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Alunite and crandallite: a structure derived from that of pyrochlore

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Abstract

The structures of the minerals alunite $KAl_3(SO_4)_2(OH)_6$ and crandallite $CaAl_3(OH)_6[PO_3(O_{1/2}(OH)_{1/2})]_2$ have been investigated from a geometric standpoint. The similarity of this structural type with the pyrochlores $A_{1+x}M_2O_6$ or $A_2M_2O_7$ is shown. The framework $KAl_3(OH)_6O_6$ is strongly related to the host lattice M_2O_6, *i.e.* M_4O_{12}: it is built up from distorted hexagonal tungsten bronze layers $Al_3(OH)_6O_3$ similar to the M_3O_9 layers observed for pyrochlores, and from KO_3 layers which correspond to the MO_3 layers of pyrochlores. The stacking sequence of the $Al_3(OH)_6O_3$ and M_3O_9 layers is however different in both structures; it yields, due to the tilting of the octahedra, a coordination number 12 for K^+ in the KO_3 layers, while M of the MO_3 layers is characterized by an octahedral coordination.

The crystal structure of the mineral alunite $KAl_3(SO_4)_2(OH)_6$ has formed the subject of several publications (Hendricks, 1937; Pabst, 1947; Rong Wang *et al.*, 1965). Crandallite $CaAl_3(OH)_6[PO_3(O_{1/2}(OH)_{1/2})]_2$ (Blount, 1974) has a structure analogous to alunite. Recently Moore and Araki (1977) have shown that the structure of mitridatite $Ca_6(H_2O)_6\ [Fe_9^{III}O_6(PO_4)_9] \cdot 3H_2O$ is topologically distinct from, but related to, alunite. Although this structure is now definitely established, no relation with other structural types has been observed. The present paper describes the relations between this structure and that of pyrochlore, $A_2M_2O_7$, which forms an important group of minerals whose classification and nomenclature has recently been revised by Hogarth (1977).

The comparison of the hexagonal cell of alunite ($a_H \simeq 7$Å and $c_H \simeq 17$Å) with the cubic cell of pyrochlore ($a_c \simeq 10$Å) admits the relations:

$$a_H \simeq a_c/\sqrt{2} \simeq 7\text{Å and } c_H \simeq a_c\sqrt{3} \simeq 17\text{Å}$$

The symmetry of alunite is in fact rhombohedral $R\bar{3}m$ with α close to 60°. Note that the cubic pyrochlores ($Fd3m$) can be equivalently described in a rhombohedral cell with the same dimensions as those of alunite and characterized by the same space group $R\bar{3}m$. From these considerations, it appears that the formula $KAl_3(OH)_6(SO_4)_2$, related to the rhombohedral cell of alunite, should be compared with $A_4M_4O_{14}$ for pyrochlores, where A is a large cation (R > 1Å) and M is a metal in octahedral coordination.

The atomic parameters of pyrochlores AM_2O_6, referred to the corresponding hexagonal cell, are listed in Table 1. They demonstrate that there is a similarity between the frameworks $KAl_3(OH)_6O_6$ and M_4O_{12}, where Al and M atoms both have the same octahedral coordination. Previous studies on nonstoichiometric pyrochlores $A_{1+x}M_2O_6$ (Babel *et al.*, 1967; Michel *et al.*, 1973) have shown that the seventh oxygen atom of the $A_2M_2O_7$ compounds is not indispensable to the stability of the structure. This can be considered as built up from a host lattice M_2O_6, *i.e.* M_4O_{12} (M = W, Ta, or Nb) based on octahedra, where the A cations (K^+, Rb^+, Tl^+) are inserted. This host framework can also be described as built up from two sorts of layers, M_3O_9 and MO_3, which are normal to the $\langle 111 \rangle$ direction of the cubic cell. The M_3O_9 layers, made from corner-sharing octahedra, are in fact distorted hexagonal tungsten bronze sheets previously described by Magneli (1953). The examination of the (001) planes of the hexagonal cell of alunite shows that the latter type of layer is also observed in alunite and crandallite (Fig. 1a) and has the composition $Al_3(OH)_6O_3$. The MO_6 and $Al(OH)_4O_2$ octahedra are almost regular in both the pyrochlore and alunite structures; they are tilted about c_H or $\langle 111 \rangle_c$ with approximately the same in-

