# THE CRYSTAL STRUCTURE OF ALUNITE AND THE JAROSITES

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Alunite is of potential economic value in the United States as a source of both aluminum and potassium compounds. Various attempts have been made to exploit the extensive deposits at Marysvale, Utah, and the U. S. Bureau of Mines is now studying the subject. A determination of the crystal structure of alunite was undertaken at the suggestion of Mr. J. Koster of that Bureau.

Alunite and the related jarosites are of mineralogical interest on account of the many types of isomorphous replacements shown by them. The composition of the various members has been summarized by Schaller[1] as follows:

*Sulphates*

| | | | | |
|---|---|---|---|---|
| Alunite | $(Al(OH)_2)_6$ | $K_2$ | $(SO_4)_2$ | $(SO_4)_2$ |
| Natroalunite | $(Al(OH)_2)_6$ | $Na_2$ | $(SO_4)_2$ | $(SO_4)_2$ |
| Jarosite | $(Fe(OH)_2)_6$ | $K_2$ | $(SO_4)_2$ | $(SO_4)_2$ |
| Natrojarosite | $(Fe(OH)_2)_6$ | $Na_2$ | $(SO_4)_2$ | $(SO_4)_2$ |
| Plumbojarosite | $(Fe(OH)_2)_6$ | $Pb$ | $(SO_4)_2$ | $(SO_4)_2$ |
| Karphosiderite | $(Fe(OH)_2)_6$ | $H_2$ | $(SO_4)_2$ | $(SO_4)_2$ |

*Phosphates*

| | | | | |
|---|---|---|---|---|
| Hamlinite | $(Al(OH)_2)_6$ | $Sr$ | $(HPO_4)_2$ | $(Sr(PO_4)_2)$ |
| Plumbogummite | $(Al(OH)_2)_6$ | $Pb$ | $(HPO_4)_2$ | $(Pb(PO_4)_2)$ |
| Gorceixite | $(Al(OH)_2)_6$ | $Ba$ | $(HPO_4)_2$ | $(Ba(PO_4)_2)$ |
| Florencite | $(Al(OH)_2)_6$ | $Ce_{2/3}$ | $(Ce_{1/3}PO_4)_2$ | $(Ce_{2/3}(PO_4)_2)$ |

*Sulphate-Phosphates*

| | | | | |
|---|---|---|---|---|
| Beudantite | $(Fe(OH)_2)_6$ | $Pb$ | $(SO_4)_2$ | $Pb(AsO_4)_2)$ |
| Corkite | $(Fe(OH)_2)_6$ | $Pb$ | $(SO_4)_2$ | $(Pb(PO_4)_2)$ |
| Svanbergite | $(Al(OH)_2)_6$ | $Sr$ | $(SO_4)_2$ | $(Sr(PO_4)_2)$ |
| Hinsdalite | $(Al(OH)_2)_6$ | $Pb$ | $(SO_4)_2$ | $(Pb(PO_4)_2)$ |
| Harttite | $\begin{cases} (Al(OH)_2)_6 \\ 2(Al(OH)_2)_6 \end{cases}$ | $Sr$ <br> $Sr$ | $(SO_4)_2$ <br> $(HPO_4)_2$ | $(SO_4)_2$ <br> $(Sr(PO_4)_2$ |

Artificial jarosites containing rubidium have also been prepared.[2] In addition to these substances the compound $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, a solid phase in the system $Fe_2O_3–SO_2–H_2O$, is also probably a jarosite and possibly corresponds to the mineral borgströmite.[3] The results of the crystal analysis lead to a structural explanation for these various replacements.

[1] Schaller, *U. S. Geol. Survey, Bull.* **509**, p. 76, 1912. *Zeits. Kryst.*, vol. **50**, p. 106, 1912. *Am. Jour. Sci.*, vol. **32**, p. 359, 1911.

[2] Fairchild, *Am. Mineral.* vol. **18**, p. 543, 1933.

[3] Posnjak and Merwin, *Jour. Am. Chem. Soc.*, vol. **44**, p. 1977, 1922.

From the structural and chemical point of view these minerals are of interest in that they are basic salts in which hydroxyl binding[4] might be expected. Their behavior upon heating[5] should be explained by their structures.

