

# Alluaudites, wyllieites, arrojadites: crystal chemistry and nomenclature

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## SYNOPSIS

A NOMENCLATURE is proposed for the alluaudite and wyllieite complex series which is based on sequentially distributing the cations in the cell according to increasing polyhedral size, matching that size with increasing ionic radii of the cations. For oxidized members, the largest site may be partly occupied to empty after all the cations have been distributed. This is supported by structural study.

For alluaudites, the cell formula is  $X(2)_4X(1)_4M(1)_4M(2)_8(PO_4)_{12}$  and is written according to decreasing size of the discrete sites. The X(1) and X(2) sites are appended as suffixes in the trivial nomenclature, that is *specific name*—X(1)X(2).

For wyllieites, the cell formula is  $X(2)_4X(1a)_2X(1b)_2M(1)_4M(2a)_4Al_4(PO_4)_{12}$ . The X(1a), X(1b), and X(2) sites are appended as suffixes in the trivial nomenclature, that is *specific name*—X(1a)X(1b)X(2).

The nomenclature proposed is:

Generic name		M(2)	M(1)
<i>alluaudites</i>	<i>wyllieites</i>		
hagendorfites	wyllieites	Fe <sup>2+</sup>	Fe <sup>2+</sup>
varulite	unnamed	Fe <sup>2+</sup>	Mn <sup>2+</sup>
alluaudites	rosemaryites	Mn <sup>2+</sup>	Mn <sup>2+</sup>
		Fe <sup>3+</sup>	Fe <sup>2+</sup>
		Fe <sup>3+</sup>	Mn <sup>2+</sup>

Specific name	
<i>alluaudites</i>	<i>wyllieites</i>
ferrohagendorfite	ferrowyllieite (1)
hagendorfite (4)	wyllieite (1)
varulite (1)	unnamed
ferroalluaudite (2)	unnamed
alluaudite (9)	rosemaryite (1)

Seventeen analyses are discussed (of which five are new) for alluaudite and four analyses (of which three are new) for wyllieites. Their distribution is given parenthetically above. One analysis revealed predominant Mg<sup>2+</sup> in M(2). It is named maghagendorfite.

Six new analyses are presented for the arrojadite family of minerals including re-examination of dickinsonite from Branchville, Connecticut. Al<sup>3+</sup> is always present. We propose  $X^{1+}Y_3^{1+}M_{14}^{2+}Al(OH,F)(PO_4)_{12}$ , Z = 4, where X = large cations (K<sup>+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, etc.), Y = Na<sup>1+</sup>, Ca<sup>2+</sup>, and M = Fe<sup>2+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>. A range of cations X, Y, M, and Al between 76.8 and 85.9 in the cell (84 for proposed formula) suggests the likelihood of some vacancies in the structure.

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The anhydrous phosphate minerals encountered in complex granitic pegmatites constitute an extremely complex and diverse group of species whose detailed crystal chemistry have been only recently understood as the result of crystal structure analysis on key phases. Next to the accessory anhydrous silicate phases such as beryl, petalite, spodumene and the garnets, the phosphates are the most widely dispersed, and scarcely a pegmatite of the complex type is wanting in at least one of the phases. Although our knowledge of their structures is fairly complete (excepting the arrojadites), but little is known of their stability fields and most information of this type has been inferred from field study. Syntheses of the structure types from oxide components have been achieved only for the triphylite,  $\text{Li}(\text{Fe,Mn})(\text{PO}_4)_2$ . This is hardly surprising since the other phases involve four or more components and the compositions of the natural phases involve the system  $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{MgO}-\text{CaO}-\text{FeO}-\text{MnO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ . Minor but persistent components include  $\text{ZnO}$ ,  $\text{BaO}$ ,  $\text{SrO}$ ,  $\text{PbO}$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$  as well.

The present study spanned one decade of field and laboratory investigation. The entire project was fraught with obstacles, the most worthy of mention including incorrectly identified phases, incorrectly labelled sources, and persistent difficulty in field identification of the species owing to uncanny similarities in gross physical appearance.

In this study, the mode of attack involves three important units: the chemical analyses, correct referral to a structure type, and nomenclature. Easily the most important are the analyses. Owing to mixed valence states, thorough wet chemical analyses were absolutely necessary, supplemented by electron microprobe analysis. Care was taken in separating out pure grains and more often than not this required extensive collection in the field since many primary phosphate phases have suffered extensive corrosion during the evolution of the pegmatite, especially in the final stages. Whenever a doubt arose, the correct structure type was established by single crystal photography. This problem arises because the discrete structure types embrace compositions quite similar to each other. Nomenclature, of course, is usually the weakest unit, and this present study is hardly without issue. We adopt a nomenclature based on two premises: structure type and selective partitioning of the cations over their non-equivalent sites according to increasing ionic radii. Short of detailed three-dimensional structure analysis on each crystal for which a chemical analysis exists, a compromise must be made and this compromise assumes that selective partitioning depends on relative polyhedral size, established earlier in two structure analyses, on an alluaudite and a wyllieite.

**Alluaudites.** Crystal chemistry of the alluaudites is complicated by the fact that several non-equivalent cation positions occur in the unit cell and that the compositions cannot be assigned to discrete specific names solely on the basis of transition metal ratios as, for example, in the triphylite-lithiophilite series. It was once asserted that the alluaudite family followed a series analogous to the triphylite-lithiophilite series and the heterosite-purpurite series and was adopted by Palache, Berman and Fendler (1951) for the basis of a parallel nomenclature. The difference was that the triphylite family embraced the series  $\text{Li}(\text{Fe,Mn})^{2+}(\text{PO}_4)_2-(\text{Fe,Mn})^{3+}(\text{PO}_4)_2$  and the alluaudite family  $\text{Na}(\text{Fe,Mn})^{2+}(\text{PO}_4)_2-(\text{Fe,Mn})^{3+}(\text{PO}_4)_2$ . Thus, the primary unoxidized material followed the series  $(\text{Ca,Na})(\text{Fe,Mn})^{2+}(\text{PO}_4)_2$  ("hühnerkobelite")- $(\text{Na,Ca})(\text{Mn,Fe})^{3+}(\text{PO}_4)_2$  ("varulite") and the alkali-

leached products  $(\text{Na,Fe}^{3+},\text{Mn}^{2+})(\text{PO}_4)_2$  ("alluaudite")- $(\text{Na,Mn}^{2+},\text{Fe}^{3+})(\text{PO}_4)_2$  ("manganalluaudite"). Presumably, these final products were  $(\text{Fe,Mn})^{3+}(\text{PO}_4)_2$  (heterosite) and  $(\text{Mn,Fe})^{3+}(\text{PO}_4)_2$  (purpurite) for both series.

Several features are undesirable about this proposed double series. First, Fisher (1955) established that the two series are not isotypic and therefore differ in a fundamental way in their crystal chemistry. Moore (1971), on structural grounds, asserted that no continuous path led to the heterosite-purpurite series from parent alluaudites. Second, both Na and Ca occur in variable amounts in the alluaudites. Strunz (1954), for example, proposed "hagendorfite" for the composition  $(\text{Na,Ca})(\text{Fe,Mn})^{2+}(\text{PO}_4)_2$ . No such analogy can be found for the triphylite family. Third, the mixed valence states over two independent octahedral sites and two large cation sites necessitated an interpretation differing from that of the triphylite family. Fisher (1957 and 1965), in detailed investigations on the subject, argued that the cell contents be expressed  $\text{W}_6\text{-}_{12}(\text{X}^{+1})_{12}(\text{PO}_4)_{12}$ , where  $\text{W} = \text{Na}$  and  $\text{Ca}$ ;  $\text{X} = \text{Mn}^{2+}, \text{Fe}^{2+}$ ; and  $\text{Y} = \text{Fe}^{3+}$ . With the unit cell data at hand, it was possible to inquire further about the partitioning of cations in the structure. Fisher (1957) proposed that the series could be defined on the basis of three end-members: "mangan-alluaudite," "ferro-alluaudite" and "ferri-alluaudite". Unfortunately, the detailed crystal structure was not known at that time.