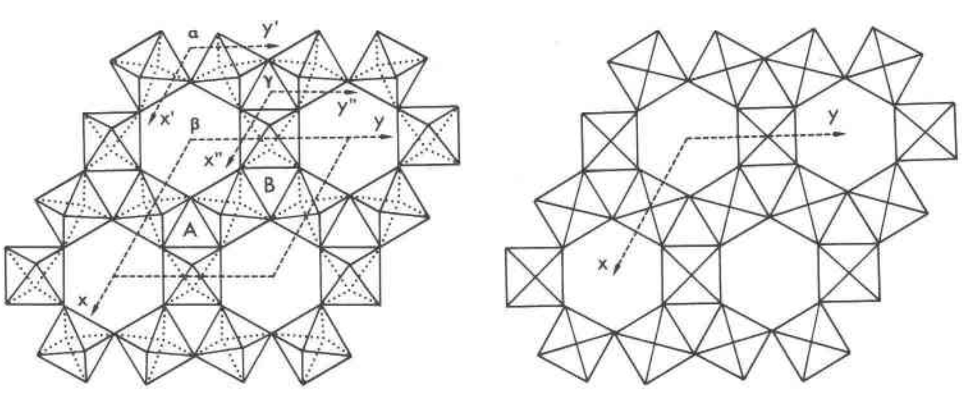
Table 1. Atomic parameters for alunite (Rong Wang *et al.*, 1965) and pyrochlore AB_2O_6 (Michel, 1974) referred to the hexagonal cell of the $R\bar{3}m$ space group

	Alunite (a = 6.97 Å, c = 17.27 Å)				Pyrochlore (a = 7.28 Å, c = 17.84 Å)			
Position	Atom	x	y	z	Atom	x	y	z
3 (a)	K	0.	0.	0.	M	0.	0.	0.
9 (d)	Al	0.5	0.	0.5	M	0.5	0.	0.5
6 (c)	S	0.	0.	0.3030	A	0.	0.	0.375
6 (c)	O(1)	0.	0.	0.3844				
18 (h)	O(2)	0.2180	-0.2180	-0.0588	O	0.2067	-0.2067	-0.2717
18 (h)	OH	0.1247	-0.1247	0.1416	O	0.1267	-0.1267	0.1883

clination with respect to that direction (18° for alunite, 17° for crandallite, and 15° for pyrochlore), differing from the hexagonal tungsten bronzes layers (Fig. 1b), whose octahedra are not (or only slightly) tilted about the *c* axis. The hexagonal tungsten bronze layers (HTB) are lying at levels $z = 1/6$, $3/6$, and $5/6$ of the hexagonal cell and, in a particular structure, correspond one with another by the translation vectors of the $R\bar{3}m$ space group. Therefore, in each compound, there are three different states α, β, and γ for the HTB layers, according to their configuration with respect to the $O\vec{x}$ and $O\vec{y}$ reference axes of the hexagonal cell. The three states are shown in Figure 1a.

Thus, the structural analysis and comparison of the structures of alunite type and pyrochlore type can be achieved in two different ways. The projections of the HTB layers at the same level *z* are identical in both structures but the tiltings of the octahedra about the $\vec{c}_H$ axis are in the opposite direction, so that both host lattices cannot be superimposed. Another way of comparison by means of HTB layer types (α, β, or γ), with the same tilting direction, shows a different stacking order along $\vec{c}_H$: $\alpha\ \beta\ \gamma$ sequence in the pyrochlore and $\gamma\ \beta\ \alpha$ sequence in alunite type.

Thus, the stacking of the $Al_3(OH)_6O_3$ or M_3O_9 layers along $\vec{c}_H$ or $\langle 111 \rangle_c$ is comparable: two consecutive layers are derived one from the other by a gliding of $a_H/\sqrt{3}$; the gliding directions are however different in both structures (Fig. 2): they are oriented at 180° one from the other. Starting from a HTB layer, chosen as a reference, a pyrochlore type structure is obtained from the stacking HTB; HTB $(+\vec{t})$; HTB $(-\vec{t})$, while the alunite type structure agrees with HTB; HTB



(a) (b)

Fig. 1. Comparison of the M_3O_9 and $Al_3(OH)_6O_3$ octahedral layers of (a) alunite and pyrochlore with that of (b) hexagonal tungsten bronze (HTB). The references α, β, and γ show the three possible positions of the distorted HTB layers in the alunite and pyrochlore structures.

