

ALLAUDITE-GROUP PHOSPHATE AND ARSENATE MINERALS

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ABSTRACT

A systematic study of alluaudite, hagendorfite, and varulite was done using single-crystal X-ray diffraction, powder diffraction, and electron probe microanalysis of samples from 12 separate localities. The crystal structures of the representative alluaudite and hagendorfite samples were refined to R_1 indices of 3.7 and 1.8%, respectively, using a Siemens P4 automated four-circle diffractometer equipped with a graphite monochromator and MoK α X-radiation. These samples and several others were analyzed with an electron microprobe to study variations in chemical composition. For the single-crystal analyses, the resulting unit formulae are $(\text{Na}_{0.11}\square_{0.89})(\text{Na}_{0.59}\text{Mn}_{0.27}\text{Ca}_{0.14})\text{Mn}_{1.00}(\text{Fe}^{3+}_{1.64}\text{Al}_{0.24}\text{Mg}_{0.13})(\text{PO}_4)_3$ for alluaudite, $(\text{Na}_{0.79}\square_{0.21})(\text{Na}_{0.81}\text{Mn}^{2+}_{0.19})(\text{Mn}_{0.70}\text{Fe}^{2+}_{0.30})(\text{Fe}^{2+}_{1.72}\text{Mg}_{0.27}\text{Al}_{0.01})(\text{PO}_4)_3$ for hagendorfite, and $(\text{Na}_{0.84}\square_{0.16})(\text{Na}_{0.71}\text{Ca}_{0.23}\square_{0.06})\text{Mn}_{1.00}(\text{Fe}^{3+}_{0.89}\text{Fe}^{2+}_{0.68}\text{Mn}_{0.42}\text{Mg}_{0.01})(\text{PO}_4)_3$ for varulite.

Originally, a nomenclature scheme was proposed for the alluaudite-group minerals that was based on sequentially distributing the cations in the cell according to increasing polyhedron size, matching that size with increasing ionic radii of the cations. For alluaudite, the structural formula was written as $X(2)_4X(1)_4M(1)_4M(2)_8(\text{PO}_4)_{12}$, with the sites ordered in decreasing size of the discrete polyhedra. Later, the formula $[A(2)A(2)'A(2)''_2][A(1)A(1)'A(1)''_2]M(1)M(2)_2(\text{PO}_4)_3$ was proposed, which takes into account the distinct crystallographic sites in the channels of the structure. More recently there has been a revision to the nomenclature of the group. The simplified structural formula for the alluaudite-type is now $A(2)'A(1)M(1)M(2)_2(\text{TO}_4)_3$; the new nomenclature scheme has been adopted by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC), based on the contents of the $M(1)$ and $M(2)$ octahedral sites, and the results are reviewed here.

Compounds belonging to the alluaudite structural family have been the focus of synthetic mineral studies for decades owing to the open-framework architecture and their unique physical properties. Improvements in synthesis methods have allowed researchers to substitute a wide range of elements into the alluaudite structure.

Keywords: alluaudite, hagendorfite, varulite, crystal structure, electron probe microanalysis, nomenclature, phosphates.

INTRODUCTION

The alluaudite-group minerals are complex primary and secondary phosphate and arsenate minerals that occur primarily in granitic pegmatites, but have also been found in scoria, phosphatic nodules, granites, and volcanic fumaroles. Except for accessory anhydrous silicate phases, such as beryl, petalite, spodumene, and garnet, phosphates are the most widely distributed accessory minerals in pegmatites. Many synthetic analogues have been made, due to the flexibility of the structure to accommodate a wide variety of cations to suit a wide range of applied materials science uses.

The alluaudite supergroup is composed of four groups: the alluaudite-, wyllieite-, bobfergusonite-, and manitobaite-groups (Hatert 2019). The minerals of these groups are topologically identical but are distinguished by different cation-ordering schemes over the octahedrally coordinated cation sites in the structure. One issue in the crystal chemistry of the alluaudite-group minerals is the choice of cell orientation; the alluaudite group can be presented in $C2/c$ or $I2/a$. The $I2/a$ space group was selected in previous studies (e.g., Tait & Hawthorne 2003) due to the smaller β angle, which is conformable with space group $P2_1/c$ for the wyllieite and manitobaite structure

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and $P2_1/n$ for the bobjergsonite structure. However, recent work (e.g., Kampf *et al.* 2019, Hatert 2019) has presented new members of the group in $C2/c$, so here we use the $C2/c$ orientation for consistency.

Transition-metal phosphates and arsenates are difficult to study, in part due to mixed valence states (that can lead to incorrectly identified phases if not examined with several different techniques) and complicated ordering of cations in the structure. Single-crystal X-ray diffraction and electron probe microanalysis (EPMA) will be the main techniques used here, with laser ablation-inductively coupled-plasma mass spectrometry (LA-ICP-MS) used as needed.

As part of a general study of the alluaudite group *sensu lato*, below we review the existing literature and examine the crystal structures and chemistries of several alluaudite-group minerals of differing chemical compositions and localities to derive detailed site populations and further the understanding of the variations of chemical composition in natural samples.

PREVIOUS WORK: ALLUAUDITE-GROUP MINERALS

The alluaudite-group minerals currently consist of six International Mineralogical Association (IMA) approved phosphates (alluaudite, ferroalluaudite, groatite, hagendorffite, maghagendorffite, and varulite) and nineteen IMA-approved arsenates (arseniopleite, badalovite, bradaczekite, calciojohillerite, canutite, camanchacaite, caryinite, erikapohlite, johillerite, hatertite, keyite, krenovite, magnesiocanutite, magnesiohatertite, nickenichite, o'danielite, paraberzeliite, yazganite, and zincobradaczekite). Endmember formulae of current species (Hatert 2019) are listed in Table 1. For some of the formulae of these minerals, there is no agreement between Hatert (2019) and the New IMA List of Minerals (updated March 2020). Where this occurs, we have used the formulae of Hatert (2019), as these have been approved by IMA-CNMNC and either the New IMA List of Minerals (updated March 2020) was not completely updated or there are errors in this list for some of these minerals.

Alluaudite and ferroalluaudite

Alluaudite was first described from Chanteloube (near Limoges), France, by Damour (1847, 1848) and was named for François Alluaud (September 21, 1778–February 18, 1866) of Limoges, France, a mining engineer and mineralogist who discovered the species. The formula was described as $(\text{Fe}^{3+}, \text{Mn}^{3+})_3 (\text{P}^{5+})_2 + 2\text{H}$. The name was relegated to varietal status (under triphylite–lithiophilite) by Dana (1920), and there it remained until Quensel (1937, 1940, 1956) characterized it from the Varuträsk

TABLE 1. ENDMEMBER FORMULAE FOR PHOSPHATE AND ARSENATE MINERALS OF THE ALLUAUDITE GROUP

	Phosphates
Alluaudite	$\text{NaMnFe}^{3+}_2(\text{PO}_4)_3$
Ferroalluaudite	$\text{NaFe}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_3$
Groatite	$\square\text{NaCaMn}_2(\text{PO}_4)(\text{HPO}_4)_2$
Hagendorffite	$\text{Na}_2\text{Mn}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$
Maghagendorffite	$\text{Na}_2\text{Mg}(\text{Fe}^{2+}, \text{Fe}^{3+})(\text{PO}_4)_3$
Varulite	$\text{Na}_2\text{Mn}(\text{MnFe}^{3+})(\text{PO}_4)_3$
	Arsenates
Arseniopleite	$\text{NaCaMnMn}_2(\text{AsO}_4)_3$
Badalovite	$\text{NaNaMg}(\text{MgFe}^{3+})(\text{AsO}_4)_3$
Bradaczekite	$\text{NaCuCuCu}_2(\text{AsO}_4)_3$
Calciojohillerite	$\text{NaCaMgMg}_2(\text{AsO}_4)_3$
Camanchacaite	$\text{Na}\square\text{CaMg}_2(\text{AsO}_4)_2[\text{AsO}_2(\text{OH})_2]$
Canutite	$\text{Na}\square\text{MnMn}_2(\text{AsO}_4)[\text{AsO}_3(\text{OH})_2]$
Caryinite	$\text{NaCaCaMn}_2(\text{AsO}_4)_3$
Erikapohlite	$(\square_{0.5}\text{Cu}_{0.5})\text{CuCaZn}_2(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$
Hatertite	$\text{NaNaCa}(\text{Cu}^{2+}\text{Fe}^{3+})(\text{AsO}_4)_3$
Johillerite	$\text{NaCuMgMg}_2(\text{AsO}_4)_3$
Keyite	$(\square_{0.5}\text{Cu}_{0.5})\text{CuCdZn}_2(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$
Krenovite	$\text{Na}_3\text{Fe}^{3+}_2(\text{AsO}_4)_3$
Magnesiocanutite	$\text{Na}\square\text{MnMg}_2(\text{AsO}_4)_2[\text{AsO}_2(\text{OH})_2]$
Magnesiohatertite	$\text{NaNaCa}(\text{MgFe}^{3+})(\text{AsO}_4)_3$
Nickenichite	$\text{Na}(\text{Ca}_{0.5}\text{Cu}_{0.5})\text{MgMg}_2(\text{AsO}_4)_3$
O'danielite	$\text{Na}\square\text{ZnZn}_2(\text{AsO}_4)[\text{AsO}_3(\text{OH})_2]$
Paraberzeliite	$\text{NaCaCaMg}_2(\text{AsO}_4)_3$
Yazganite	$\text{NaMgFe}^{3+}_2(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$
Zincobradaczekite	$\text{NaCuCuZn}_2(\text{AsO}_4)_3$

pegmatite, Sweden. Alluaudite was then described from the Hühnerkobel pegmatite, Bavaria (Mason 1942) and the Buranga pegmatite, Rwanda (Thoreau 1954). Fisher (1955) reported the first occurrence of alluaudite in the United States at the Green pegmatite, 3 miles northeast of Pringle, South Dakota. He compared this material to alluaudite from Buranga and Chanteloube, gave the space group as $C2/c$, and reported the cell dimensions. Fisher (1956) re-analyzed this material, confirmed that it is isostructural with alluaudite, and reoriented the hagendorffite cell to $I2/a$ in accord with the $I2/a$ orientation used for alluaudite from Buranga. Moore (1965) described single crystals and granular greenish-black masses of “hühnerkobelite” from the Palermo No. 1 pegmatite, North Groton, New Hampshire, USA, and gave cell dimensions for alluaudite in the space group $I2/a$. Fisher (1966) discredited the name “hühnerkobelite”, stating that it is “alluaudite”. Moore (1966) defended “hühnerkobelite” (= Fisher’s “ferroan-alluaudite”) as used by Palache *et al.* (1951) and as implied by the composition in Strunz (1954) and suggested that the

International Committee on Mineral Names review the situation. Moore & Ito (1979) proposed a nomenclature scheme for the alluaudite and wylieite minerals based on the *M*(1) and *M*(2) sites, for which ferroalluaudite was identified as a separate species, based on Fe^{2+} dominance at the *M*(2) site as compared to alluaudite with Mn^{2+} dominant at the *M*(1) site.

