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The crystal structures of jarosite and svanbergite

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ABSTRACT

The crystal structures of jarosite and svanbergite have been refined. It was revealed that geometry of the sulphur tetrahedra in jarosite and alunite is much affected by the octahedral cations. The sulphur tetrahedra in jarosite expand nearly to maximum, and they are comparable in size to those of phosphorus tetrahedra. The six refined crystal structures of the alunite-type minerals, alunite, goyazite, crandallite, woodhouseite and these two minerals, are compared. It was found that jarosite which has Fe octahedra behaves in an exceptional manner. It seems that the geometry of other five structures which have Al octahedra is in right order from the view point of crystal chemistry.

Introduction

The alunite-type structures are of mineralogical and crystallographical interest on account of the many types of isomorphous substitutions shown by them. The minerals of this structure type are classified into the following three groups: (1) alunite group (sulphates), (2) woodhouseite group (sulphate-phosphates or sulphate-arsenates), and (3) crandallite group (phosphates or arsenates).

The broad features of the alunite-type structures have been known since alunite, $KAl_3(SO_4)_2(OH)_6$, itself was studied by Hendricks (1937), although he assigned this structure to the space group $R3m$ on the basis of a pyroelectric test. Pabst (1947) considered that the structures of the alunite-type minerals are in the space group $R\bar{3}m$, and determined atomic positional parameters of alunite, svanbergite, $SrAl_3(PO_4)(SO_4)(OH)_6$, and woodhouseite, $CaAl_3(PO_4)(SO_4)(OH)_6$. An accurate refinement of the alunite structure was carried out by Wang, Bradley and Steinfink (1965). Kato (1971, 1977) refined the crystal structures of goyazite, $SrAl_3(PO_4)_2(OH)_5 \cdot H_2O$, and woodhouseite. Blount (1974) refined the crystal structure of crandallite, $CaAl_3[PO_3(O_{0.5}(OH)_{0.5})_2](OH)_6$. It is to be noticed that the Ca ions in this structure are not located at the origin.

Hendricks (1937) considered that jarosite, $KFe_3(SO_4)(OH)_6$, is isostructural with alunite but the presence of iron did not allow him to determine positional parameters of the atoms from the X-ray data. It was considered to be necessary to refine further the svanbergite structure using single crystal diffractometer data because a cell parameter of this mineral ($c \cong 17$Å) is very large and small shifts of atomic positional parameters may make substantial change in the interatomic distances as pointed out by Pabst (1947). This paper reports the detail of the crystal structures of jarosite and svanbergite together with a comparison of these structures with other refined structures of this structure type.

Experimental

A jarosite crystal of 0.18×0.18×0.10 mm in size was chosen from the sample from Meadow Valley 1, Pioche, Nevada provided by U.S. National Museum (USNMR 94406). A svanbergite crystal of 0.25×0.20×0.20 mm in size was selected from the sample from the Dover Andalusite Mine, Nevada provided by British Museum (BM 17702).

Intensities of 294 non-zero reflections for jarosite and 283 reflections for svanbergite were measured with a Syntex P$\bar{1}$ auto diffractometer using 2θ scans in the variable scan speed mode. Graphite monochromatized MoKα radiation was used, and only reflections for which $I>3\sigma(I)$ were taken into account. Reflections up to maximum $2\theta=60°$ were collected. Intensities were corrected for Lorentz-polarization effects and for absorption. The cell parameters based on least squares refinement of 15 high 2θ reflections are compared in Table 1 together with those of previous works.

Table 1. Unit cell parameters (in Å).

	a	*c*
alunite		
Hendricks (1937)	6.97	17.38
Pabst (1947)	6.97	17.38
Wang et al. (1965)	6.970(1)	17.27(1)
jarosite		
Hendricks (1937)	7.21	17.03
synthesized*	7.29	17.16
this study	7.304(2)	17.268(5)
svanbergite		
Ygberg (1945)	6.96	16.8
this study	6.992(2)	16.567(5)

* A.S.T.M. 22-827

Refinement

The atomic coordinates of alunite determined by Wang *et al.* (1965) and those of svanbergite determined by Pabst (1947) were used for the refinement of jarosite and svanbergite structures, respectively, by the full-matrix least squares program FLS-4 written by Sakurai (1967). The refinement adopting the space group $R\bar{3}m$ successfully converged to give the values of $R=0.060$ for jarosite and 0.085 for svanbergite. In Table 2 the final atomic coordinates are compared with reported values. The calculated bond distances and angles with error are given in Table 3.

