

## NOMENCLATURE OF THE ALUNITE SUPERGROUP

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### ABSTRACT

The alunite supergroup consists of more than 40 mineral species with the general formula  $DG_3(TO_4)_2(OH,H_2O)_6$ , in which  $D$  is occupied by monovalent (*e.g.*, K, Na,  $NH_4$ ,  $H_3O$ ), divalent (*e.g.*, Ca, Ba, Pb), or trivalent (*e.g.*, Bi, REE) ions,  $G$  is typically  $Al^{3+}$  or  $Fe^{3+}$ , and  $T$  is  $S^{6+}$ ,  $As^{5+}$ , or  $P^{5+}$ . The current nomenclature classification is unusual in that, within the ternary system defined by the  $SO_4$ ,  $AsO_4$ , and  $PO_4$  apices, compositions are divided into five fields rather than the three that are conventionally recommended for such systems by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association. The current compositional boundaries are arbitrary, and the supergroup is examined to determine the repercussions that would ensue from adoption of a conventional ternary compositional system. As a result of the review, several inconsistencies have been revealed; for example, beaverite and osarizawaite, which are commonly formulated as  $Pb(Cu,Fe)_3(SO_4)_2(OH)_6$  and  $Pb(Cu,Al)_3(SO_4)_2(OH)_6$ , respectively, not only have formula  $Fe > Cu$  and  $Al > Cu$ , but the amount of substitutional Cu also is variable. Beaverite is therefore compositionally equivalent to Cu-bearing plumbojarosite. The CNMMN system also permits the introduction of new mineral names if a supercell is present; within the alunite supergroup, the supercell is typically manifested by a doubling of the  $c$  axis to  $\sim 34$  Å, and the effect is evident on X-ray powder patterns by the appearance of a diffraction line or peak at 11 Å. In addition to the supercell, however, several other departures from the standard trigonal cell with space group  $R\bar{3}m$  have been observed. To accommodate these structural variations, thereby minimizing the introduction of numerous potential new mineral names, the possibility of incorporating a suffix modifier is explored. To keep within CNMMN nomenclature protocols, potential solutions are offered, but none is proposed.

*Keywords:* alunite supergroup, nomenclature, alunite group, beudantite group, crandallite group, compositions, structures.

### SOMMAIRE

Le supergroupe de l'alunite comprend plus de quarante espèces minérales répondant à la formule générale  $DG_3(TO_4)_2(OH,H_2O)_6$ ; le site  $D$  contient des ions monovalents (*e.g.*, K, Na,  $NH_4$ ,  $H_3O$ ), divalents (*e.g.*, Ca, Ba, Pb), ou trivalents (*e.g.*, Bi, terres rares),  $G$  contient en général  $Al^{3+}$  ou  $Fe^{3+}$ , et  $T$  représente  $S^{6+}$ ,  $As^{5+}$ , ou  $P^{5+}$ . Le système de classification en vigueur actuellement est anormal: dans le contexte d'un système ternaire défini par les pôles  $SO_4$ ,  $AsO_4$ , et  $PO_4$ , les compositions sont réparties en cinq domaines plutôt que trois, comme le recommande la Commission sur les Nouveaux Minéraux et Noms de Minéraux de l'Association Minéralogique Internationale. La délimitation des divers champs est arbitraire. Les répercussions de l'adoption d'un système ternaire de nomenclature de ce supergroupe sont ici passées sous revue. Plusieurs cas de non concordance sont relevés; à titre d'exemple, la beaverite et l'osarizawaite, auxquelles on attribue couramment les formules  $Pb(Cu,Fe)_3(SO_4)_2(OH)_6$  et  $Pb(Cu,Al)_3(SO_4)_2(OH)_6$ , respectivement, ont une teneur en Fe et en Al supérieure à celle du Cu, mais cette teneur en cuivre peut aussi être variable. La beaverite serait donc équivalente en composition à une plumbojarosite cuprifère. Le système en place actuellement permet l'introduction de nouveaux noms de minéraux si une supermaille est manifestée. Au sein du supergroupe de l'alunite, la présence d'une supermaille se voit par le dédoublement de la période  $c$  jusqu'à environ 34 Å, et par la présence d'un pic ou d'une raie à 11 Å dans un spectre de diffraction. En plus de la supermaille, toutefois, on observe plusieurs autres écarts par rapport à la maille trigonale standard dans le groupe spatial  $R\bar{3}m$ . Afin d'accommoder ces variations structurales, et ainsi de minimiser l'introduction potentielle de plusieurs nouveaux noms de minéraux, il est possible d'ajouter un suffixe au nom. Afin de satisfaire aux exigences de la Commission, des solutions possibles au dilemme sont présentées, mais aucune n'est proposée.

(Traduit par la Rédaction)

*Mots-clés:* supergroupe de l'alunite, nomenclature, groupe de l'alunite, groupe de la beudantite, groupe de la crandallite, compositions, structures.

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## INTRODUCTION

The alunite supergroup consists of three mineral groups that, combined, contain more than 40 mineral species with the general formula  $DG_3(TO_4)_2(OH, H_2O)_6$ , wherein  $D$  represents cations with a coordination number greater or equal to 9, and  $G$  and  $T$  represent sites with octahedral and tetrahedral coordination, respectively (Smith *et al.* 1998). The supergroup consists of the alunite group, the beudantite group, and the crandallite group (Mandarino 1999). In all three, the  $T$  in  $(TO_4)_2$  is dominated by one or more of  $S^{6+}$ ,  $As^{5+}$ , or  $P^{5+}$ . The alunite group is characterized by  $(SO_4)_2$ -dominant minerals, whereas in the beudantite group, one of the two  $SO_4$  groups is replaced by  $PO_4$  or  $AsO_4$ . In the crandallite group, the  $(TO_4)_2$  represents one or both of  $PO_4$  and  $AsO_4$ . Thus the change from the alunite to the beudantite group, and thence to the crandallite group, can be viewed as a progression from  $(SO_4)_2$ , to  $(SO_4)(PO_4)$  or  $(SO_4)(AsO_4)$ , and thence to either  $(PO_4)_2$  or  $(AsO_4)_2$ . This progression follows that in *The System of Mineralogy* (Palache *et al.* 1951), wherein the alunite group is classified with the sulfates, the beudantite group falls within the category of "compound phosphates, *etc.*", and the plumbogummite group is equivalent to the current crandallite group. In the beudantite group, a small departure from the 1:1 ratio for  $(TO_4):(TO_4)$  was recognized (Palache *et al.* 1951), and this variation is evident in all of the compositions listed therein. For example, the two compositions chosen for beudantite *sensu stricto* have  $SO_3$  contents of 12.30 and 14.82 wt%, whereas the appropriate value is 11.24 wt% for  $(SO_4):(AsO_4) = 1:1$ . Under the current rules of nomenclature for such a binary system, these compositions fail to meet the "50% rule" in that they are sulfate-dominant rather than precisely at the 50:50 boundary that separates them from the arsenate-dominant mineral species. Compositions of some of the other minerals within the group, however, exceed the 50% requirement and fall within the  $PO_4$ -dominant field.

After publication of *The System of Mineralogy*, it became apparent that the 1:1 ratio of anions was not a

meaningful compositional boundary, and that mutual substitutions of  $SO_4$ ,  $PO_4$ , and  $AsO_4$  are extensive within the alunite supergroup. To rationalize the previously indefinite boundaries between the  $SO_4$ -dominant and other members of the family, Scott (1987) proposed that the boundaries be set at 0.5 formula  $(SO_4)_2$  and 1.5 formula  $(SO_4)_2$ ; these values are 25% and 75% of total  $TO_4$ , as shown in Figure 1. The proposal was accepted by the Commission on New Minerals and Mineral Names (CNMMN). The effect of Scott's classification is that each  $SO_4$ - $AsO_4$ - $PO_4$  "ternary" diagram incorporates five compositional fields and mineral names, four of which are partly governed by the  $PO_4$ - $AsO_4$  binary dividing line (Fig. 1). Novák *et al.* (1994) proposed that the  $SO_4$ - $PO_4$ - $AsO_4$  field be divided into six units (Fig. 1), a system that requires the redefinition of several minerals. Their system has not been submitted to the CNMMN for a vote, but its usage has been propagated in several publications (Novák & Jansa 1997, Novák *et al.* 1997, 1998, Sejkora *et al.* 1998).

The nomenclature of the alunite supergroup is complex and promises to be increasingly so if the CNMMN-approved system is not modified to take account of the crystal-structure variations that have been recognized to occur within the supergroup. In the following discussion, the nomenclature is evaluated to explore not only what happens in a ternary compositional system, but also to explore the repercussions of designating the crystal-structure variations by suffixes. In the compositional system herein, the ternary series is divided into three equal fields (Fig. 1, left), which is in accord with current CNMMN recommendations for naming ternary solid-solutions that are complete and without structural order of the ions defining the end members (Nickel 1992).

## THE ALUNITE GROUP

The minerals of the alunite group are listed in Table 1. Figure 2 shows that little substitution of  $SO_4$  by  $PO_4$  and  $AsO_4$  occurs for members in which  $D$  is monovalent; where  $D$  is divalent, however,  $TO_4$  substi-

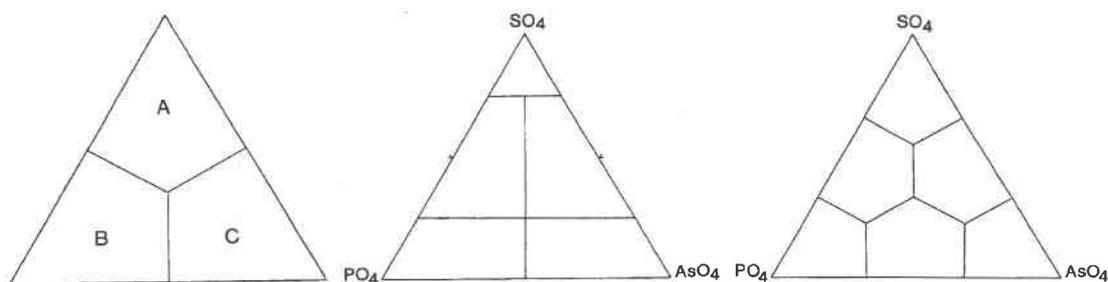


FIG. 1. Left diagram shows the nomenclature scheme for complete ternary solid-solutions according to recommendations by the CNMMN (Nickel 1992). Middle diagram is the system in current use for the alunite supergroup (Scott 1987), and the diagram on the right shows the composition fields proposed by Novák *et al.* (1994).

