

## NOMENCLATURE OF THE ALUNITE SUPERGROUP: DISCUSSION

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The alunite–jarosite minerals are defined as having the general formula  $AB_3(XO_4)_2(OH)_6$ , where  $A$  is a large ion in 12-fold coordination (e.g., K, Na, Ca, Pb, REE),  $B$  is usually Fe or Al, and the  $XO_4$  anions are usually  $SO_4$ ,  $PO_4$  or  $AsO_4$ . Because of the potential for a large number of complex substitutions in the supergroup and to avoid a proliferation of mineral names, Scott (1987) proposed that compositional limits be set on some previously ill-defined alunite–jarosite minerals (*viz.*, alunite, jarosite, hinsdalite, corkite, goyazite, plumbogummite, florencite and the now discredited “lusungite”). Those boundaries were set at 0.5 and 1.5 formula units of ( $SO_4$ ) in the  $XO_4$  sites. That proposal was accepted by the Commission on New Minerals and Mineral Names (CNMNMN) of the International Mineralogical Association and used as the basis for a classification system for the alunite–jarosite minerals. That system is based on 1) Fe or Al dominance in  $B$  sites for the initial subdivision (because that is reflected crystallographically and is easily measured by X-ray diffractometry), and then 2) the dominant cation in the  $A$  site, 3) the proportion of  $SO_4$ ,  $AsO_4$  and  $PO_4$  in  $XO_4$  sites with boundaries at 0.5 and 1.5 formula units of  $SO_4$ , and 4) the use of adjectival modifiers to indicate significant amounts of other ions in  $A$  or  $B$  sites. The system was intended to be a practical one which, at least in the initial subdivision into Al- and Fe-rich groups (using differences in cell dimensions, which can be determined by X-ray diffractometry), did not need full chemical analysis. However, it does not seem to have gotten widespread acceptance, with most subsequent authors preferring to retain the historical division into alunite, beudantite and crandallite groups (e.g., Mandarin 1999, Gaines *et al.* 1997), *i.e.*, grouping Fe- and Al-rich analogues together and requiring compositional data for even preliminary classification. Thus it is gratifying that the classification outlined by Jambor (1999) relies upon the  $B$ -site occupancy, at least for its secondary divisions.

Since my proposal, there have been many more members of the alunite–jarosite family reported; there are now more than 40 members, and so Jambor’s (1999)

review is timely. His systematic examination of minerals relative to each different  $A$ -site-dominant cation is very clear and succinct. This careful work has led to a call for critical appraisal of currently used names, like kemmlitzite, which plot outside their ideal fields, and a cessation of the use of discredited names like “weilerite”. I concur with such a call. However, he also advocates a new system of classification based on a ternary system for the  $SO_4$ ,  $AsO_4$  and  $PO_4$  anions. Such a system is in accord with current general CNMNMN recommendations for solid solutions (Nickel 1992), and could reduce the need for named members of a particular  $A$ -site-dominant group of minerals from 10 to 6. For the whole alunite–jarosite family, this could potentially reduce mineral names by 40%. This initially attractive proposition needs further evaluation. Does it significantly reduce mineral names, and does it really help workers in the field? For minerals with cations other than Pb in  $A$  sites, apart from the elimination of kemmlitzite (for which the type material plots in the field of arsenogoyazite in any case), only huangite would be eliminated if his proposal were accepted. For Pb-rich minerals, where 11 named species are currently recognized, five minerals could be potentially eliminated (Fig. 1). Thus this Pb-rich grouping will be considered in more detail below.