## SOURCE OF MATERIALS

The work was greatly facilitated by the excellent material available for study. Dr. W. F. Foshag of the U. S. National Museum kindly furnished crystals of alunite (USNMR 6290) from Rosita Hills, Colorado, and jarosite (USNMR 6299) from Meadow Valley Mine, Pioche, Nevada. These crystals, which were from the Roebling collection, showed predominant development of $c(00.1)$ and $r(10.1)$. They measured as much as 2 mm. on the edge and a number of well formed ones about $.3 \times .3 \times .1$ mm. were selected for $x$-ray work. Dr. Foshag also supplied samples of the original analyzed natrojarosite[6] (USNM 86932), analyzed ammoniojarosite[7] (USNM 95654) from Panguitch, Utah, plumbojarosite from the original locality, Cook's Peak, New Mexico[6] (USNMR 6308), karphosiderite (USNMR 6266) from Greenland, borgströmite (USNMR 6312) from Otrovaara, Finland, and hamlinite (USNMR 4051) from Serra de Congonhas Minas Geraes, Brazil. The samples of ammoniojarosite, karphosiderite, and borgströmite were microcrystalline. Individual crystals of natro- and plumbojarosite measured about $.08 \times .08 \times .01$ mm. and those of the other minerals were as large as 1 mm. Crystals of plumbojarosite, from the Tintic Standard Mine, Dividend Utah, measuring as much as 0.5 mm. on the edge were supplied by Dr. W. T. Schaller of the U. S. Geological Survey.

Mr. J. G. Fairchild of the U. S. Geological Survey very kindly supplied samples of microcrystalline artificial silver and lead jarosites.[2] Dr. E. Posnjak of the Geophysical Laboratory, Carnegie Institution of Washington, furnished single crystals of the compound $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ that he had prepared. Analyzed samples of commercial grades of alunite from Marysvale, Utah, containing from 1.2 to 45.0% $SiO_2$ were made available by Mr. J. Koster of the U. S. Bureau of Mines.

## EXPERIMENTAL PROCEDURE, LATTICE DIMENSIONS AND SPACE GROUP

Lattice dimensions of alunite were obtained from layer line photographs about the orthohexagonal $c$ and $a$ axes and from high angle

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[4] For a discussion of the role of hydroxyl binding in structural chemistry see Bernal and Megaw, *Proc. Roy. Soc.*, vol. **A151**, p. 384, 1935.

[5] Fink, Van Horn, and Pazour, *Ind. Eng. Chem.* vol. **23**, p. 1248, 1931.

[6] Hillebrand and Penfield, *Am. Jour. Sci.* (5), vol. **14**, p. 211, 1902.

[7] Shannon, *Proc. U. S. National Museum* #2758, 1928.

reflections from $(hk.0)$ and $(00.1)$ on Weissenberg photographs. These dimensions are listed in Table 1 together with the results obtained from the other minerals that were examined. The value of $c/a$ for alunite agrees to within the limit of experimental error with $2 \times c/a$ as obtained from reflection goniometer measurements. Weissenberg photographs were taken with at least two different crystal orientations for jarosite, natrojarosite and $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, and powder photographs were made, with FeK radiation, from these minerals as well as from argento- and ammoniojarosites, karphosiderite, borgströmite, and hamlinite. Agreement between $x$-ray and reflection goniometer measurements for jarosite is very poor and considerably exceeds the apparent experimental error.

TABLE 1

| Mineral | Composition | Lattice dimensions | | $c/a$ | | | Density | |
|---------|-------------|------|------|-----------------|---------------------|-----------------|-------|------|
| | | $a$ | $c$ | $x$-ray | Morpho-logical | $\frac{x\text{-ray}}{n}$ | calc. | obs. |
| Alunite | $KAl_3(SO_4)_2(OH)_6$ | 6.96 | 17.35 | 2.492 | 1.252 | 1.246 | 2.80 | 2.75 |
| Jarosite | $KFe_3(SO_4)_2(OH)_6$ | 7.20 | 17.00 | 2.361 | 1.245 | 1.18 | 3.24 | 3.26 |
| Argento-jarosite[1] | $AgFe_3(SO_4)_2(OH)_6$ | 7.22 | 16.40 | 2.27 | 1.106[5] | 1.13 | 3.80 | |
| Natro-jarosite[2] | $NaFe_3(SO_4)_2(OH)_6$ | 7.18 | 16.30 | 2.27 | 1.104 | 1.13 | 3.29 | 3.2 |
| Ammonio-jarosite[3] | $NH_4Fe_3(SO_4)_2(OH)_6$ | 7.20 | 17.00 | 2.36 | | | 3.09 | |
| Plumbo-jarosite[4] | $Pb(Fe_3(SO_4)_2(OH)_6)_2$ | 7.20 | 33.60 | 4.67 | 1.147[5] | 1.17 | 3.71 | 3.67 |
| _____[1] | $H_2OFe_3(SO_4)_2(OH)_5H_2O$ | 7.16 | 16.90 | 2.36 | 1.14 | 1.18 | | |