TABLE 1. MINERALS OF THE ALUNITE GROUP (CURRENT USAGE)

|                  |                                      |                    |                                    |
|------------------|--------------------------------------|--------------------|------------------------------------|
| alunite          | $KAl_3(SO_4)_2(OH)_6$                | jarosite           | $KFe_3(SO_4)_2(OH)_6$              |
| natroalunite     | $NaAl_3(SO_4)_2(OH)_6$               | natrojarosite      | $NaFe_3(SO_4)_2(OH)_6$             |
| ammonioalunite   | $(NH_4)Al_3(SO_4)_2(OH)_6$           | ammoniojarosite    | $(NH_4)Fe_3(SO_4)_2(OH)_6$         |
| schlossmacherite | $(H_3O, Ca)Al_3(SO_4)_2(OH)_6$       | hydronium jarosite | $(H_3O)Fe_3(SO_4)_2(OH)_6$         |
| —                | —                                    | argentojarosite    | $AgFe_3(SO_4)_2(OH)_6$             |
| —                | —                                    | dorallcharite      | $TlFe_3(SO_4)_2(OH)_6$             |
| osarizawaite     | $Pb(Al, Cu)_3(SO_4)_2(OH, H_2O)_6$   | beaverite          | $Pb(Fe, Cu)_3(SO_4)_2(OH, H_2O)_6$ |
| —                | —                                    | plumbojarosite*    | $PbFe_6(SO_4)_4(OH)_{12}$          |
| minamiite*       | $(Na, Ca, K)_2Al_6(SO_4)_4(OH)_{12}$ | —                  | —                                  |
| huangite*        | $CaAl_6(SO_4)_4(OH)_{12}$            | —                  | —                                  |
| walthierite*     | $BaAl_6(SO_4)_4(OH)_{12}$            | —                  | —                                  |

\* Length of *c* unit-cell parameter is double that of the other members of the group.

tution may be substantial, and these minerals are discussed separately. In the synthetic alunite-jarosite series, Fe-for-Al solid solution is complete (Brophy *et al.* 1962, Härtig *et al.* 1984); although natural members with intermediate compositions are known (Palache *et al.* 1951, van Tassel 1958), the degree of Fe-for-Al substitution in most occurrences is limited, and compositions are close to those of either the Fe or Al end-members.

Solid solution involving  $K^+$ ,  $Na^+$ , and  $(H_3O)^+$  is extensive in both alunite and jarosite (Brophy *et al.* 1962, Parker 1962, Brophy & Sheridan 1965, Kubisz 1960, 1970, Stoffregen & Cygan 1990, Li *et al.* 1992). Substitution involving  $K^+$  and  $Pb^{2+}$  has been shown by Scott (1987) to be extensive in alunite, and by de Oliveira *et al.* (1996) and Roca *et al.* (1999) to be equally extensive in jarosite. The incorporation of  $NH_4$  in ammonioalunite (Altaner *et al.* 1988) and ammoniojarosite (Odum *et al.* 1982) seems to be mainly at the expense of  $K^+$  and  $(H_3O)^+$ . Apparent deficiencies in  $K + Na + NH_4$  D-site occupancy are generally attributed to  $(H_3O)^+$ .

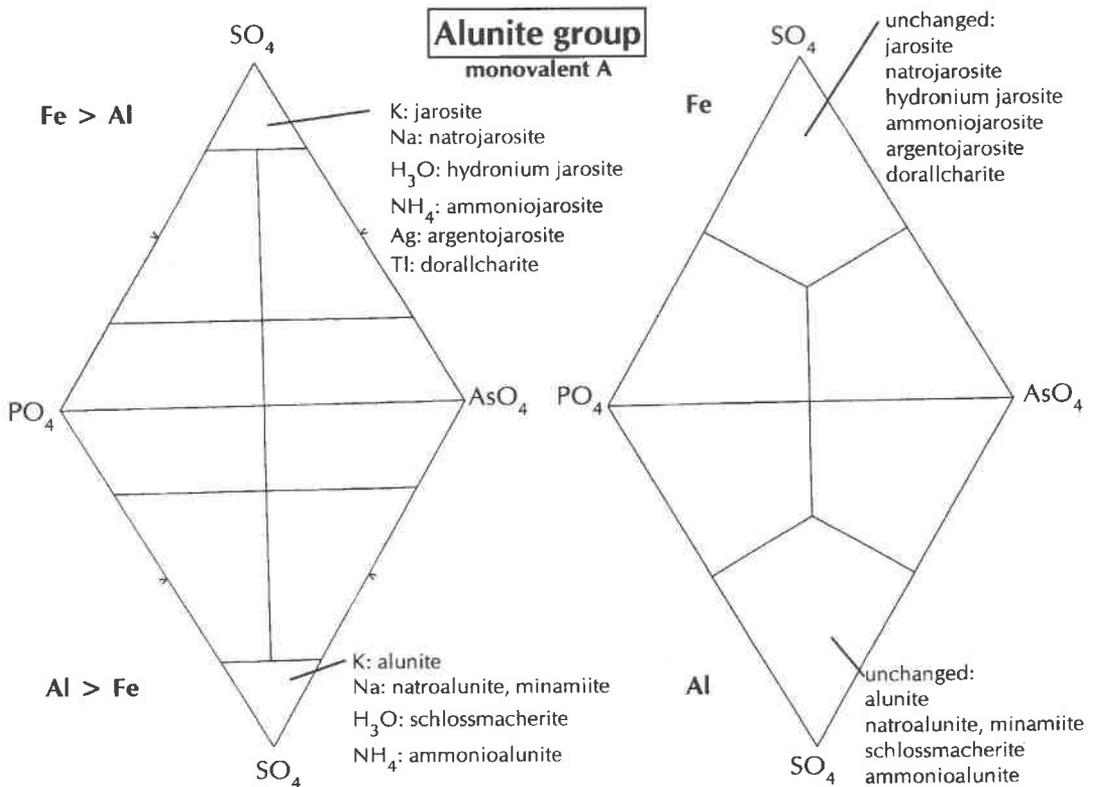


FIG. 2. Minerals of the alunite supergroup with monovalent ions predominant as the D-site cation. Left diagram shows the current system of nomenclature, and diagram on the right shows the effects of adopting a ternary system. Minerals with Fe > Al and with Al > Fe are, respectively, jarosite – alunite, natrojarosite – natroalunite, ammoniojarosite – ammonioalunite, hydronium jarosite – schlossmacherite. Argentojarosite and dorallcharite do not have Al > Fe analogues.

Natural argentojarosite is generally near the end-member composition, although in synthetic systems the solid solution between Ag–Pb ( $\pm$  H<sub>3</sub>O) and Ag–K ( $\pm$  H<sub>3</sub>O) has been shown to be complete (Idefonse *et al.* 1986, Dutrizac & Jambor 1984). The Tl<sup>+</sup> member, dorallcharite, is known only from one locality, and the mean occupancy of the *D* site is (Tl<sub>0.81</sub>K<sub>0.19</sub>) (Balić Žunić *et al.* 1994). The remaining members of the alunite group, except minamiite and schlossmacherite, contain a predominance of divalent *D*-site cations. As these minerals present some difficulties in nomenclature, the species are discussed individually.

### Minamiite

The ideal formula of minamiite is (Na,Ca,K)<sub>2</sub>Al<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH)<sub>12</sub>. Chemical analysis of the type specimen gave (Na<sub>0.46</sub>K<sub>0.19</sub>Ca<sub>0.14</sub>□<sub>0.14</sub>)Σ<sub>0.93</sub>Al<sub>3.11</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>5.70</sub> on the basis of SO<sub>4</sub> = 2, and the ideal formula of the crystal used for the X-ray structure study (Ossaka *et al.* 1982) was determined to be (Na<sub>0.36</sub>K<sub>0.1</sub>Ca<sub>0.27</sub>□<sub>0.27</sub>)Σ<sub>0.93</sub>Al<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>. The □ in the formula represents vacancies that compensate for the presence of the divalent ion (Ca<sup>2+</sup>) in the *D* position. The mineral was determined to be trigonal, space group *R* $\bar{3}m$ , *a* = 6.981, *c* = 33.490 Å. Thus, type minamiite is compositionally equivalent to a Ca-rich natroalunite, but the *c* axis in minamiite is doubled because of partial order of the *D* cations. This results in a superstructure that yields a characteristic powder-diffraction line (or peak) at about 11 Å (Okada *et al.* 1987).

Although type minamiite is Na-dominant (Ossaka *et al.* 1982), the same authors subsequently synthesized the Ca-dominant analogue, and they explicitly referred to the end-member composition of minamiite as Ca<sub>0.5</sub>Al<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> (Ossaka *et al.* 1987, Okada *et al.* 1987). Nevertheless, although Ossaka *et al.* (1987) showed that extensive substitution involving Na–K–Ca occurs in natural minamiite, none of the compositions indicated a predominance of Ca as the *D*-site cation.

Most minerals of the alunite group have *D* occupied by a monovalent ion, and for these minerals the substitution of SO<sub>4</sub> by PO<sub>4</sub> or AsO<sub>4</sub> is extremely limited (Fig. 2). Adoption of a ternary system SO<sub>4</sub>–PO<sub>4</sub>–AsO<sub>4</sub> for these minerals therefore would not affect the nomenclature of the existing species. The three divalent elements predominating at the *D* site in the alunite-group minerals are Ba, Ca, and Pb.

### Huangite and walthierite

The mineral with Ca predominant, ideally Ca<sub>0.5</sub>Al<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>, was named huangite, and that with Ba predominant, ideally Ba<sub>0.5</sub>Al<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>, was named walthierite (Li *et al.* 1992). X-ray powder patterns of both minerals show an 11 Å diffraction effect, indicating that their *c* axis is doubled to 33–34 Å. Acceptance of huangite as a new mineral indicated that the CNMNMN

regarded minamiite to be compositionally equivalent to calcian natroalunite, but with the *c* axis doubled in minamiite. A plot by Matsubara *et al.* (1998) of Na + K (alunite–natroalunite) versus Ca (huangite) does not show significant compositional gaps to be present in the series. Because of small grain-size, however, X-ray data have not been obtained for all compositions. Thus, if ordering of Ca is assumed to be the sole cause for the doubling of *c*, the lower limit to trigger the change has not been established.

### Beaverite and osarizawaite

Beaverite is typically assigned the formula PbCuFe<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> or Pb(Cu<sup>2+</sup>,Fe<sup>3+</sup>,Al)<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> (Palache *et al.* 1951, Gaines *et al.* 1997). Osarizawaite is the Al-dominant analogue of beaverite, *i.e.*, Al > Fe (Taguchi 1961). As all compositions of beaverite and osarizawaite have Fe > Cu or Al > Cu, the respective formulas should be written as Pb(Fe,Cu,Al)<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> and Pb(Al,Cu,Fe)<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>. Most compositions of beaverite have Cu:(Fe,Al) near 33:67, but both higher and lower values have been reported (van Tassel 1958, Yakhontova *et al.* 1988, Breidenstein *et al.* 1992). As summarized by Yakhontova *et al.* (1988), the values of the relevant ratio range from 36:64 to 25:75.

As for beaverite, most analyses of the Al > Fe analogue, osarizawaite, indicate Cu:(Al,Fe) near 33:67. However, Paar *et al.* (1980) reported an occurrence of osarizawaite for which the ratio is 25:75. [The mineral described by Cortelezzi (1977) as osarizawaite seems to be a Pb–Cu-rich alunite, requiring re-analysis].