In the Pb–Fe-rich members of the supergroup, the classification proposed by Jambor (1999) leads to corkite having a possible composition  $PbFe_3H(PO_4)_2(OH)_6$  rather than  $PbFe_3(PO_4)(SO_4)(OH)_6$ , as currently defined. His proposed classification implies that there is nothing special about having one divalent and one trivalent anion in the  $XO_4$  sites. However, the work of Blount (1974) and Radoslovich (1982) indicates that one of the  $PO_4$  anions in the “double phosphate” members is actually protonated and divalent, *i.e.*,  $(PO_3OH)^{2-}$ . Thus the major change in moving from a Pb–Fe– $SO_4$  to Pb–Fe– $PO_4$  mineral occurs where one of the sulfate groups is replaced. Ideally, the change can be envisaged as  $Pb_{0.5}Fe_3(SO_4)_2(OH)_6 \rightarrow PbFe_3(PO_4)(SO_4)(OH)_6 \rightarrow PbFe_3H(PO_4)_2(OH)_6$ , with the first step involving the

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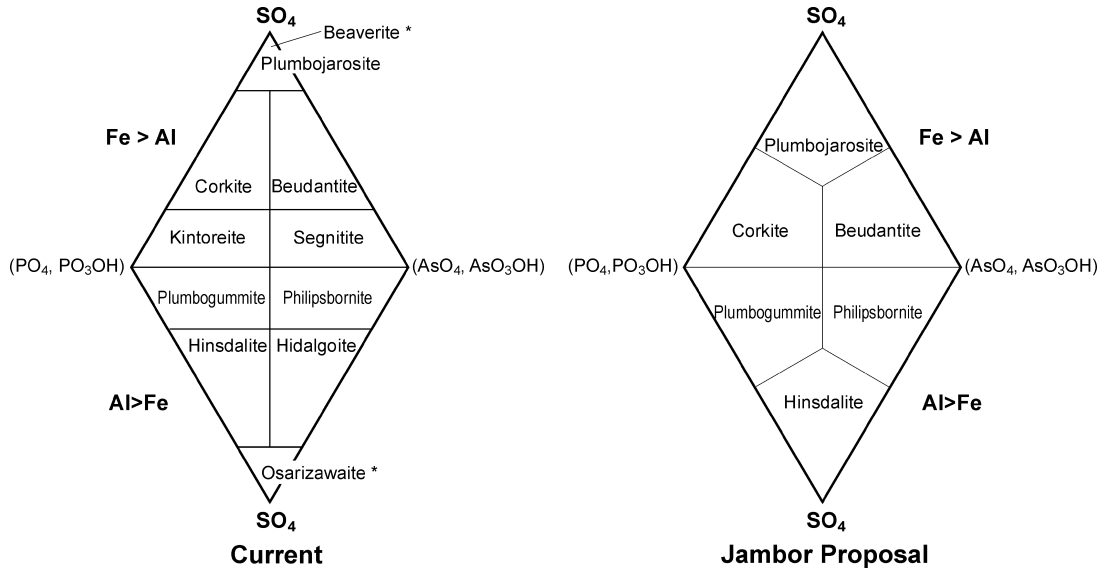


FIG. 1. Minerals of the alunitic–jarosite family with dominant Pb in the *A* sites (modified from Jambor 1999). \* substantial Cu present in *B* sites in these minerals.