Moore (1971) announced the crystal structure of alluaudite and specified the cell contents according to the general formula  $\text{X}(2)_4\text{X}(1)_4\text{M}(1)_4\text{M}(2)_4(\text{PO}_4)_{12}$ , the discrete cation sites written according to decreasing size. For a composition  $\text{Na}_2.5\text{Li}_0.5\text{Ca}_0.5\text{Mn}^{2+}_4\text{Mg}_0.5\text{Fe}^{3+}_4(\text{PO}_4)_{12}$  of a crystal from the Buranga pegmatite, the proposed site distributions based on refined site occupancies were established as  $\text{X}(1)_4 = 2.5 \text{ Na} + 0.7 \text{ Mn}^{2+} + 0.5 \text{ Ca} + 0.3 \text{ Li}$ ;  $\text{X}(2)_4 = 4.0 \text{ Mn}^{2+} + 0.1 \text{ Mg} + 0.1 \text{ Li}$ ; and  $\text{M}(2)_4 = 7.9 \text{ Fe}^{3+} + 0.1 \text{ Mg}$ . The polyhedral interatomic distance averages were  $\text{M}(2)-\text{O} 2.04$ ,  $\text{M}(1)-\text{O} 2.21$ ,  $\text{X}(1)-\text{O} 2.54\text{\AA}$ . Owing to the oxidized aspect of the crystal, it was not possible to locate any atoms on the  $\text{X}(2)$  sites and the assignment of large cations in other alluaudites was tentative. There the matter stood until Moore and Molin-Case (1974) investigated the ordered structure of wyllieite. For this crystal, the space group is reduced to  $\text{P}2_1/\text{n}$  which is one of the "same cell" maximal subgroups of  $\text{C}2/\text{c}$  and results from ordering over equivalent positions in the alluaudite structure type. Symmetry and the general formula require split  $\text{X}(1)$  and  $\text{M}(2)$  positions and

TABLE I. Alluaudite family. Proposed nomenclature<sup>†</sup>

M(2)	M(1)	X(1)	X(2)	M(2)	M(1)	X(1)	X(2)
FERROHAGENDORFITES				VARULITES			
Fe <sup>2+</sup>	Fe <sup>2+</sup>	Na	Na	(3) Mn <sup>2+</sup>	Mn <sup>2+</sup>	Na	Na
* Fe <sup>3+</sup>	Fe <sup>2+</sup>	Na	Ca	* Mn <sup>2+</sup>	Mn <sup>2+</sup>	Na	Ca
✓ Fe <sup>3+</sup>	Fe <sup>2+</sup>	Ca	Na	✓ Mn <sup>2+</sup>	Mn <sup>2+</sup>	Ca	Na
** Fe <sup>3+</sup>	Fe <sup>2+</sup>	Ca	Ca	*** Mn <sup>2+</sup>	Mn <sup>2+</sup>	Ca	Ca
Fe <sup>3+</sup>	Fe <sup>2+</sup>	Na	□	Mn <sup>2+</sup>	Mn <sup>2+</sup>	Na	□
Fe <sup>3+</sup>	Fe <sup>2+</sup>	Ca	□	Mn <sup>2+</sup>	Mn <sup>2+</sup>	Ca	□
HAGENDORFITES				FERROALLUAUDITES			
(1,2,4,12) Fe <sup>2+</sup>	Mn <sup>2+</sup>	Na	Na	(5) Fe <sup>3+</sup>	Fe <sup>2+</sup>	Na	Na
* Fe <sup>3+</sup>	Mn <sup>2+</sup>	Na	Ca	* Fe <sup>3+</sup>	Fe <sup>2+</sup>	Na	Ca
✓ Fe <sup>3+</sup>	Mn <sup>2+</sup>	Ca	Na	✓ Fe <sup>3+</sup>	Fe <sup>2+</sup>	Ca	Na
** Fe <sup>3+</sup>	Mn <sup>2+</sup>	Ca	Ca	*** Fe <sup>3+</sup>	Fe <sup>2+</sup>	Ca	Ca
Fe <sup>3+</sup>	Mn <sup>2+</sup>	Na	□	✓(16) Fe <sup>3+</sup>	Fe <sup>2+</sup>	Na	□
Fe <sup>3+</sup>	Mn <sup>2+</sup>	Ca	□	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Ca	□
UNNAMED (UNSTABLE?)				ALLUAUDITES			
** Mn <sup>2+</sup>	Fe <sup>2+</sup>	Na	Na	(7,15) Fe <sup>3+</sup>	Mn <sup>2+</sup>	Na	Na
* Mn <sup>2+</sup>	Fe <sup>2+</sup>	Na	Ca	* Fe <sup>3+</sup>	Mn <sup>2+</sup>	Na	Ca
** Mn <sup>2+</sup>	Fe <sup>2+</sup>	Ca	Na	✓ Fe <sup>3+</sup>	Mn <sup>2+</sup>	Ca	Na
*** Mn <sup>2+</sup>	Fe <sup>2+</sup>	Ca	Ca	*** Fe <sup>3+</sup>	Mn <sup>2+</sup>	Ca	Ca
** Mn <sup>2+</sup>	Fe <sup>2+</sup>	Na	□	✓(6,8,10,11,13,17) Fe <sup>3+</sup>	Mn <sup>2+</sup>	Na	□
** Mn <sup>2+</sup>	Fe <sup>2+</sup>	Ca	□	(9) Fe <sup>3+</sup>	Mn <sup>2+</sup>	Ca	□

<sup>†</sup>Numbers in parentheses refer to end-member compositions suggested by Table 2. \*Bond distances unstable, since  $\text{X}(2) < \text{X}(1)$ . \*\*Bond distances unstable, since Ca is in  $\text{X}(2)$ . \*\*\*Possible pure end-member compositions.

the approximate site occupancies were established as X(1a) = 1.82 Na + 0.18Ca; X(1b) = 1.0 Ca + 1.0 Mn<sup>2+</sup>; X(2) = 2.78 Na + 1.22Mg; M(1) = 3.0 Fe<sup>2+</sup> + 1.0 Mg; M(2a) = 4.0 Fe<sup>2+</sup>; and M(2b) = 3.0 Al + 1.0 Fe<sup>3+</sup>. Since all sites were at least partly occupied, it was possible by analogy to write an unambiguous formula for the alluaudites as well as the wyllieites. More detailed discussion on the polyhedra in wyllieite is found under that heading.

In alluaudites, the X(1) polyhedron is a distorted cube, X(2) a distorted square antiprism, M(1) a curiously distorted octahedron (described as a square pyramid with a bifurcated apex) and M(2) a slightly distorted regular octahedron. The two structure studies established the following order in ionic size: M(2) < M(1) < X(1) < X(2). For cations recorded in alluaudite analyses, the order of increasing radius is Al<sup>3+</sup> < Fe<sup>3+</sup> < Mg<sup>2+</sup> < Li<sup>+</sup> < Fe<sup>2+</sup> < Mn<sup>2+</sup> < Ca<sup>2+</sup> < Na<sup>+</sup> < K<sup>+</sup>. Moore (1971) and Moore and Molin-Case (1974) then proposed to systematically partition the cell contents of alluaudites by progressively filling the non-equivalent sites starting with the smallest sites and cations first. The structure studies established the following possible substitutions: M(2) = Al,Fe<sup>3+</sup>,Mg,Li,Fe<sup>2+</sup>,Mn<sup>2+</sup>; M(1) = Mg,Li,Fe<sup>2+</sup>,Mn<sup>2+</sup>,Ca; X(1) = Mn<sup>2+</sup>,Ca,Na,K,Ca; and X(2) = Na,K,Ca. Preferential leaching of alkalis proceeds from the X(2) position until it is emptied and then to X(1). There is no evidence that emptying of sites proceeds beyond X(2) and X(1).

The following cations are proposed as the major constituents in alluaudites: M(2) = Fe<sup>3+</sup>,Fe<sup>2+</sup>,Mn<sup>2+</sup>; M(1) = Fe<sup>2+</sup>,Mn<sup>2+</sup>; X(2) = Ca,Na; and X(1) = Ca,Na,Ca. There are 6x2 + 6x2 + 6x2 = 36 possible ordered compositions and these are listed in Table I. Of these, some are predicted unstable, such as the coexisting pairs X(1) = Na and X(2) = Ca; M(1) = Fe<sup>2+</sup> and M(2) = Mn<sup>2+</sup>; since these schemes contradict the relative site sizes found in the structure studies. Eliminating these, 25 compositions remain. X(2) = Ca is probably also unstable since the distance average  $\frac{1}{6}\sum(X_2-O) = 2.84\text{\AA}$  in wyllieite is much too large for Ca<sup>2+</sup> in eight-fold coordination. Eliminating these compositions, 20 discrete compositions remain which are predicted stable as those representing the greatest fractional occupancy at each site. The eleven analyses in Moore (1971), cited from Fisher (1965); five new analyses on material from the Palermo mine, Dyke Lode, Townsite, Pleasant Valley, and Tsaboisumnd pegmatites; and the analysis of "ferrialluaudite" from Sidi-Bou-Othmane (Huvelin, Orlic and Permingeat, 1972) are arranged (based on O = 48) according to the procedure of site distribution assignments above in Table II. Table III lists the new chemical analyses based on weight percentages of the oxide components.

The site assignments lead to a pattern consistent with the facts at hand for the available analyses on alluaudites. Table II reveals that all analyses lead to either predominant Na<sup>+</sup> or Ca<sup>2+</sup> over X(2). For the X(1) position, sixteen samples contain predominant Na<sup>+</sup> with sample 9 containing

predominant Ca<sup>2+</sup>. This is the nominate "Hühnerkobelite" of Lindberg (1950). Furthermore, fifteen samples contain predominant Mn<sup>2+</sup> in the M(1) position. The exceptions, samples 5 and 16, are the "Hühnerkobelite" of Lindberg (1950) from Norrö and the Pleasant Valley material, both of which contain predominant Fe<sup>2+</sup>. Over the M(2) positions, four samples possess predominant Fe<sup>2+</sup> and eleven predominant Fe<sup>3+</sup>. Sample 3 from Lemmäs contains predominant Mn<sup>2+</sup> and is the mangan-alluaudite of Quesnel (1937) (= "Lemmäsite" of Pehrman, 1939). Sample 14 contains predominant Mg<sup>2+</sup> in the M(2) position but its amount is not much larger than Fe<sup>2+</sup> and Fe<sup>3+</sup>. Nevertheless we are forced to conclude that predominant Mg<sup>2+</sup> in the M(2) position is possible for the alluaudite structure type and to be consistent with our proposed nomenclature, a new trivial name for this material will be introduced further on. Of the twenty possible alluaudite predominant cation compositions in Table I, seven of them are represented in Table II.