The compositional variations in beaverite–osarizawaite indicate that the ratio of divalent (Cu<sup>2+</sup> and Zn<sup>2+</sup>) to trivalent (Fe<sup>3+</sup> and Al<sup>3+</sup>) ions need not be strictly 33:67. In synthetic beaverite–plumbojarosite, substitution of Cu<sup>2+</sup> for Fe<sup>3+</sup> was found to be complete over the range Cu:Fe = 0:100 to Cu:Fe = 33:67 (Jambor & Dutrizac 1985). Up to 0.76 mol (Zn + Cu) has been reported for Pb-rich alunite (Scott 1987). For corkite, which is also in the supergroup and is described farther below, substitution of 0.42 to 0.64 mol Cu has been reported by de Bruijn *et al.* (1990) and Tsvetanova (1995), respectively.

Giuseppetti & Tadini (1980) solved the structure of osarizawaite of composition Pb(Al<sub>1.62</sub>Cu<sub>0.98</sub>Fe<sub>0.38</sub>Zn<sub>0.02</sub>)Σ<sub>3.00</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> in space group *R* $\bar{3}m$ , which requires that the Cu and Al–Fe be disordered. X-ray powder-diffraction patterns reported for natural beaverite–osarizawaite have so far conformed to a basic cell of *a* = ~7, *c* = ~17 Å, but as Cu<sup>2+</sup> decreases, Pb content also must decrease to maintain charge balance. At some point, therefore, the unit cell must transform to the doubled *c* of ~34 Å that is commonly accepted as characteristic of plumbojarosite. In synthetic plumbojarosite–beaverite, however, doubled cells appeared randomly along the series (Jambor & Dutrizac 1983).

In terms of composition, beaverite is a Cu-rich plumbojarosite. All occurrences of natural plumbojarosite have so far been reported to have a doubled *c* axis, but in synthetic hydronium-bearing plumbojarosite, the *c* may be either 17 or 34 Å, apparently depending on whether Pb is ordered or disordered. The degree of order can be variable, and this is readily indicated by variations in the intensity of the 11 Å diffraction line or peak in the X-ray pattern.

*Schlossmacherite*

Schlossmacherite contains substantial amounts of both SO<sub>4</sub> and AsO<sub>4</sub>; thus the mineral has been variably assigned to the alunite group (Gaines *et al.* 1997) or the beudantite group (Mandarino 1999; Table 2). Recalculation of the only analytical data available (Schmetzer *et al.* 1980) gives [(H<sub>3</sub>O)<sub>0.32</sub>□<sub>0.28</sub>Ca<sub>0.26</sub>Na<sub>0.07</sub>K<sub>0.05</sub>Sr<sub>0.01</sub>Ba<sub>0.01</sub>]<sub>Σ1.00</sub>(Al<sub>2.94</sub>Fe<sub>0.02</sub>Cu<sub>0.06</sub>)<sub>Σ3.02</sub>[(SO<sub>4</sub>)<sub>1.51</sub>(AsO<sub>4</sub>)<sub>0.49</sub>](OH)<sub>5.26</sub> on the basis of TO<sub>4</sub> = 2 and after reassignment of Cu from the *D* to the *G* position. The formula conforms with that generalized by the authors (Schmetzer *et al.* 1980). The ratio of SO<sub>4</sub>:AsO<sub>4</sub> is 75.6:24.4, thus placing schlossmacherite in the SO<sub>4</sub>-AsO<sub>4</sub>-dominant field in Figure 2. The mineral is therefore the Al-dominant analogue of hydronium jarosite. Cell dimensions are *a* = 6.998, *c* = 16.67 Å.

THE CRANDALLITE GROUP

The minerals of the crandallite group are listed in Table 3. Nine of the members have Ba, Sr, or Ca domi-

TABLE 2. MINERALS OF THE BEUDANTITE GROUP (CURRENT USAGE)

|   |  |
|---|--|
| beudantite<br>PbFe <sub>3</sub> [(As,S)O <sub>4</sub> ] <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>       | corkite<br>PbFe <sub>3</sub> [(P,S)O <sub>4</sub> ] <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>      |
| hidalgoite<br>PbAl <sub>3</sub> [(As,S)O <sub>4</sub> ] <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>       | hinsdalite<br>PbAl <sub>3</sub> [(P,S)O <sub>4</sub> ] <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>   |
| kemmlitzite<br>(Sr,Ce)Al <sub>3</sub> [(As,S)O <sub>4</sub> ] <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub> | svanbergite<br>SrAl <sub>3</sub> [(P,S)O <sub>4</sub> ] <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>  |
| —   | woodhouseite<br>CaAl <sub>3</sub> [(P,S)O <sub>4</sub> ] <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub> |
| gallobeudantite<br>PbGa <sub>3</sub> [(As,S)O <sub>4</sub> ] <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>  | —  |

Either As or S may be predominant in (As,S)O<sub>4</sub>, and either P or S may be predominant in (P,S)O<sub>4</sub>.

nant in *D* (three members for each of these cations), four members have Pb dominant, and the remainder has REE, Ca, or Th dominant. As in the alunite group, a primary distinction rests on whether the proportion of Fe is greater than that of Al or *vice versa*.

*Ba predominance*

The Ba-dominant member of the alunite group is walthierite Ba<sub>0.5</sub>Al<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>, and its relationship to other Ba-dominant members of the alunite supergroup is shown in Figure 3. Although Li *et al.* (1992) obtained *a* = 7.08, *c* = 17.18 Å by electron-diffraction study of walthierite, X-ray powder patterns of bulk samples show an 11 Å diffraction peak, requiring that the length of *c* be doubled. The inconsistency was attributed to disorder induced by the electron-diffraction beam.

TABLE 3. MINERALS OF THE CRANDALLITE GROUP (CURRENT USAGE)

| Al > Fe   |  | Fe > Al   |  |
|---|--|---|--|
| gorceixite<br>BaAl <sub>3</sub> (PO <sub>4</sub> )(PO <sub>3</sub> -OH)(OH) <sub>6</sub>                                  | arsenogorceixite<br>BaAl <sub>3</sub> (AsO <sub>4</sub> )(AsO <sub>3</sub> -OH)(OH) <sub>6</sub>                                 | —   | dussertite<br>BaFe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                 |
| crandallite<br>CaAl <sub>3</sub> [PO <sub>3</sub> (O <sub>1/2</sub> (OH) <sub>1/2</sub> )] <sub>2</sub> (OH) <sub>6</sub> | arsenocrandallite<br>CaAl <sub>3</sub> [AsO <sub>3</sub> (O <sub>1/2</sub> (OH) <sub>1/2</sub> )] <sub>2</sub> (OH) <sub>6</sub> | —   | —  |
| goyazite<br>SrAl <sub>3</sub> [PO <sub>3</sub> (O <sub>1/2</sub> (OH) <sub>1/2</sub> )] <sub>2</sub> (OH) <sub>6</sub>    | arsenogoyazite<br>SrAl <sub>3</sub> [AsO <sub>3</sub> (O <sub>1/2</sub> (OH) <sub>1/2</sub> )] <sub>2</sub> (OH) <sub>6</sub>    | benauite<br>SrFe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>      | —  |
| plumbogummite<br>PbAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>                     | philipsbornite<br>PbAl <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>                          | kintoreite<br>PbFe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>    | segnitite<br>PbFe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub> |
| florencite-(Ce)<br>CeAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                                    | arsenoflorencite-(Ce)<br>CeAl <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                                    | —   | —  |
| florencite-(La)<br>LaAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                                    | "arsenoflorencite-(La)"*<br>LaAl <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                                 | —   | —  |
| florencite-(Nd)<br>NdAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                                    | "arsenoflorencite-(Nd)"*<br>NdAl <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                                 | —   | —  |
| waylandite<br>(Bi,Ca)Al <sub>3</sub> (PO <sub>4</sub> ,SiO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                  | "arsenowaylandite"*<br>(Bi,Ca)Al <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>                | zairite<br>BiFe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                        | —  |
| eylettersite<br>(Th,Pb)Al <sub>3</sub> (PO <sub>4</sub> ,SiO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                | —  | —   | Others   |
| —   | —  | springcreekite<br>BaV <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub> | —  |

\* not CNMNMN-approved, but included here for completeness.

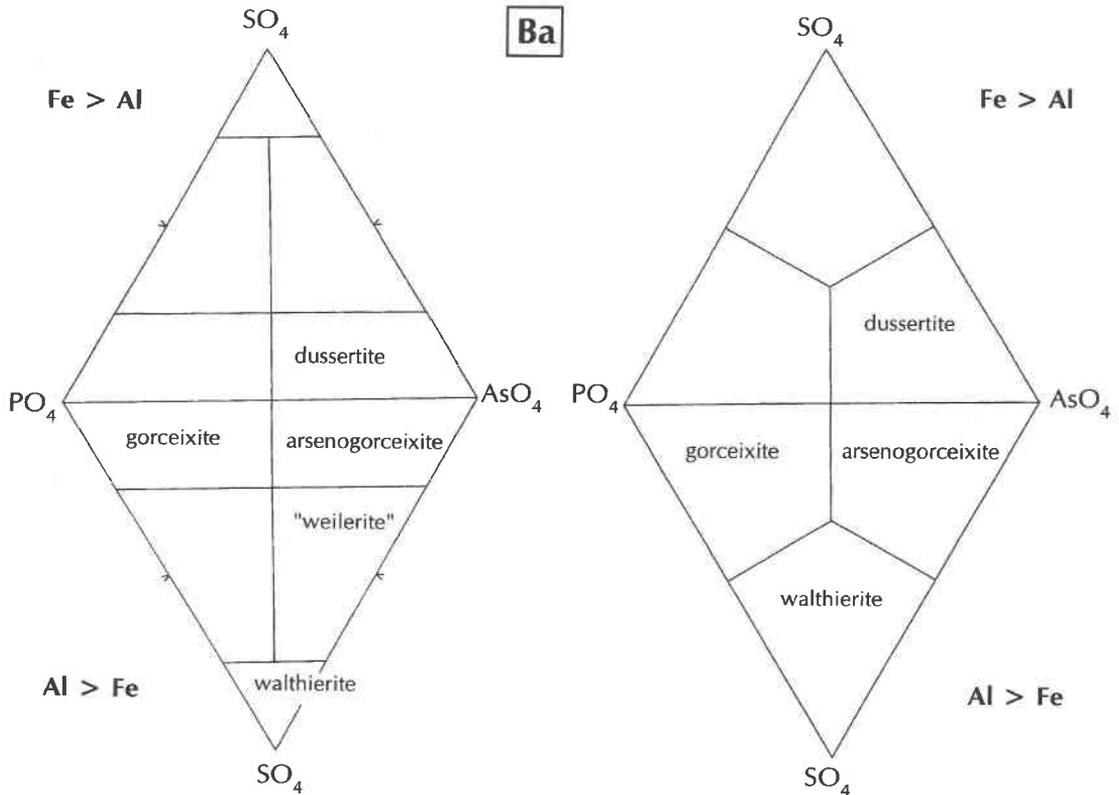


FIG. 3. Minerals of the alunite supergroup with Ba as the predominant *D*-site cation. Left diagram shows the current nomenclature, and diagram on right shows the effects of adopting a ternary system. "Weilerite" is not a valid species (see text).