Varulite

Pebrman (1939) reported a new mineral (which he called “lemnäsité”) from a pegmatite in the Lemnäs parish, Kimito, SW Finland. “Lemnäsité” is a Mn-rich alluaudite and has been referred to as such in more recent literature. A dull-green fine-grained mineral was found associated with alluaudite, which Quensel (1937) proposed to call varulite after the Varuträsk pegmatite. Björling & Westgren (1938) gave X-ray powder-diffraction photographs of triphylite, varulite, and their oxidation products and showed that varulite and alluaudite seem to be related to each other in the same way as triphylite and ferrisicklerite but contain Na instead of Li. Mason (1940) described dark-green varulite from the Skruppetorp pegmatite and alluaudite (originally called “pseudotriphylite” by Mäkinen 1913) from Sukula, near Tammela, Finland. Material from Hühnerkobel and Norrö, Sweden, originally described as arrojadite, is not isostructural with arrojadite from the Nickel Plate pegmatite and the Serra Branca pegmatite. Lindberg (1950) proposed a new mineral, “hühnerkobelite”, $(\text{Na}_2, \text{Ca})\text{O} \cdot 2(\text{Fe}, \text{Mn})\text{O} \cdot \text{P}_2\text{O}_5$ to describe this “partly oxidized” material. Varulite from Skruppetorp is isostructural with “hühnerkobelite” and with the yellowish-green varulite from Varuträsk (Lindberg 1950).

Hagendorfite and maghagendorfite

Strunz (1954) described hagendorfite from the Hagendorf-Süd pegmatite, Bavaria, as belonging to the varulite-“hühnerkobelite” series, with the chemical formula $(\text{Na}, \text{Ca})(\text{Fe}^{2+}, \text{Fe}^{3+})_{1+n}\text{Mn}_{1-n}(\text{PO}_4)_2$. It occurs in the Hagendorf-Süd pegmatite as greenish-black sparry masses together with triphylite–lithiophilite, $\text{Li}(\text{Fe}, \text{Mn})(\text{PO}_4)$, or wolfeite, $\text{Fe}^{2+}_2(\text{PO}_4)(\text{OH})$. Fleisher *et al.* (1980) proposed a new name, maghagendorfite, with type material from the Dyke Lode, Custer, South Dakota. Hagendorfite was identified as one of the rare phosphates present at Big Fish River, Yukon (Robinson *et al.* 1992). Redhammer *et al.* (2005) examined hagendorfite and alluaudite by ^{57}Fe Mössbauer spectroscopy; more recently, Dyar *et al.* (2014) compared spectroscopic properties of iron phosphates at Mars conditions, where hagendorfite, alluaudite, and varulite were part of the study.

Groatite

The newest member of the phosphate alluaudite-group is a protonated alluaudite-phosphate: groatite, ideally, $\text{NaCaMn}_2(\text{PO}_4)[\text{PO}_3(\text{OH})]_2$. It was described from the Tanco pegmatite, Bernic Lake, Manitoba, Canada (Cooper *et al.* 2009). At the time of publication, this is the only locality where it has been found. Hatert (2019) revised the chemical formula to $\text{NaCaMn}_2(\text{PO}_4)(\text{HPO}_4)_2$.

Arseniopleite and caryinite

Arseniopleite was originally described by Igelström (1888) from the Sjö Mine, near Gythyttan, Örebro, Sweden. “Sjögruvite” was described by Igelström (1892), but Henriques (1963) re-described “sjögruvite” as arseniopleite after reanalysis of the original mineral. Caryinite was originally described by Lundström (1874) from Långban, Sweden.

Moore (1968) showed that arseniopleite and caryinite are structurally related and proposed that arseniopleite is a “water-rich” variety of caryinite. Dunn & Peacor (1987) re-analyzed both arseniopleite and caryinite and showed that both are anhydrous. Dunn & Peacor (1987) stated that “If the cation assignments follow the scheme proposed by Moore (1966) for alluaudite, then [their formula for arseniopleite] might define arseniopleite as a species with Mn dominant in the *M*(1) site instead of Ca/Mn which apparently occupies that site in caryinite”. However, they stressed that until such a site occupancy is confirmed, the species status of arseniopleite remains uncertain. Ercit (1993) refined the crystal structure of caryinite from Långban, Sweden; he showed that the *M*(1) site is occupied by Ca and Mn with Ca dominant and supported the proposal of Dunn & Peacor (1987) that arseniopleite is isostructural with caryinite (and alluaudite) with Mn dominant at *M*(1). However, the status of arseniopleite was still considered somewhat uncertain (Nysten *et al.* 1999). Tait & Hawthorne (2003) confirmed the validity of arseniopleite as a member of the alluaudite group and distinct from caryinite by the presence of dominant Mn rather than Ca (as in caryinite) at the *M*(1) site. Hatert (2019) changed the formula to $\text{NaCaMnMn}_2(\text{AsO}_4)_3$.

O’danielite, johillerite, and calciojohillerite

O’danielite was found as a secondary mineral in corroded copper ore in the Tsumeb mine, Namibia (Keller *et al.* 1981), in association with koritnigite, prosperite, and Cu-bearing adamite. It has only been reported from this locality. Johillerite is also found in the Tsumeb mine, Namibia (Keller *et al.* 1982), in radiating masses together with Cu-rich adamite and

conichalcite in oxidized copper ore. Keller & Hess (1988) described the two structures from Tsumeb, Namibia. Glavatskikh & Bykova (1998) were first to describe johillerite from the Tolbachik volcano, Kamchatka Peninsula, Russia, and then Tait & Hawthorne (2004) presented detailed site populations and further examined the incorporation of Cu into the alluaudite-type structure from this locality. Pekov *et al.* (2016c) described the Ca-analogue of johillerite, calciojohillerite, from the Arsenatnaya fumarole, second scoria cone of the Northern Breakthrough of the Great Tolbachik, Kamchatka Peninsula, Russia.

Bradaczekite, zincobradaczekite, hatertite, magnesiohatertite, badalovite, khrenovite, and paraberzeliite: Minerals from the Tolbachik volcano

Filatov *et al.* (2001) described a new Cu^{2+} -bearing dark-blue alluaudite-group mineral, bradaczekite, from the Tolbachik volcano, that forms intergrowths with johillerite. In this environment, the exhalative minerals form at high temperatures on cooling volcanoes (Filatov *et al.* 2009). Krivovichev *et al.* (2001) described in detail the three symmetrically independent Cu atoms in the bradaczekite structure and the Jahn-Teller distorted octahedra. Hatertite, $\text{Na}_2(\text{Ca}, \text{Na})(\text{Fe}^{3+}, \text{Cu})_2(\text{AsO}_4)_3$, was also described by Krivovichev *et al.* (2013) from the Tolbachik fumaroles in Russia. This honey-yellow mineral was originally found in 1983 in fumarolic activity, associated with johillerite and bradaczekite (Krivovichev *et al.* 2013). Pekov *et al.* (2016a) described a Zn-analogue of bradaczekite, zincobradaczekite, also from the Tolbachik fumaroles. Magnesiohatertite, $(\text{Na}, \text{Ca})_2\text{Ca}(\text{Mg}, \text{Fe}^{3+})_2(\text{AsO}_4)_3$, was described from the Arsenatnaya fumarole, Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka peninsula, Far-Eastern Region, Russia (Pekov *et al.* 2016d). The formula of magnesiohatertite was recently changed to $\text{NaNaCa}(\text{MgFe}^{3+})(\text{AsO}_4)_3$ (Hatert 2019). Badalovite $\text{Na}_2\text{Mg}_2\text{Fe}^{3+}(\text{AsO}_4)_3$ is another mineral described from the Arsenatnaya fumarole in Russia (Pekov *et al.* 2016b). Hatert (2019) revised the chemical formula to $\text{NaNaMg}(\text{MgFe}^{3+})(\text{AsO}_4)_3$. Pekov *et al.* (2018a) described the new mineral khrenovite, $\text{Na}_3\text{Fe}^{3+}_2(\text{AsO}_4)_3$, from Tolbachik and Pekov *et al.* (2018b) described the new mineral paraberzeliite, $\text{NaCa}_2\text{Mg}_2(\text{AsO}_4)_3$.

Keyite and erikapohlite, alluaudite arsenates from the Tsumeb mine

Keyite, $(\text{Cu}, \text{Zn}, \text{Cd})_3(\text{AsO}_4)_2$, was first described by Embrey *et al.* (1977) and occurs as small blue prisms in cavities in tennantite ore from Tsumeb, Southwest

Africa. Cooper & Hawthorne (1996) solved the crystal structure of keyite, which resulted in an extensive revision of the chemical formula to $\text{Cu}_3\text{Zn}_4\text{Cd}_2(\text{AsO}_4)_6 \cdot 2\text{H}_2\text{O}$. Malcherek & Schlüter (2013) described the keyite structure as triclinic, as H_2O within one of the channels of the alluaudite heteropolyhedral framework reduces the symmetry and gives rise to weak X-ray diffraction maxima forbidden in space group $\text{C2}/c$. Hatert (2019) revised the chemical formula to $(\square_{0.5}\text{Cu}_{0.5})\text{CuCdZn}_2(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$. Erikapohlite, $\text{Cu}_3(\text{Zn}, \text{Cu}, \text{Mg})_4\text{Ca}_2(\text{AsO}_4)_6 \cdot 2\text{H}_2\text{O}$, the Ca-dominant analogue of keyite (Schlüter *et al.* 2013), is also found at Tsumeb and had been described previously as the Ca-Cu-Zn-As mineral (GS 5) found on level 44 at Tsumeb by Gebhard (1999). Hatert (2019) revised the chemical formula to $(\square_{0.5}\text{Cu}_{0.5})\text{CuCaZn}_2(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$.

Canutite, magnesiocanutite, and camachacite, minerals of the Torrecillas mine, Chile

Kampf *et al.* (2014) described canutite as a reddish-brown mineral with the formula $\text{NaMn}_3(\text{AsO}_4)[\text{AsO}_3(\text{OH})]_2$ which occurs as a secondary alteration phase at the Torrecillas mine, Salar Grande, Iquique Province, Chile. Hatert (2019) revised the chemical formula to $\text{NaMnMn}_2(\text{AsO}_4)[\text{AsO}_3(\text{OH})]_2$. Magnesio-canutite, $\text{NaMnMg}_2(\text{AsO}_4)_2[\text{AsO}_2(\text{OH})_2]$, is the Mg-analogue of canutite and is also from the Torrecillas mine, Chile (Kampf *et al.* 2017). Magnesio-canutite occurs as pale brownish-pink to rose-pink lozenge-shaped tablets that often form tightly intergrown aggregates as a secondary phase in association with anhydrite, canutite, halite, lavendulan, and magnesio-koritnigite (Kampf *et al.* 2017). Hatert (2019) revised the chemical formula to $\text{Na}\square\text{MnMg}_2(\text{AsO}_4)_2[\text{AsO}_2(\text{OH})_2]$. Kampf *et al.* (2019) described camanchacite, $\text{Na}\square\text{CaMg}_2(\text{AsO}_4)_2[\text{AsO}_2(\text{OH})_2]$, named after “camanchaca”, a dense fog that forms along the northern Chilean coast where the Atacama Desert reaches the Pacific Ocean. Camanchacite forms balls with compact radial structure up to ~ 1 mm in diameter; due to the nature of the mineral, Kampf *et al.* (2019) were unable to obtain a structure refinement.

Yazganite

Sarp & Černý (2005) described the brown-to-black yazganite, $\text{NaFe}^{3+}_2(\text{Mg}, \text{Mn})(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$, from the Erciyes volcanic complex, Central Anatolia Region, Turkey; to date, this is the only locality at which this mineral has been found. Hatert (2019) revised the chemical formula to $\text{NaMgFe}^{3+}_2(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$.