Table 2. Atomic coordinates.

	x	y	z	B
jarosite				
K	0	0	0	1.04
S	0	0	0.3084(1)	0.58
Al	1/6	−1/6	−1/6	0.58
O(1)	0	0	0.3934(4)	1.00
O(2)	0.2180(7)	−0.2180	−0.0543(2)	1.23
OH	0.1247(7)	−0.1247	0.1351(2)	0.80
svanbergite				
Pabst (1947)				
Sr	0	0	0	
P, S	0	0	0.29	
Al	1/6	−1/6	−1/6	
O(1)	0	0	0.38	
O(2)	0.213	−0.213	−0.08	
OH	0.14	−0.14	0.14	
This study				
Sr	0	0	0	1.29
P, S	0	0	0.3095(4)	0.11
Al	1/6	−1/6	−1/6	0.21
O(1)	0	0	0.3993(11)	0.36
O(2)	0.2180(17)	−0.2180	−0.0558(6)	0.46
OH	0.1247(17)	−0.1247	0.1358(6)	0.13

Discussion

The alunite-type structures belong to the rhombohedral space group $R\bar{3}m$, and are described in terms of the hexagonal cell in which $a=7\,\text{Å}$, $c=17\,\text{Å}$ approximately. Their most obvious feature is the sheet of octahedral group (joined corner-to-corner) parallel to the (001) plane. The central cation is either Al^{3+} or Fe^{3+}, depending on the mineral, and four anions shared with other octahedral group

Table 3. Bond lengths and angles.

jarosite		svanbergite	
S-O(1)	1.468(8) Å	(P, S)-O(1)	1.488(19) Å
S-O(2)	1.545(6)	(P, S)-O(2)	1.493(10)
O(1)-O(2)	2.455(8)	O(1)-O(2)	2.453(18)
O(2)-O(2′)	2.527(8)	O(2)-O(2′)	2.419(19)
Fe-O(2)	2.047(4)	Al-O(2)	1.939(10)
Fe-OH	1.977(5)	Al-OH	1.889(12)
O(2′)-OH	2.915(6)	O(2′)-OH	2.674(13)
O(2′′)-OH	2.773(7)	O(2′′)-OH	2.650(17)
OH-OH′	2.732(5)	OH-OH′	2.616(12)
OH′-OH′′	2.857(6)	OH′-OH′′	2.727(20)
K-O(2)	2.913(6)	Sr-O(2)	2.797(14)
O(2)-O(2′)	4.777(6)	O(2)-O(2′)	4.573(19)
K-OH	2.816(4)	Sr-OH	2.710(10)
OH-OH′	2.732(5)	OH-OH′	2.616(12)
Fe-S	3.230(2)	Al-(P, S)	3.110(5)
Fe-K	3.568(8)	Al-Sr	3.421(8)
O(2)-S-O(2′)	109.79(26)°	O(2)-(P, S)-O(2′)	108.17(64)°
O(2)-S-O(1)	109.11(18)	O(2)-(P, S)-O(1)	110.71(44)
O(2)-Fe-OH	87.13(18)	O(2)-Al-OH	87.57(46)
O(2′)-Fe-OH	92.87(18)	O(2′)-Al-OH	92.43(46)
OH-Fe-OH′	87.45(19)	OH-Al-OH′	87.61(48)
OH′-Fe-OH′′	92.55(19)	OH′-Al-OH′′	92.39(48)
S-O(2)-Fe	127.60(31)	(P, S)-O(2)-Al	129.40(76)
O(1)-OH	2.940(7) Å	O(1)-OH	2.778(16) Å

are hydroxyl. The hydroxyls arrange in a plane which is roughly parallel to the (001) plane. The remaining two anions are oxygens, lying on opposite sides of the layers of hydroxyls. The octahedra form six and three membered rings; and the three apical oxygens from each triad of octahedra form the base of phosphate, sulphate or arsenate tetrahedral groups, with which the oxygens are shared