Sample 12 from the Palermo mine is remarkable in possessing the least oxidized character with all sites occupied save 0.09O at X(2). Crystals of this material were examined in detail and single crystal study established beyond doubt the space group  $C2/c$ .

Table II also suggests that there is a limit to the degree of transition metal oxidation and alkali deficit which the alluaudite structure type can tolerate. No M<sup>3+</sup> cations appear to enter into the M(1) position and vacancies over the X(1) position also appear to be quite limited in extent. From these observations, is it possible to propose a classification of alluaudites which conserves both chronological priority and which follows the crystal-chemical arguments from the structure studies? Table IV clearly shows that this is impossible. The proposed nomenclature of Fisher (1957) can hardly apply since it is based on the sum of both M(1) and M(2), the results of which are quite different than obtained when M(1) and M(2) are selectively partitioned.

Analogous to the triphylite-lithiophilite series, Li(Fe,Mn)<sup>2+</sup>(PO<sub>4</sub>) and the alkali-leached oxidized products heterosite-purpurite, (Fe,Mn)<sup>2+</sup>(PO<sub>4</sub>), it is desirable to propose at most four trivial names embracing each of the end-members Fe<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>3+</sup> in the M(2) position. However, not one but two independent positions must be specified. If specific status includes the X(1) and X(2) positions as well, then there exists the possibility of twenty trivial names (Table I). To minimize the profusion of trivial names, a generic name based on M(2) is proposed. A specific name applies to the predominant cation in M(1) and is given as a prefix to the generic name. Further splitting into subspecific terms is facilitated by suffixes, that is ferrohagendorfite--X(1)X(2) for the composition X(2)X(1)Fe<sub>2</sub><sup>2+</sup>Fe<sup>3+</sup>(PO<sub>4</sub>), and so on.

The following nomenclature is proposed:

TABLE II. Alluaudite family. Partitioning of the cations.\*

Sample	M(2)					M(1)				X(1)					X(2)			Echarge-36
	Fe <sup>3+</sup>	Mg	Li	Fe <sup>2+</sup>	Mn <sup>2+</sup>	Mg	Fe <sup>2+</sup>	Mn <sup>2+</sup>	Ca	Mn <sup>2+</sup>	Ca	Na	K	□	Na	K	□	
2	1.86	0.05	1.18	2.80	2.11	----	----	4.00	----	0.98	0.90	2.22	----	----	3.28	----	0.68	-2.15
1	1.63	0.04	----	3.37	2.96	----	----	3.03	0.97	----	0.32	3.68	----	----	2.65	0.03	1.35	-3.37
4	3.33	0.33	----	4.30	0.04	----	----	4.00	----	1.18	0.60	2.22	----	----	3.25	0.07	0.68	+0.43
12	0.77	1.59	----	5.64	----	----	0.62	3.58	----	1.09	0.79	2.12	----	----	3.21	----	0.09	-3.02
3	3.27	0.27	0.03	0.55	3.88	----	----	4.00	----	0.16	1.67	2.17	----	----	3.78	0.18	0.06	+1.01
14	2.31	2.39†	0.07	2.27	0.96	----	----	4.00	----	0.41	0.29	3.30	----	----	0.39	----	3.67	-4.67
5	3.63	1.27	0.34	2.76	----	----	2.32	1.69	----	1.08	0.48	2.44	----	----	3.88	0.03	0.15	+0.70
6	4.16	----	0.38	0.56	2.90	----	----	4.00	----	0.58	0.78	2.74	----	----	1.79	0.05	2.16	-0.92
15	4.57	0.19	----	1.88	1.36	----	----	4.00	----	0.01	0.39	3.60	----	----	2.25	----	1.75	-0.78
7	6.74	0.05	0.09	0.89	1.83	----	----	3.98	0.02	----	0.94	3.06	----	----	2.22	----	1.78	+0.21
17	6.84	0.90	----	1.56	----	----	0.94	3.06	----	0.39	0.76	2.85	----	----	0.99	----	3.02	-0.32
13	6.31	0.01	----	1.22	0.36	----	----	3.35	0.65	----	1.93	2.07	----	----	0.37	----	3.63	+0.41
8	6.51	----	----	1.49	----	----	----	4.00	----	1.39	0.58	2.03	----	----	0.51	----	3.49	+0.99
16	6.78	0.94	0.05	0.25	----	----	2.78	1.82	----	0.14	0.54	3.22	----	----	0.95	----	2.05	-0.05
9	6.81	0.35	0.49	0.35	----	----	1.68	1.86	0.46	----	3.09	0.91	----	----	2.42	0.02	1.56	+3.85
10	7.87	0.19	----	0.24	----	----	0.20	3.58	0.24	----	1.17	2.78	0.01	0.04	----	----	4.00	+0.70
11	7.88	0.14	----	----	----	----	0.21†	3.79	----	0.75	0.50	2.53	0.01	0.24	----	----	4.00	+0.87

\*Cations listed according to increasing ionic radius. The predominant cation at each site is italicized. †Includes 0.05 Zn added to Mg. ‡Contains 0.12 Li added to Mg.

Generic Name	M(2)	M(1)	Specific Name
hagendorffites	Fe <sup>2+</sup>	Fe <sup>2+</sup>	ferrohagendorffite
	Fe <sup>2+</sup>	Mn <sup>2+</sup>	hagendorffite
varulite	Mn <sup>2+</sup>	Mn <sup>2+</sup>	varulite
alluaudites	Fe <sup>3+</sup>	Fe <sup>2+</sup>	ferroalluaudite
	Fe <sup>3+</sup>	Mn <sup>2+</sup>	alluaudite

Although Moore (1971) tabulated existing compositions for alluaudites, he did not propose a trivial nomenclature. Fisher (1957 and 1965) divided alluaudites into a triangular set based on  $(X+Y)_{12}$ ; these are the "ferro-alluaudites" (Fe<sup>2+</sup>), the "manganoalluaudites" (Mn<sup>2+</sup>), and the "ferri-alluaudites" (Fe<sup>3+</sup>). Other names in the literature include "hagendorffite," "hühnerkobelite," "varulite," "alluaudite" and "mangan-alluaudite". On the basis of the nomenclature proposed herein, there are five contradictions.

TABLE III. Chemical analyses of alluaudites and wyllieites\*

	ALLUAUDITE FAMILY					WYLLIEITE FAMILY			
	12	14	15	16	17	1	2	3	4
Al <sub>2</sub> O <sub>3</sub>	nil	0.01	0.01	0.01	0.07	7.9	7.1	6.48	6.90
Fe <sub>2</sub> O <sub>3</sub>	1.1	9.89	18.53	28.15	22.31	0.33	4.8	10.62	14.58
FeO	24.3	8.75	6.86	9.12	9.11	29.2	20.2	14.73	11.64
MnO	15.8	20.42	19.32	7.25	12.42	4.3	9.6	11.22	13.62
MgO	3.2	5.06	0.39	1.98	1.84	1.97	4.8	1.71	0.47
ZnO	nil	0.23	0.03	0.06	0.05	0.04	0.08	0.41	0.02
CaO	2.2	0.86	1.11	1.59	2.17	2.5	0.95	3.12	1.81
Li <sub>2</sub> O	----	0.06	0.00	0.04	0.01	0.01	0.01	0.004	0.04
Na <sub>2</sub> O	9.3	6.12	9.20	6.90	6.03	8.0	7.1	3.93	3.40
K <sub>2</sub> O	nil	0.00	0.03	0.00	0.05	0.05	nil	0.05	0.00
P <sub>2</sub> O <sub>5</sub>	43.4	44.32	(43.3)	(43.1)	43.18	43.8	44.6	45.41	43.84
SiO <sub>2</sub>	nil	----	----	----	----	0.8	0.1	----	----
H <sub>2</sub> O	----	3.06	0.30	0.64	0.62	0.70	0.60	0.92	1.73
Insol.	nil	1.05	0.93	1.19	1.54	nil	nil	1.22	1.78
	99.3	99.83	(100.0)	(100.0)	99.43	99.56	99.94	99.82	99.83

\*Samples 1 to 11 for alluaudites are discussed in Fisher (1965). Sample 13 is discussed by Huvelin *et al.* (1972).

<sup>12</sup>Palermo No. 1 mine, North Groton, New Hampshire. A. J. Irving, analyst. Fe<sub>2</sub>O<sub>3</sub> determined by J. Ito.

<sup>14</sup>Dyke Lode, Custer, South Dakota. J. Ito, analyst.

<sup>15</sup>Townsite pegmatite, Pringle, South Dakota. P<sub>2</sub>O<sub>5</sub> determined by difference. J. Ito, analyst.

<sup>16</sup>Pleasant Valley pegmatite, Custer, South Dakota. P<sub>2</sub>O<sub>5</sub> determined by difference. J. Ito, analyst.