Nickenichite

Nickenichite, $\text{Na}_x\text{Ca}_y\text{Cu}_z(\text{Mg,Fe,Al})_3(\text{AsO}_4)_3$, $x \approx 0.8$, $y \approx 0.4$, $z \approx 0.4$, was found close to the village of Nickenich at the Nickenicher Sattel, Eifel, Germany, in a cavity in scoria (Auernhammer *et al.* 1993). Nickenichite occurs at the top (roof) of an inclined chimney associated with cerussite, malachite, and chrysocolla; crusts of vanadinite cover the crystals (Auernhammer *et al.* 1993). Nickenichite has also been reported from the Tolbachik volcano, Russia (Mindat.org). Hatert (2019) updated the mineral formula to $\text{Na}(\text{Ca}_{0.5}\text{Cu}_{0.5})\text{MgMg}_2(\text{AsO}_4)_3$.

PREVIOUS WORK: SYNTHETIC ALLUAUDITE STRUCTURES

Compounds with structures related to those of the alluaudite-supergroup minerals have been the focus of synthesis studies for decades owing to the significant flexibility of the framework, which allows cation substitution at the *A* and *M* sites and tolerates a wide range of compositional variation. Because of this, compounds with this structure type have a wide range of practical applications, for example as corrosion inhibitors, passivators of metal surfaces, and catalysts (Korzenski *et al.* 1998). Interest in alluaudite structures with monovalent cations has continued to grow in the electrochemical field, where they have application as positive electrodes in lithium and sodium batteries (Trad *et al.* 2010a). Improvements in synthesis methods have allowed incorporation into the alluaudite structure of a wide range of elements not observed in alluaudite-supergroup minerals to date. There is an extensive literature on sulfate, molybdenate, and vanadinite alluaudite structures that are beyond the scope of this paper. A few examples of structural types are compared here, together with a comprehensive list of all synthetic phosphate- (Table 2) and arsenate-alluaudite structures (Table 3).

Transition-metal alluaudite structures

A series of synthetic alluaudites that are similar to natural analogues have also been studied in order to look systematically at structural variation with changing chemical composition; examples are $\text{Na}_2\text{Mn}_2\text{Fe}(\text{PO}_4)_3$, $\text{NaMnFe}_2(\text{PO}_4)_3$, and $\text{Na}_2\text{MnFe}^{\text{II}}\text{Fe}^{\text{III}}(\text{PO}_4)_3$ (Hatert *et al.* 2004); $\text{Na}_2(\text{Mn}_{1-x}\text{Fe}_{2+x})_2\text{Fe}^{3+}(\text{PO}_4)_3$ ($x = 0$ to 1) (Hatert *et al.* 2005); $\text{Na}_{1.5}\text{Mn}_{2.48}\text{Al}_{0.85}(\text{PO}_4)_3$ (Hatert 2005) and $\text{Na}_2(\text{Mn}_{2-2x}\text{Fe}_{1+2x})(\text{PO}_4)_3$ ($x = 0$ to 1) (Hatert *et al.* 2006); and $\text{Na}_{1.67}\text{Zn}_{1.67}\text{Fe}_{1.33}(\text{PO}_4)_3$ (Khmiyas *et al.* 2015). The effect of particle size on physical properties has also been examined, e.g., $\text{Na}_2\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ (Karegeya *et al.* 2017) and $\text{Na}_2\text{Fe}_{3-x}\text{Mn}_x(\text{PO}_4)_3$ (Huang *et al.* 2015).

Cadmium

Cadmium has been used as the main divalent cation in a series of compounds including $\text{NaCdIn}_2(\text{PO}_4)_3$ (Antenucci *et al.* 1993), $\text{NaCaCdMg}_2(\text{PO}_4)_3$ (Antenucci *et al.* 1995), $\text{NaCaCdMg}_2(\text{PO}_4)_3$ (Antenucci *et al.* 1996), $\text{Na}_{1.5}(\text{Mn}_{1-x}\text{M}^{2+}_x)_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ ($x = 0$ to 1, $\text{M}^{2+} = \text{Cd}^{2+}$, Zn^{2+}) (Hatert 2008), $\text{Na}_2\text{Mn}_{2(1-x)}\text{Cd}_{2x}\text{Fe}(\text{PO}_4)_3$ (Hidouri *et al.* 2011), and $\text{AgCaCdMg}_2(\text{PO}_4)_3$ and $\text{AgCd}_2\text{Mg}_2(\text{PO}_4)_3$ (Kacimi *et al.* 2005).

Copper

Copper in the synthetic alluaudite structure-types has been shown to occupy different sites compared to the alkali and alkaline-earth metal ions in nature, e.g., $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$ and $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$ (Warner *et al.* 1993, Warner & Maier 1994).

Lithium

The strong covalent P–O bond in the alluaudite-structure type leads to high safety and stability in battery applications, and Li-rechargeable batteries are promising candidates for environmentally friendly vehicles (Kim *et al.* 2014). The first synthetic alluaudite with lithium was reported in 2000, $\text{Na}_{1-x}\text{Li}_x\text{MnFe}_2(\text{PO}_4)_3$ ($x = 0$ to 1) (Hatert *et al.* 2000), followed by other synthetic phosphate materials with lithium such as $(\text{Na}_{1-x}\text{Li}_x)\text{CdIn}_2(\text{PO}_4)_3$ (Hatert *et al.* 2002), $(\text{Na}_{1-x}\text{Li}_x)_{1.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ (Hatert 2004), $\text{Li}_{0.5}\text{Na}_{0.5}\text{MnFe}_2(\text{PO}_4)_3$ and $\text{Li}_{0.75}\text{Na}_{0.25}\text{MnFe}_2(\text{PO}_4)_3$ (Trad *et al.* 2010a), and LiMnPO_4 (Kim *et al.* 2014).

Silver

By incorporating another monovalent cation into the structure where Na^+ usually occurs in nature, another group of alluaudite-structure types can be made: $\text{Ag}_{1.49}\text{Mn}_{1.49}\text{Mn}^{3+}_{1.51}(\text{AsO}_4)_3$ (Brahim & Amor 2003), $\text{AgCaCdMg}_2(\text{PO}_4)_3$ and $\text{AgCd}_2\text{Mg}_2(\text{PO}_4)_3$ (Kacimi *et al.* 2005), $\text{Ag}_2\text{FeMn}_2(\text{PO}_4)_3$ (Chouaibi *et al.* 2001), and $\text{Ag}_{1.655}\text{Co}_{1.64}\text{Fe}_{1.36}(\text{PO}_4)_3$ (Bouraima *et al.* 2017).

Potassium

The presence of cations, such as potassium, located in the tunnels in the alluaudite structure has the potential to provide interesting ionic mobility (Chaalia *et al.* 2012). A few examples of potassium-bearing alluaudite structures are $\text{K}_2\text{Mn}_3(\text{AsO}_4)_3$ (Chaalia *et al.* 2012), $\text{K}_3\text{Bi}_2(\text{AsO}_4)_3$ (Falah *et al.* 2004), and $\text{K}_{0.53}\text{Mn}_{2.37}\text{Fe}_{1.24}(\text{PO}_4)_3$ (Hidouri & Amara 2011).

