

THE CRYSTAL STRUCTURE OF AUGELITE

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ABSTRACT

An augelite, $\text{Al}_2(\text{PO}_4)(\text{OH})_3$, from Mono County, California, has unit cell $a=13.124 \pm 0.006$, $b=7.988 \pm 0.005$, $c=5.066 \pm 0.003$ Å, $\beta=112.25 \pm 0.02^\circ$ and its space group is $C2/m$, in agreement with Peacock and Moddle (1941).

Patterson maps were calculated from three-dimensional intensities and solved by the minimum function method. The structure was refined by a sequence of Fourier syntheses and least-squares techniques to an R value of 6.6 percent for all and 5.0 percent for all but the eight strongest reflections.

Al has two different coordinations in this structure. One is coordinated to four OH and two O and the other to three OH and two O. The P atom is coordinated to four O. Four Al polyhedra, two of each type, are linked together by sharing OH-OH edges. These groups in turn are connected to P-tetrahedra sharing corner O atoms.

EXPERIMENTAL PROCEDURE

A cleavage fragment from a large crystal from Mono County, California, measuring 0.65, 0.65 and 1.0 mm along the a -, b - and c -axes respectively, was mounted on the goniometer with the c -axis as rotation axis.

The precession photographs offered a choice between the pseudoorthorhombic body centered unit cell with $a=12.14 \pm 0.02$, $b=7.98 \pm 0.02$, $c=5.07 \pm 0.02$ Å and $\beta=90.3 \pm 0.1^\circ$ and the monoclinic C -centered unit cell with $a=13.13 \pm 0.02$, $b=7.98 \pm 0.02$, $c=5.07 \pm 0.02$ Å and $\beta=112.4 \pm 0.15^\circ$. These cell parameters were refined from powder diffractometry data with least-squares techniques and the following parameters were obtained for the C -centered monoclinic unit cell: $a=13.124 \pm 0.006$ Å, $b=7.988 \pm 0.005$ Å, $c=5.066 \pm 0.003$ Å, $\beta=112.25 \pm 0.02^\circ$, $Z=4$. The diffraction symmetry of the crystal and the systematic absences of diffraction spot indicated the possible space groups of $C2/m$, Cm , or $C2$. All the above data are in agreement with those determined by Peacock and Moddle (1941).

Intensities of 1474 reflections were collected on an equi-inclination, single-crystal diffractometer using molybdenum radiation and Zr-Y balanced filters within the upper half of the reciprocal lattice limited to $\sin \theta=0.503$. Three reflections (202), (404) and (606), however, were not scanned because these reciprocal points are too close to the rotation axis. The usual corrections were applied for absorption and Lorentz-polarization with the aid of Charles W. Burnham's (1966) computer program written for an arbitrary-shaped crystal, but no attempt was made to correct for extinction effects at this stage. For the 26 unobserved reflections, the value of the standard deviation of the intensity measurements was used as the intensities, giving a total of 782 independent observed reflections.

STRUCTURE DETERMINATION

The $N(z)$ test of Howells, Phillips and Rogers (1950), using all reflections, disclosed that the structure is centric. Accordingly the three dimensional Patterson maps were solved for the centric space group of $C2/m$.

The tracing of image lines and the judgment of the heights of the prominent peaks on the Patterson maps led to the locations of four Al atoms on two-fold axes, and another four Al and the P atoms on mirror planes. Accordingly the coordinates of the Al and P atoms were obtained directly from the Patterson maps. The coordinates of the oxygen atoms and the hydroxyl groups, however, could not be determined, because of peak broadening in areas where they could be expected. Using the observed Al-Al and P-P inversion vectors M_6 maps were prepared which re-

TABLE 1. ATOMIC PARAMETERS IN AUGELITE

Standard deviations at lower rows, x, y, z 's multiplied by 10^4 , β 's by 10^6

Atom	Number of atoms in the unit cell	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al(1)	4	0	1989	0	95	136	574	0	144	0
		0	2	0	8	18	43	0	14	0
Al(2)	4	1889	0	9792	74	186	238	0	64	0
		1	0	2	8	18	42	0	14	0
P	4	3528	0	6278	56	126	108	0	41	0
		1	0	2	6	15	35	0	16	0
O(1)	4	2576	0	7322	137	464	627	0	173	0
		2	0	6	19	49	101	0	37	0
O(2)	4	3038	0	3003	126	1027	267	0	78	0
		2	0	6	19	65	96	0	36	0
O(3)	8	4215	1563	7170	280	469	2054	-230	510	-650
		2	3	5	16	37	93	21	33	49
OH(1)	4	0853	0	1980	126	284	367	0	57	0
		2	0	5	18	44	96	0	34	0
OH(2)	8	1071	1813	8431	163	273	1080	51	266	145
		2	3	4	13	33	78	18	26	40