[1] Synthetic materials.

[2] Analysis 6.28% $Na_2O$, 0.37% $K_2O$ (Hillebrand).

[3] Analysis 0.22% $Na_2O$, 1.56% $K_2O$, 4.23% $(NH_4)_2O$ (Shannon).

[4] Crystals from the two localities mentioned in the introduction gave closely the same constants.

[5] Unpublished data from Dr. W. T. Schaller.

Failure of obtaining agreement in crystallographic constants as measured on optical and $x$-ray goniometers is probably due to difficulties in both methods. In substances, such as the jarosites, in which extensive solid solution formation is possible, individual crystals might show zoning in composition, particularly on the surface and thus give fortuitous, but consistent, values for crystal angles. While $x$-ray measurements are not susceptible to this error they are influenced by the fact

that observations are made on only a few crystals. Even though the sample is an analyzed one the individual crystals selected for study might show considerable departure in composition from the mass of the material, particularly since preference is given to very well formed ones. Measurement of refractive indices for the crystal examined can partially protect against such error.[8]

Dr. W. T. Schaller of the U. S. Geological Survey has graciously given permission to quote from unpublished work by him as follows. "Axial ratios obtained on crystals of argento- and plumbojarosites from the Tintic Standard Mine, Dividend, Utah, are $c/a = 1.106$ and $1.147$, respectively. Individual crystals gave fair signals but the reflections were not entirely satisfactory." The value found for plumbojarosite is considerably lower than that given by Penfield,[6] namely 1.216; it agrees with the $x$-ray goniometer measurements within the limits of error of the two measurements.

Observed and calculated densities are in close agreement for all the compounds save natrojarosite. Experimental determination of density is of course always open to serious error and the best procedure is to take the maximum value obtained provided the material is homogeneous. This has been done for the observed values of Table 1 which are all taken from the literature.

Laue photographs of alunite made with the $x$-ray beam accurately normal to (00.1) showed the symmetry $D_{3d} - 3m$. Various sized crystals of alunite, jarosite, plumbojarosite, hamlinite, and $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ did not give a piezoelectric effect when tested by the method of Giebe and Scheibe.[9] Individual crystals of alunite and jarosite showed strong pyroelectric properties when tested after the Martin method.[10] It should be emphasized here that a negative pyroelectric or piezoelectric test is without significance for determination of crystal symmetry.

All the minerals examined gave reflections from $(h\bar{h}.l)$ with $l$ odd and absences from all planes having $(h - k + l) = 3n$. The space group based on this criterion and the crystal symmetry as shown by Laue and Weissenberg photographs is $D_3^7 - R32$, $C_{3v}^5 - R3m$, or $D_{3d}^5 - R\bar{3}m$. Intensities of $(hk.0)$ for the jarosites could not be explained by $R32$. The observation that alunite is pyroelectric requires its space group to be $C_{3v}^5 - R3m$ and the univalent jarosites probably have the same structure.

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[8] This discussion is based upon conversations with Dr. H. E. Merwin of the Geophysical Laboratory, Carnegie Institution of Washington.

[9] Giebe and Scheibe, *Zeitz. phys.*, vol. **33,** p. 760, 1925.

[10] Martin, A. J. P., *Mineral. Mag.*, vol. **22,** p. 519, 1931.

### STRUCTURE DETERMINATION FOR ALUNITE AND JAROSITE

The rhombohedral unit of structure contains $1R'R'''_3(SO_4)_2(OH)_6$. In the space group $R\,3m^{11}$ referred to hexagonal axes there are sets of three equivalent positions on the three fold axes at $00z\overline{)}$, nine equivalent ones about these axes at $x\bar{x}z$, $x2xx$, $2\bar{x}\bar{x}z\overline{)}$ and the eighteen general positions. Potassium atoms can be placed at $000\overline{)}$ and two sets of $S$ and $O$ atoms of $SO_4$ groups are on the trigonal axes, $00z\overline{)}$. Aluminum, or iron, atoms and two sets of oxygen atoms of $SO_4$ groups are in the nine equivalent positions.