<sup>17</sup>Tsaobismund, S. W. Africa. J. Ito, analyst. Includes 0.03% CuO.

Wyllieite (type). Victory mine, Custer, South Dakota. Moore and Ito (1973). Trace elements include Sr, Ba, Pb, Be.

<sup>2</sup>Smith mine, Newport, New Hampshire. J. Ito, analyst. H<sub>2</sub>O (700°C) = 0.40, H<sub>2</sub>O (1100°C) = 0.2. Trace elements include Cu, Co, Ni, Ti, Ag, Pb, Sc.

<sup>3</sup>Old Mike mine, Custer, South Dakota. J. Ito, analyst. Insol. = muscovite. Trace elements include Pb, Ba, Sr, Sn, Ti, Sc.

<sup>8</sup>Rock Ridge pegmatite, Custer, South Dakota. J. Ito, analyst.

"Hühnerkobelite" was named by Lindberg (1950) to apply to partly oxidized material with formula  $(Ca,Na)(Fe,Mn)_2^{2+}(PO_4)_2$ . It is clear, however, that both hühnerkobelites, from Hühnerkobel (sample 9) and Norrö (5) are in fact alluaudites. According to the proposed nomenclature, they are alluaudite and ferroalluaudite respectively. "Varulite" (Quensel, 1937) has been retained for the  $(Na,Ca)(Mn,Fe)_2^{2+}(PO_4)_2$  portion of the series (Palache *et al.*, 1951) but the partitioning of cations into M(1) and M(2) positions shows that in fact the Skruppetorp (1) and Varuträsk (2) materials are Fe<sup>2+</sup>-predominant in the M(2) position. These are hagendorffite according to the proposed nomenclature. The Lemnäs (3) material, referred to as "mangan-alluaudite" is, according to the proposed nomenclature, varulite. The hagendorffite of Strunz (1954), Hagendorf (4), has predominant Fe<sup>2+</sup> in M(2) and Mn<sup>2+</sup> in M(1) and, on the basis of chronological priority, is retained. Distinction between Fe<sup>2+</sup> and Mn<sup>2+</sup> in M(1) is desirable, however; the Fe<sup>2+</sup>-predominant material is accordingly defined as ferrohagendorffite.

From the partitioning of cations on the basis of ionic radii and non-equivalent positions in the structure, sample 14 must contain predominant Mg<sup>2+</sup> in the M(2) position. Although Mg<sup>2+</sup> occupies only 30 mole % of the site, consistency nevertheless dictates that a Mg<sup>2+</sup> end-member be named. The end-member composition of sample 14 would be M(2) = Mg, M(1) = Mn, X(1) = Na and X(2) = □. We propose the generic term maghagendorffite since  $(Mg,Fe)_2^{2+}$  solution is expected to be extensive, if not complete, over the M(2) position in such a series.\* The specific name, including the suffix qualifiers, is maghagendorffite-NaCa. Twelve additional end-member compositions are possible but four of these are predicted to be unstable.

Thus, six trivial names are proposed for the known compositions of the alluaudite group of minerals. Varulite does not require a prefix since the distribution M(2) = Mn<sup>2+</sup> and M(1) = Fe<sup>2+</sup> is predicted unstable. The full terms are therefore hagendorffite-NaNa (samples 1, 2, 4, 12); varulite-NaNa (3); ferroalluaudite-NaNa (5); ferroalluaudite-NaCa (16); alluaudite-NaNa (7,15); alluaudite-NaCa (6, 8, 10, 11, 13, 17); alluaudite-CaCa (9); maghagendorffite-NaCa (14). Of the six proposed trivial names, one has not yet been characterized and this is ferrohagendorffite. It is noted that sample 5, however, is sufficiently close to this member that its existence is very likely. In addition, it is the unoxidized equivalent of both 5 and 16 and parallels the progressive oxidation and alkali-leaching found for the triphylite-heterosites.

\*This new generic term intentionally exploits "mag", distinct from "magnesium" (cf. "ferro") which would imply predominant Mg<sup>2+</sup> at the M(1) site.

TABLE IV. Alluaudites and wyllieites. Samples discussed.\*

Sample	Alluaudite Family	Wyllieite Family
1. Skruppetorp, Sweden (= "varulite")	Fisher (1965); Mason (1940)	
2. Varuträsk, Sweden (= "varulite")	do. ; Quensel (1940)	
3. Lemnäs, Finland (= "lemnäsite")	do. ; Pehrman (1939)	
4. Hagendorf, Bavaria (= "hagendorffite")	do. ; Strunz (1954)	
5. Norrö, Sweden (= "hühnerkobelite")	do. ; Eriksson (1946); Lindberg (1950)	
6. Varuträsk, Sweden (= "mangan-alluaudite")	do. ; Quensel (1940)	
7. Sukuis, Finland (= "alluaudite")	do. ; Mason (1940)	
8. Chanteloube, France (= "alluaudite")	do. ; Damour (1848)	
9. Hühnerkobel, Bavaria (= "hühnerkobelite")	do. ; Mason (1942); Lindberg (1950)	
10. Pringle, South Dakota (= "alluaudite")	do. ; Fisher (1965)	
11. Buranga, Rwanda (= "alluaudite")	do. ; Thoresau and Bastien (1954)	
12. North Groton, New Hampshire (= "hühnerkobelite")	This study; Moore (1965)	
13. Sidi-Bou-Othmane, Morocco (= "ferri-alluaudite")	Huvelin, Orliac and Permingeat (1972)	
14. Dyke Lode, Custer, South Dakota	This study	
15. Townsite pegmatite, Pringle, South Dakota	do.	
16. Pleasant Valley pegmatite, Custer, South Dakota	do.	
17. Tsaobismund, Southwest Africa	do.	
WYLLIEITE FAMILY		
1. Victory mine, Custer, South Dakota (= "wyllieite")	Moore and Ito (1973)	
2. Smith mine, near Newport, New Hampshire	This study	
3. Old Mike mine, Custer, South Dakota	do.	
4. Rock Ridge pegmatite, Custer, South Dakota	do.	

There is no doubt that the proper characterization of the alluaudite group requires special precautions. First, single crystal study is desirable to discriminate between the C2/c structures (alluaudites) and the P2<sub>1</sub>/n structures (wyllieites). Second, a complete wet chemical analysis is necessary to establish the end-member composition of Table I. Arranging the cations through progressive filling of the sites, from smallest size to largest, establishes the specific trivial name. The advantage of the proposed classification is that sufficient flexibility is available to mitigate yet new trivial names which do not in fact convey to the investigator any structural information about the alluaudite complex series. In the event that a sample has not been chemically characterized, it is advised to use the family name: alluaudite.

A condensed nomenclature can be immediately proposed but chronological priorities challenge it. This nomenclature adopts all non-equivalent sites as suffixes and all specific end-members would be referred to alluaudite-M(2)M(1)X(1)X(2).

Owing to mixed charges distributed over equivalent sites, some pure end-member compositions are impossible and exist only for nomenclatural reasons. The possible pure compositions are X(2)<sup>1+</sup>X(1)<sup>2+</sup>M(1)<sup>2+</sup>M(2)<sup>2+</sup>(PO<sub>4</sub>)<sub>3</sub> and X(1)<sup>1+</sup>M(1)<sup>2+</sup>M(2)<sup>2+</sup>(PO<sub>4</sub>)<sub>3</sub>. In Table I, five possible compositions fulfill this criterion with samples 10 and 11 coming as close as any. We note that the relatively unoxidized samples, the hagendorfites and varulites, extensively exploit mixed valences over equivalent sites, further emphasizing the versatility of the alluaudite structure type.

**Conclusions.** The alluaudite complex series has, in the limit, the range X(2)<sup>1+</sup>X(1)<sup>2+</sup>M(1)<sup>2+</sup>M(2)<sup>2+</sup>(PO<sub>4</sub>)<sub>3</sub>-X(1)<sup>1+</sup>M(1)<sup>2+</sup>M(2)<sup>2+</sup>(PO<sub>4</sub>)<sub>3</sub>. In this respect, the series resembles the triphylite-heterosite series, LiM<sup>2+</sup>(PO<sub>4</sub>)-M<sup>2+</sup>(PO<sub>4</sub>). It does not proceed, however, to completely oxidized end-members owing to the M(1) position which for fifteen analyses is predominantly Mn<sup>2+</sup> and the remaining two Fe<sup>2+</sup>. The peculiar nature of the polyhedron, described as a square pyramid with bifurcated apex, probably inhibits stable compositions with higher oxidation states.

Owing to two kinds of six-coordinated sites, two kinds of cations, and two valence states, the nomenclature requires not four but eight specific terms. As yet no Mn<sup>3+</sup> members have been found and one, with M(2) = Mn<sup>2+</sup> and M(1) = Fe<sup>2+</sup>, is predicted to be unstable. Thus, five specific terms are required.

The alluaudite complex series is further complicated by the fact that two non-equivalent large cation sites are available and these can accommodate both Ca<sup>2+</sup> and Na<sup>1+</sup>. Twenty possible stable end-member compositions are predicted on this basis. Owing to distinctly different shapes and sizes of the M(2), M(1), X(1) and X(2) polyhedra, it appears possible to refer any alluaudite sample to one of these twenty compositions based on progressive partitioning of the cations over these sites according to their relative ionic radii. For alluaudites with Na >> Ca, the progressive emptying of the X(2) position roughly follows the degree of oxidation of M(2)<sup>2+</sup> to M(2)<sup>3+</sup>.