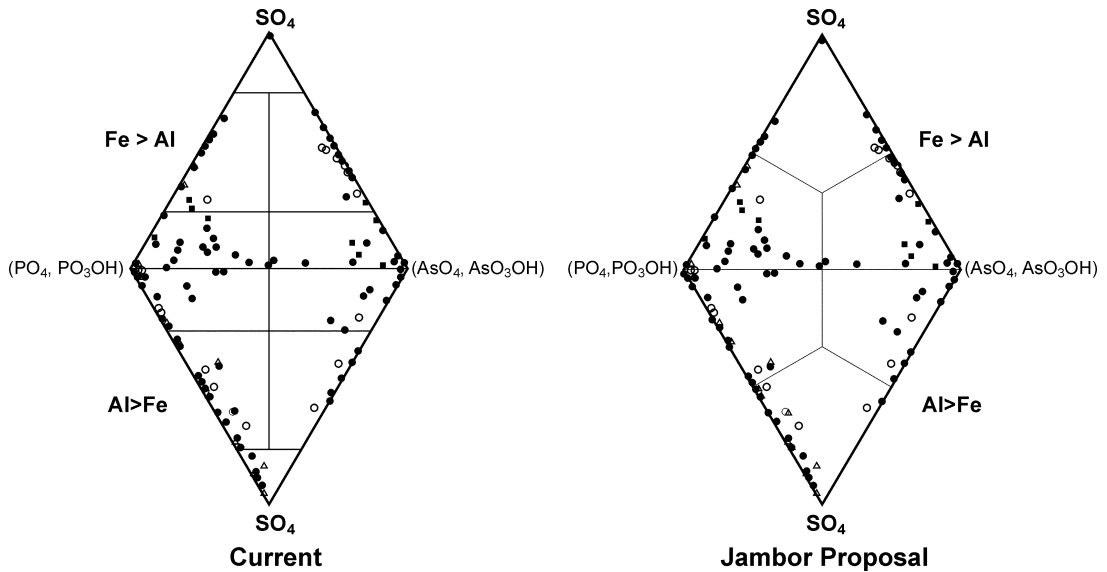


FIG. 2. Compositions of Pb-rich alunitic–jarosite minerals, showing the restricted extent of  $\text{PO}_4$ – $\text{AsO}_4$  solid solution once  $\text{SO}_4$  exceeds 25% [modified from Jambor (1999), and with more data added]. Data points: black dot: Sejkora *et al.* (1998), black square: Rattray *et al.* (1996), open triangle: Scott (1987), open circle: Scott (unpubl. data, Cobarr region).

introduction of the trivalent anion being balanced by the addition of 0.5 Pb in the *A* site, and the second step merely involving an interchange of divalent anions,  $\text{SO}_4$  and  $\text{PO}_3\text{OH}$ . Alternatively, if beaverite,  $\text{Pb}(\text{Fe,Cu})_3(\text{SO}_4)_2(\text{OH})_6$ , is taken as the starting material, the introduction of the trivalent anion is balanced by the replacement of the divalent Cu in the *B* site by trivalent Fe to form corkite,  $\text{PbFe}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$ . The current classification recognizes this significant change in the substitution process, where approximately equal amounts of divalent and trivalent anions occur as corkite, but this change is hidden by the system proposed by Jambor (1999).

Furthermore, consideration of naturally occurring material (Fig. 2) suggests that solid solution involving the  $\text{PO}_4$  and  $\text{AsO}_4$  anions is not generally significant unless  $\text{SO}_4$  occupies less than 25% of the  $\text{XO}_4$  sites. Hence a boundary at 0.5 formula units  $\text{SO}_4$  may represent a real compositional break that is recognized by Scott's (1987) system but not by Jambor's (1999) proposed system (Fig. 2). Above this boundary, recognition of corkite and beudantite as  $\text{Pb-Fe-PO}_4\text{-SO}_4$  and  $\text{Pb-Fe-AsO}_4\text{-SO}_4$  minerals, with 1:1 divalent and trivalent anions and generally little incorporation of a second trivalent anion, thus appears useful. Hence, further work to demonstrate extensive mixing of  $\text{PO}_4$  and  $\text{AsO}_4$  in minerals like corkite and beudantite is needed before changes to the currently approved nomenclature should be considered. Furthermore, even if additional work leads to the discovery of more compositions like that of the published corkite with significant  $\text{AsO}_4$  and hinsdalite with significant  $\text{AsO}_4$  (Fig. 2), retaining the

current names rather than describing them as plumbojarosite and plumbogummite, respectively (Jambor's proposal) is more informative about their compositions.

Of the various members of the alunite-jarosite family, the Pb-rich are the best documented, with the full range of compositions being recognized, and thus Jambor's (1999) proposal potentially has the most impact upon their nomenclature. Therefore, in the above argument, I have concentrated on them. His proposal hides the importance of the 1:1 divalent-trivalent anion mechanism of substitution in these minerals to form corkite and beudantite. In addition, the general paucity of published data for minerals containing significant amounts of both  $\text{PO}_4$  and  $\text{AsO}_4$ , unless these anions together occupy 75% of the  $\text{XO}_4$  sites, favors the retention of a division at 25%  $\text{SO}_4$  (0.5 formula units of  $\text{SO}_4$ ), at least until the importance of solid solution between minerals like corkite and beudantite is established. Thus I contend that the current system of nomenclature is actually more informative about the substitutions present within particular members of the alunite-jarosite family, and should be retained despite the slightly greater number of mineral names it allows.

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