TABLE 2. SYNTHETIC PHOSPHATE ALLUAUDITE STRUCTURES

Chemical Formula	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)	Ref
NaMg ₃ (HPO ₄) ₂ (PO ₄)	11.8064(6)	12.0625(7)	6.4969(4)	113.805(2)	846.54(8)	1
AgNi ₃ (PO ₄) ₂ (HPO ₄) ₂	11.865(4)	12.117(3)	6.467(2)	113.82(3)	850.6(4)	2
AgMg ₃ (PO ₄)(HPO ₄) ₂	11.9126(5)	12.1197(6)	6.4780(3)	113.812(2)	855.66(7)	3
NaCo ₃ (PO ₄)(HPO ₄) ₂	11.865(2)	12.137(2)	6.512(1)	114.12(1)	855.9(2)	4
Na _{1.25} Mg _{1.10} Fe _{1.90} (PO ₄) ₃	11.7831(3)	12.4740(3)	6.3761(2)	113.643(2)	858.51(4)	5
Na ₂ Ni ₂ Fe(PO ₄) ₃	11.729(7)	12.433(5)	6.431(2)	113.66(4)	858.9(6)	6
Na _{1.5} Zn _{1.5} Fe ³⁺ _{1.5} (PO ₄) ₃	11.737(1)	12.503(2)	6.386(1)	113.54(1)	859.16*	7
Na ₂ Co ₂ Fe(PO ₄) ₃	11.7599(3)	12.4522(3)	6.44063(16)	113.913(2)	862.18(4)	8
(Na _{0.38} Ca _{0.31})MgFe ₂ (PO ₄) ₃	11.852(2)	12.458(1)	6.3861(6)	113.84(1)	862.5(2)	9
Na _{1.67} Zn _{1.67} Fe _{1.33} (PO ₄) ₃	11.7545(4)	12.5080(4)	6.4014(2)	113.507(1)	863.06(5)	10
Na _{1.79} Mg _{1.79} Fe _{1.21} (PO ₄) ₃	11.791(3)	12.489(3)	6.4191(10)	113.82(2)	864.7(4)	11
Li _{0.75} Na _{0.25} MnFe ₂ (PO ₄) ₃	11.9822(2)	12.4672(1)	6.3787(1)	114.800(6)	865.01(3)	12
Na _{1.5} (Mn _{0.25} Zn _{0.75}) _{1.5} Fe ³⁺ _{1.5} (PO ₄) ₃	11.802(3)	12.515(3)	6.396(2)	113.70(2)	865.04*	7
Li _{0.5} Na _{0.5} MnFe ₂ (PO ₄) ₃	11.9892(2)	12.4927(2)	6.3859(1)	114.639(1)	869.39(4)	12
Cu ₂ Mg ₃ (PO ₄) ₃	11.726(5)	12.613(4)	6.457(3)	114.43(4)	869.50*	13
Li _{1.5} Mn _{1.5} Fe _{1.5} (PO ₄) ₃	11.982(3)	12.514(2)	6.409(2)	115.12(2)	870.1(2)	14
Na ₂ VFe ₂ (PO ₄) ₃ /C	11.914	12.464	6.456	114.54	872.11*	15
Na _{1.5} (Mn _{0.5} Zn _{0.5}) _{1.5} Fe ³⁺ _{1.5} (PO ₄) ₃	11.883(2)	12.530(2)	6.412(1)	113.93(1)	872.66*	7
(Na _{0.25} Li _{0.75}) _{1.5} Mn _{1.5} Fe _{1.5} (PO ₄) ₃	12.002(2)	12.510(2)	6.428(2)	114.96(1)	875.0(2)	14
Cu _{1.35} Fe ₃ (PO ₄) ₃	11.894(4)	12.629(4)	6.440(1)	115.24(2)	875.1(5)	16
Na _{1.860.14} Fe ₃ (PO ₄) ₃	11.8656(6)	12.5335(8)	6.4703(3)	114.530(4)	875.39(8)	17
Na ₂ Fe ²⁺ Fe ³⁺ (PO ₄) ₃	11.849(2)	12.539(1)	6.486(1)	114.51(1)	876.8(1)	18
Ag _{1.655} Co _{1.64} Fe _{1.36} (PO ₄) ₃	11.8680(3)	12.5514(3)	6.4386(2)	114.012(1)	876.09(4)	19
(Na _{0.5} Li _{0.5}) _{1.5} Mn _{1.5} Fe _{1.5} (PO ₄) ₃	12.006(2)	12.515(2)	6.426(1)	114.78(1)	876.6(2)	14
NaMnFe ₂ (PO ₄) ₃	11.9878(2)	12.5364(2)	6.3980(1)	114.22(1)	876.88(4)	20
NaMnFe ₂ (PO ₄) ₃	12.010(3)	12.530(3)	6.407(2)	114.54(2)	877.2(3)	21
NaMnFe ₂ (PO ₄) ₃	12.001(2)	12.538(2)	6.405(1)	114.45(1)	877.3(2)	22
Na ₂ Mn _{0.5} Fe ²⁺ _{1.5} Fe ³⁺ (PO ₄) ₃	11.894(4)	12.536(3)	6.471(2)	114.49(2)	878.1(3)	18
Na _{1.5} (Mn _{0.75} Zn _{0.25}) _{1.5} Fe ³⁺ _{1.5} (PO ₄) ₃	11.950(3)	12.555(3)	6.420(1)	114.07(2)	879.47*	7
(Na _{0.75} Li _{0.25}) _{1.5} Mn _{1.5} Fe _{1.5} (PO ₄) ₃	12.013(2)	12.543(2)	6.427(1)	114.57(1)	880.7(2)	14
NaFe _{3.67} (PO ₄) ₃	11.881(4)	12.564(3)	6.522(2)	115.09(2)	881.7(5)	23
NaMn(Fe _{0.90} In _{0.12}) ₂ (PO ₄) ₃	12.013(2)	12.572(3)	6.416(1)	114.45(2)	882.1(2)	22
Na ₂ MnFe ²⁺ Fe ³⁺ (PO ₄) ₃	11.944(2)	12.560(2)	6.480(1)	114.52(1)	884.4(2)	18
Na ₄ CaFe ₄ (PO ₄) ₆	12.099(5)	12.480(5)	6.404(2)	113.77(3)	884.9(6)	24
Na _{1.5} Mn _{1.5} Fe ³⁺ _{1.5} (PO ₄) ₃	12.018(2)	12.591(2)	6.442(1)	114.27(1)	888.6(2)	14
Na ₂ GaMn ₂ (PO ₄) ₃	12.019(4)	12.559(2)	6.495(5)	114.63(3)	891.19(3)	25
NaMn(Fe _{0.75} In _{0.25}) ₂ (PO ₄) ₃	12.064(2)	12.641(2)	6.428(1)	114.63(1)	891.2(2)	22
Na ₂ Mn _{1.5} Fe ²⁺ _{0.5} Fe ³⁺ (PO ₄) ₃	11.995(3)	12.596(4)	6.495(2)	114.60(3)	892.3(3)	18
Na _{1.5} (Mn _{0.75} Cd _{0.25}) _{1.5} Fe ³⁺ _{1.5} (PO ₄) ₃	12.064(2)	12.599(2)	6.442(1)	114.31(1)	892.34*	7
LiMnPO ₄	12.071(6)	12.4416(6)	6.6475(4)	115.715(6)	899.48*	26
Na ₂ Mn ₂ Fe ³⁺ (PO ₄) ₃	12.024(4)	12.629(6)	6.515(3)	114.58(4)	899.6(5)	18
Na _{1.5} (Mn _{0.50} Cd _{0.50})Fe ³⁺ _{1.5} (PO ₄) ₃	12.132(2)	12.620(2)	6.451(2)	114.34(2)	899.91*	7
Na ₂ Mn ₂ Fe(PO ₄) ₃	12.039(3)	12.625(3)	6.511(2)	114.54(2)	900.21(4)	27
Na ₂ FeMn ₂ (PO ₄) ₃	12.049(5)	12.624(1)	6.507(3)	114.559(3)	900.347(2)	28
K _{0.53} Mn _{2.37} Fe _{1.24} (PO ₄) ₃	12.272(2)	12.606(2)	6.416(4)	114.87(2)	900.5(6)	29
NaCaCdMg ₂ (PO ₄) ₃	12.005(2)	12.675(3)	6.546(1)	114.55(1)	906.03*	30
AgNaFeMn ₂ (PO ₄) ₃	12.085(1)	12.684(0)	6.498(4)	114.535(3)	906.250(3)	28
AgCd ₂ Mg ₂ (PO ₄) ₃	12.089(3)	12.653(2)	6.530(1)	114.71(2)	907.4(2)	31
Ag ₂ FeMn ₂ (PO ₄) ₃	12.1466(3)	12.7328(4)	6.4999(5)	114.5323(3)	907.85(2)	32
NaMn(Fe _{0.50} In _{0.52}) ₂ (PO ₄) ₃	12.131(2)	12.746(2)	6.470(1)	114.84(1)	907.9(2)	22
Na _{1.5} (Mn _{0.25} Cd _{0.75})Fe _{1.5} (PO ₄) ₃	12.188(3)	12.660(3)	6.463(2)	114.41(2)	908.11*	7
AgCaCdMg ₂ (PO ₄) ₃	12.106(3)	12.677(2)	6.525(1)	114.67(2)	909.9(2)	31
NaMn ₃ (PO ₄)(HPO ₄) ₂	12.179(2)	12.405(1)	6.6602(8)	114.616(7)	914.7(2)	33
Na _{1.5} Cd _{1.5} Fe ³⁺ _{1.5} (PO ₄) ₃	12.234(2)	12.696(2)	6.475(1)	114.50(1)	915.18*	7

TABLE 2. CONTINUED.

Chemical Formula	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)	Ref
Na ₂ FeMnCd(PO ₄) ₃	12.169(5)	12.685(3)	6.524(4)	114.51(2)	916.32(3)	25
Na ₂ MnCdFe(PO ₄) ₃	12.169(4)	12.692(4)	6.530(2)	114.56(2)	917.58(5)	27
AgMn ₃ (PO ₄)(HPO ₄) ₂	12.263(1)	12.446(1)	6.649(1)	114.708(8)	921.9(2)	34
Na ₂ CaMnFe(PO ₄) ₃	12.283(1)	12.736(1)	6.494(5)	114.76(3)	922.5(7)	35
NaMn(Fe _{0.25} In _{0.75}) ₂ (PO ₄) ₃	12.222(3)	12.845(2)	6.507(1)	115.11(2)	925.0(2)	22
Na ₂ GaCd ₂ (PO ₄) ₃	12.188(3)	12.799(1)	6.547(3)	114.75(2)	926.44(2)	25
NaMn(Fe _{0.1} In _{0.90}) ₂ (PO ₄) ₃	12.261(3)	12.911(2)	6.535(1)	115.20(2)	936.1(2)	22
Na ₂ Cd ₂ Fe(PO ₄) ₃	12.297(4)	12.799(4)	6.562(2)	114.85(2)	937.06(2)	27
Na ₂ InMn ₂ (PO ₄) ₃	12.248(1)	12.823(4)	6.607(2)	114.97(3)	940.64(4)	25
NaMnIn ₂ (PO ₄) ₃	12.282(2)	12.948(2)	6.552(1)	115.21(1)	942.8(2)	22
LiCdIn ₂ (PO ₄) ₃	12.476(3)	12.906(3)	6.571(2)	115.74(2)	953.0(3)	36
Na _{0.25} Li _{0.75} CdIn ₂ (PO ₄) ₃	12.472(2)	12.905(2)	6.574(1)	115.67(1)	953.8(2)	36
Na _{0.3} Li _{0.7} CdIn ₂ (PO ₄) ₃	12.470(2)	12.907(2)	6.575(1)	115.64(1)	954.1(2)	36
Na _{0.4} Li _{0.6} CdIn ₂ (PO ₄) ₃	12.474(3)	12.909(2)	6.573(1)	115.61(1)	954.5(2)	36
Na _{0.5} Li _{0.5} CdIn ₂ (PO ₄) ₃	12.479(2)	12.917(2)	6.571(1)	115.55(1)	955.6(2)	36
Na _{0.75} Li _{0.25} CdIn ₂ (PO ₄) ₃	12.502(2)	12.944(2)	6.572(1)	115.44(2)	960.4(2)	36
NaCdIn ₂ (PO ₄) ₃	12.517(3)	12.966(3)	6.571(2)	115.36(2)	963.7(3)	36
NaCdIn ₂ (PO ₄) ₃	12.519(2)	12.959(3)	6.575(1)	115.17(1)	965.42*	37

1. Saleck *et al.* (2015); 2. Smail & Jouini (2002); 3. Assani *et al.* (2011); 4. Lii & Shih (1994); 5. Hidouri *et al.* (2008); 6. Essehli *et al.* (2011); 7. Hatert (2008); 8. Essehli *et al.* (2015); 9. Zid & Jouini (2005); 10. Khmias *et al.* (2015); 11. Hidouri *et al.* (2003); 12. Trad *et al.* (2010a); 13. Warner & Maier (1994); 14. Hatert (2004); 15. Wen *et al.* (2018); 16. Warner *et al.* (1993); 17. Essehli *et al.* (2016); 18. Hatert *et al.* (2005); 19. Bouraima *et al.* (2017); 20. Trad *et al.* (2010b); 21. Hatert *et al.* (2004); 22. Hatert *et al.* (2003); 23. Korzenski *et al.* (1998); 24. Hidouri *et al.* (2004); 25. Durio *et al.* (2002); 26. Kim *et al.* (2014); 27. Hidouri *et al.* (2011); 28. Daidouh *et al.* (2002); 29. Hidouri & Amara (2011); 30. Antenucci *et al.* (1995); 31. Kacimi *et al.* (2005); 32. Chouaibi *et al.* (2001); 33. Leroux *et al.* (1995); 34. Leroux *et al.* (1995); 35. Jebli *et al.* (2016); 36. Hatert *et al.* (2002); 37. Antenucci *et al.* (1993).

* Volume not reported in manuscript, calculated from cell dimensions.

Indium

In nature, indium tends to favor sulfide minerals rather than oxides, and no indium-bearing alluaudite structures have been discovered in nature. The influence of indium on the structure has been explored in NaMn(Fe_{1-x}In_x)₂(PO₄)₃ (Hatert *et al.* 2003) and Na₃In₂(AsO₄)₃ (Khorari *et al.* 1997).

Unoxidized variants

A series of unoxidized variants have been synthesized which are related to the alluaudite-structure type, with a few important differences. The tightly bonded framework is composed of complex $M^{2+}O_6$ distorted octahedra and PO₄ tetrahedra, as with the other alluaudite structures. The differences referred to above pertain to the *P*(2)O₄ tetrahedron which shares two vertices with one chain and one vertex with an adjacent chain; the fourth vertex points outward, away from the plane of the pleated sheet. These sheets are linked together through this last vertex of the *P*(2)O₄ tetrahedra, together with hydrogen bonds, to form a three-dimensional framework (Leroux *et al.* 1995). By incorporating a monovalent cation at the *A* site and

divalent cations at the *B* site, several structures have been prepared, such as NaMn₃(PO₄)(HPO₄)₂ (Leroux *et al.* 1995), AgNi₃(PO₄)(HPO₄)₂ (Smail & Jouini 2002), AgMn₃(AsO₄)(HAsO₄)₂ (Stock & Bein 2003), AgMg₃(PO₄)(HPO₄)₂ (Assani *et al.* 2011), NaMg₃(HPO₄)₂(PO₄) (Saleck *et al.* 2015), NaCo₃(PO₄)(HPO₄)₂ and NaCo₃(AsO₄)(HAsO₄)₂ (Lii & Shih 1994), and NaMn₃(AsO₄)(HAsO₄)₂ and KMn₃(AsO₄)(HAsO₄)₂ (Stock *et al.* 2001). Structures with divalent cations at the *A* and *B* sites have also been prepared, such as Cd_{1.16}Zn_{2.34}(AsO₄)_{1.5}(HAsO₄)(H₂AsO₄)_{0.5} and Cd_{0.74}Mg_{2.76}(AsO₄)_{1.5}(HAsO₄)(H₂AsO₄)_{0.5} (Stojanović *et al.* 2012).