**Wyllieites.** The wyllieite family embraces coarsely crystalline primary phases which possess ordered crystal structures allied to the disordered alluaudites. Four analyses are presented, one previously reported on material from the type locality at the Victory mine pegmatite, Custer, South Dakota (Moore and Ito, 1973) and three previously unreported results from the Smith mine pegmatite, Chandler's Mills, near Newport, New Hampshire; the Old Mike pegmatite and the Rock Ridge pegmatite, both near Custer, South Dakota. Table IV summarizes the occurrences and specimen numbers.

As with the alluaudites, the crystal chemistry of the wyllieites must proceed from structural knowledge. In a detailed crystal structure analysis, Moore and Molin-Case (1974) have shown that wyllieite crystallizes in space group P2<sub>1</sub>/n which is a nearest "same cell" subgroup of C2/c, the space group for alluaudites. Single crystal precession photographs of a

wyllieite (Old Mike mine) and an alluaudite (Palermo mine) are shown in Figure I to illustrate this. The additional reflections, incompatible with C2/c, are not insubstantial and can be immediately recognized. Structure analysis revealed that X(1) in alluaudite splits into two independent positions, X(1a) and X(1b); and M(2) splits likewise into M(2a) and M(2b). The ideal cell formula is X(2)<sub>2</sub>X(1a)<sub>2</sub>X(1b)<sub>2</sub>M(1)<sub>2</sub>M(2a)<sub>2</sub>M(2b)<sub>2</sub>(PO<sub>4</sub>)<sub>12</sub>. The relative sizes of the ions at these sites is M(2b) < M(2a) < M(1) < X(1b) < X(1a) < X(2) and is exemplified by the average M-O and X-O distances: 1.97, 2.10, 2.23, 2.46(2.21), 2.53 and 2.84(2.72) Å respectively. The structure analysis also showed that all Al is concentrated on the M(2b) site. The X(1) polyhedra are distorted cubes, with X(1b) evincing site disorder or splitting leading to a collapsed inner coordination shell of six anions whose average distance is given in parentheses. In the type crystal examined, X(2) was shown to be substantially occupied (see under alluaudites for the refined site distributions). The remaining polyhedra are similar to those found in alluaudite. Thus, the structural evidence at hand appears to strongly favor the distribution of cations of increasing size in the same order as the increase in size of the polyhedra and it follows that the same kind of scheme will be adopted for arranging wyllieite site distributions as for those in alluaudites. The four chemical analyses are presented in Table III and the site distributions in Table V.

TABLE V. *Wyllieite family. Partitioning of the cations.*

	M(2b)			M(2a)				M(1)		
	Al	Fe <sup>3+</sup>	Mg	Fe <sup>3+</sup>	Mg	Li	Zn	Fe <sup>2+</sup>	Fe <sup>2+</sup>	Mn <sup>2+</sup>
3	2.37	1.63	----	0.85	0.79	----	0.09	2.27	1.46	2.54
4	2.53	1.47	----	1.94	0.22	0.05	----	1.79	1.23	2.77
2	2.60	1.12	0.28	----	1.94	0.13	0.02	1.91	3.84	0.66
1	3.01	0.08	0.91	----	0.04	0.13	0.01	3.22	4.00	----

	X(1b)			X(1a)			X(2)				
	Fe <sup>2+</sup>	Mn <sup>2+</sup>	Ca	Ca	Na	K	□	Na	K	□	
3	----	0.42	1.04	0.54	----	1.83	0.02	0.15	----	----	4.00
4	----	0.21	0.60	0.59	----	1.46	----	0.54	----	----	4.00
2	----	1.73	0.27	----	0.05	1.95	----	----	2.33	----	1.67
1	0.06	1.18	0.76	----	0.10	1.90	----	----	3.10	----	0.90

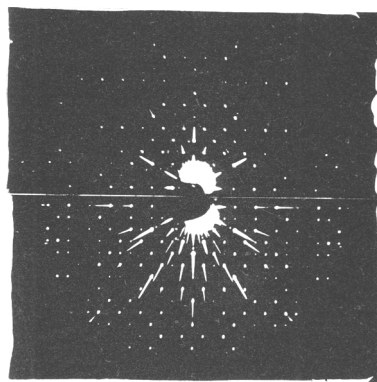


Fig. 1.--Precession photographs of the (hk0) levels for hagendorfite (Palermo No. 1 Mine, sample 12), upper photograph; and wyllieite (Old Mike Mine, sample 3), lower photograph. Extinction criteria: hagendorfite, hk0, h+k ≠ 2n; wyllieite, hk0, no extinctions. Minor contamination by small randomly oriented grains occur for the hagendorfite specimen. Mo/Zr, Kα radiation.

All four wyllieites were examined by X-ray precession photography and their (hko) projections reveal the additional reflections compatible only with a primitive cell. Table V suggests that Al is the predominant cation in M(2b). M(2a) and M(1) closely resemble the alluaudites with M(2a) capable of oxidation of Fe<sup>2+</sup> and M(1) with predominant Fe<sup>2+</sup> and Mn<sup>2+</sup>. The X(1b) site appears to be populated primarily by divalent cations of intermediate size (Mn<sup>2+</sup>, Ca) and X(1a) is predominantly occupied by Na<sup>+</sup>. The X(2) site, as in the alluaudite family, is only partly occupied by Na<sup>+</sup> and is vacant in more oxidized members.

The nomenclature for the wyllieites follows directly from the alluaudites: since M(2b) is predominantly Al<sup>3+</sup>, M(2a) establishes the generic term and M(1) the specific term. The qualifying suffixes include X(1b)X(1a)X(2) in that order. As with alluaudites, there are Fe<sup>2+</sup>-predominant members (samples 1 and 3), a Mg-predominant member (sample 2) and an Fe<sup>3+</sup>-predominant member (sample 4) with respect to the M(2a) position. The type wyllieite (sample 1) is analogous to ferrohagendorfite. We propose the name ferrowyllieite by analogy. Thus, sample 3, which is analogous to hagendorfite, is wyllieite. Sample 2 is analogous to maghagendorfite but with predominant Fe<sup>2+</sup> in M(1). Discussion at the end of this study forces us not to propose a new trivial name, however. Sample 4 is analogous to alluaudite; we propose the name rosemaryite for those wyllieites in which Fe<sup>3+</sup> is the end-member composition over the M(2a) position. The name is for Mrs. F. Rosemary Wyllie, the wife of Professor Peter J. Wyllie.

The following nomenclature is recommended:

Generic Name	M(2a)	M(1)	Specific Name
wyllieites	Fe <sup>2+</sup>	Fe <sup>2+</sup>	ferrowyllieite
	Fe <sup>2+</sup>	Mn <sup>2+</sup>	wyllieite
unnamed	Mn <sup>2+</sup>	Mn <sup>2+</sup>	unnamed
rosemaryites	Fe <sup>3+</sup>	Fe <sup>2+</sup>	unnamed
	Fe <sup>3+</sup>	Mn <sup>2+</sup>	rosemaryite

Thus, the known wyllieites include ferrowyllieite-Mn<sup>2+</sup>NaNa (sample 1 and 2), wyllieite-CaNa□ (sample 3), and rosemaryite-Mn<sup>2+</sup>Na□ (sample 4). Although the analogue of ferroalluaudite is not as yet known, we recommend ferrosemaryite by analogy with the alluaudites. The analogue of varulite is not yet known; when found, it will require a novel trivial name.

A condensed nomenclature can be proposed but priority and analogy with the alluaudites challenge it. This nomenclature adopts all non-equivalent sites as suffixes and all specific end-members would be referred to wyllieite-M(2a)M(1)X(1a)X(1b)X(2).

As with the alluaudites, mixed charges over equivalent sites limit the possible pure end-member compositions. The series can be written X(2)<sub>1/2</sub>X(1a)<sup>1+</sup>X(1b)<sup>2+</sup>M(1)<sub>1/2</sub>M(2a)<sub>1/2</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>-Ca□X(1b)<sup>2+</sup>M(1)<sub>1/2</sub>M(2a)<sub>1/2</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>. All known wyllieites appear to possess only fractional occupancies over the X(2) positions which, like alluaudites, allow considerable flexibility in admissible compositions.