(Fig. 1). When a further octahedral network is added to the structure it is located so that two triads of hydroxyls enclose a site in which a larger cation such as K^+, Sr^{2+}, Pb^{2+}, Ce^{3+}, Ca^{2+}, Na^+ may be located in twelve coordination. The remaining anions of interest are the apex oxygens on each of the tetrahedral groups. These point alternately up and down the *c*-axis, projecting into the six-membered rings of octahedral hydroxyls, to which they are probably lightly bonded, by long hydrogen bonds.

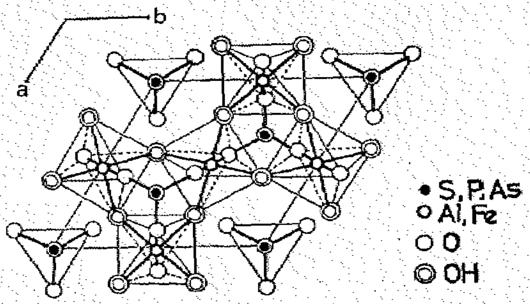

Fig. 1. *c*-axis projection of alunite-type structure. Only polyhedral contacts between $z=1/3$ and $z=2/3$ and the positions of tetrahedra near the origin are shown.

Wang *et al.* (1965) concluded that in the alunite structure protons would be at $x\bar{x}z$ $x=0.20$ and $z=0.11$. Kiriyama (1965) determined the distances of neighboring protons in the alunite structure by NMR data (Fig. 2).

The jarosite structure is derived from the alunite structure by replacing Al by Fe. It was found that this replacement gives a very profound effect on the geometry of octahedra and simultaneously on tetrahedra. Although Hendricks (1937) obtained 17.03Å as the *c* parameter of jarosite, that obtained in this study is 17.268Å. Synthesized jarosite (A. S. T. M. Card No. 22-827) also gives 17.16Å.

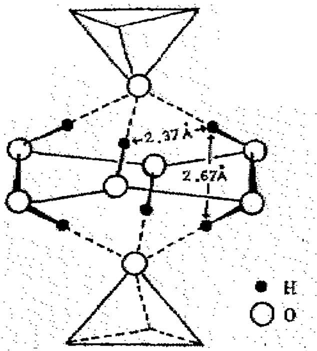

Fig. 2. Configuration of six neighboring H in alunite (Kiriyama (1965)).

It is hard to find the reason why substantial decrease must occur in the *c* parameter of jarosite compared to that of alunite.

In the jarosite structure, the ferric iron is coordinated in slightly distorted octahedra formed by four OH and two oxygen atoms from two separate SO_4 groups. The distance between iron and oxygen is 2.047Å. The Fe-OH bond length is 1.977Å. The OH-OH edge distances are 2.732 and 2.857Å; O-OH edge distances are 2.773 and 2.915Å. Each iron atom is at a symmetry center with paired internal angle O-Fe-OH 87.13° and 92.87° and OH-Fe-OH 87.45° and 92.55°. The configuration of a single octahedron is illustrated in Fig. 3(b).

In the jarosite structure, iron octahedra show a considerable expansion than aluminum octahedra of alunite, resulting in giving an expansion of sulphur tetrahedra. The three equivalent bonds from sulphur atom to basal oxygens, S-O(2), has a distance of 1.545Å, while the bond length between the sulphur atom and the apical oxygen, O(1), is 1.468Å, and this bond is considered to be the 'doubly' bonded one as pointed out by Wang *et al.* (1966) in the

Table 4. Bond lengths and angles of refined alunite-type structures.