NOMENCLATURE

Moore & Ito (1979) proposed a nomenclature scheme for the alluaudite-group minerals that is based on sequentially distributing the cations in the cell according to increasing polyhedron size, matching that size with increasing ionic radii of the cations. For alluaudite, the structural formula was written as $X(2)_4X(1)_4M(1)_4M(2)_8(PO_4)_{12}$, with the sites ordered in decreasing size of the corresponding polyhedra. A

TABLE 3. SYNTHETIC ARSENATE-ALLUAUDITE STRUCTURES

Chemical Formula	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)	Ref
NaMg ₃ (AsO ₄)(AsO ₃ OH) ₂	11.972(2)	12.367(3)	6.743(2)	112.67(3)	921.3(4)	1
Cd _{0.74} Mg _{2.76} (AsO ₄) _{1.5} (HAsO ₄)(H ₂ AsO ₄) _{0.5}	11.992(2)	12.429(3)	6.7462(13)	112.92(3)	926.1(4)	2
NaZn ₃ (AsO ₄)(AsO ₃ OH) ₂	12.023(2)	12.385(3)	6.750(2)	112.79(3)	926.7(4)	1
NaCo ₃ (AsO ₄)(HAsO ₄) ₂	12.054(1)	12.378(1)	6.780(2)	113.03(1)	931.0(3)	3
AgZn ₃ H ₂ (AsO ₄) ₃	12.159(6)	12.438(7)	6.782(3)	113.16(3)	943.02*	4
AgCo ₃ H ₂ (AsO ₄) ₃	12.169(2)	12.495(3)	6.755(1)	112.77(1)	947.08*	4
NaCaMg ₃ (AsO ₄) ₃	11.880(1)	12.817(1)	6.741(2)	112.45(1)	948.7(3)	5
Cd _{1.16} Zn _{2.34} (AsO ₄) _{1.5} (HAsO ₄)(H ₂ AsO ₄) _{0.5}	12.250(3)	12.491(3)	6.816(1)	113.62(3)	955.6(4)	2
Na _{1.6} Zn _{2.4} (H _{0.6} AsO ₄)(AsO ₃ OH) ₂	12.458(3)	12.484(3)	6.839(2)	113.83(3)	973.0(4)	1
Ag _{1.49} Mn _{2.49} Mn _{1.51} ³⁺ (AsO ₄) ₃	12.262(2)	12.934(3)	6.7070(9)	113.690(2)	974.1(3)	6
NaCaCdMg ₂ (AsO ₄) ₃	12.2363(1)	12.9869(1)	6.7742(1)	113.7985(3)	984.98*	7
NaMn ₃ (AsO ₄)(HAsO ₄) ₂	12.299(3)	12.735(3)	6.893(2)	113.587(4)	989.5(4)	8
Na _{0.25} Ca _{2.375} Mg ₂ (AsO ₄) ₃	12.288	13.0627	6.7672	113.747	994.267	9
NaCa ₂ Ni ₂ (AsO ₄) ₃	12.304	13.033	6.781	113.84	994.6	9
AgMn ₃ (AsO ₄)(HAsO ₄) ₂	12.397(2)	12.707(2)	6.8904(6)	113.57(1)	994.8(2)	10
Ca _{2.5} Mg ₂ (AsO ₄) ₃	12.3169	13.0736	6.7623	113.873	995.747	9
Na _{0.5} Ca _{2.5} Mg ₂ (AsO ₄) ₃	12.2912	13.0685	6.7801	113.821	996.285	9
NaCa ₂ Co ₂ ²⁺ (AsO ₄) ₃	12.264	13.103	6.790	114.00	996.8	9
Na _{0.9} Ca _{2.05} Mg ₂ (AsO ₄) ₃	12.2797(8)	13.0701(6)	6.7850(4)	113.72(33)	997.013	9
Na _{0.75} Ca _{2.125} Mg ₂ (AsO ₄) ₃	12.2893	13.0768	6.7816	113.794	997.195	9
Na _{0.8} Ca _{2.1} Mg ₂ (AsO ₄) ₃	12.2941	13.0821	6.7813	113.776	998.085	9
NaCa ₂ Mg ₂ (AsO ₄) ₃	12.2897(10)	13.0770(10)	6.7913(5)	113.74(40)	999.09(10)	9
NaCa ₂ Mg ₂ ²⁺ (AsO ₄) ₃	12.290	13.077	6.791	113.74	999.1	9
KCa ₂ Ni ₂ ²⁺ (AsO ₄) ₃	12.458	12.974	6.767	113.45	1003.4	9
AgCa ₂ Mg ₂ (AsO ₄) ₃	12.346	13.086	6.789	113.77	1003.8	9
KCa ₂ Co ₂ (AsO ₄) ₃	12.499	13.084	6.815	114.06	1017.6	9
K ₂ Mn ₃ (AsO ₄) ₃	12.490(1)	13.013(1)	6.888(1)	114.460(1)	1019.2(8)	11
KMn ₃ (AsO ₄)(HAsO ₄) ₂	12.706(3)	12.731(3)	6.937(2)	113.175(5)	1031.6(4)	8
TiCa ₂ Mg ₂ (AsO ₄) ₃	12.775	13.112	6.777	113.98	1037.2	9
Na ₃ In ₂ (AsO ₄) ₃	12.6025(1)	13.1699(1)	6.8335(1)	113.7422(5)	1037.66(9)	9
Na ₃ Bi ₂ (AsO ₄) ₃	13.673(2)	13.474(3)	6.885(2)	116.22(2)	1137.9*	12
K ₃ Bi ₂ (AsO ₄) ₃	14.030(2)	13.773(2)	7.009(2)	114.71(2)	1230.4(3)	13

1. Đorđević *et al.* (2015); 2. Stojanović *et al.* (2012); 3. Lii & Shih (1994); 4. Keller *et al.* (1981); 5. Adballah & Haddad (2008); 6. Brahim & Amor (2003); 7. Khorari *et al.* (1997); 8. Stock *et al.* (2001); 9. Khorari *et al.* (1997); 10. Stock & Bein (2003); 11. Chaalia *et al.* (2012); 12. Bdey *et al.* (2018); Falah *et al.* (2004).

* Calculated volume from unit cell.

generic name based on the occupancy of the *M*(2) site was proposed, with a specific name referring to the predominant cation at *M*(1) and given as a prefix to the root name. Further splitting into sub-specific names is facilitated by suffixes [e.g., ferrohagendorfite-*X*(1)-*X*(2)]. Leroux *et al.* (1995) proposed a new nomenclature, relabeling *X*(1) and *X*(2) as *A*(1) and *A*(2), respectively. *A*(1) occurs in channel 1 that extends around (1/2, 0, *z*) and (0, 1/2, *z*), and *A*(2) occurs in channel 2 that extends around (0, 0, *z*) and (1/2, 1/2, *z*). The first new cation site described by Leroux *et al.* (1995) was named *A*(2)⁺. Its position corresponds to (0, *y*, 1/4) with *y* ≈ 0, in channel 2. Large cations such as Na, Ag, and Ca can occupy this site, which exhibits [4+2] (distorted trigonal prism) or [4+4] (distorted

gable disphenoid) coordination polyhedra (Antenucci *et al.* 1993, Antenucci *et al.* 1995, Leroux *et al.* 1995). The *A*(1)⁺ site has a square-planar environment, corresponds to the *A*(4) site of Keller *et al.* (1981), and occurs at (0, *y*, 1/4) with *y* ≈ 0.5, in channel 1. The last *A*(1)⁺ site occurs on the general (*x*, *y*, *z*) position in channel 1 and accommodates [2]-coordinated H or [4+2]-coordinated Cu (Warner *et al.* 1993, Leroux *et al.* 1995). Hatert *et al.* (2000) introduced a new crystallochemical formula for the alluaudite-type compounds: $[A(2)A(2)^+][A(1)A(1)^+A(1)^+{}_2]M(1)M(2)_2[(P,As)O_4]_3$. In contrast to the *M* sites, the *A* sites can be partly or totally empty. The majority of the alluaudite minerals have atoms at *A*(1) and *A*(1)⁺, with vacancies at *A*(2), *A*(1)⁺, and *A*(1)⁺. The general

TABLE 4. SAMPLE NUMBERS AND LOCALITIES FOR ALLUAUDITE, HAGENDORFITE, AND VARULITE

Single-crystal refinements			
alluaudite	A-1	Buranga pegmatite, Burundi, Rwanda	ROM 36223
hagendorfite	H-1	Palermo #1, North Groton, New Hampshire, USA	Har 131270
Hand samples			
alluaudite	A-2	Helen Beryl Mine, South Dakota, USA	UM museum
alluaudite	A-3	White Elephant pegmatite, South Dakota, USA	UM museum
alluaudite	A-4	Buranga pegmatite, Burundi, Rwanda	CMNMC 39380
alluaudite	A-5	Chanteloube, Haute-Vienne, France	Har 129255
alluaudite	A-6	Pleasant Valley, South Dakota, USA	Har 118885
alluaudite	A-7	Norrö, Sweden	Har 100820
alluaudite	A-8	Ross mine, Custer Co., South Dakota, USA	ROM 26019
hagendorfite	H-2	Hagendorf pegmatite, Bavaria, Germany	CMNMC 58688
hagendorfite	H-3	Big Fish River, Yukon, Canada	CMNMC 48733
varulite	V-1	Skrumpetorp, Sweden	Har 104346
varulite	V-2	Varuträsk, Västerbotten, Sweden	AMNH 20944

formula for protonated members of the supergroup is $A1A2M1M2_2(X1O_4)(X2O_3OH)_2$ (Dordević *et al.* 2015). In minerals, the *A* sites are occupied by Na, Ca, Mn, whereas the *M* sites are occupied by Mn, Fe, Al, and Mg. Tetrahedrally coordinated *X* sites are occupied by either P or As.

Hatert (2019) proposed a new nomenclature scheme and a new general formula: $A(2)'A(1)M(1)M(2)_2(TO_4)_3$. The new nomenclature scheme is based mainly on the contents of the octahedrally coordinated *M*(1) and *M*(2) sites. For phosphates, the root name is defined on the basis of the content of the *M*(2) site, allowing a valency-imposed double-site occupancy for that site: $M(2)(Fe^{3+}Fe^{3+})$ = alluaudites *s.l.*, $M(2)(Fe^{2+}Fe^{3+})$ = hagendorfites *s.l.*, and $M(2)(Mn^{2+}Fe^{3+})$ = varulites *s.l.* (Hatert 2019). The root name is used without prefix if the *M*(1) site is occupied by Mn, but the prefix “ferro-” is added where *M*(1) is predominantly occupied by Fe^{2+} . For arsenates, the nomenclature is more complicated, as numerous root names are already defined in the literature. Hatert (2019) recommended preferentially adding prefixes to these existing root names in order to differentiate arsenates with identical *M*(2) contents but with different *M*(1) contents.

EXPERIMENTAL

Minerals from several localities were studied by a variety of analytical methods to examine chemical and structural variations. We now know from the numerous studies on synthetic materials that the alluaudite framework is extremely flexible and can incorporate a variety of elements. A systematic study was done to examine major- and minor-element variations in natural samples and to expand the amount of available

structural data for the alluaudite-group minerals. Sample localities are given in Table 4, together with the original sample numbers and more convenient sample numbers used in this work.