The main concern in the Ba-dominant group is substitution at the *T* site; for walthierite, such substitution was not detected (Li *et al.* 1992). Likewise, compositions of gorceixite are typically close to, or at, the  $\text{PO}_4$  end-member. For arsenogorceixite, however, the type material shows  $\text{AsO}_4:\text{PO}_4 = 74:26$  (Walenta & Dunn 1993). The  $\text{AsO}_4$  (arsenogorceixite) and  $\text{PO}_4$  (gorceixite) end-members have been synthesized by Schwab *et al.* (1990, 1991).

"Weilerite" is included as a valid species in some modern compilations (Clark 1993, Gaines *et al.* 1997), but the mineral was discredited by the CNMMN (IMA 1968). As no quantitative chemical data had been published for the mineral (Fleischer 1962, 1967), the position on the  $\text{AsO}_4$ – $\text{SO}_4$  join is uncertain, and the mineral may have been identical to the more recently described arsenogorceixite. The removal of "weilerite" from the system is appropriate, thus leaving a gap between gorceixite–arsenogorceixite and walthierite (Fig. 3).

Dussertite is the only known member with  $\text{Fe} > \text{Al}$ , thus theoretically allowing six additional names to be introduced in the left diagram of Figure 3. In a ternary system, the potential six are reduced to two.

#### Ca predominance

All Ca-dominant minerals in the alunite supergroup are also Al-dominant (Fig. 4). Numerous compositions of crandallite are near that of the  $\text{PO}_4$  end-member, but substitution of S for P is extensive, and compositions extend well into the current field for woodhouseite (Stoffregen & Alpers 1987, Spötl 1990, Li *et al.* 1992), including compositions with formula  $\text{SO}_4 > \text{PO}_4$  (Wise 1975). For arsenocrandallite (Walenta 1981), the type material contains substantial Si in the *T* position:  $(\text{As}_{0.99}\text{P}_{0.75}\text{Si}_{0.26})$ . The As:P ratio is 57:43, which is well within the field for arsenocrandallite.

Adoption of a ternary system for the Ca–Al-dominant minerals would pose the problem of whether woodhouseite or huangite is to be used to designate the  $\text{SO}_4$  end-member. Type woodhouseite has  $\text{PO}_4:\text{SO}_4 = 54:46$  (Lemmon 1937), but it has long been accepted that either formula S or P can be predominant. The only composition given by Palache *et al.* (1951) has  $\text{P} > \text{S}$ , but more modern analyses, by electron microprobe, of woodhouseite from the type locality have shown both formula  $\text{P} > \text{S}$  and  $\text{S} > \text{P}$  (Wise 1975). Moreover, the

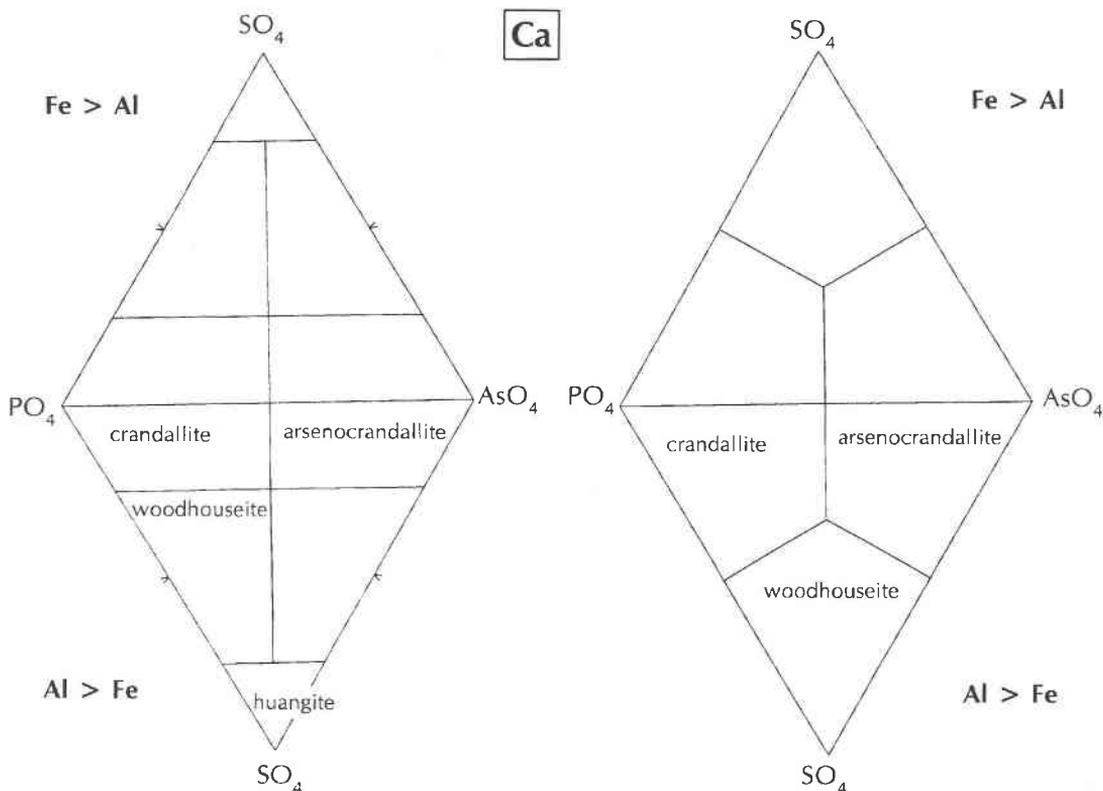


FIG. 4. Minerals of the alunite supergroup with Ca as the predominant *D*-site cation. Left diagram shows the current nomenclature, and diagram on right shows the effects of adopting a ternary system.

current CNMMN-approved nomenclature extends the composition of woodhouseite well into the  $\text{SO}_4$ -dominant field (Fig. 4). Accordingly, woodhouseite has been adopted to designate the field with  $\text{S} > \text{P}$  in the ternary system (Fig. 4).

#### *Sr* predominance

The minerals with Sr predominant in the *D* site are shown in Figure 5. The two minerals with  $\text{Fe} > \text{Al}$  are benauite and an associated unnamed mineral richer in  $\text{SO}_4$  (Walenta *et al.* 1996). The empirical formula for benauite is  $(\text{Sr}_{0.67}\text{Ba}_{0.16}\text{Pb}_{0.07}\text{Ca}_{0.01}\text{K}_{0.01})_{\Sigma 0.92}(\text{Fe}_{2.90}\text{Al}_{0.03})_{\Sigma 2.93}[(\text{PO}_4)_{1.48}(\text{SO}_4)_{0.48}(\text{AsO}_4)_{0.04}](\text{OH},\text{H}_2\text{O})_{8.3}$ , which was simplified by Walenta *et al.* (1996) as  $\text{SrFe}_3(\text{PO}_4)_2(\text{OH},\text{H}_2\text{O})_6$ . The proportion of atoms in the *T* site, however, is  $\text{P}:\text{S}:\text{As} = 74:24:2$ , which places the mineral just beyond the boundary designated by the simplified formula, and into the field of the unnamed  $\text{SO}_4$ -richer mineral (Fig. 5). The range in compositions (wt%) reported by Walenta *et al.* (1996) is  $\text{P}_2\text{O}_5$  17.98–19.93 (mean 18.53 used to calculate the formula),  $\text{As}_2\text{O}_5$  0.64–0.94 (mean 0.78),  $\text{SO}_3$  6.24–7.37 (mean 6.79), and thus

the compositions probably straddle the aforementioned boundary. The formula of the unnamed mineral is  $(\text{Sr}_{2.81}\text{Ba}_{0.06})\text{Fe}_{3.13}(\text{PO}_4)_{1.35}(\text{SO}_4)_{0.65}(\text{OH},\text{H}_2\text{O})_n$ , which places the mineral well beyond the field of benauite. If Scott's (1987) nomenclature system is to be adhered to, benauite requires redefinition as ideally  $\text{SrFe}_3[(\text{P},\text{S})\text{O}_4]_2(\text{OH},\text{H}_2\text{O})_6$ . The field shown as occupied by benauite in Figure 5 would therefore remain vacant.

For the Al-dominant group (Fig. 5), goyazite and svanbergite have long been used to indicate the  $\text{PO}_4$  and  $\text{PO}_4$ – $\text{SO}_4$  minerals, respectively. For svanbergite, the compositions listed in Palache *et al.* (1951) have formula  $\text{P} > \text{S}$ , but compositions with  $\text{S} > \text{P}$  also are known (Wise 1975); the CNMMN-approved system accepts that either S or P may predominate (Fig. 5). Type arsenogoyazite (Walenta & Dunn 1984) has  $\text{AsO}_4:\text{PO}_4 = 64:36$ , but the pure end-member has also been described (Zhang *et al.* 1987). Kemmlitzite (Hak *et al.* 1969) was regarded by Fleischer (1970) to be the arsenate analogue of svanbergite; analysis of type material, however, gave  $[(\text{AsO}_4)_{0.98}(\text{PO}_4)_{0.42}(\text{SO}_4)_{0.39}(\text{SiO}_4)_{0.19}]_{\Sigma 1.98}$ , which places kemmlitzite in the field of arsenogoyazite (Fig. 5). Re-examination of the holotype speci-