The $SO_4$ groups are assumed to have the dimensions found in other sulfates,[12] the S–O distance being 1.52A. There are two possible orientations in both the $a$ and $c$ directions for each set of sulfate groups. The only parameters in the $a$ direction are those of the hydroxyl groups and the $R'''$ atoms. Consideration of the $(hk.0)$ reflections from jarosite shows that $x_{Fe} = .167$. With this limitation the intensities of $(hk.0)$ for alunite require the two sets of $SO_4$ groups to be rotated 60° with respect to one another in the projection on $(00.1)$ and the hydroxyl groups to be in two non-equivalent sets with $x_{OH}$ near .13 and $-.13$. Parameter values in the $c$ direction can be fixed from this projection, an approximate knowledge of interatomic distances, and the intensities of the $(00.1)$ reflections. Final parameter values for alunite are:

|        | $x$  | $z$   |         | $x$   | $z$   |        | $x$    | $z$    |
|--------|------|-------|---------|-------|-------|--------|--------|--------|
| 3 K    |      | 0     | 3 $O_1'$  |       | .060  | 9 OH   | $-.150$ | .126   |
| 3 S'   |      | .305  | 3 $O_1''$ |       | $-.060$ | 9 OH   | .150   | $-.126$ |
| 3 S''  |      | $-.305$ | 9 $O'$    | $-.215$ | $-.058$ |        |        |        |
| 3 Al   | .167 | .167  | 9 $O''$   | .215  | .058  |        |        |        |

These values are to be slightly changed for jarosite, but because of the predominant effect of iron correct ones cannot be found from the $x$-ray data. Calculated values of $F^2/100$ for some reflections from alunite and jarosite are listed together with observed intensities in Table 2. Scattering factors used from $\sin\theta/\lambda = .10$ to $.30$ for $Al^{+++}$ and $O^{--}$ are those given by Wyckoff,[13] other values were taken from the *I.T.D.C.S.* No temperature correction was made in the calculations.

[11] *The International Tables for the Determination of Crystal Structures*, Chemical Catalogue Company, New York, **1935**, are used throughout. (Later referred to as *I.T.D.C.S.*)

[12] *Strukturbericht II, Ergänzungsband II*, Leipzig **1936**. See also C. A. Beevers and C. M. Schwartz, *Zeits. Krist.*, vol. **91**, p. 157, 1935. W. A. Wooster, *ibid.*, vol. **94**, p. 375, 1936.

[13] Wyckoff, R. W. G., *The Structure of Crystals*, p. 100. New York, **1931**.