TABLE 2. ELLIPSOIDS OF THERMAL VIBRATIONS

Atom	<i>B</i>	axis	<i>r</i> (Å)	$\phi(a)$	$\phi(b)$	$\phi(c)$
Al(1)	0.43 0.02	1	0.064 0.004	140° 6°	90° 0	28° 6°
		2	.066 .004	90 0	180 0	90 0
		3	.089 .003	50 6	90 0	62 6
Al(2)	0.37 0.02	1	.049 .005	108 7	90 0	5 7
		2	.075 .004	162 7	90 0	85 7
		3	.077 .004	90 0	0 0	90 0
P	0.25 0.02	1	.032 .006	104 5	90 0	8 5
		2	.064 .004	90 0	180 0	90 0
		3	.065 .004	14 5	90 0	98 5
O(1)	0.81 0.05	1	.072 .007	126 10	90 0	14 10
		2	.103 .007	144 10	90 0	104 10
		3	.122 .007	90 0	0 0	90 0
O(2)	1.20 0.06	1	.052 .010	100 8	90 0	12 8
		2	.098 .007	170 8	90 0	78 8
		3	.182 .006	90 0	0 0	90 0
O(3)	1.40 0.04	1	.074 .007	73 7	34 2	70 7
		2	.107 .004	30 5	91 6	143 5
		3	.190 .004	66 2	124 2	59 2
OH(1)	0.62 0.05	1	.064 .008	91 9	90 0	21 9
		2	.096 .007	90 0	180 0	90 0
		3	.101 .007	1 9	90 0	111 9
OH(2)	0.80 0.03	1	.084 .005	128 59	116 69	33 28
		2	.087 .006	127 60	37 56	79 66
		3	.126 .004	60 5	66 5	59 5

B = equivalent isotropic temperature factors.

r = rms displacement along the principal axes, 1, 2, or 3.

ϕ = angles between the principal axes and the crystallographic axes.

vealed the positions of the missing oxygens and hydroxyls. A single run of Fourier synthesis using the coordinates thus obtained, confirmed the location of all the atoms. At this stage, the *R*-factor was 18.7 percent.

Using these atomic coordinates and all reflections a cycle of least squares refinement was calculated which gave negative temperature factors for P and Al (2) and unreasonably low values for other atoms. After removing 81 strong reflections, two cycles of least-squares refinement were calculated. This refinement yielded reasonable isotropic tem-

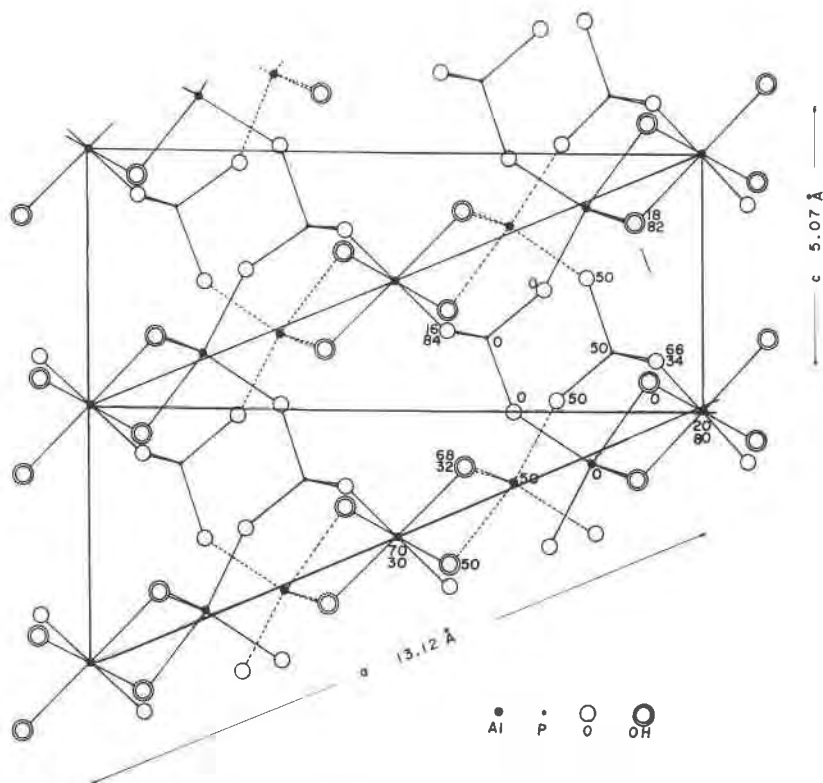


FIG. 1. *b*-axis projection of the augelite structure.