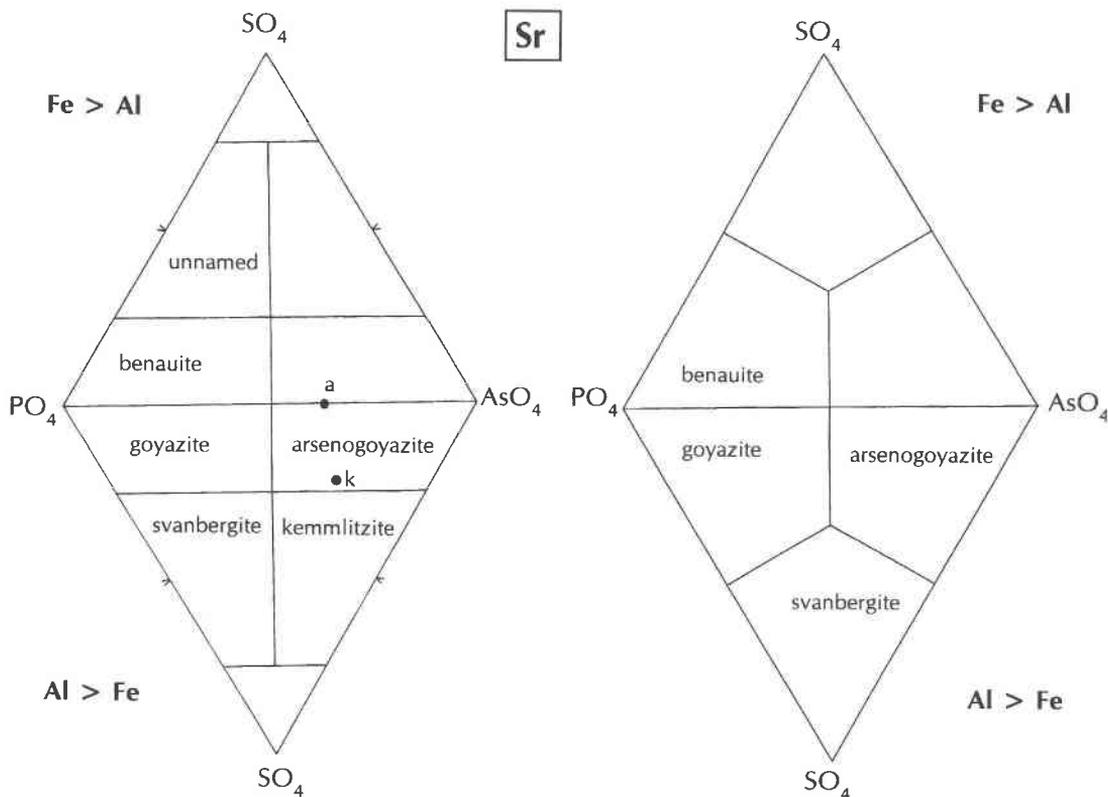


FIG. 5. Minerals of the alunite supergroup with Sr as the predominant *D*-site cation. Left diagram shows the current nomenclature; unnamed mineral is that of Walenta *et al.* (1996), point "a" is the composition of type arsenogoyazite, and "k" is that for type kemmlitzite. Right diagram shows the effects of adopting a ternary system.

men of kemmlitzite has shown it to be zoned and inhomogeneous (Novák *et al.* 1994). Kemmlitzite predates arsenogoyazite, and the latter was specifically defined as occupying the  $AsO_4$ -dominant field because adoption of the current (Scott) system of nomenclature had the effect of entrenching kemmlitzite as representative of  $SO_4$ -rich compositions (Fig. 5). Such a  $SO_4$ -rich composition has been reported by Novák *et al.* (1997). In view of the reported zoning and lack of homogeneity in type kemmlitzite, retention of the name arsenogoyazite would seem, arguably, to be preferred. In a ternary system, therefore, the most appropriate names are considered to be goyazite, arsenogoyazite, and svanbergite for the Al-dominant members, and benauite for the Fe-dominant mineral with  $PO_4$  greater than  $AsO_4$  or  $SO_4$  (Fig. 5).

#### *Bi* predominance

Minerals with Bi predominant in *D* are shown in Figure 6. Analyses of waylandite (Clark *et al.* 1986) and

zairite (van Wambeke 1975) are within the designated compositional fields. "Arsenowaylandite" is an unofficial name (Scharm *et al.* 1994) that has not been submitted to the CNMMN for approval. The anhydrous composition for  $TO_4 = 2$  varies from  $(Bi_{0.89}Sr_{0.05}Ca_{0.03})_{\Sigma 0.97}(Al_{2.90}Fe_{0.10})[(AsO_4)_{1.61}(SO_4)_{0.22}(PO_4)_{0.17}]$  to  $(Bi_{0.99}Sr_{0.05})_{\Sigma 1.04}(Al_{2.98}Fe_{0.04})[(AsO_4)_{1.81}(SO_4)_{0.19}]$ .

#### *Pb* predominance

Figure 7 is illustrative of the profusion of mineral names possible as the compositional fields within the alunite supergroup are filled. For Fe-dominant minerals, plumbojarosite, corkite, and beudantite have been in use for many years, and corkite and beudantite occupy the bulk of the field. Segnitite (Birch *et al.* 1992) and kintoreite (Pring *et al.* 1995) occupy the  $SO_4$ -poor fields that opened only as a consequence of the adoption of the current CNMMN-approved system of nomenclature. For Al-dominant minerals, plumbogummite and hinsdalite have been known for many years (Palache

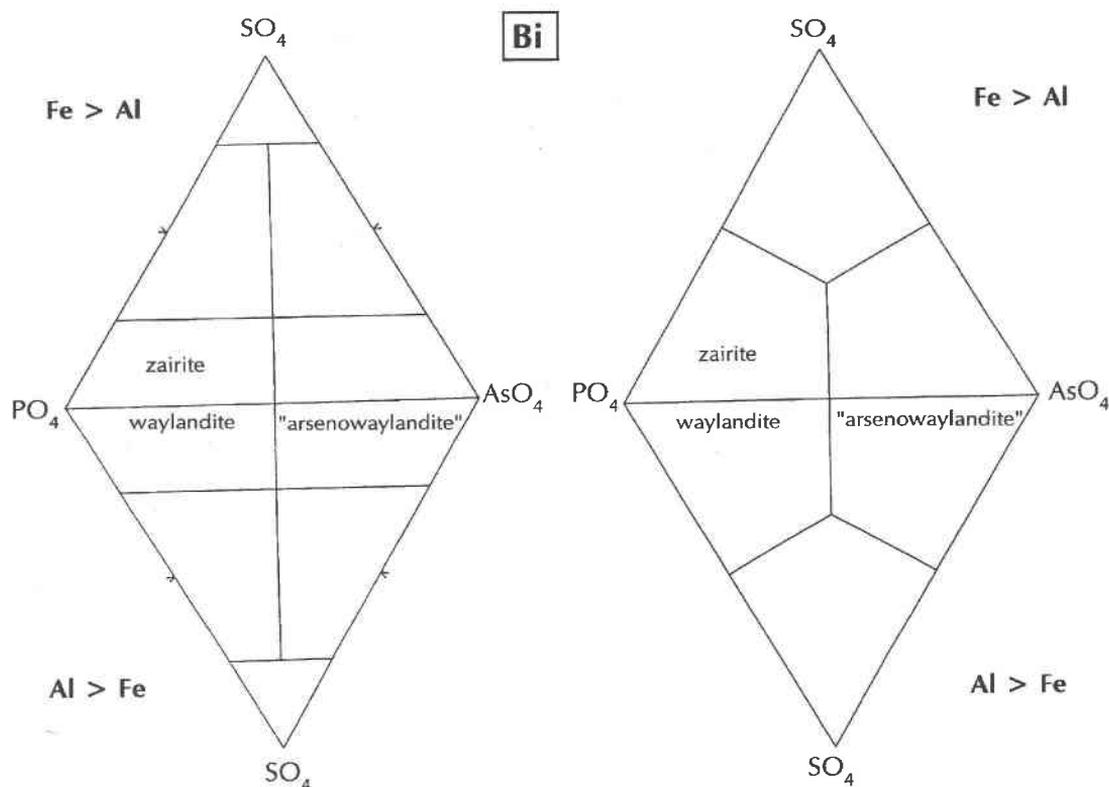


FIG. 6. Minerals of the alunite supergroup with Bi as the predominant *D*-site cation. Left diagram shows current nomenclature, and that on the right shows the effects of adopting a ternary system. "Arsenowaylandite" (Scharm *et al.* 1994) is not an approved name.

*et al.* 1951). Hidalgoite has the formula ratio  $SO_4:AsO_4 = 59:41$ , and the mineral was specifically named as the arsenate analogue of hinsdalite (Smith *et al.* 1953). Philipsbornite (Walenta *et al.* 1982) is somewhat unusual in its high Cr content in  $TO_4$ , for which  $AsO_4:CrO_4:SO_4 = 76:19:5$ . The small field at the  $SO_4$  apex (Figs. 7, 8) has been referred to as "plumboalunite" (Novák *et al.* 1994) and "plumbian alunite" (Sejkora *et al.* 1998). However, if it is accepted that (Cu + Zn) substitution is non-essential, then the Pb–Al sulfate in this field is osarizawaite.

Adoption of a ternary system for the Pb-dominant members would pose some difficulties. In the system with Fe predominant in *G*, corkite and beudantite have priority, thereby requiring the abandonment of the recently named kintoreite and segnitite. In the system with Al predominant in *G*, plumbogummite and hinsdalite have priority. Osarizawaite was named as the Al analogue of beaverite, but the requirement, as will be discussed, is that neither be retained as a mineral name. Plumbogummite and hinsdalite thus occupy the  $PO_4$ –

$SO_4$  join as shown in Figure 7. The consequence is that the field for hidalgoite, which includes the composition of type hidalgoite, would be overlapped by the new field for hinsdalite. Therefore, as was done for arsenogoyazite, philipsbornite would be retained to designate the As-dominant member.

#### REE predominance

The REE-bearing minerals are characterized by a predominance of trivalent cations in *D*, and it has been suggested (Scott 1987) that such minerals be classified as the florencite group. Accepted minerals within the group (Fig. 9) are florencite-(Ce), florencite-(La), florencite-(Nd), and arsenoflorencite-(Ce). Compositions corresponding to the La and Nd analogues of arsenoflorencite-(Ce) have been reported by Scharm *et al.* (1991, 1994), but the new names have not been submitted to the CNMMN for approval. Adoption of a ternary system for the REE-dominant members would not affect the current nomenclature.

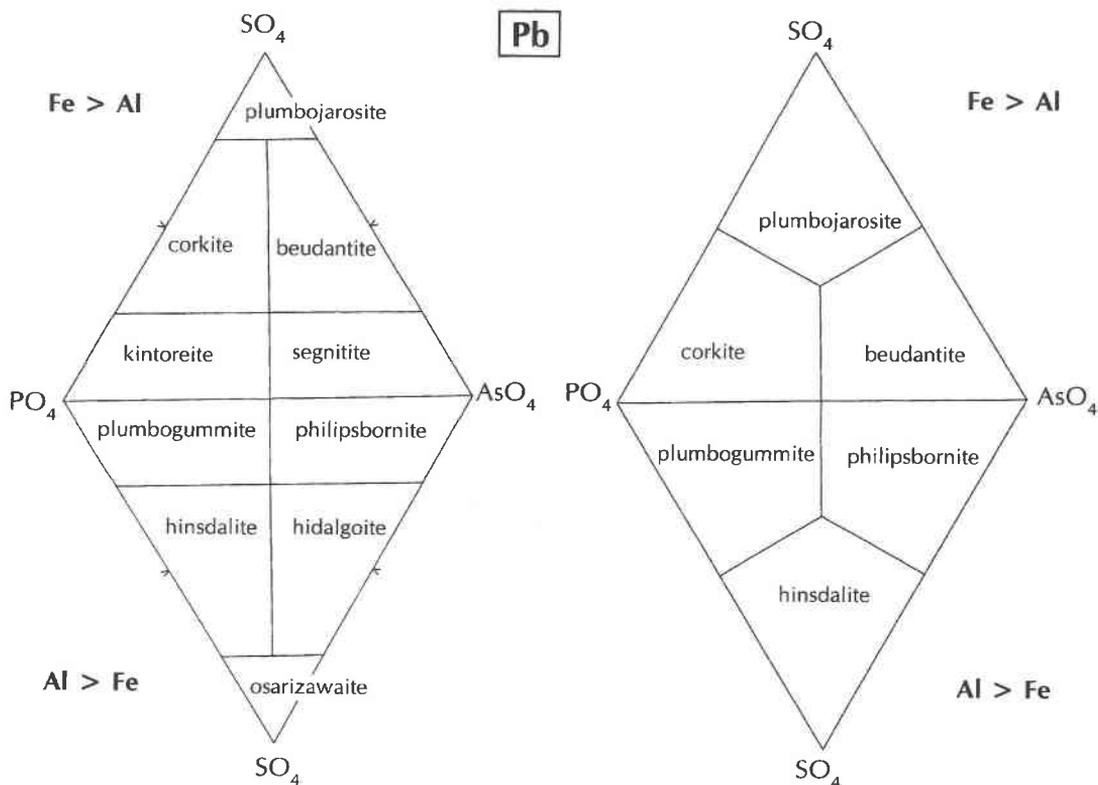


FIG. 7. Minerals of the alunite supergroup with Pb predominant as the *D*-site cation. Left diagram shows current nomenclature. The mineral at the Al–SO<sub>4</sub> apex is osarizawaite if it is accepted that Cu is non-essential. Compositions are shown by Sejkora *et al.* (1998) as extending into this field, which has been named “plumboalunite” by Novák *et al.* (1994). Diagram on right shows the results of adopting a ternary system.