	goyazite Kato (1971)	crandallite Blount (1974)	woodhouseite Kato (1977)	svanbergite This study	alunite Wang Rong *et al.* (1965)	jarosite This study
Tetrahedron	P	P	P, S	P, S	S	S
X-O(1) (×1)	1.551Å	1.520Å	1.483Å	1.488Å	1.406Å	1.468Å
X-O(2) (×3)	1.522	1.543	1.492	1.493	1.477	1.545
Mean	1.529	1.537	1.490	1.492	1.459	1.526
O(2)-X-O(2′)	110.11°	110.4°	108.45°	108.17°	109.49°	109.79°
O(2)-X-O(1)	110.10	108.5	110.45	110.71	109.45	109.11
Mean	110.11	109.5	109.45	109.44	109.47	109.45
Octahedron	Al	Al	Al	Al	Al	Fe
B-O(2) (×2)	1.907Å	1.931Å	1.939Å	1.939Å	1.963Å	2.047Å
B-OH(×4)	1.896	1.888	1.892	1.889	1.864	1.977
Mean	1.900	1.902	1.908	1.914	1.897	2.012
Mean O(2)-OH	2.688	2.700	2.709	2.662	2.707	2.844
Mean OH-OH	2.682	2.669	2.675	2.672	2.636	2.795
Mean	2.685	2.685	2.692	2.667	2.672	2.820
Twelve coordinated ion						
	Sr	Ca	Ca	Sr	K	K
A-O(2)	2.788	Mean 2.748	2.788	2.797	2.821	2.913
A-OH	2.729	Mean 2.674	2.688	2.710	2.871	2.816
Mean	2.759	2.711	2.738	2.754	2.846	2.865
O(1)-OH	2.759	2.728	2.767	2.778	2.964	2.940

alunite structure. The mean bond length of S-O in jarosite is 1.526 Å, while that of alunite is 1.459 Å. Baur (1970) stated that the bond lengths between sulphur and oxygen range 1.42 to 1.61 Å with the mean value of 1.473 Å, and that those between phosphorus and oxygen range 1.44 to 1.64 Å with the mean value of 1.537 Å. The sulphur tetrahedra in jarosite expand nearly to maximum, and they are comparable in size to those of phosphorus tetrahedra in other alunite-type structures (Table 4 and Fig. 3 (a) and (b)).

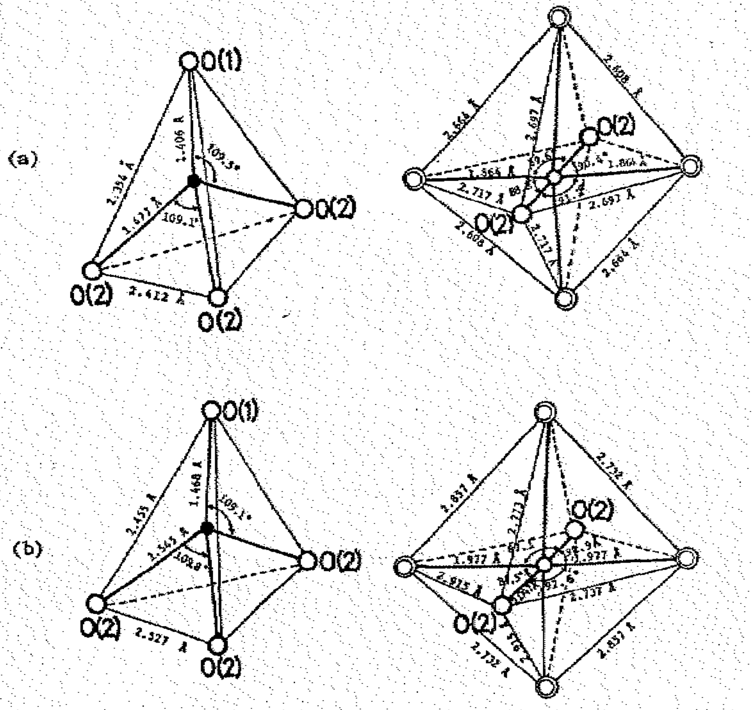

Fig. 3. Geometry of tetrahedra and octahedra. (a) alunite (Wang *et al.* (1965)), (b) jarosite.