TABLE 2. CALCULATED VALUES OF $F^2/100$ AND ESTIMATED INTENSITIES OF REFLECTION

| | Jarosite | | | Alunite | | |
|---|---|---|---|---|---|---|
| Plane | $F^2/100$ | Estimated Int. MoK | | Plane | $F^2/100$ | Estimated Int. NiK |
| $1\bar{2}.0$ | 50 | mw | | | 100 | s |
| $2\bar{4}.0$ | 700 | vs | | | 400 | vs |
| $3\bar{6}.0$ | 210 | m | | | 250 | s |
| $4\bar{8}.0$ | 250 | m | | | 120 | s |
| $5\ \bar{10}.0$ | 40 | vw | | $3\ \bar{3}.0$ | 1 | a |
| $6\ \bar{12}.0$ | 220 | mw | | $6\ \bar{6}.0$ | 100 | s |
| $7\ \bar{14}.0$ | 10 | a | | $5\ \bar{4}.0$ | 50 | mw |
| $8\ \bar{16}.0$ | 100 | w | | $7\ \bar{8}.0$ | 50 | w |
| | | MoK | FeK | | | CuK |
| $00.3$ | 131 | | ms | | 6 | w |
| $00.6$ | 200 | s | vs | | 37 | ms |
| $00.9$ | 210 | ms | s | | 66 | ms |
| $00.12$ | 36 | a | w | | 3 | a |
| $00.15$ | 23 | a | w | | 3 | a |
| $00.18$ | 82 | w | | | 21 | mw |
| $1\ \bar{1}.1$ | 330 | | | | 230 | s |
| $2\ \bar{2}.2$ | 100 | ms | | | 2 | vw |
| $3\ \bar{3}.3$ | 21 | w | | | 5 | w |
| $4\ \bar{4}.4$ | 290 | ms | | | 110 | ms |
| $5\ \bar{5}.5$ | 1 | a | | | 5 | w |
| $6\ \bar{6}.6$ | 145 | m | | $2\ \bar{2}.\bar{1}$ | 145 | s |
| $7\ 7.7$ | 40 | w | | $2\ \bar{2}.\bar{4}$ | 105 | m |
| $8\ \bar{8}.8$ | 65 | w | | $2\ \bar{2}.7$ | 57 | w |
| $9\ \bar{9}.9$ | 6 | a | | $1\ \bar{1}.2$ | 48 | ms |
| $10\ \bar{10}.10$ | 82 | mw | | $1\ \bar{1}.4$ | 9 | a |
| $11.\bar{11}.11$ | 4 | a | | $1\ \bar{1}.5$ | 26 | mw |
| $12\ \bar{12}.12$ | 26 | w | | $3\ \bar{3}.3$ | 380 | vs |

## STRUCTURE DETERMINATION FOR PLUMBOJAROSITE

Equatorial zone Weissenberg photographs were taken about the $c$ axis and the normal to $(\bar{1}2.0)$, FeK radiation being used. Data from the latter are listed in Table 3. The lattice is rhombohedral and the unit of structure contains one $Pb[Fe_3(SO_4)_2(OH)_6]_2$. The value of $a_0$ (hexagonal cell) for plumbojarosite is closely the same as that of jarosite while $c_0$ is approximately twice as great.

TABLE 3. WEISSENBERG PHOTOGRAPHIC DATA FROM PLUMBOJAROSITE, FeK RADIATION

| $n$ | $(00.(3n+3))$ | $(10.(3n+2))$ | $(20.(3n+1))$ | $(30.3n)$ | $(40.(3n+2))$ | $(50.(3n+1))$ | $(50.3n)$ |
|---|---|---|---|---|---|---|---|
| 0 | m | s | m | vw | vw | a | m–ms |
| 1 | vw | ms | ms–s | vw–w | a | a | a |
| 2 | m | a | w | mw | m | a | a |
| 3 | vs | vw | vw | w–vw | a | a | a |
| 4 | w | ms–s | w | vw | a | a | m |
| 5 | mw | vw | mw | a | a | a | |
| 6 | mw | w | a | a | m | | |
| 7 | w | a | vw | a | a | | |
| 8 | a | mw | vw | mw–w | a | | |
| 9 | a | vw | mw | vw | | | |
| 10 | w–mw | w | a | mw–w | | | |

| $n$ | $(10.(3n-1))$ | $(20.(3n-2))$ | $(30.3n)$ |
|---|---|---|---|
| 0 | s | s | vw |
| 1 | mw | m | mw |
| 2 | m | s | s |
| 3 | a | w | w |
| 4 | vw | vw | vw |
| 5 | a | a | vw |
| 6 | w | ms | m |
| 7 | w | a | a |
| 8 | vw | a | a |
| 9 | a | w | |
| 10 | w | ms | |

Since the ionic radius of $Pb^{++}$ differs but slightly from that of $K^+$ it would be expected that the plumbojarosite structure would differ from that of jarosite by replacement of half the potassium atoms with lead atoms, the other half of the positions remaining vacant and the remainder of the structure practically undisturbed. Such a change, however, increases the symmetry to that of the point group $D_{3d} - \bar{3}m$, the space group being $D_{3d}^5 - R\bar{3}m$. Lead atoms without loss of generality are at $000$; $\frac{1}{3} \frac{2}{3} \frac{1}{3}$; $\frac{2}{3} \frac{1}{3} \frac{2}{3}$; and iron atoms are at $18(h)$ (*I.T.D.C.S.*) with $x = .167$ and $z = .417$. This is strikingly shown by the fact that strong reflections are present from planes having complex indices only when $(h/6 + 5l/12) = n$; thus:

| | | | |
|---|---|---|---|
| (10.2)s | (20.4)ms-s | (30.6)mw | (40.8)m |
| (10.14)ms-s | (20.16)mw | | (40.8)m |
| (10.26)mw | (20.28)mw | (30.30)mw-w | |