Single-crystal diffraction

Crystals were selected under a binocular microscope and then examined for suitability for diffraction experiments in plane-polarized and cross-polarized light. Suitable crystals were attached to glass fibers and mounted on a Siemens *P4* automated four-circle diffractometer equipped with a graphite monochromator and $MoK\alpha$ X-radiation. The data were corrected for Lorentz, polarization, and background effects, averaged and reduced to structure factors. Reflections were measured out to $\sim 60^\circ 2\theta$ with index ranges $-9 \leq h \leq 0$, $0 \leq k \leq 17$, $-15 \leq l \leq 15$; details are given in Table 5, together with other information concerning data collection and structure refinement.

Electron probe microanalysis

The crystals used for X-ray diffraction, together with representative pieces from all samples, were mounted on a Perspex disk, ground, polished, carbon-coated, and analyzed with a CAMECA SX-50 electron microprobe operating under the following conditions in wavelength-dispersion mode: excitation voltage: 15 kV, specimen current 20 nA, beam size: 15 μ m, peak count-time: 20 s, background count-time: 10 s. The following standards (all $K\alpha$ X-ray lines) and crystals were used for the elements sought: Na: maričite, TAP; Mg: forsterite, TAP; Si: diopside, PET; P: maričite, PET; Ca: apatite, PET; Mn: spessartine, LiF; Fe: maričite, LiF; Zn: gahnite, LiF; As: mimetite, TAP.

TABLE 5. MISCELLANEOUS INFORMATION FOR ALLUAUDITE A-1 AND HAGENDORFITE H-1

	A-1	H-1		A-1	H-1
<i>a</i> (Å)	12.013(3)	11.896(2)	Crystal size (μm)	0.20 × 0.12 × 0.03	0.14 × 0.04 × 0.04
<i>b</i> (Å)	12.475(2)	12.578(3)	Radiation	MoKα/Gr	
<i>c</i> (Å)	6.374(2)	6.512(3)	No. of reflections	1381	1407
<i>V</i> (Å ³)	868.3(3)	886.0(5)	No. unique reflections	1275	1301
<i>B</i>	114.63(2)	98.22(3)	Refinement method	least-squares on <i>F</i> ² ; fixed weights 1/(σ(<i>F</i>))	
Sp. Gr.	<i>C2/c</i>	<i>C2/c</i>	No. * <i>F</i> _o * > 4σ(* <i>F</i> _o *)	1127	1189
<i>Z</i>	4	4	<i>R</i> _{merge} (%)	3.1	2.1
Φ (mm ⁻¹)	5.02	4.08	<i>R</i> ₁ (* <i>F</i> _o * > 4σ(<i>F</i>)) (%)	3.7	1.8
<i>D</i> _{calc} (g/cm ³)	3.859	3.471	<i>wR</i> ₂ (<i>F</i> _o ²) (%)	8.4	4.4

$$R = \frac{\sum (*F_o* - *F_c*)}{\sum *F_o*}$$

$$wR = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}, w = 1/F_o^2$$

Ten points were analyzed for each crystal, and the mean chemical compositions are given in Table 6. The unit formulae were calculated on the basis of 3 P *apfu* (atoms per formula unit).

LA-ICP-MS

Several samples were analyzed for Li by laser ablation-inductively coupled-plasma mass spectrometry (LA-ICP-MS). Table 7 shows the instrument parameters used for the analysis. Sodium, Ca, and Mn were determined independently by EPMA and were used as internal standards for the lithium measurements. Lithium intensities were processed using GLITTER (Van Achterbergh *et al.* 2001). Three standard signals were collected before and after the data acquisition from nine points. The standard signals were averaged, and local backgrounds used for all signals.

SINGLE-CRYSTAL STRUCTURE REFINEMENT

All calculations were done with the SHELXTL PC (Plus) suite of programs; *R* indices are of the form given in Table 5 and are expressed as percentages. For each structure, the atom positions, anisotropic-displacement parameters, and site-scattering values for the *A*(2)', *A*(1), *M*(1) and *M*(2) sites were considered as variables, and full-matrix least-squares refinement converged to *R* indices of 3.7% for A-1 and 1.8% for H-1. Atom positions and displacement parameters are listed in Table 8, selected interatomic distances are given in Table 9, and refined site-scattering values (Hawthorne *et al.* 1995) are given in Table 10. Observed and calculated structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

Site populations

In the alluaudite structure, there are four cation sites, *A*(2)', *A*(1), *M*(1), and *M*(2), that contain the non-tetrahedrally coordinated cations of the formula unit. The site populations may be assigned to these sites in accord with the refined site-scattering values and the observed mean bond-lengths at these sites.

Alluaudite

Inspection of the mean bond-lengths in alluaudite (Table 9) indicates that the large (low-valence) cations occupy the *A* sites and the small- and intermediate-sized cations occupy the *M* sites. The calculated scattering values for these two groups of cations are 17.3 and 72.0 *epfu* (electrons per formula unit), respectively, whereas the refined scattering values at the *A* and *M* sites are 17.5 and 72.3 *epfu*. The total scattering values from the refinement and the unit formula are very close (89.8 and 89.3 *epfu*) whereas the values for each group of sites differ significantly from the calculated scattering of each of the two groups of cations (17.5 *versus* 10.5 and 72.3 *versus* 78.8 *epfu*). These differences indicate that some of the smaller, more strongly scattering cations must occur at the *A* sites, in accord with the excess number of medium-sized divalent and trivalent cations relative to the number of available sites: 0.27 *apfu*. As Mn²⁺ is the largest of the smaller cations, 0.27 Mn²⁺ was assigned to the *A* sites to bring the aggregate site-scattering values into accord (Table 10). The refined site-scattering values at *A*(2)' and *A*(1) (Table 10) indicate that the majority of the large low-valence cations must occur at the *A*(2)' site. As <*A*(1)–O> is less than <*A*(2)–O>, the smaller cations Ca and Mn²⁺ were assigned to *A*(2)' together with the Na remaining after Na was assigned to *A*(1) sufficient to agree with

TABLE 6. CHEMICAL COMPOSITIONS (wt.%) AND UNIT FORMULAE* (*apfu*) FOR ALLUAUDITE, HAGENDORFITE, AND VARULITE

	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	H-1	H-2	V-1	V-2
P ₂ O ₅	43.65	45.69	43.91	43.48	44.40	45.85	44.23	43.27	42.49	44.03	41.67	43.01
FeO**	—	0.15	1.77	3.08	2.10	3.40	11.36	10.95	10.12	14.09	9.66	6.38
Fe ₂ O ₃ **	26.78	32.56	29.91	24.64	27.97	35.42	21.60	24.02	18.79	12.53	14.05	16.75
MnO	18.42	11.12	16.50	19.65	17.72	8.16	9.18	13.41	12.54	13.31	20.76	21.84
CaO	1.56	0.27	0.07	1.56	0.63	—	0.13	0.17	2.74	2.75	2.52	1.82
Al ₂ O ₃	2.49	—	—	—	0.05	—	—	—	0.08	1.53	—	—
MgO	1.11	2.76	0.29	0.94	0.37	1.47	2.70	0.37	2.21	3.13	0.06	—
Na ₂ O	4.44	7.52	6.06	5.07	6.86	6.44	10.71	6.55	9.88	8.58	9.50	10.08
Total	98.45	100.07	98.51	98.42	100.10	100.74	99.97	98.94	98.85	99.95	98.22	99.88
P*	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Fe ³⁺	1.63	1.90	1.82	1.51	1.68	2.00	1.30	1.48	1.30	0.76	0.89	1.04
Al	0.24	—	—	—	0.01	—	—	—	—	0.15	—	—
Mg	0.13	0.10	0.04	0.11	0.04	—	0.32	0.05	0.28	0.38	0.01	—
Fe ²⁺	—	—	0.12	0.21	0.14	—	0.38	0.47	0.42	0.71	0.68	0.44
Mn	—	—	0.02	0.17	0.13	—	—	—	—	—	0.42	0.52
Σ <i>M</i> (2)	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Fe ²⁺	—	—	—	—	—	0.06	—	—	0.29	—	—	—
Mg	—	0.22	—	—	—	0.17	—	—	—	—	—	—
Mn ²⁺	0.99	0.01	—	—	—	0.22	0.38	0.28	0.71	0.23	—	—
Zn	0.01	0.73	1.00	1.00	1.00	0.53	0.62	0.72	—	0.77	1.00	1.00
Σ <i>M</i> (1)	1.00	0.96	1.00	1.00	1.00	0.98	1.00	1.00	1.00	1.00	1.00	1.00
Mn ²⁺	0.27	—	0.11	0.19	0.20	—	—	0.21	0.14	0.14	0.06	—
Na	0.44	0.98	0.88	0.67	0.75	0.97	0.99	0.77	0.62	0.62	0.71	0.84
Ca	0.14	0.02	0.01	0.14	0.05	—	—	0.02	0.24	0.24	0.23	0.16
□	0.15	—	—	—	—	—	—	—	—	—	—	—
Σ <i>A</i> (1)	1.00	1.00	1.00	1.00	1.00	0.97	0.99	1.00	1.00	1.00	1.00	1.00
Na	0.26	0.14	0.07	0.14	0.39	—	0.67	0.28	0.98	0.72	0.84	0.77
□	0.74	0.86	0.93	0.86	0.61	1.00	0.34	0.72	0.02	0.28	0.16	0.23
Σ <i>A</i> (2)'	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

the refined site-scattering value. The resulting site-populations show aggregate scattering values that are very close to the refined values (Table 10).

Comparison of the $\langle M-O \rangle$ bond-lengths in alluaudite (Table 9) indicates that the larger *M*-type cations occupy the *M*(1) site and the smaller *M*-type cations occupy the *M*(2) site. The *M*-type cations are predominantly Mn and Fe, and the $\langle M-O \rangle$ distances indicate that there must be mainly divalent cations at *M*(1) and trivalent cations at *M*(2). As Mn³⁺ octahedra show strong Jahn-Teller distortion (*cf.* Burns *et al.* 1994) and the *M*(2) octahedron does not have a geometry typical of Jahn-Teller distortion, we may conclude that Mn is divalent and occurs at *M*(1), and that Fe is trivalent and occurs at *M*(2). The refined site-scattering values at the *M* sites are in accord with complete occupancy of *M*(1) by Mn, and the remaining amounts of Al and Mg were assigned to *M*(2) together with Fe as Fe³⁺. The effective site-

scattering values calculated from the assigned site-populations (Table 10) are in close agreement with the corresponding refined values.