#### Other minerals

Eylettersite is considered to be a Th-dominant member of the crandallite group, with P as the main cation in *TO*<sub>4</sub> (Table 3). However, the calculated formulas also incorporate substantial (H<sub>4</sub>O<sub>4</sub>) in *TO*<sub>4</sub>, and show excessive Al (≥3.5 mol) for *G* (Van Wambeke 1972). Such a *G*-cation excess is untenable for an alunite-type mineral, and eylettersite is considered to need restudy.

Gallobaudantite was defined as having subequal values of AsO<sub>4</sub> and SO<sub>4</sub>, and a predominance of Ga in *G* (Jambor *et al.* 1996). However, *TO*<sub>4</sub> compositions extend into the fields encompassed by Ga analogues of segnitite, corkite, and kintoreite, thus permitting the introduction of three additional new names for the Ga-dominant minerals. The distribution of *TO*<sub>4</sub> values in the Ga minerals is such that adoption of a ternary system would not reduce the number of potential new names. Also present with gallobaudantite is the Ga analogue of arsenocrandallite.

#### Other analogues

Numerous members of the alunite supergroup have been synthesized. Among those not known as minerals are the Rb<sup>+</sup> and Hg<sup>2+</sup> analogues of jarosite; the Hg-dominant and Pb-dominant phases described by Dutrizac & Kaiman (1976) and Dutrizac *et al.* (1980) are indexed with *c* = 33 Å, but no diffraction line at 11 Å was reported. Mumme & Scott (1966) also noted that the 11 Å line is absent from their synthetic plumbojarosite.

Tananaev *et al.* (1967) prepared analogues with Na, K, Rb, H<sub>3</sub>O, and NH<sub>4</sub> in *D*, and Ga in *G*. Only small amounts of various divalent metals other than Cu<sup>2+</sup> and Zn<sup>2+</sup> have been reported to be taken up by the alunite supergroup. The In<sup>3+</sup>, V<sup>3+</sup>, and Cr<sup>3+</sup> analogues have been synthesized (Dutrizac 1982, Dutrizac & Dinardo 1983, Lengauer *et al.* 1994); up to 0.6 mol V<sup>3+</sup> and 0.18 mol Cr<sup>3+</sup> have been reported in natural gorceixite (Johan *et al.* 1995), and V<sup>3+</sup> predominates at the *G* site in

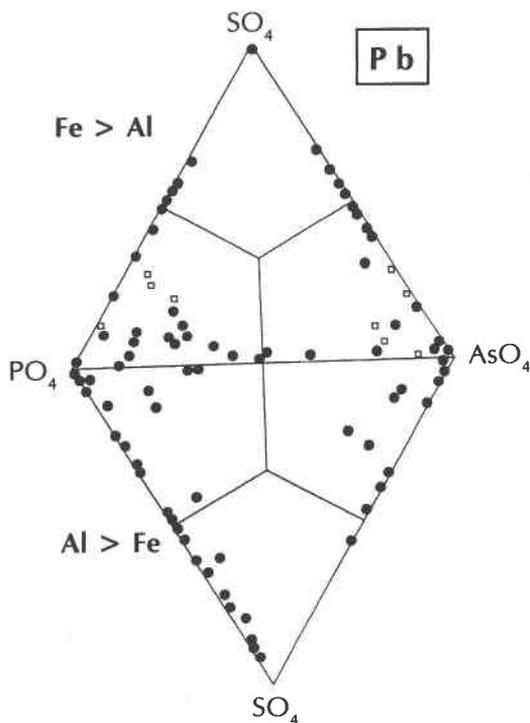


FIG. 8. Compositions of minerals within the Pb-dominant field, as in Figure 7, illustrating the extensive range of  $TO_4$  solid solution. Solid circles: abridged data from Sejkora *et al.* (1998); open squares are compositions from Rattray *et al.* (1996).

springcreekite (Table 3; Kolitsch *et al.* 1999a). Substantial  $Sb^{5+}$ -for- $Fe^{3+}$  substitution in dussertite has been documented by Kolitsch *et al.* (1999b).

The vanadate (Tudo *et al.* 1973), chromate (Powers *et al.* 1976, Cudennec *et al.* 1980), and selenate (Dutrizac *et al.* 1981, Breitinger *et al.* 1997) analogues have been synthesized, and substantial Cr has been reported in the  $T$  site in philipsbornite (Walenta *et al.* 1982). Some analyses reveal Si, which has been assigned either as  $SiO_4$  (as in kemmlitzite and eylettersite) or as amorphous  $SiO_2$ . Other substitutions, such as Nb (Lottermoser 1990) and  $CO_3$ , are possible but generally not significant; analyses showing percentage quantities of  $CO_2$  (*e.g.*, Förtisch 1967) predate the widespread use of the electron microprobe, and the high values reported in a few older analyses may be the result of inclusions of carbonate minerals.

Substitution of Cl for OH is rarely reported and, where detected, amounts are small. Accounts of F substitution are more common, and up to 4.7 wt% F has been determined to be present in gorceixite (Taylor *et al.* 1984).

## STRUCTURAL ASPECTS

The classification of the alunite supergroup discussed to this point has been mainly chemical, and structural aspects have been largely ignored. Numerous single-crystal X-ray structure studies of the supergroup have been done, and the findings are summarized in Table 4. Most of these studies have revealed that the minerals have trigonal symmetry, with  $a \approx 7$ ,  $c \approx 17$  Å, space group  $R\bar{3}m$ , but several exceptions have been documented.

The structures of alunite, jarosite, and plumbojarosite were first determined by Hendricks (1937), who concluded that because alunite and jarosite show strong pyroelectric properties, their space group must be  $R3m$  rather than  $R\bar{3}m$ . In contrast, plumbojarosite was determined to belong to  $R\bar{3}m$ , and the Pb atoms showed an ordered arrangement that had the effect of doubling the  $c$  axis, *i.e.*, the typical cell of  $a \approx 7$ ,  $c \approx 17$  Å increased to  $a \approx 7$ ,  $c \approx 34$  Å.

In addition to the data given in Table 4, several studies of synthetic analogues have been done, either by single-crystal or Rietveld methods. All of the studies, both on minerals and their synthetic equivalents, and on those not known as minerals, confirm that the basic topology of the structure remains the same regardless of chemical composition. Even where a monoclinic or triclinic system has been established, the structures are strongly pseudotrigonal.

The basic structural motif of the supergroup consists of  $TO_4$  tetrahedra and variably distorted  $R$ -cation octahedra, the latter corner-shared to form sheets perpendicular to the  $c$  axis. Substitutions involving  $G$  therefore mainly affect the  $a$  dimension, and  $a$  increases as Fe-for-Al substitution increases. The  $TO_4$  tetrahedra, which are aligned along  $[001]$ , occur as two crystallographically independent sets within a layer; one set of  $TO_4$  points upward along  $c$ , and this set alternates with another pointing downward. The oxygen and hydroxyl form an icosahedron, amidst which is the  $D$  cation. For compositions with identical  $T$  in  $TO_4$ , the length of  $c$  is mainly influenced by the size of the  $D$  cation.

Symmetry changes arise principally because of order-disorder relationships among the  $TO_4$  tetrahedra, or because of order-disorder or distortion involving  $D$  sites. To maintain the space group  $R\bar{3}m$ , the  $SO_4$ - $PO_4$ - $AsO_4$  tetrahedra must be disordered; ordering, as has been found in corkite and gallobeudantite, reduces the symmetry to  $R3m$ .

A second principal effect is related to the presence of a divalent cation in  $D$ . In such a case, the standard jarosite-type formula  $D^+G^{3+}_3(SO_4)_2(OH)_6$  becomes either  $D^{2+}[G^{3+}_3(SO_4)_2(OH)_6]_2$  (ordered) or,  $D^{2+}_{1/2}G^{3+}_3(SO_4)_2(OH)_6$  (disordered). Thus in plumbojarosite, for example, the  $D$ -site cation is  $Pb^{2+}$ , and to maintain electroneutrality, half of the  $D$  sites are vacant. Ordering of the Pb and these vacancies produces a supercell, which is manifested as a doubling of the  $c$  axis to 33–34 Å.