*Arrojadite family.* Thirteen analyses are presented for the arrojadite family, six reported for the first time. Published analyses include material from the Nickel Plate mine, Keystone, South Dakota (Lindberg, 1950); Sidi-Bou-Othmane, Morocco (Huvelin, Orliac and Permingeat, 1972); and Buranga mine, Rwanda (von Knorring, 1969); the Victory mine, Custer, South Dakota (Moore and Ito, 1973); two early analyses on dickinsonite from Branchville, Connecticut (Brush and Dana, 1890); and one early analysis on dickinsonite from the Berry quarry, Poland, Maine (Berman and Gonyer, 1930). The supposed arrojadite from Serra Branca, Parafba district, Brazil (Guimarães, 1942) appears to be so highly altered as to constitute a probable mixture or possibly some other species. The new analyses include four wet chemical analyses (Sapucaia pegmatite, Minas Gerais, Brazil; Smith Mine, Newport, New Hampshire; Palermo No. 1 mine, North Groton, New Hampshire; Nancy Mine, North Groton, New Hampshire) and two electron probe analyses (Sapucaia

TABLE VI. *Arrojadite family. Chemical analyses.*

	1	2	3	4	5	5a	6	7	8	9	10	11	12
Al <sub>2</sub> O <sub>3</sub>	2.66	2.41	1.96	2.85	2.23	2.2	2.30	2.33	2.37	2.0	-----	-----	-----
Fe <sub>2</sub> O <sub>3</sub>	-----	nil	1.34	n.d.	1.7	-----	0.2	nil	nil	-----	-----	-----	-----
FeO	28.22	28.05	19.36	37.01	17.6	17.9	28.7	34.9	30.09	13.3	13.25	12.96	12.33
MnO	15.78	14.12	19.45	3.62	14.6	14.9	7.43	7.76	12.6	32.0	31.58	31.83	31.83
MgO	1.04	1.53	2.80	1.38	6.78	6.0	4.55	3.37	2.49	nil	-----	-----	1.67
ZnO	-----	0.25	-----	nil	0.20	nil	0.17	0.24	0.06	nil	-----	-----	-----
CaO	2.46	0.82	2.28	5.39	2.57	2.5	2.28	3.65	1.31	2.3	2.15	2.09	2.01
BaO	-----	4.32	5.36	nil	1.5	1.9	2.32	0.02	0.20	nil	-----	-----	-----
SrO	-----	0.31	-----	nil	0.34	0.3	0.13	0.05	0.65	nil	-----	-----	-----
PbO	-----	0.76	-----	nil	4.42	n.d.	0.88	0.37	nil	nil	-----	-----	-----
Li <sub>2</sub> O	0.09	0.33	0.20	n.d.	0.70	n.d.	0.25	0.52	0.08	(0.17)	0.17	0.22	0.20
Na <sub>2</sub> O	6.40	5.47	4.97	7.55	4.53	4.6	5.50	5.36	6.59	7.8	7.46	7.37	7.41
K <sub>2</sub> O	1.74	0.56	0.63	1.09	0.58	0.7	0.95	1.43	1.59	1.1	1.52	1.80	1.73
P <sub>2</sub> O <sub>5</sub>	40.00	39.07	39.34	42.26	40.6	41.2	42.3	40.1	40.8	39.5	39.57	40.89	40.78
SiO <sub>2</sub>	-----	-----	-----	nil	nil	nil	1.05	nil	nil	nil	-----	-----	-----
H <sub>2</sub> O <sup>+</sup>	0.91	0.81	1.45	n.d.	n.d.	n.d.	0.98	0.14	n.d.	(1.65)	1.65	1.63	1.82
H <sub>2</sub> O <sup>-</sup>	-----	0.45	0.10	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
F	0.80	0.95	0.47	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-----	-----	-----	-----
Insol.	0.11	nil	nil	-----	-----	-----	-----	-----	-----	-----	2.58	0.82	1.00
F=O	-0.34	-0.41	-0.20	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
	99.87	99.80	99.51	101.15	98.35	92.2	99.99	100.29	99.44	99.9	99.93	99.61	100.78

<sup>1</sup>Nickel Plate mine, Keystone, South Dakota. Lindberg (1950).

<sup>2</sup>Sidi-Bou-Kricha, Morocco. Huvelin, Orliac and Permingeat (1972).

<sup>3</sup>Buranga mine, Gatumba, Rwanda. Von Knorring (1969).

<sup>4</sup>Victory mine, Custer, South Dakota. Moore and Ito (1973).

<sup>5</sup>Sapucaia pegmatite, Minas Gerais, Brazil. J. Ito, analyst (this study). Trace Ti, Mo and Be.

<sup>6</sup>Sapucaia pegmatite, Minas Gerais, Brazil. A. J. Irving, analyst (this study). Note Pb and Li were not determined.

<sup>7</sup>Smith mine, Newport, New Hampshire. J. Ito, analyst (this study). Trace Be.

<sup>8</sup>Nancy mine, North Groton, New Hampshire. J. Ito, analyst (this study). Trace Sn, Ti, V, Si, B, Be.

<sup>9</sup>Palermo No. 1 mine, North Groton, New Hampshire. J. Ito, analyst (this study). Trace Ti, Pb, Si.

<sup>10</sup>Dickinsonite, Branchville, Connecticut. A. J. Irving, analyst (this study). H<sub>2</sub>O<sup>+</sup> and Li<sub>2</sub>O from (10) were added.

<sup>11</sup>Branchville, Connecticut. Wells analysis in Brush and Dana (1890).

<sup>12</sup>Berry quarry, Poland, Maine. Gonyer analysis in Berman and Gonyer (1930).

TABLE VII. *Arrojadite family. Cations based on 196 (O<sup>2-</sup>+P<sup>5+</sup>) anions.*

	1	2	3	4	5	6	7	8	9
Al <sup>3+</sup>	4.41	4.03	3.21	4.56	3.54	3.68	3.80	3.91	3.25
Fe <sup>3+</sup>	-----	-----	1.41	-----	1.72	0.20	-----	-----	-----
Fe <sup>2+</sup>	33.22	33.24	22.66	42.03	19.83	32.58	40.39	36.16	15.36
Mn <sup>2+</sup>	18.81	16.94	23.05	4.16	16.65	8.54	9.10	14.93	37.43
Mg <sup>2+</sup>	2.18	3.23	5.83	2.79	13.61	9.20	6.95	5.19	-----
Zn <sup>2+</sup>	-----	0.26	-----	-----	0.20	0.18	0.24	0.06	-----
Ca <sup>2+</sup>	3.71	1.24	3.41	7.84	3.71	3.31	5.41	1.96	3.40
Ba <sup>2+</sup>	-----	2.40	2.94	-----	0.79	1.23	0.01	0.11	-----
Sr <sup>2+</sup>	-----	0.26	-----	-----	0.27	0.10	0.04	0.53	-----
Pb <sup>2+</sup>	-----	0.29	-----	-----	1.60	0.32	0.13	-----	-----
Li <sup>+</sup>	0.51	1.88	1.13	-----	3.80	1.36	2.89	0.46	0.95
Na <sup>+</sup>	17.47	15.03	15.48	19.87	11.83	14.48	14.39	17.87	20.89
K <sup>+</sup>	-----	3.12	1.01	1.13	1.88	1.00	1.65	2.53	2.48
P <sup>5+</sup>	47.65	46.87	46.60	48.58	46.29	48.61	46.99	48.32	46.18
H <sup>+</sup>	8.55	7.66	13.54	-----	14.84*	8.87	1.30	-----	15.21
(F <sup>-</sup> )	(3.56)	(4.26)	(2.07)	-----	-----	-----	-----	-----	-----

\* By difference.

pegmatite, Minas Gerais, Brazil; Branchville pegmatite, Branchville, Connecticut).

Arrojadites are the most chemically complex of primary pegmatite phosphates and no less than sixteen elements may play a significant role. All arrojadites consistently contain Al<sub>2</sub>O<sub>3</sub> which we propose is an essential cation in the structure. Alkalies and alkaline earths occur in variable amounts: Na<sup>+</sup> and Ca<sup>2+</sup> are consistently present as major constituents but variable amounts of Li<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> are also present. The Sapucaia material is noteworthy for its high P<sub>2</sub>O<sub>5</sub> (4.2%) content. The transition metals include Fe<sup>2+</sup> and Mn<sup>2+</sup> with minor amounts of Zn<sup>2+</sup>. Highly variable amounts of water (up to 1.8%) and fluorine (up to 1.0%) have been reported for arrojadites. Like the alluaudites, a limited range of mixed valences evidently occurs over equivalent positions. Unlike the alluaudites, the arrojadite family appears to be highly resistant to oxidation and alkali leaching and oxidized equivalents are not known: the highest Fe<sub>2</sub>O<sub>3</sub> content is 1.7% for material from the Sapucaia pegmatite.

Table VI lists the analytical results and Table VII affords the atomic contents based on 196 anions. Analysis 9 is a refined electron probe study of a specimen of dickinsonite from Branchville, Connecticut. All the components utilized an arrojadite standard (analysis 5). The results are in excellent agreement with analysis 10 except that Al<sub>2</sub>O<sub>3</sub> was overlooked in the earlier study by Brush and Dana (1890). The material from Poland, Maine was not re-investigated; the three earlier analyses on dickinsonites are not included in Table VII owing to the uncertainty in Al<sub>2</sub>O<sub>3</sub>. Fisher (1965), in his study on the sodium iron manganese phosphates, based his computations on 48 (PO<sub>4</sub>) in the unit cell which is tolerably consistent with specific gravity and cell volume determinations. We believe that the consistent presence of water and fluorine represents in part additional anionic positions in the cell. A better fit with the minimum equivalent point rank number of 4 in the space group C<sub>2</sub>/c is obtained with 196 anions in the cell instead of 192.