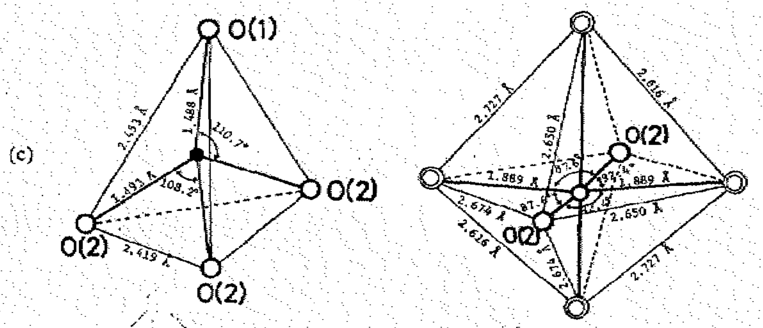

Fig. 3. (Continued). (c) svanbergite.

The environment of potassium is presumably considered as twelve coordinated. Six oxygen neighbors from six sulphate groups afford a flattened octahedron about each potassium of jarosite with a bond length of 2.913 Å (2.821 Å in alunite); while the six OH neighbors of iron octahedra in the elongated octahedral arrangement about each potassium are at the distances of 2.816 Å (2.871 Å in alunite); the K–OH bond lengths in jarosite are shorter than those of K–O. This situation is the reverse of the alunite structure, and the alunite case is exceptional among the refined alunite-type structures (Table 4). The apical sulphate oxygen has three OH neighbors distant 2.940 Å and these three associations are presumed to be hydrogen bonds.

The svanbergite structure can be compared with that of woodhouseite. The replacement of Ca in the woodhouseite structure by Sr results in the svanbergite structure. Aluminum is coordinated by O and OH in the form of a slightly distorted octahedron. The distance between aluminum and oxygen is 1.939 Å which is the same as that of woodhouseite. The Al–OH bond length of 1.889 Å is almost the same as the value of 1.892 Å in woodhouseite. The OH–OH edge distances of the octahedron is 2.616 and 2.717 Å which agree well with 2.616 and 2.734 Å in woodhouseite; O–OH edge distances are 2.650 and 2.674 Å, corresponding values in woodhouseite are 2.645 and 2.772 Å, respectively. Each aluminum atom has paired internal angles O–Al–OH 87.57° and 92.43° and OH–Al–OH 87.61° and 92.73°. These values compare well with those of woodhouseite, 87.32°, 92.68°, 87.47° and 91.33°, respectively (Fig. 3 (c)).

The P, S tetrahedra (P and S are disordered) in the svanbergite structure are also similar to those in woodhouseite. The bond lengths from P, S to the basal oxygen atoms are 1.493 Å, and that to the apical oxygen is 1.488 Å (Fig. 3 (c)).

The strontium ion appears to be 12-coordinated, to six O(2) at 2.797 Å and six OH at 2.710 Å. These values compare well with those of goyazite, 2.788 and 2.729 Å, respectively. The bond length between the apical oxygen and OH is 2.778 Å.

The principal bond lengths and angles of six refined alunite-type structures including jarosite and svanbergite are listed in Table 4.

Among these structures only jarosite has Fe octahedra and all others have Al octahedra. As already mentioned, jarosite behaves in an exceptional manner. Comparing the remaining five structures the geometry of tetrahedra, octahedra, and 12-coordinated ion surroundings seems to be in right order from the view point of crystal chemistry.

The mean P–O, (P, S)–O and S–O values by Baur (1970) are 1.537, 1.505 and 1.473 Å, respectively. The refined results, 1.537 (crandallite, Blount (1974), 1.529 (goyazite); 1.492 (svanbergite), 1.490 (woodhouseite); 1.459 (alunite, Wang *et al.* (1965)) agree with these expected values. The geometry of Al octahedra of these five structures is similar. The distances between 12-coordinated ions and O(2) and OH increase with increasing cation radii. As already mentioned, the distances between cation and O(2) are longer than those of cation to

OH except the case of alunite.

Finally, we can state that the alunite-type structure is so flexible that (1) various ions can construct this structure and (2) even the same ion can have different geometry to adapt this structure as revealed by the jarosite structure. This flexibility is the reason why so many minerals of various composition can crystallize in the alunite-type structure.

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