If the remainder of the plumbojarosite structure was unchanged from that of jarosite reflections from $(h0.l)$ with $l$ odd should show, for particular values of $h$, normal decline of $F$ as $l$ increases, since lead atoms alone would contribute to such reflections. This is not quite true as perhaps

can be seen from the intensities of (00.$l$), thus 3rd m, 9th m, 15th w, 21st mw, 27th a. These rather suggest that the $SO_4$ and possibly the OH groups about the vacant potassium positions are slightly displaced along the $c$ axis, by an amount, however, that probably does not exceed .01 $c_0$ = .34A.

### STRUCTURES OF NATRO- , ARGENTO- , AMMONIOJAROSITES, HAMLINITE, KARPHOSIDERITE, BORGSTRÖMITE, AND $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$.

Powder photographs with FeK radiation of these minerals showed that they all are correctly classified as jarosites. The photograph of $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ in particular was very closely similar to that of jarosite. Borgströmite gave a powder photograph closely related to these but distinctly different from them. Limited isomorphous replacement in the natural mineral is sufficient to account for the observed differences. This is also true for karphosiderite the diffraction pattern of which is distinctly different from that of any of the above mentioned minerals. Powder photographs of hamlinite, on the other hand, showed considerable displacement of the interference maxima and change of intensities from those of the jarosites. These changes are to be expected as a result of replacing $Fe^{+++}$ by $Al^{+++}$. In the absence of analyses it was thought unwise to use these powder diffraction data for determination of lattice dimensions. The argento- and ammoniojarosites, however, were materials of known composition. Lattice dimensions obtained from their powder diffraction data are listed in Table 1.

Equatorial zone Weissenberg photographs (FeK radiation) about the normal to (10.0) and to (01.0) showed that the structure of $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ must be closely the same as that of jarosite. The rhombohedral unit of structure thus contains one $Fe_3(SO_4)_2 \cdot 4\frac{1}{2}H_2O$ which corresponds to $Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O$. This change in composition is brought about without apparent change of symmetry or change in the parameter values for jarosite. It would seem, therefore, that half of the $H_2O$ molecules replace potassium at $000\overline{)}$ and that of the other half replace hydroxyl groups in a random manner.

### DISCUSSION

The structure of alunite projected to scale on (00.1) is shown as Fig. 1. In Fig. 2 an attempt has been made to show the immediate surroundings of some atoms. Inspection of these figures and consideration of the structure as a whole show that electrostatic requirements are well satisfied. An $Al^{+3}$ ion is at the maximum possible distance, permitted by the

crystal symmetry, from other $Al^{+3}$ ions and near the maximum possible distance from $S^{+6}$ that still permits an $Al^{+3}$ to oxygen of $SO_4^{--}$ distance of *ca.* 2.0Å. Aluminum has the expected coordination number, six, being surrounded at the corners of an approximately regular octahedron by four $OH^-$ groups and two oxygen atoms of $SO_4^{--}$ ions. The coordination number of potassium is twelve, there being six oxygen atoms at 2.80Å and six hydroxyl groups at 2.85Å.
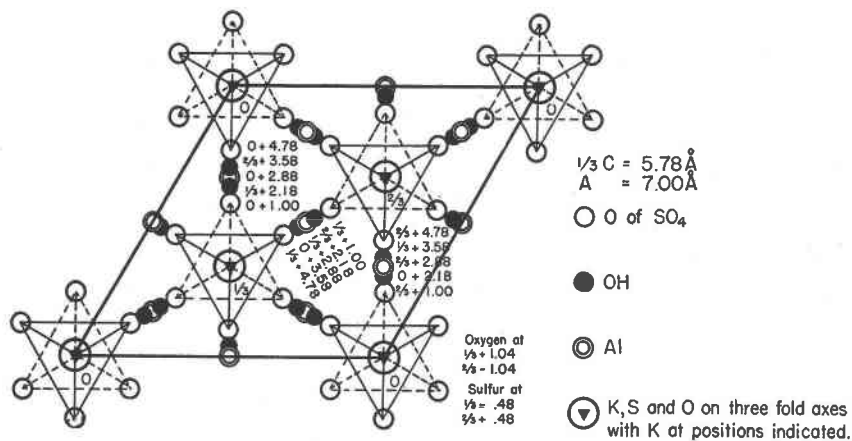


Fig. 1—Projection of the alunite structure in (00.1). Distances above the plane of projection are indicated on the figure.

