii:

- **M(2a):** Fe^{3+} , and then successively Mn^{3+} , Al, Mg, and eventually Zn, Fe^{2+} or Mn^{2+} to fill the site (1 *apfu*).
- **M(2b):** Eventually the remaining Fe^{3+} , Mn^{3+} , Mg or Zn. If necessary, the site is then filled by Fe^{2+} first, then by Mn^{2+} .
- **M(1):** In rare analyses of very oxidized alluaudites, small amounts of Fe^{3+} or Mn^{3+} may be attributed to that site. Then, Mg, Fe^{2+} and Mn^{2+} are successively added here. If the site is not yet filled, Ca and then Na are added.
- **A(1):** Remnants of Mn^{2+} are located here, as well as Ca and Na. If the site is not yet filled, K or Li may also be added here. Generally, this site is filled, but in a few analyses, small amounts of vacancies may occur here.
- **A(2)′:** Remnants of Na, as well as K and Li, are located on that site. Generally, significant amounts of vacancies also occur on that site.

Once the cations are distributed, it is necessary to determine the name of the mineral.

The root-name is based on the content of *M(2)*, and a prefix may be added, depending on the content of the *M(1)* site. Generally, large *A* sites are occupied by Na and/or vacancies, and the contents of these constituents may vary significantly, since they are very sensitive to the complex substitution mechanisms affecting alluaudites. So, generally, the contents of *A(1)* and *A(2)′* sites are not considered for nomenclature purposes. However, if the *A(1)* site of hagen-dorfites, varulites and root2 is mainly occupied by divalent cations (${}^{A(1)}M^{2+} > 0.5$), a suffix is added to the name to designate this cation.

Mineral names of alluaudite-type phosphates may be determined according to the following scheme:

$$1. {}^{M(2)}M^{2+} \leq 0.5 \text{ apfu:}$$

$$1.a. {}^{M(2)}M^{3+} \text{ dominantly } \text{Fe}^{3+}: \text{Alluaudites}$$

$$1.a.a. {}^{M(1)}M^{2+} \text{ dominantly } \text{Mn}^{2+}: \text{Alluaudite}$$

$$1.a.b. {}^{M(1)}M^{2+} \text{ dominantly } \text{Fe}^{2+}: \text{Ferroalluaudite}$$

- 1.b. $M^{(2)}M^{3+}$ dominantly Mn^{3+} : *Root1 s.l.*
- 1.b.a: $M^{(1)}M^{2+}$ dominantly Mn^{2+} : *Root1*
 1.b.b: $M^{(1)}M^{2+}$ dominantly Fe^{2+} : *Ferroroot1*
2. $0.5 \leq M^{(2)}M^{2+} \leq 1.5$ apfu, and $A^{(1)}M^{2+} \leq 0.5$ apfu:
- 2.a. $M^{(2)}M^{3+}$ dominantly Fe^{3+} , and $M^{(2)}M^{2+}$ dominantly Fe^{2+} : *Hagendorfites*
- 2.a.a: $M^{(1)}M^{2+}$ dominantly Mn^{2+} : *Hagendorfite*
- 2.b. $M^{(2)}M^{3+}$ dominantly Fe^{3+} , and $M^{(2)}M^{2+}$ dominantly Mn^{2+} : *Varulites*
- 2.b.a: $M^{(1)}M^{2+}$ dominantly Mn^{2+} : *Varulite*
 2.b.b: $M^{(1)}M^{2+}$ dominantly Fe^{2+} : *Ferrovarulite*
- 2.c. $M^{(2)}M^{3+}$ dominantly Fe^{3+} , and $M^{(2)}M^{2+}$ dominantly Mg^{2+} : *Root2 s.l.*
- 2.c.a: $M^{(1)}M^{2+}$ dominantly Mn^{2+} : *Root2*
 2.c.b: $M^{(1)}M^{2+}$ dominantly Fe^{2+} : *Ferroroot2*
3. $0.5 \leq M^{(2)}M^{2+} \leq 1.5$ apfu, and $A^{(1)}M^{2+} \geq 0.5$ apfu:
- 3.a. $A^{(1)}M^{2+}$ dominantly Ca: Add a suffix “-Ca” to the names mentioned above (point 2).
- 3.b. $A^{(1)}M^{2+}$ dominantly Mn: Add a suffix “-Mn” to the names mentioned above (point 2).
4. $M^{(2)}M^{2+} \geq 1.5$ apfu, and $A^{(1)}M^{2+}$ dominantly Ca:
- 4.a. $M^{(2)}M^{2+}$ dominantly Fe^{2+} : *Root3 s.l.*
- 4.a.a: $M^{(1)}M^{2+}$ dominantly Mn^{2+} : *Root3*
 4.a.b: $M^{(1)}M^{2+}$ dominantly Fe^{2+} : *Ferroroot3*
- 4.b. $M^{(2)}M^{2+}$ dominantly Mg: *Root4 s.l.*
- 4.b.a: $M^{(1)}M^{2+}$ dominantly Mn^{2+} : *Root4*
 4.b.b: $M^{(1)}M^{2+}$ dominantly Fe^{2+} : *Ferroroot4*
- 4.c. $M^{(2)}M^{2+}$ dominantly Mn: *Root5 s.l.*
- 4.c.a: $M^{(1)}M^{2+}$ dominantly Mn^{2+} : *Root5*
 4.c.b: $M^{(1)}M^{2+}$ dominantly Fe^{2+} : *Ferroroot5*