The atomic cell contents for arrojadites vary widely and range between 76.8 and 85.9 cations other than P<sup>5+</sup> and H<sup>+</sup> per 196 anions. The simplest interpretations of this range include partial site occupancies, especially for positions rich in alkalies and other large cations; the substitution of water as (H<sub>3</sub>O)<sup>+</sup> or (H<sub>4</sub>O)<sub>2</sub><sup>2+</sup> clusters for large cations and tetrahedra; and the presence of highly aquated impurities. On grounds of ionic radii, it is sensible to group M<sup>3+</sup> = (Al<sup>3+</sup> and Fe<sup>3+</sup>); M<sup>2+</sup> = (Fe<sup>2+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup> and Zn<sup>2+</sup>); X = (K<sup>+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup> and Pb<sup>2+</sup>); and Y = (Na<sup>+</sup> and Ca<sup>2+</sup>) together as indicated by the parentheses. The highly variable Li<sup>+</sup>

TABLE VIII. *Arrojadite family. Partitioning of cations based on 196 anions.\**

	1	2	3	4	5	6	7	8	9	10
Zn <sup>2+</sup>	4.41	4.03	4.62	4.56	5.26	3.88	3.80	3.91	3.25	4.00
Mn <sup>2+</sup>	54.21	53.67	51.54	48.98	50.29	50.50	56.68	56.34	52.79	56.00
ZLi	0.51	1.88	1.13	?	3.80	1.36	2.89	0.46	0.95	
ECa+Na	21.18	16.27	16.89	27.71	15.54	17.79	19.80	19.83	24.29	20.00
EBa+Sr+Pb+K	3.12	5.96	4.07	1.88	3.66	3.30	2.71	5.12	1.94	4.00
Total Σ	83.43	79.81	78.25	85.13	78.55	76.83	85.88	83.66	83.22	84.00
ΔH	8.55	7.66	13.54	?	?	8.87	1.30	?	15.21	4.00

\* M<sup>3+</sup> = Al<sup>3+</sup>, Fe<sup>3+</sup>; M<sup>2+</sup> = Fe<sup>2+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>. Column 10 is the proposed ideal limit.

content is treated separately. These groupings are compiled in Table VIII. Substitutions between these groupings are quite likely, especially between M<sup>2+</sup> and M<sup>3+</sup>, and M<sup>2+</sup> and Y. The role of Li<sup>+</sup> is uncertain: it may be present as an impurity such as triphylite or it may substitute in the M<sup>2+</sup> positions. Water content is highly variable: in addition to its presence as a constituent and substituent, arrojadites often show thin films along joints and cracks of pale blue vivianite. Finally, vacancies probably occur over the large cation positions, assuming greater flexibility in accommodating cations of mixed valences. Samuelsenite, (Ba,C)(Ca,C)<sub>2</sub>(Mn<sup>2+</sup>,Fe<sup>2+</sup>,Na)<sub>4</sub>Ca<sub>9</sub>Al<sub>2</sub>(OH)<sub>2</sub>(PO<sub>4</sub>)<sub>18</sub>, a phase which occurs in association with arrojadite at the Palerma pegmatite, was shown by Moore and Araki (1977), in a detailed crystal structure analysis, to possess partial occupancies over large cation positions and Na<sup>+</sup> + (Mn,Fe)<sup>2+</sup> substitution as well. Despite the difficulties inherent in a structure as complex as arrojadite, any effort at unravelling its atomic positions will be most welcome.

We propose the ideal formula, X<sup>+</sup>Y<sup>+</sup>M<sup>3+</sup>M<sup>2+</sup>Al(OH,F)(PO<sub>4</sub>)<sub>12</sub>, Z = 4, for the arrojadites. This sets an upper limit of 84 cations other than P<sup>5+</sup> and H<sup>+</sup> in the cell. An ideal end-member composition KNa<sub>2</sub>Fe<sub>2</sub>Al(OH)(PO<sub>4</sub>)<sub>12</sub> is suggested for arrojadite. Note that grouping the alkalies; and the octahedral cations; and disregarding water, we obtain Na<sub>2</sub>Fes(PO<sub>4</sub>)<sub>4</sub>, Z = 12, which was suggested by Palache et al. (1951). To appreciate its complexity, at least twelve non-equivalent cation positions (other than P<sup>5+</sup> and H<sup>+</sup>) may occur in its structure. Table VIII reveals that analyses 1, 4, 7, 8, and 9 approach the limit of 84 cations in the cell. Analyses 2 and 5 indicate that Li<sup>+</sup> may substitute at the M<sup>2+</sup> positions. Analyses 1, 2, 3, 5, 6, and 9, are high in water content and possess a deficit of cations in Y positions, suggesting that OH<sup>-</sup> substitutions probably occur in the anion frame. In addition, 2, 3, 5, and 9 are low in P<sup>5+</sup>, indicating OH<sup>-</sup> substitution at tetrahedral vertices. Several analyses (4, 5, and 8), however, did not seek water content owing to limited amount of reasonably pure material. Analysis 4 represents the highest content of Na<sup>+</sup> and Ca<sup>2+</sup> recorded for arrojadites and indicates extensive substitution at M<sup>2+</sup> positions by Y cations, probably Ca<sup>2+</sup>.

Owing to lack of knowledge of the crystal structure, we do not advise further splitting of the arrojadite nomenclature and retain arrojadite for M<sup>2+</sup> = (Fe,Mn)<sup>2+</sup> and dickinsonite for M<sup>2+</sup> = (Mn,Fe)<sup>2+</sup>.

*More problems: continuous alkali-leaching versus recrystallization.* Consider now the possible routes of oxidation of the alluaudites and wyllieites. It was asserted earlier (Moore, 1971; Moore and Molin-Case, 1974) that alluaudites are metasomatic products, formed by alkali exchange, oxidation, and fine-grained recrystallization from earlier formed primary phases, in particular triphylites and lithiophilites while the wyllieites are themselves primary phases which crystallized directly from the pegmatite fluid and appeared as large euhedral crystals. The order scheme for the cations proposed earlier assumed that the present composition found for the material is precisely that of the originally formed crystal. The scheme, however, would change significantly if the present composition is

TABLE IX. *Alluaudites* and *Wyllieites*. Partitioning of Cations After  $Fe^{3+} + Fe^{2+}$ ,  $\square + Na^{+}$ .

Sample	ALLUAUDITES*											Excess $Na^{+}$	$\Sigma$	Change			
	M(2)				M(1)			X(1)			X(2)						
	Mg	Li	$Fe^{2+}$	$Mn^{2+}$	$Fe^{2+}$	$Mn^{2+}$	Ca	$Mn^{2+}$	Ca	Na	Na				K	$\square$	
2	0.05	1.18	4.66	2.11	---	4.00	---	0.98	0.90	2.12	4.00	---	---	1.18	1.88	0000	
1	0.04	---	5.00	2.96	---	3.05	0.97	---	0.32	3.68	3.97	0.03	---	0.28	0.32	0000	
4	0.33	---	7.63	0.04	---	4.00	---	1.18	0.60	2.29	3.93	0.07	---	2.65	1.78	0000	
12	1.59	---	6.41	---	---	0.62	3.38	---	1.09	0.79	2.12	4.00	---	0.68	1.88	0000	
3	0.27	0.03	3.82	3.88	---	4.00	---	0.16	1.67	2.17	3.82	0.18	---	3.21	1.83	0000	
14	2.39 <sup>†</sup>	0.07	4.68	0.96	---	4.00	---	0.41	0.29	3.30	2.70	---	1.30	0.00	0.70	1001	
5	1.27	0.34	6.39	---	---	2.31	1.69	---	1.08	0.48	2.44	3.97	0.03	---	3.48	1.56	1000
6	---	0.38	4.72	2.90	---	4.00	---	0.58	0.78	2.74	3.95	0.05	---	2.00	1.36	1001	
15	0.19	---	6.46	1.36	---	4.00	---	0.01	0.39	3.60	4.00	---	---	2.82	0.40	1000	
7	0.05	0.09	6.03	1.83	---	3.98	0.02	---	0.94	3.06	4.00	---	---	3.36	0.94	1000	
17	0.90	---	7.10	---	---	0.94	3.08	---	0.39	0.76	2.86	4.00	---	2.53	1.15	1001	
15	0.01	---	7.53	0.36	---	3.36	0.65	---	1.93	2.07	4.00	---	---	2.68	1.93	1001	
8	---	---	6.51	1.49	---	4.00	---	1.39	0.56	2.03	4.00	---	---	3.02	1.97	1001	
16	0.54	0.05	7.01	---	---	2.18	1.82	---	0.14	0.54	3.38	4.00	---	3.71	0.68	1001	
9	0.35	0.49	7.16	---	---	1.68	1.86	0.46	---	3.09	0.91	3.98	0.02	---	5.25	3.09	1000
10	0.19	---	7.81	---	---	0.20	3.66	0.24	---	1.17	2.83	3.99	0.01	---	3.53	1.17	1001
11	0.23	0.12	7.66	---	---	0.21	3.79	---	0.75	0.50	2.76	4.00	---	3.62	1.25	1001	

\* The cations are partitioned after  $Fe^{3+} + Fe^{2+}$ ,  $\square + Na^{+}$ . The predominant cation at each site is italicized. The "Excess  $Na^{+}$ " is that amount remaining after all available sites are filled. The " $\Sigma$ " is the sum of  $Mn^{2+}$  and Ca in X(1). " $\Sigma$ " refers to end-member compositional change from distribution in Table II, 1 meaning a change and 0 meaning no change. The order is M(2), M(1), X(1), X(2). All changes occur at M(2) and X(2) which, excepting for sample 14, involve  $Fe^{3+} \rightarrow Fe^{2+}$  (predominant) and  $\square \rightarrow Na^{+}$  (predominant).