Sulfate oxygen atoms on trigonal axes are surrounded by three $OH^-$ groups at 2.52Å, the error being possibly as great as 0.15Å. It would seem that the hydrogen atoms must be so placed as to give hydroxyl binding to these oxygen atoms since no other ions, other than $S^{+6}$, approach them closely. Hydroxyl groups are near: 2 Al at 2.04Å, 1 K at 2.85Å, 1 oxygen at 2.52Å, 2 oxygen at 2.65Å, two other hydroxyl groups at 2.65Å, and two other hydroxyl groups at 2.68Å. These distances are near the expected values.

Before discussing the isomorphous replacements leading to the various minerals it might be best to list the ionic radii of the elements involved: these, as taken from Pauling[14] are:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $Na^+$ | 0.95Å | $Pb^{++}$ | 1.21 | $Ce^{+++}$ | 1.18 | $S^{+6}$ | 0.29 |
| $K^+$ | 1.33 | $Sr^{++}$ | 1.13 | $Al^{+++}$ | 0.50 | $P^{+5}$ | 0.34 |
| $Rb^+$ | 1.48 | $Ba^{++}$ | 1.35 | $Fe^{+++}$ | 0.67 | $As^{+5}$ | 0.47 |
| $Ag^+$ | 1.26 | | | | | | |

[14] Pauling, *Jour. Am. Chem. Soc.*, vol. **49**, p. 765, 1927.

It is to be noted that the $SO_4^{--}$, $PO_4^{---}$, and $AsO_4^{---}$ differ but slightly in dimensions and that the positive ions $Na^+$ to $Ce^{+++}$ vary from $r$ $=0.95\text{Å}$ to $1.48\text{Å}$, which is considerably greater than usually is found in an isomorphous series.
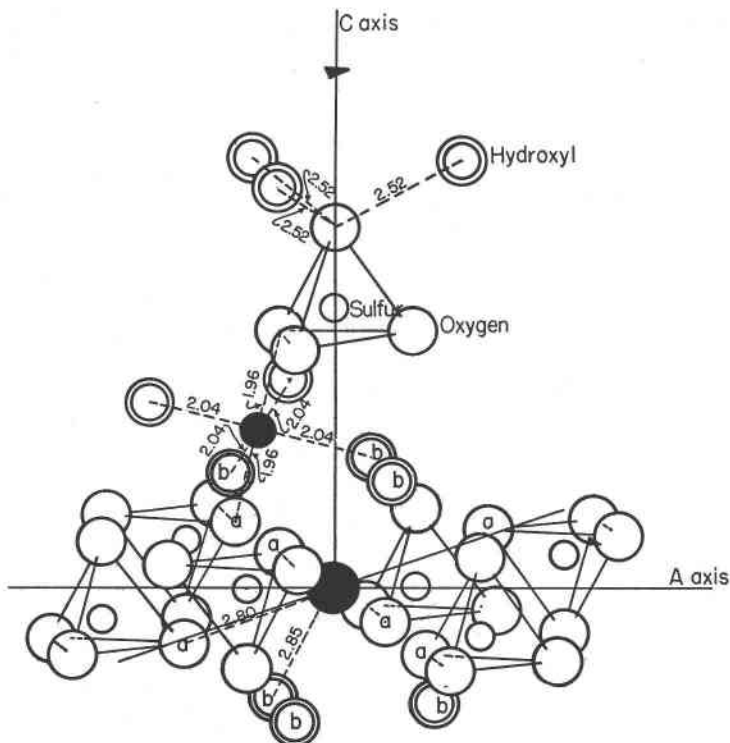


Fig. 2—The surroundings of potassium (large black circles), aluminum (small black circles), and oxygen at 00z. Potassium is at the indicated distances from six oxygen atoms of $SO_4$ groups (marked $a$) and six hydroxyl groups (marked $b$).