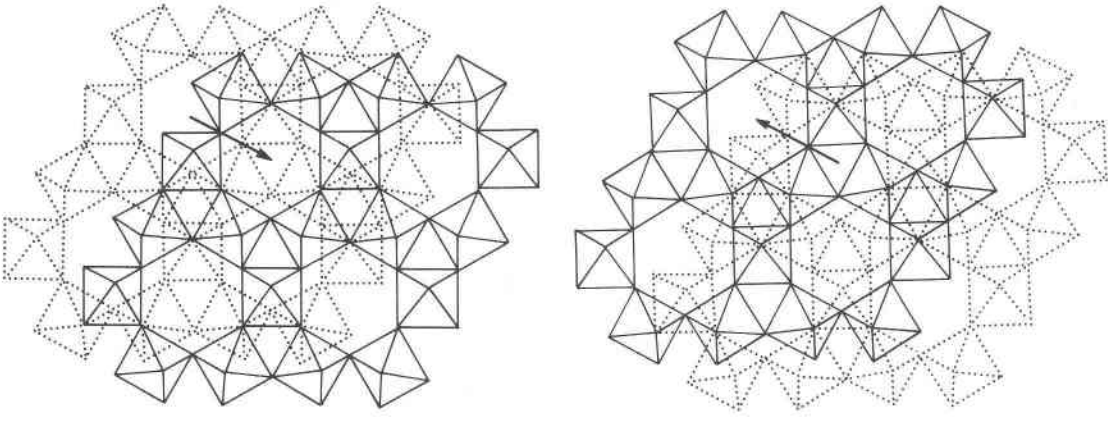
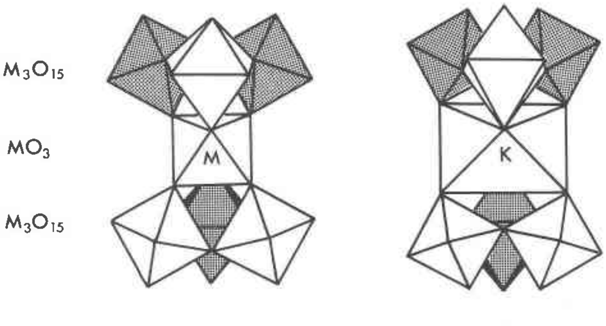

(a) (b)

Fig. 2. Stacking of two adjacent distorted HTB layers (a) in pyrochlore (b) in alunite and crandallite.

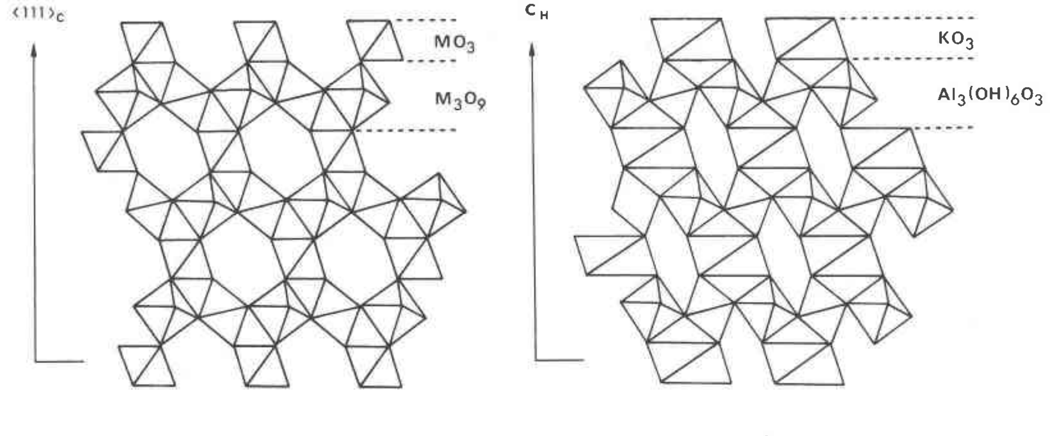
$(-\vec{t})$; HTB $(+\vec{t})$ where $\vec{t} = (1/3)\vec{a}_H + (2/3)\vec{b}_H$. As a consequence, the main difference appears on the KO_3 and MO_3 layers connecting two consecutive M_3O_9 or $Al_3(OH)_6O_3$ layers. The tilting about $\vec{c}_H$ in the blocks "M_3O_{15}" of three corner-sharing octahedra defines two sorts of triangles whose apices are oxygen atoms located at the surface of a layer—small triangles noted A and large triangles noted B (Fig. 1a); this is in contrast to the ideal hexagonal bronze structure, where all the triangles are equivalent (Fig. 1b). The different stacking modes generate two sorts of sites which are available for M and K cations. In pyrochlore, two A triangles belonging to neighboring M_3O_9 sheets are one above the other, forming an octahedron (Fig. 3a) whose ternary axis is parallel to the $\langle 111\rangle_c$ direction, where the M ion is located. An analogous disposition is obtained for the B triangles in alunite, forming trigonal antiprisms (Fig. 3b) where the K^+ ions (or Ca^{2+} in crandallite) are located. In fact, the opposite directions of the tilting of octahedra in Figures 3a and 3b lead to a six-coordinated M cation in pyrochlore, while K^+ (or Ca^{2+}) is twelve-coordinated in alunite, since the oxygen atoms which are common to the octahedra of a "M_3O_{15}" group are not at the same z level in both structures: they are neighbors for K^+, but not for M. The polyhedra KO_{12} can be considered as built from flattened octahedra KO_6 (antiprisms) having the same disposition in KO_3 layers as the MO_6 octahedra in MO_3 layers. Both structural families can thus be regarded as forming strongly related host lattices which are built up from the stacking of MO_3 and M_3O_9 layers along $\langle 111\rangle_c$ for the M_4O_{12} framework (Fig. 4a) and from the stacking of KO_3 and $Al_3(OH)_6O_3$ layers along c_H for the alunite framework (Fig. 4b).