Hagendorfite

The site populations in hagendorfite were assigned in the same manner as for alluaudite. The total refined scattering at the *A* and *M* sites, 101.2 *epfu*, is in close agreement with the aggregate scattering from the cations of the unit formula: 100.5 *epfu*. The $\langle M(2)-O \rangle$ bond length indicates that Fe is present at this site as both Fe³⁺ and Fe²⁺. Using the ideal bond-lengths for $\langle [^{61}\text{Fe}^{2+}-\text{O}^{2-}] \rangle$ and $\langle [^{61}\text{Fe}^{3+}-\text{O}^{2-}] \rangle$ (Gagné & Hawthorne 2020), we may calculate the Fe³⁺ and Fe²⁺ contents to give a $\langle M(2)-O \rangle$ bond length of 2.080 Å (the observed value, Table 9). The resulting site-populations are given in Table 10; the calculated site-scattering values are in close agreement with the refined values. The *M*(2) site is occupied by

TABLE 7. LA-ICP-MS OPERATING AND DATA-ACQUISITION PARAMETERS

ICP-MS	
Model	Element 2
Forward Power	1336 W
Gas flows:	
Plasma (Ar)	16 L min ⁻¹
Auxiliary (Ar)	0.80 L min ⁻¹
Carrier (Ar)	1.26 L min ⁻¹
LAM	
Model	Merchantek LUV 213
Wavelength	213 nm
Repetition rate	10 and 20 Hz
Pre-ablation warm-up	None
Pulse duration	5 ns
Spot size	40 & 60 mm
Incident pulse energy	~0.137 and 0.287 mJ
Energy density on sample	~10.93 and 9.95 J cm ⁻²
Data-Acquisition Parameters	
Data-acquisition protocol	time resolved analysis
Scanning mode	BScan and EScan
Detector mode	analog and counting
Isotopes	⁶ Li, ⁷ Li, ²³ Na, ⁴⁴ Ca, ⁵⁵ Mn *
Dwell time (segment duration)	100 ms
Magnet setting time	0.001–0.3 s
Time/scan	0.927 s
Runs/passess**	50-3
Data acquisition(s)	40 s gas blank, 60 s ablation

* Internal standard.

** A pass is a measurement cycle through the mass spectrum, they are averaged and combined into one run 50 times to create 50 blocks of data per sample.

Fe³⁺_{1.30}(Fe²⁺_{0.42}Mg_{0.28}), which is closer to the *M*(2) content of ideal hagedorfite: Fe³⁺_{1.0} Fe²⁺_{1.0} [this is more apparent if we write the *M*(2) content of H-1 as Fe³⁺_{1.30} M²⁺_{0.70}].

Mean bond-lengths

In most groups of chemically complicated minerals (e.g., olivine, pyroxene, amphibole), there are relations between the observed mean bond-lengths at the cation sites and the mean radii of the constituent cations at those sites. When a lot of data is available, linear relations between these variables can be developed. For structures in which not much data is available, the observed mean bond-lengths may be compared with the aggregate average observed mean bond-lengths for the constituent cations; [⁷Na²⁺–O^{2–}, [⁸Na²⁺–O^{2–}, [⁶Mg²⁺–O^{2–}, [⁷Ca²⁺–O^{2–} (Gagné & Hawthorne 2016); [⁶Al³⁺–O^{2–} (Gagné & Hawthorne 2018); and

[⁶Mn²⁺–O^{2–}, [⁷Mn²⁺–O^{2–}, [⁶Fe²⁺–O^{2–}, [⁶Fe³⁺–O^{2–} (Gagné & Hawthorne 2020); this is done in Table 11. The observed and calculated bond-lengths are generally within 0.02 Å, and the deviations are consistent in both structures, suggesting that these differences arise from structural strain (Gagné & Hawthorne 2020). This is not the case for the *A*(1) polyhedron where the deviations are ~0.12 Å (Table 11); in part, this may be assigned to the fact that the site can be only partly occupied, but this is not the case for H-1—it is probable that the extremely distorted nature of the *A*(1) polyhedron plays a role.

CHEMICAL COMPOSITION OF ALLUAUDITE-GROUP MINERALS

Eight crystals of alluaudite, four crystals of hagedorfite, and two crystals of varulite were selected from several localities (Table 4) for electron probe microanalysis; chemical compositions and unit formulae are given in Table 6. In the new nomenclature scheme for the alluaudite subgroup, alluaudite *s.l.* is defined by ^{*M*(2)}(Fe³⁺Fe³⁺), hagedorfites *s.l.* by ^{*M*(2)}(Fe²⁺Fe³⁺), and varulites *s.l.* by ^{*M*(2)}(Mn²⁺Fe³⁺) (Hatert 2019). Hatert (2019) defined alluaudite as ^{*M*(2)}M²⁺ < 0.5 (Type 1) with the trivalent cation at the *M*(2) site and a vacancy at the *A*(2)' site to charge-balance the structure. Alluaudite and ferroalluaudite have Fe³⁺ as the main constituent at the *M*(2) site but differ at the *M*(1) site: alluaudite is Mn²⁺ dominant, ferroalluaudite is Fe²⁺ dominant. The only alluaudites that have considerable Al³⁺ are those from the Buranga pegmatite with 2.39–2.57 wt.% Al₂O₃, and Fransolet (1980) reported up to 4.68 wt.% Al₂O₃ in alluaudite from the beryl-muscovite-albite zone of the pegmatite (Association I). ⁵⁷Fe Mössbauer spectroscopy of the Buranga alluaudite showed that iron is exclusively at the trivalent site (Redhammer *et al.* 2005). Robinson *et al.* (1992) reported 2.94 wt.% Al₂O₃ in alluaudite from Rapid Creek, Yukon, Canada, where thick deposits of siderite and phosphatic ironstone in shale form an iron-rich host for the alluaudite minerals. Can there be Al analogues of Fe³⁺-bearing species in this group? At the present time, this is not clear; the data of Fransolet (1977) suggest that this could be the case, but higher amounts of Al promote crystallization of wylleite-group minerals.

Hagedorfite *s.l.* has Fe²⁺ dominant at the *M*(2) site; "ROOT3" (Hatert 2019) *M*(1) = Fe²⁺, hagedorfite has *M*(1) = Mn²⁺, and maghagedorfite has *M*(1) = Mg; varulite *s.l.* has ^{*M*(2)}(Mn²⁺Fe³⁺). Magnesium is a rare major constituent in alluaudite-group minerals. As a consequence, the role of Mg in alluaudite-group minerals is not well-characterized. Rondeux & Hatert

TABLE 8. ATOM COORDINATES AND ANISOTROPIC-DISPLACEMENT PARAMETERS FOR ALLUAUDITE A-1 AND HAGENDORFITE H-1

	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	U _{eq}
A-1										
A(2)'	1/2	0	0	0.0494(12)	0.0076(7)	0.0393(11)	-0.0026(6)	-0.0321(8)	0.0018(6)	0.0491(9)
A(1)	0	-0.0154(7)	1/4	0.019(4)	0.028(5)	0.036(5)	0	-0.002(3)	0	0.032(3)
M(1)	0	0.2609(5)	1/4	0.0110(3)	0.0120(3)	0.0167(4)	0	0.00685(24)	0	0.01281(22)
M(2)	0.2796(6)	0.65302(4)	0.36878(7)	0.00890(23)	0.00980(24)	0.0111(3)	-0.00226(14)	0.003322(17)	-0.00073(14)	0.01021(17)
T(1)	0	-0.28518(8)	1/4	0.0077(4)	0.0065(4)	0.0080(4)	0	-0.0006(3)	0	0.00869(22)
T(2)	0.24213(6)	-0.10741(6)	0.13348(12)	0.0091(3)	0.0087(3)	0.0103(3)	-0.00324(22)	0.0020(3)	-0.00074(22)	0.01007(20)
O(1)	0.45124(19)	0.71439(17)	0.5326(3)	0.01112(9)	0.0124(9)	0.0101(9)	-0.0043(7)	0.0025(7)	0.0008(7)	0.0119(4)
O(2)	0.09774(21)	0.63963(18)	0.2356(4)	0.0167(10)	0.0159(10)	0.0173(11)	-0.0073(8)	0.0005(9)	0.0060(8)	0.0189(5)
O(3)	0.32704(22)	0.66375(17)	0.1012(4)	0.0240(11)	0.0104(10)	0.0107(9)	-0.0028(7)	0.0062(8)	-0.0062(8)	0.015(4)
O(4)	0.12182(21)	0.40043(19)	0.3097(5)	0.0120(11)	0.0135(11)	0.0496(16)	0.0036(11)	0.0124(11)	0.0012(8)	0.0252(6)
O(5)	0.22673(20)	0.82221(18)	0.3210(4)	0.0138(10)	0.0156(10)	0.0106(9)	0.0004(8)	0.0026(8)	0.0021(8)	0.0141(4)
O(6)	0.31304(21)	0.50309(18)	0.3750(4)	0.0164(10)	0.0117(9)	0.0184(10)	0.0051(8)	0.0044(8)	-0.0026(8)	0.0165(5)
H-1										
A(2)'	1/2	0	0	0.414(5)	0.0119(4)	0.0170(4)	-0.0004(3)	-0.0062(3)	-0.0016(3)	0.0296(3)
A(1)	0	-0.02037(11)	1/4	0.0209(7)	0.0455(9)	0.0185(7)	0	0.0039(5)	0	0.0297(4)
M(1)	0	0.26587(3)	1/4	0.00973(18)	0.00989(18)	0.01179(19)	0	0.00592(14)	0	0.00999(11)
M(2)	0.27993(2)	0.65815(2)	0.36658(4)	0.00741(13)	0.00852(13)	0.00848(14)	-0.00038(8)	0.00359(10)	0	0.00804(9)
T(1)	0	-0.28841(4)	1/4	0.00633(24)	0.00671(24)	0.0059(3)	0	0.00170(20)	0	0.00658(12)
T(2)	0.23405(4)	-0.10826(3)	0.12542(7)	0.00721(19)	0.00673(19)	0.00610(19)	-0.00027(13)	0.00225(15)	-0.00005(13)	0.00685(10)
O(1)	0.45702(11)	0.71800(9)	0.53757(19)	0.0078(5)	0.0123(5)	0.0065(5)	-0.0027(4)	0.0021(4)	-0.0001(4)	0.00914(23)
O(2)	0.09929(12)	0.63528(10)	0.24557(23)	0.0107(6)	0.0108(6)	0.0120(7)	-0.0062(5)	0.0027(5)	0.0028(4)	0.0150(3)
O(3)	0.33658(11)	0.66423(9)	0.10457(20)	0.0139(6)	0.0099(5)	0.0076(5)	-0.0022(4)	0.0033(5)	-0.0034(4)	0.01089(24)
O(4)	0.12813(11)	0.40278(10)	0.32408(21)	0.0082(6)	0.0106(6)	0.0201(7)	0.0004(5)	0.0060(5)	0.0003(4)	0.0130(3)
O(5)	0.22313(11)	0.82420(10)	0.31329(20)	0.0125(6)	0.0158(6)	0.0083(5)	0.0028(5)	0.0042(5)	-0.0014(5)	0.0123(3)
O(6)	0.32802(12)	0.49984(10)	0.38703(21)	0.0131(6)	0.0110(5)	0.0129(6)	0.0032(5)	0.0042(5)	-0.0032(5)	0.0128(3)

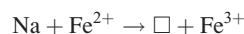
TABLE 9. SELECTED INTERATOMIC DISTANCES (Å) IN ALLUAUDITE A-1 AND HAGENDORFITE H-1

	A-1	H-1
A(2)'-O(2)	2.288(7)	2.282(20)
A(2)'-O(2)	2.299(7)	2.321(19)
A(2)'-O(2)	2.797(6)	2.821(13)
A(2)'-O(4)	2.261(7)	2.361(19)
A(2)'-O(4)	2.357(5)	2.378(19)
A(2)'-O(4)	2.315(7)	2.456(16)
A(2)'-O(4)	2.798(5)	2.679(16)
<A(2)'-O>	2.445	2.471
A(1)-O(1) ×2	2.783(7)	2.787(2)
A(1)-O(3) ×2	2.928(7)	2.922(2)
A(1)-O(6) ×2	2.689(3)	2.563(1)
A(1)-O(6) ×2	2.512(2)	2.412(1)
<A(1)-O>	2.728	2.671
M(1)-O(1) ×2	2.192(2)	2.220(1)
M(1)-O(3) ×2	2.246(2)	2.186(1)
M(1)-O(4) ×2	2.202(2)	2.216(1)
<M(1)-O>	2.213	2.207
M(2)-O(1)	2.033(2)	2.072(1)
M(2)-O(2)	1.995(2)	1.978(1)
M(2)-O(3)	2.015(2)	2.081(1)
M(2)-O(5)	2.189(2)	2.178(1)
M(2)-O(5)	2.034(2)	2.112(2)
M(2)-O(6)	1.910(2)	2.061(1)
<M(2)-O>	2.030	2.080
T(1)-O(1) ×2	1.538(2)	1.540(1)
T(1)-O(2) ×2	1.535(2)	1.532(1)
<T(1)-O>	1.537	1.536
T(2)-O(3)	1.544(2)	1.549(1)
T(2)-O(4)	1.523(2)	1.538(1)
T(2)-O(5)	1.555(2)	1.539(1)
T(2)-O(6)	1.521(2)	1.533(1)
<T(2)-O>	1.536	1.540

(2010) showed experimentally that Mg has a preference for the *M*(2) site, so Hatert (2019) considered maghagendorfite to be questionable. Inspection of the available refined crystal structures of this group suggests that Mg is not likely to occur at the *M*(2) site, so it seems that maghagendorfite should remain a valid species.