The various $Na^+$, $K^+$, $Rb^+$, $Ag^+$, $NH_4^+$, $Fe^{+++}$, and $Al^{+++}$ minerals, alunite, jarosite, natroalunite, argentojarosite, ammoniojarosite, and natrojarosite, are of course simple replacement compounds. Large variation in the ionic radii of the ion in the potassium position is allowed by the structure. In the case of plumbojarosite, as mentioned above, one $Pb^{++}$ replaces $K^+$ and the other $K^+$ position remains vacant. It is possible that this vacant position is sometimes filled with a water molecule. In the sulfate-phosphates, beudantite, corkite, svanbergite, hinsdalite, and harttite replacement of $SO_4^{--}$ by $PO_4^{---}$ or $AsO_4^{---}$ is accompanied by the filling of this vacant position with $Sr^{++}$ or $Pb^{++}$, the limit being the 1:1 ratio of $SO_4$ to $PO_4$ or $AsO_4$. The cerium compound, the mineral florencite, is a continuation of this series in which $PO_4^{---}$ replaces

$SO_4^{--}$ and $Ce^{+++}$ the $K^+$ ions; $4PO_4^{---} + 2Ce^{+++}$ having the same charge as $4SO_4^{---} + 2K^+$ and occupying the same positions.

The most interesting isomorphous replacement of all is that afforded by $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$. This compound can be written as $H_2O \cdot Fe_3$ $(SO_4)_2(OH)_5H_2O$ to show its relationship to jarosite $K Fe_3(SO_4)_2(OH)_5$ $(OH)$. Thus an $H_2O$ molecule replaces $K^+$ and a hydroxyl ion is changed to $H_2O$, preserving the balance of charge. Such a change is permitted by the size of the water molecule. In karphosiderite the formula could be written as $Fe_3(SO_4)_2(OH)_5 \cdot H_2O$, the potassium positions remaining vacant. Similarly the minerals listed as acid phosphates by Schaller, namely, hamlinite, plumbogummite, gorceixite etc., and harttite are probably related to the above compounds. For example, plumbogummite probably is $PbAl_3(PO_4)_2(OH)_5H_2O$, which is related to jarosite by replacement of $K^+$ by $Pb^{++}$, $SO_4^{--}$ by $PO_4^{---}$ and $OH^-$ by $H_2O$ neutral. In all of these minerals hydroxyl is probably statistically replaced by water and the crystal symmetry is retained.

A particular mineral has the possibility of showing any of the various types of replacement. Thus plumbojarosite might show variation toward corkite, plumbogummite, or a hydrous form in which the vacant positions are filled with water.[15] There is no explanation in the structure for the observation that the various minerals are usually found free of extensive isomorphous replacement.

Powder photographs of the alunite ores from Marysvale, Utah, all showed diffraction lines of quartz. The intensity variation of the quartz pattern was, moreover, that to be expected from the $SiO_2$ content of the samples. It would seem therefore that the silica is present as a separate very finely divided crystalline phase. Alunite has also been shown to occur associated with halloysite $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$[16] and more commonly with diaspore $(AlO(OH))$. These observations indicate that alunite does not form appreciable solid solutions containing excess $Al^{+++}$, i.e. replacing $K^+$, in which $SiO_4$ replaces $SO_4$. This is to be expected from the structure, but introduction of some $SiO_4$ as a replacement of $SO_4$ with accompanying substitution of something like $Ca^{++}$ for $K^+$ might be possible.

[15] Mr. E. P. Henderson of the U. S. National Museum has given permission to quote some unpublished results obtained by him while working with the U. S. Geological Survey. "Upon measuring the loss on ignition in presence of PbO of several samples of plumbojarosites one was found in which the loss was 12.70% at 600° and even at 450° had lost 11.09% (calculated per cent of water in plumbojarosite is 9.57)." It might be suggested that if this loss is truly due to water then replacements of the type mentioned are probably present.

[16] Ross, C. S. and Kerr, P. F. *Professional Paper* **1856**, U. S. Dept. of Interior, p. 135–148.

## Summary

$X$-ray diffraction data have been obtained from alunite, jarosite, natro-, argento-, ammonio- and plumbojarosites, karphosiderite, borgströmite, hamlinite, and the compound $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$. The crystal structure of the alunite-jarosite group of minerals is derived from these data and an explanation is advanced for the various types of isomorphous replacements shown by the group. These structures are characterized by binding between hydroxyl groups and an oxygen atom of a sulfate group.