These frameworks delimit cavities which are different in each structure. In the case of pyrochlore, a large triangle B is sited directly above and below the hexagon formed by six octahedra (Fig. 2a), while for alunite such a hexagon is surrounded on both sides by small triangles A (Fig. 2b). Hence the cavities of the pyrochlore structure, bounded by 18 oxygen atoms, are limited by the hexagonal crowns of six octahedra and the "M_3O_{15}" blocks of two successive M_3O_9 layers (Fig. 5a) and share their distorted hexagonal faces, forming tunnels parallel to the $\langle 110\rangle_c$ direction. In the non-stoichiometric pyrochlores $A_{1+x}B_2O_6$, the large A cations (K, Rb, Cs, Tl, *etc.* . . .) are located inside these cavities, whereas they are located on the common faces in $A_2M_2O_7$ pyrochlores,



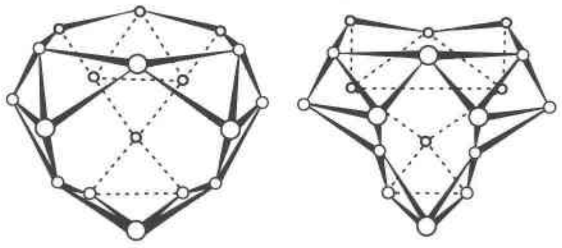
(a) (b)

Fig. 3. Coordination of M and K^+ respectively in MO_3 and KO_3 layers: (a) the MO_6 octahedron of pyrochlore; (b) the KO_6 antiprism of alunite; the K^+ ion has however six additional close neighbors at equal distances, belonging to the "M_3O_{15}" blocks above and under the antiprism.



(a) (b)

Fig. 4. Stacking of (a) the MO_3 and M_3O_9 layers in pyrochlore as seen along $[110]_H$, (b) the KO_3 and $Al_3(OH)_6O_3$ layers in the alunite as seen along $[\overline{1}\overline{1}0]_H$.



(a) (b)

Fig. 5. The cavities bounded by 18 oxygen atoms and (or) hydroxyl groups (a) in pyrochlore (b) in alunite.

the seventh oxygen atom being situated at the center of the cavities.

The cavities of alunite are less open so that the tunnels no longer exist. Among the 18 oxygen atoms, we can consider that 9 have nearly the same disposition as in pyrocholore (Fig. 5b). The other nine atoms belong to the A and B triangles which are permuted from one structure type to the other. Each cavity contains one "SO" or "PO" group. The oxygen atom of this group is directed towards the distorted hexagonal face so that it forms, with the three oxygen atoms of the A triangle, a tetrahedron where the sulfur or phosphorus atom is located.

These structural relations show the importance of the hexagonal tungsten bronze framework, which can be considered as an elementary part of the structure of a great number of compounds. The possibility of intergrowths of alunite and pyrochlore structures, corresponding to different stackings of the M_3O_9 and $Al_3(OH)_6O_3$ layers, should be considered.

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