Substitution mechanisms

The Na content at the *A* sites in alluaudite, hagendorfite, and varulite follows the relation:



As hagendorfite and varulite have Fe^{2+} dominant at the *M*(2) site, $^{[4]}\text{Na} > 0.5$ apfu does not occur. The trend between Na and vacancy is generally close to 1:1; the few exceptions to this trend are a small number of samples of varulite with up to 3.29 wt.% CaO. Calcium does not seem to be a major component of the alluaudite-group minerals, and Mn^{2+} preferentially occurs at the octahedrally coordinated *M*(1) and *M*(2) sites in the structure. On a ternary plot of ($\text{Mn}^{2+} + \text{Ca}$) versus vacancy versus Na (apfu) (Fig. 1), the samples plot on the left side of the diagram, away from the ($\text{Mn}^{2+} + \text{Ca}$) vertex. Given this, a plot of Na versus vacancy is more appropriate to show the variations at the *A* sites (Fig. 2). Hatert (2019) allowed for future additions to the alluaudite group by considering the replacement of two Na^+ cations by Ca and vacancy, with the hypothetical root names hagendorfite-Ca [$\square\text{CaM}^{2+}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$], varulite-Ca [$\square\text{CaM}^{2+}(\text{Mn}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$], and ROOT2-Ca [$\square\text{CaM}^{2+}(\text{MgFe}^{3+})(\text{PO}_4)_3$].

Yazganite (Sarp & Černý 2005) is unique among the alluaudite-group phosphate minerals *sensu lato* in having essential H_2O . This H_2O resides in a channel in the structure; the O atom of the (H_2O) group is not

TABLE 10. REFINED SITE-SCATTERING VALUES* (RSS *epfu*), MEAN BOND-LENGTHS (Å), ASSIGNED SITE-POPULATIONS (*apfu*), AND CORRESPONDING CALCULATED SITE-SCATTERING VALUES (CSS *epfu*) AND MEAN BOND-LENGTHS (Å) FOR ALLUAUDITE A-1 AND HAGENDORFITE H-1

	RSS	<M,A-O>	Site populations	CSS	<M,A-O> _{calc}
A-1					
A(1)	14.6(3)	2.445	0.14 Ca + 0.44 Na + 0.27 Mn^{2+} + 0.15 $\square$	14.4	2.466
A(2)'	2.9(1)	2.728	0.26 Na + 0.74 $\square$	2.9	2.599
M(1)	24.7(1)	2.213	0.99 Mn^{2+} + 0.01 Zn	24.7	2.199
M(2)	47.6(2)	2.030	1.63 Fe^{3+} + 0.24 Al + 0.13 Mg	47.3	2.006
H-1					
A(1)	16.2(8)	2.470	0.62 Na + 0.24 Ca + 0.14 Mn^{2+}	16.2	2.52
A(2)'	10.74(6)	2.671	0.98 Na + 0.02 $\square$	10.7	2.60
M(1)	25.65(5)	2.207	0.71 Mn^{2+} + 0.29 Fe^{2+}	25.3	2.23
M(2)	48.6(1)	2.080	1.30 Fe^{3+} + 0.42 Fe^{2+} + 0.28 Mg	48.1	2.08

TABLE 11. OBSERVED AND CALCULATED MEAN BOND-LENGTHS FOR ALLUAUDITE A-1 AND HAGENDORFITE H-1

	Alluaudite A-1			Hagendorfite H-1		
	Observed (Å)	Calculated (Å)	Difference (Å)	Observed (Å)	Calculated (Å)	Difference (Å)
M(1)	2.213	2.199	0.014	2.207	2.184	0.023
M(2)	2.030	2.006	0.024	2.080	2.080	0
A(2)'	2.455	2.466	-0.021	2.470	2.493	-0.023
A(1)	2.728	2.599	0.129	2.671	2.547	0.124

bonded to any cation in the structure (apart from H), and the (H₂O) group is held in the structure by hydrogen bonds alone. Hydroxyl-bearing and (H₂O)-bearing minerals are more common in the alluaudite-group arsenate minerals: keyite, erikapohlite, o'danielite, canutite, magnesiocanutite, and camanchacaite. In keyite and erikapohlite, the substitution mechanism is as follows: in protonated arsenates, channel 1 is occupied by H atoms of the [AsO₃(OH)] and [AsO₂(OH)₂] groups, explaining the presence of vacancies at the A(1) sites of o'danielite, canutite, magnesiocanutite, and camanchacaite. Other arsenate or phosphate compositions will give rise to distinct species if (H₂O) is dominant over vacancy at the channel site.

Lithium

Lithium is a common constituent of rare-element pegmatites and a significant component of some

primary phosphates such as triphylite-lithiophilite, Li(Fe,Mn)PO₄. Several synthesis studies have been done on alluaudite compounds, where it has been shown that the alluaudite structure can accommodate Li (Hatert *et al.* 2000, 2003). We analyzed several samples of alluaudite, hagendorfite, and varulite by LA-ICP-MS but found Li only in trace amounts. Thus, although synthetic equivalents of alluaudite can show Li replacing Na at the A(2)' site, alluaudite-group minerals (to date) only incorporate trace amounts of Li.

SUMMARY

The alluaudite supergroup is composed of four groups: the alluaudite-, wyllieite-, bobfergusonite-, and manitobaite-groups. The minerals of these groups are topologically identical but are distinguished by different cation-ordering schemes over the octahedrally coordinated cation sites in the structure and the

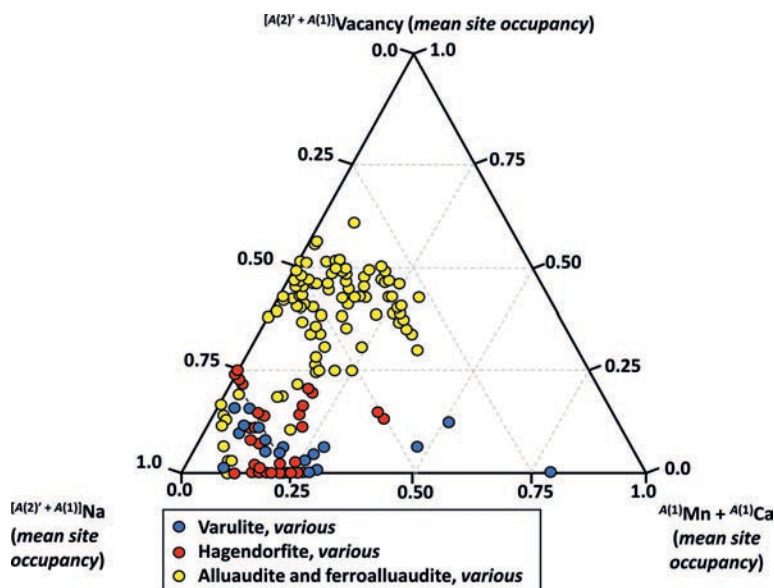


Fig. 1. Normalized ternary plot of (Mn + Ca) versus vacancy versus Na (apfu) for alluaudite, hagendorfite, and varulite.

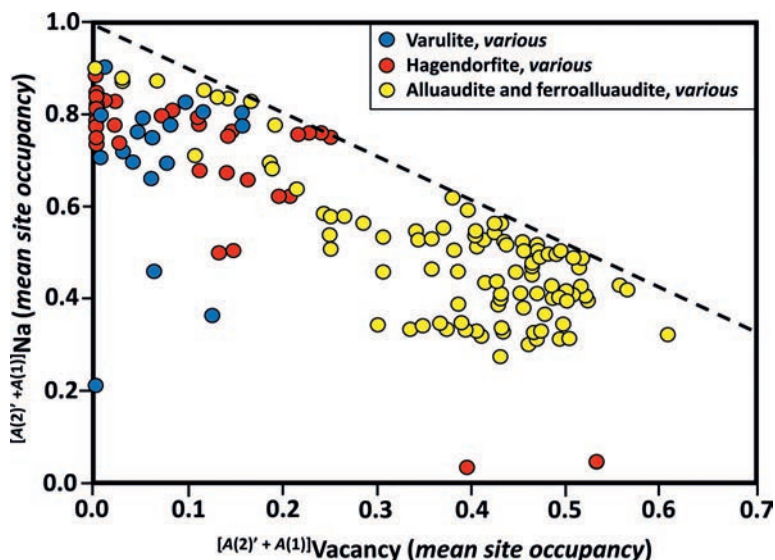


FIG. 2. Vacancy versus Na (apfu) in alluaudite, hagendorfite, and varulite.

resulting differences in the sizes and space-group symmetries of the unit cells. The minerals of the alluaudite group are ubiquitous in granitic pegmatites, but have also been found in scoria, phosphatic nodules, granites, and volcanic fumaroles. The alluaudite group currently consists of six IMA-approved phosphates (alluaudite, ferroalluaudite, hagendorfite, maghendorfite, varulite, and groatite) and 19 IMA-approved arsenates (arseniopleite, badalovite, bradaczekite, calciojohillerite, canutite, camanchacaite, caryinite, erikapohlite, johillerite, hatertite, keyite, krenovite, magnesiocanutite, magnesiohatertite, nickenichite, o'danielite, paraberzeliite, yazganite, and zincobradaczekite). Due to the extremely flexible nature of the open-framework architecture in the alluaudite structure, many synthetic analogues have been made with unique physical properties.

Alluaudite and ferroalluaudite have Fe^{3+} as the main constituent at the $M(2)$ site but differ at the $M(1)$ site: alluaudite is Mn^{2+} dominant, ferroalluaudite is Fe^{2+} dominant, and significant Al is uncommon in both. The Na content at the A sites in alluaudite, hagendorfite, and varulite follows the relation $\text{Na} + \text{Fe}^{2+} \rightarrow \square + \text{Fe}^{3+}$. The trend between Na and vacancy is generally close to 1:1; the few exceptions to this trend are a small number of samples of varulite, with up to 3.29 wt.% CaO in the structure. Yazganite (Sarp & Černý 2005) is unique among the alluaudite-group phosphate minerals *sensu lato* in having essential H_2O . Hydroxyl-bearing and (H_2O) -bearing minerals are more common in the alluaudite-group arsenate minerals:

keyite, erikapohlite, o'danielite, canutite, magnesiocanutite, and camanchacaite.

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