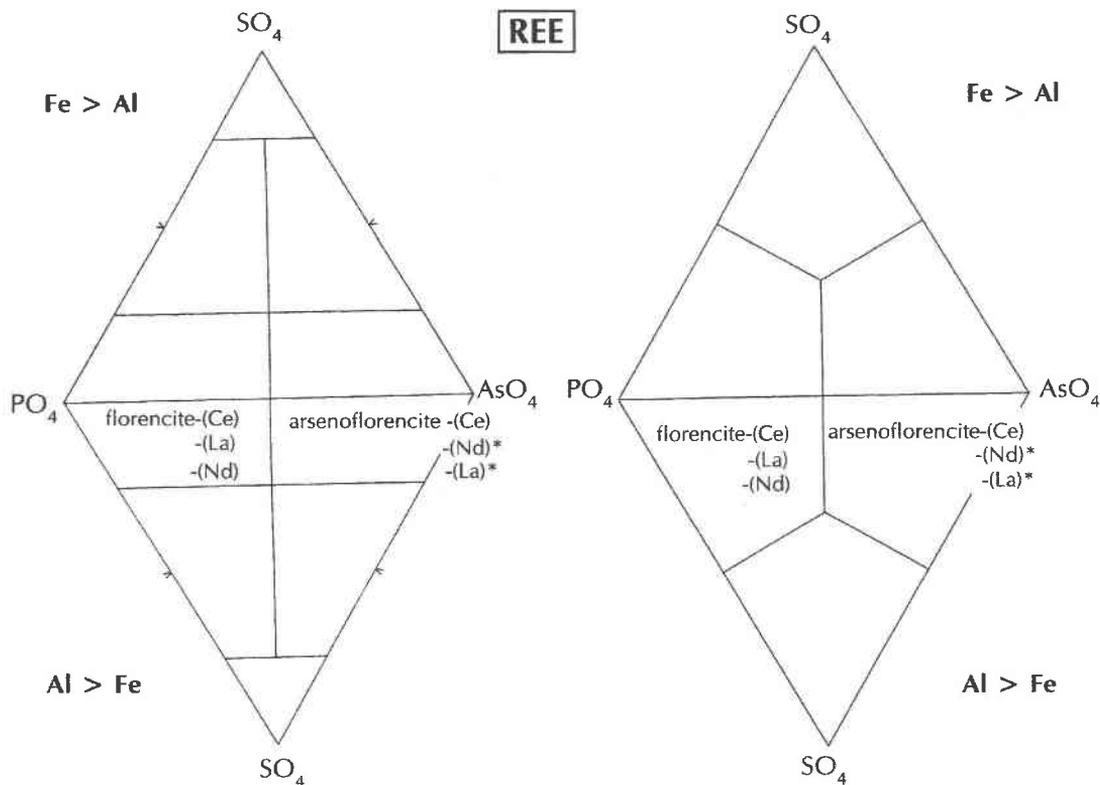


FIG. 9. Minerals of the alunite–jarosite supergroup with *REE* as the predominant *D*-site cations. “Arsenoflorencite-(La)\*” and “arsenoflorencite-(Nd)\*” are names (Scharm *et al.* 1991, 1994) that have not been submitted to the CNMMN for a vote. Diagram on right shows the effects of adopting a ternary system.

A third principal effect is related to the charge of the  $TO_4$  group. Where  $TO_4$  is  $PO_4$  or  $AsO_4$  rather than  $SO_4$ , an extra proton is required to maintain charge balance. In crandallite, Blount (1974) concluded that the formula takes the form  $CaAl_3[PO_3O_{1/2}(OH)_{1/2}]_2(OH)_6$ , thereby achieving compensation by having partial substitution of hydroxyl for oxygen of the  $PO_4$  tetrahedron. Radoslovich (1982), however, determined that such a configuration would not be permitted in gorceixite because of the larger size of Ba. He therefore concluded that the formula of gorceixite is best represented by  $BaAl_3(PO_4)(PO_3\cdot OH)(OH)_6$ .

It is possible, therefore, that order may exist without the necessity of having the *T* site occupied by different elements (As, P, S). Furthermore, the crystal-structure determination ( $R = 0.0195$ ) of unnamed  $PbFe_3(PO_4)_2(OH, H_2O)_6$  by J.T. Szymański (Table 4) revealed that distortion at the Pb sites leads to two independent Pb atoms in the structure. Thus, a superstructure is formed in this mineral without the necessity of having *D*-site vacancies.

Szymański (1985) has pointed out additional aspects relevant to the crystal chemistry of the alunite supergroup. Among these is the report by Loiacono *et al.* (1982) that the space group of their natural alunite is  $R\bar{3}m$ . For hydronium jarosite – schlossmacherite, Szymański (1985) pointed out that “... the hydronium ion, whether it remains in its original  $H_3O^+$  form or whether it is reduced to water, cannot have a centre of symmetry and cannot be located at a centre of symmetry. Any hydronium-for-cation substitution will destroy the symmetry, and reduce the space group to  $R\bar{3}m$  or lower. This is not to say that the hydrogen atoms of the hydronium ion or the water molecule cannot be statistically distributed or dynamically disordered, and hence give the structure the overall appearance of having a centre of symmetry.”

As with hydronium, the  $NH_4$  ion cannot be accommodated within  $R\bar{3}m$  (Arkhipenko *et al.* 1985, Serna *et al.* 1986). However, as discussed by Szymański (1985), in the absence of incontrovertible structural data, the space group of alunite minerals should be considered as  $R\bar{3}m$ .

TABLE 4. SINGLE-CRYSTAL X-RAY STRUCTURE STUDIES OF MINERALS IN THE ALUNITE SUPERGROUP

| Name            | Composition, comments   | $a$ , Å | $c$ , Å | space group | Ref. |
|-----------------|---|---------|---------|-------------|------|
| alunite         | composition not given   | 6.970   | 17.27   | $R\bar{3}m$ | 1    |
| natroalunite    | $(\text{Na}_{0.56}\text{K}_{0.42})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$  | 6.990   | 16.095  | $R\bar{3}m$ | 2    |
| minamiite       | $(\text{Na}_{0.36}\text{K}_{0.1}\text{Ca}_{0.27}\square_{0.27})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$   | 6.981   | 33.490  | $R\bar{3}m$ | 3    |
| jarosite        | not given; synthetic  | 7.305   | 17.190  | $R\bar{3}m$ | 4    |
|                 | not given; natural  | 7.304   | 17.268  | $R\bar{3}m$ | 5    |
| gorceixite      | —   |         |         | monoclinic  | 6    |
|                 | $\text{BaAl}_3(\text{PO}_4)(\text{PO}_3\text{-OH})(\text{OH})_6$  |         |         | monoclinic* | 7    |
| crandallite     | $\text{Ca}_{0.99}\text{Al}_{2.99}\text{P}_{2.00}\text{CaAl}_3[\text{PO}_3(\text{O}_{1/2}(\text{OH})_{1/2})_2](\text{OH})_6$                                     | 7.005   | 16.192  | $R\bar{3}m$ | 8    |
| woodhouseite    | not given; $\text{CaAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$   | 6.993   | 16.386  | $R\bar{3}m$ | 9    |
| goyazite        | not given; $\text{SrAl}_3[\text{PO}_3(\text{O}_{1/2}(\text{OH})_{1/2})_2](\text{OH})_6$   | 7.015   | 16.558  | $R\bar{3}m$ | 10   |
| svanbergite     | not given; $\text{SrAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$   | 6.992   | 16.567  | $R\bar{3}m$ | 5    |
| osarizawaite    | $\text{Pb}(\text{Al}_{1.62}\text{Cu}_{0.98}\text{Fe}_{0.15}\text{Zn}_{0.02})(\text{SO}_4)_2(\text{OH})_6$   | 7.075   | 17.248  | $R\bar{3}m$ | 11   |
| plumbojarosite  | not given; structure formula as below   | 7.20    | 33.60   | $R\bar{3}m$ | 12   |
|                 | $\text{Pb}_{0.99}\text{Fe}_{3.85}\text{S}_{4.06}\text{Pb}[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]_2$   | 7.3055  | 33.675  | $R\bar{3}m$ | 13   |
| beudantite      | $\text{Pb}_{0.99}(\text{Fe}_{2.96}\text{Cu}_{0.02}\text{Zn}_{0.01})(\text{SO}_4)_{0.99}(\text{AsO}_4)_{0.99}(\text{OH})_{6.07}$                                 | 7.339   | 17.034  | $R\bar{3}m$ | 14   |
|                 | $\text{Pb}_{1.00}(\text{Fe}_{2.54}\text{Al}_{0.46})(\text{AsO}_4)_{1.07}(\text{SO}_4)_{0.99}(\text{OH},\text{H}_2\text{O})_6$                                   | 7.3151  | 17.0355 | $R\bar{3}m$ | 15   |
|                 | $\text{Pb}_{1.00}(\text{Fe}_{2.45}\text{Al}_{0.55})(\text{AsO}_4)_{1.05}(\text{SO}_4)_{0.97}(\text{OH},\text{H}_2\text{O})_6$                                   |         |         | triclinic** | 15   |
| corkite         | $\text{Pb}_{0.96}(\text{Fe}_{2.99}\text{Cu}_{0.02})[(\text{PO}_4)_{1.00}(\text{SO}_4)_{0.96}(\text{AsO}_4)_{0.02}](\text{OH})_{6.04}$                           | 7.280   | 16.821  | $R\bar{3}m$ | 16   |
| hinsdalite      | $\text{PbAl}_3[(\text{PO}_4)_{1.31}(\text{SO}_4)_{0.62}](\text{OH},\text{H}_2\text{O})_6$   | 7.029   | 16.789  | $R\bar{3}m$ | 17   |
| gallobeudantite | $\text{Pb}_{1.04}(\text{Ga}_{1.51}\text{Al}_{1.14}\text{Fe}_{0.33}\text{Zn}_{0.18}\text{Ge}_{0.03})(\text{AsO}_4)_{1.04}(\text{SO}_4)_{0.96}(\text{OH})_{6.50}$ | 7.225   | 17.03   | $R\bar{3}m$ | 18   |
| plumbogummite   | $\text{PbAl}_3[(\text{PO}_4)_{1.30}(\text{AsO}_4)_{0.10}](\text{OH},\text{H}_2\text{O})_6$  | 7.039   | 16.761  | $R\bar{3}m$ | 17   |
| kintoreite      | $\text{PbFe}_3(\text{PO}_4)_3(\text{AsO}_4)_4(\text{SO}_4)_{0.3}(\text{OH},\text{H}_2\text{O})_6$   | 7.3310  | 16.885  | $R\bar{3}m$ | 19   |
| dusserite       | $\text{Ba}(\text{Fe}^{3+}_{0.84}\text{Sb}^{5+}_{0.16})(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_6$   | 7.410   | 17.484  | $R\bar{3}m$ | 20   |
| unnamed         | $\text{Pb}_{0.99}\text{Fe}_{2.91}(\text{PO}_4)_{1.91}(\text{SO}_4)_{0.09}(\text{OH},\text{H}_2\text{O})_{5.92}$   | 7.2885  | 33.680  | $R\bar{3}m$ | 21   |
| florencite-(Ce) | $(\text{Ce}_{0.54}\text{La}_{0.27}\text{Nd}_{0.11}\text{Sm}_{0.04}\text{Ca}_{0.04})\text{Al}_3(\text{PO}_4)_2(\text{OH})_6$                                     | 6.972   | 16.261  | $R\bar{3}m$ | 22   |

\*  $a$  12.195,  $b$  7.040,  $c$  7.055 Å,  $\beta$  125.10°. See also Blanchard (1989).

\*\*  $a$  7.319,  $b$  7.309,  $c$  17.032 Å,  $\alpha$  90.004,  $\beta$  90.022,  $\gamma$  119.974°.