<sup>†</sup> Includes 0.05 Zn added to Mg.

Sample	WYLLIEITES <sup>†</sup>															Change						
	M(2b)					M(2a)				M(1)			X(1b)		X(1a)			X(2)				
	Al	Mg	Li	Zn	$Fe^{2+}$	Mg	Li	Zn	$Fe^{2+}$	$Fe^{2+}$	$Mn^{2+}$	$Fe^{2+}$	$Mn^{2+}$	Ca	Na		Ca	Na	K	Na	K	$\square$
3	2.37	0.79	---	0.09	0.75	---	---	---	4.00	1.46	2.54	---	0.42	1.04	0.54	---	2.00	---	2.31	0.02	1.67	000001
4	2.63	0.22	0.05	---	1.20	---	---	---	4.00	1.23	2.77	---	0.81	0.60	0.59	---	2.00	---	2.87	---	1.13	010001
2	2.60	1.40	---	---	---	0.82	0.13	0.02	3.03	3.33	0.66	---	2.73	0.27	---	0.05	1.96	---	3.45	---	0.55	010000
1	3.01	0.95	0.04	---	---	---	0.09	0.01	3.80	4.00	---	0.06	1.18	0.76	---	0.10	1.20	---	3.18	---	0.82	000000

Sample	M(2b)						M(2a)				
	Al	$Fe^{3+}$	Mg	Li	Zn	$Fe^{2+}$	$Fe^{3+}$	Mg	Li	Zn	$Fe^{2+}$
3	2.37	0.75	0.79	---	0.09	---	1.73	---	---	---	2.27
4	2.63	1.20	0.22	0.05	---	---	2.21	---	---	---	1.79
2	2.60	1.40	---	---	---	---	1.12	0.82	0.13	0.02	1.91
1	3.01	0.95	0.04	---	---	---	0.08	---	0.09	0.01	3.88

<sup>†</sup> The cations are partitioned after  $Fe^{3+} + Fe^{2+}$ ,  $\square + Na^{+}$ . The predominant cation at each site is italicized. " $\Sigma$ " refers to end-member compositional change from distribution in Table V, 1 meaning change and 0 meaning no change. The order is M(2b), M(2a), M(1), X(1b), X(1a), X(2). Note changes occur at M(2a) and X(2) and involve  $Fe^{3+} \rightarrow Fe^{2+}$  (predominant) and  $\square \rightarrow Na^{+}$  (predominant). The second set of M(2b)'s and M(2a)'s adopt the distribution above but the exact amount of  $Fe^{2+} \rightarrow Fe^{3+}$  in Table V is adjusted accordingly, with M(2b) oxidized before M(2a).

in fact the result of a continuous oxidation and alkali-leaching of a more reduced original crystal. In this latter case, we assume a sequence akin to that established on structural grounds (Eventoff et al., 1972; Alberti, 1976) for the triphylite-heterosite series, that is  $LiFe^{2+}PO_4 - Fe^{3+}PO_4$ , where  $\square$  is the ordered vacancy in the M(1) position, previously occupied by  $Li^{+}$ . This sequence suggests that progressive leaching of alkali is coupled with oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  with the original cations remaining immobile in the process.

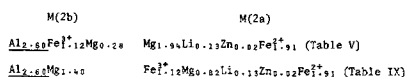
Thus, Table II and Table V are recast into a partitioning of the cations, starting with all  $Fe^{3+} + Fe^{2+}$  and balanced by  $\square + Na^{+}$  (Table IX). The most striking result is the appearance of excess  $Na^{+}$  beyond the amount the alluaudite structure type can tolerate for 16 of the 17 analyses. Only in sample 14 is the additional  $Na^{+}$  accommodated in the structure. This is contrasted by the wyllieites where, in all four analyses, a partial vacancy in the X(2) site still remains. Thus, we are forced to conclude that alluaudites are indeed metasonic products and that their present compositions evidently represent an approximation to original compositions at the time of their formation. We remark that in Table II, the variations in the cell charge from zero based on  $\Sigma$  charge (cations)-36 arises from the fact that all computations were based on  $\Sigma O = 48$ ; clearly, the presence of  $H^{+}$  (which we did not compute) would lead to negative values in "residual cell charge" and the presence of  $Fe_2O_3$  impurity would lead to positive

values. Twelve analyses are within the range  $\pm 1.0e$  and are therefore not serious departures. Nevertheless, the consistent trend of a sodium excess for ferrous equivalents cannot be disputed; it relates to the trend  $E(Mn^{2+} + Ca^{2+})$  in  $X(1) < 4.0$  (Table IX). That is to say, the composition  $4NaCa(Fe,Mn)_2(Mn,Fe)^{2+}(PO_4)_3$  is the limit for a series with no Na excess whereas the alluaudites appear to represent the hypothetical end-member  $4(Na)Na_2Ca(Fe,Mn)_2(Mn,Fe)^{2+}(PO_4)_3$ , that is a series where such an excess exists but one which the structure cannot tolerate owing the absence of an extra atomic position.

Although ordering of the alluaudites in this fashion does not lead to nonmenclatrical contradictions, contradictions exist for the wyllieites (Table IX). This is because in the latter, the rearrangement of Mg distributions lead to sample 2 - ferrowyllieite instead of a possible "ferromagwylieite" (see Table V) since in wyllieites M(2) is split into M(2b) and M(2a). We prefer to adopt the site distributions in wyllieites according to Table IX since we believe the presence of  $Fe^{3+}$  is the result of partial alkali-leaching postdating the growth of the crystal, in precisely the same manner that the triphylite-ferrisicklerite-heterosite series represents a progressive leaching and oxidation of our initially ferrous-rich crystal. The ferrowyllieite of sample 2 would be an ideal candidate for further detailed study since the following outline suggests that differences in scattering by X-rays and average polyhedral sizes would



be easily testable by a detailed structure analysis, *viz.*:



*Concluding remarks.* Alluaudites and wyllieites possess complex solid solution series over four independent sites in the former and six in the latter. The series is further complicated by the presence of iron in two oxidation states. Nomenclature of the series is based on partitioning of cations according to ionic size and site size.

If the iron in alluaudites and wyllieites is reduced  $Fe^{3+} + Fe^{2+}$  with concomitant  $\square + Na^{+}$  filled, an interesting pattern emerges: alluaudites reveal an excess of  $Na^{+}$  beyond the available sites but the sites in wyllieites are not all completely filled. This observation supports the statement that alluaudites are products of Na-metasomatism while wyllieites are truly primary phases and perhaps suffer some subsequent oxidation and alkali-leaching at a later stage in much the same manner as found in the triphylite-heterosite series. This statement is further supported by the observations in Moore (1971) that alluaudites are late products, formed by Na-metasomatism of triphylites and even heterosites. It is quite likely that the oxidation grades reported in analyses reflect the original oxidation grades of their crystals during growth. The broad paragenetic scheme for these complex series in Moore (1973) is also substantiated by these observations.

Arrojadites are complex early phosphates with probable ideal formula  $X^{1+}Y_3^{1+}M_3^{1+}Al(OH,F)(PO_4)_Z$ ,  $Z = 4$ , where  $X = K^{+}$ ,  $Ba^{2+}$ ,  $Pb^{2+}$ ,  $Ca^{2+}$ ,  $Li^{+}$ ,  $M^{2+} = Fe^{2+}$ ,  $Mn^{2+}$ ,  $Li^{+}$ ,  $Mg^{2+}$ . It is further shown that dickinsonites apparently contain essential  $Al_2O_3$  which is present in virtually all arrojadite analyses.

*Approval of nomenclature and deposition of type material.* The proposed nomenclature for the alluaudites and wyllieites was brought before the Commission on New Minerals and New Mineral Names (IMA). Type wyllieite was renamed ferrowyllieite so that the alluaudite-wyllieite nomenclature would be parallel and self-consistent. A true wyllieite from the Old Mike mine was subsequently found and encouraged this desirable revision. In addition, new trivial names were introduced: rosemaryite and maghagendorfite, rosemaryite logically forced by the parallel alluaudites; and maghagendorfite owing to predominant  $Mg^{2+}$  in one site. Although the objections raised were not scant, the nomenclature and species were nevertheless approved.

Ferrowyllieite (holotype: Victory mine), wyllieite (holotype: Old Mike mine); rosemaryite (holotype: Rock Ridge pegmatite), and maghagendorfite (holotype: Dyke Lode) are deposited in the collection of types, the U.S. National Museum of Natural History (Smithsonian Institution).

*Acknowledgments.* The problems of nomenclature of the alluaudites and wyllieites were many and we deeply appreciate the considerable body of communication with Dr. Max H. Hey whose valuable suggestions helped crystallize our own thoughts.

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