References: 1 Wang *et al.* (1965), 2 Okada *et al.* (1982), 3 Ossaka *et al.* (1982), 4 Menchetti & Sabelli (1976), 5 Kato & Miura (1977), 6 Radoslovich & Slade (1980), 7 Radoslovich (1982), 8 Blount (1974), 9 Kato (1971, 1977), 10 Kato (1971, 1987), 11 Giuseppetti & Tadini (1980), 12 Hendricks (1937), who also gave results for alunite and jarosite, 13 Szymański (1985), 14 Giuseppetti & Tadini (1989), 15 Szymański (1988), 16 Giuseppetti & Tadini (1987), 17 Kolitsch *et al.* (1999c), 18 Jambor *et al.* (1996), 19 Kharisun *et al.* (1997), 20 Kolitsch *et al.* (1999b), 21 IMA No. 93-039, 22 Kato (1990).

### Formula calculations

Various methods have been used to calculate the formulas of minerals in the alunite supergroup. Among the most common are normalization to 14 oxygen atoms, or to  $\text{TO}_4 = 2$ . Some authors (*e.g.*, Scharm *et al.* 1991, Novák & Jansa 1997, Sejkora *et al.* 1998) have used  $G_3(\text{TO}_4)_2 = 5$ . Use of  $\text{TO}_4 = 2$  is preferred here because nonstoichiometry in both  $D$  and  $G$  is common, particularly in synthetic samples. To paraphrase Szymański (1985), use of  $\text{TO}_4 = 2$  has a sound structural basis because "... it is inconceivable to visualize a stable jarosite structure with vacancies in the  $[\text{TO}_4]$  layers as well."

A second difficulty in formula calculations is that hydronium cannot be determined directly. This problem is not significant for most of the minerals in the supergroup, but it does emphasize the precarious status of the sole composition available for schlossmacherite, for which  $D$  is  $[(\text{H}_3\text{O})_{0.32}\square_{0.28}\text{Ca}_{0.26}\text{Na}_{0.07}\text{K}_{0.05}\text{Sr}_{0.01}\text{Ba}_{0.01}]$ .

### Significance of the supercell

Regardless of symmetry variations (Table 4), the topology of the unit cell of all minerals in the family can be related to a rhombohedral cell that has hexagonal dimensions of  $a \approx 7$ ,  $c \approx 17$  Å. The development of a supercell with  $c = 2 \times 17$  Å can arise because of ordering of  $D$ -site cations, regardless of whether  $D$  contains vacancies or is filled completely. Moreover, order does not require the presence of a combination of monovalent and divalent cations in  $D$ , but can take place solely with monovalent ions (Dutrizac & Jambor 1984). Many rapidly crystallized synthetic products show signs of an ordered structure, and it is inconceivable that some of the commonly more slowly crystallized natural minerals would not be ordered. On the other hand, synthetic  $\text{Pb-H}_3\text{O}$  systems show various degrees of disorder, and synthetic plumbojarosite without detectable diffraction effects due to a superstructure is well known. At the opposite extreme, in their X-ray structure studies both

Hendricks (1937) and Szymański (1985) used plumbojarosite from the Tintic Standard mine, Utah, for which an exceptionally high degree of order was found; in the case of the latter author at least, the material was selected specifically because X-ray powder patterns had previously indicated an exceptionally high degree of order to be present.

If minerals in the alunite supergroup are to be named simply on the presence or absence of the *c*-axis superstructure, the potential for the introduction of "trivial" names will increase enormously. I believe that detection of the superstructure will become more common once there is an increased awareness of the significance of the 11 Å powder-diffraction line or peak.

#### RECOMMENDATIONS ON NOMENCLATURE

If the proliferation of mineral names in the alunite supergroup is to be avoided, two properties or factors must be addressed: (a) crystallographic, and (b) chemical. In some cases these factors are independent, as for example minamiite and as-yet-unnamed mineral IMA No. 93-039, both of which are distinguished from previously named minerals solely on the presence of standard cell *versus* supercell relationships. The fundamental topology of the alunite structure remains the same regardless of space group or symmetry changes. The fundamental cell is rhombohedral, space group  $R\bar{3}m$ , with  $a \approx 7$  and  $c = 17$  Å as expressed with hexagonal parameters. Slight distortion of this cell can lead to orthorhombic (Jambor & Dutrizac 1983), monoclinic (Radoslovich 1982), or triclinic (Szymański 1988) polymorphs, and patterns of order of various kinds can lead to a doubling of *c*.

#### Crystallographic aspects

Various systems have been used to accommodate structural changes within a mineral group while maintaining a comprehensible nomenclature. For example, Pring *et al.* (1990) used the CNMMN-approved name *baumhauerite-2a* to designate a silver-bearing mineral having a superstructure derived from a *baumhauerite-*

like structure. For minerals of the alunite supergroup, a similarly simplified system of nomenclature system could be adopted such that: (a) no modifier accompany the mineral name if the unit cell has not been determined, or if only one structure type is known; (b) if there is a need to distinguish between the conventional cell and the supercell, the former should be designated *1c*, and the latter *2c*, each followed by the standard (CNMMN-approved) abbreviation for the unit-cell type [*H*: hexagonal, *R*: rhombohedral, *M*: monoclinic, *A*: triclinic (anorthic), *etc.*]. Note that it is important to retain the *c* to avoid confusion with the nomenclature designations for polytypes. Thus, for example, rhombohedral plumbojarosite lacking a superstructure would be named *plumbojarosite-1cR*, and that with a superstructure would be *plumbojarosite-2cR*. Monoclinic *gorceixite* remains as *gorceixite*, but if a doubled *c* axis for the monoclinic cell were to be found, the nomenclature would distinguish *gorceixite-1cM* and *gorceixite-2cM*. It has not yet been proved that *gorceixite* with a conventional rhombohedral cell exists, but such a mineral would simply be designated as *gorceixite-1cR*.

Adoption of such a system would involve the following nomenclature changes or revisions in:

1. Minamiite, which is fundamentally different from natroalunite only in order-disorder relationships, is *natroalunite-2cR*.
2. Monoclinic *gorceixite*, assuming that the rhombohedral form also exists, would not be entitled to a trivial name.
3. Triclinic *crandallite*, reported by Cowgill *et al.* (1963), if verified, would be designated *crandallite-1cA*.
4. Triclinic *beudantite* reported by Szymański (1988) would be designated with the suffix *1cA*.
5. Unnamed rhombohedral mineral IMA No. 93-039 would likewise adopt the appropriate already established name, together with the suffix *2cR*.
6. *Beaverite* is cuprian plumbojarosite without superstructure reflections. *Beaverite* is therefore cuprian plumbojarosite-*1cR*.
7. Orthorhombic *jarosite* with the doubled *c* and composition  $K_{0.96}Fe_{2.90}(SO_4)_2(OH)_{6.18}$  (Jambor & Dutrizac 1983) is *jarosite-2cO*.

TABLE 5. SUMMARY OF POTENTIALLY CHANGED NOMENCLATURE FOR A TERNARY COMPOSITIONAL SYSTEM

| Previous name | New                               | Previously unnamed             | New                    |
|---------------|-----------------------------------|--------------------------------|------------------------|
| minamiite     | <i>natroalunite-2cR</i>           | triclinic <i>crandallite</i>   | <i>crandallite-1cA</i> |
| huangite      | <i>woodhouseite-2cR</i>           | triclinic <i>beudantite</i>    | <i>beudantite-1cA</i>  |
| kemmlitzite   | <i>arsenogoyazite</i>             | rhombohedral <i>kintoreite</i> | <i>corkite-2cR</i>     |
| beaverite     | cuprian <i>plumbojarosite-1cR</i> | orthorhombic <i>jarosite</i>   | <i>jarosite-2cO</i>    |
| kintoreite    | <i>corkite</i>                    |                                |                        |
| segnite       | <i>beudantite</i>                 |                                |                        |
| hidalgoite    | <i>hinsdalite</i>                 |                                |                        |
| osarizawaite  | <i>hinsdalite</i>                 |                                |                        |

### Compositional aspects

Two approaches are used, namely, (a) an evaluation in terms of the existing (Scott 1987) system of nomenclature, and (b) an evaluation on the basis of a ternary compositional system. Neither system takes into account possible miscibility gaps, which have not been proved to exist within the alunite supergroup, although such a possibility is highly likely. For example, Stoffregen & Cygan (1990) have argued that a miscibility gap may exist on the simple alunite–natroalunite binary join if these minerals crystallize under equilibrium conditions. Under nonequilibrium conditions, however, a gap is not evident. Numerous proposals for miscibility gaps among minerals other than the alunite supergroup can be found in the literature, but in many cases the purported gaps simply reflect plots of existing chemical data, without good evidence that the gaps cannot be breached. For the alunite supergroup, it is likely that it will be many years before miscibility gaps can be incontrovertibly demonstrated to exist. This aspect, therefore, is not taken into consideration in this review of nomenclature; nevertheless, it is evident that, over the long term, the multicompartiment system in current use for alunite nomenclature would fare less well in terms of avoiding complexity than would a ternary system.

If a ternary system of nomenclature, combined with the superstructure–symmetry notation, were adopted for the alunite supergroup, the following would result:

1. Alunite group with monovalent ions in *D*: removal of minamiite, beaverite, and osarizawaite, and expansion of the compositional fields as shown in Figure 2 (right).

2. Ba predominant in *D* (Fig. 3): the compositional field available for a “weilerite”-type mineral disappears.

3. Ca predominant in *D* (Fig. 4): huangite is woodhouseite-2*cR*.

4. Sr predominant in *D* (Fig. 5): kemmlitzite is no longer retained.

5. Bi predominant in *D* (Fig. 6): no change other than expansion of the compositional fields.

6. Pb predominant in *D* (Fig. 7): for  $Fe > Al$ , corkite and beudantite have priority, so that kintoreite and segnitite are no longer retained. Similarly, hinsdalite has priority over hidalgote, and the latter is no longer retained.

7. REE predominant in *D* (Fig. 8): no change other than expansion of the compositional fields.

The nomenclature changes are summarized in Table 5.

### CONCLUSIONS

Independent of any *new* nomenclature proposals, the following minerals and names require reappraisal:

(a) Beaverite:  $Cu:(Fe,Al)$  is not 1:2, and Fe is predominant.

(b) Osarizawaite:  $Cu:(Al,Fe)$  is not 1:2, and Al is predominant.

(c) Minamiite is compositionally equivalent to natroalunite, but has  $c \approx 33 \text{ \AA}$ . Mineral IMA No. 93–039 (Table 4) could be given a trivial name on identical grounds.

(d) Benauite: the compositional field does not coincide with that of the ideal formula.

(e) Eylettersite requires re-examination because the formula(s) exceed acceptable limits for minerals of the alunite supergroup.

(f) The possible triclinic analogue of crandallite (Cowgill *et al.* 1963, Blount 1974) requires re-examination both with respect to composition and symmetry; no single-crystal X-ray study has been done, and the formula deviates significantly from that of the alunite supergroup.

(g) Orpheite, a Pb–Al phosphate-sulfate, is variously classified as in (Gaines *et al.* 1997) or out (Mandarino 1999) of the alunite supergroup. Fleischer (in Fleischer *et al.* 1976) concluded that orpheite is hinsdalite, but orpheite has retained species status.

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