perature factors. In the next two cycles anisotropic temperature factors were calculated. Although the data obtained appeared to be reasonable, the negative $|F_o| - |F_c|$ differences of the strong reflections indicated the presence of strong extinction effects. In order to remedy that, the scale coefficients of secondary extinction corrections (Zachariasen, 1963) were plotted for the strong reflections with $\sin \theta$ as the abscissa of the chart. The results showed that the strong reflections are dispersed in the lower angle region, especially below $\sin \theta = 0.12$ which can be attributed to the effect of extinction. In order to correct for that a weighted mean of scale coefficient was obtained from the 70 strong high angle reflections and was applied for all reflections using Zachariasen's formula, with C (the coefficient for secondary extinction correction) $= (1.756 \pm 0.132) \times 10^{-6}$. After applying this correction and using all reflections, a cycle of least-squares refinement was calculated which resulted in slightly lowered temperature factors.

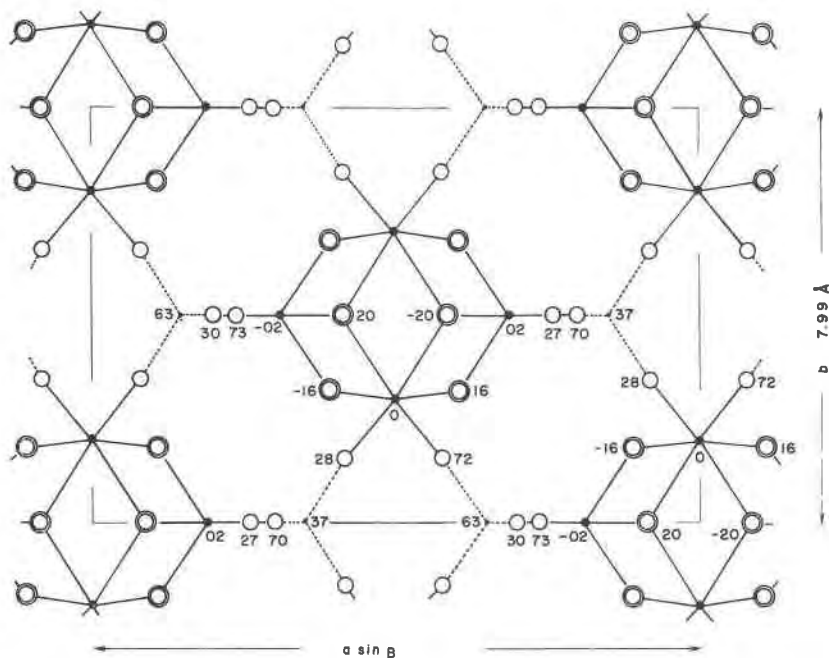


FIG. 2. c -axis projection of the augelite structure.

The eight strong reflections which still had negative $|F_o| - |F_c|$ differences were removed and three more cycles of least-squares refinement were calculated. Reasonable temperature factors and significantly smaller standard deviations for atomic parameters were then obtained.

All the above computations were performed with the University of Minnesota's CDC 6600 computer using L. W. Finger's program.¹ Throughout the calculations, neutral atomic scattering factors (Cromer and Waber, 1965) were used, and the contribution of the hydrogen atoms to the structure factors was neglected. Weights were set as the reciprocals of $\sigma(F^2)$. The final R factors were 5.0 and 6.6 percent respectively for the unrejected and for all reflections.

The final atomic parameters are tabulated in Table 1 and the ellipsoids of thermal vibration in Table 2. Lists of observed and calculated structure factors are available from the authors on request.

DESCRIPTION OF THE STRUCTURE

The structure of augelite projected along the b - and c -axes is illustrated in Figures 1 and 2, and a stereoscopic view of the bonding polyhedra is

¹ Least-squares and Fourier synthesis programs (1965)

TABLE 3. SELECTED BOND DISTANCES (LESS THAN 2.95 Å)

PO ₄ —tetrahedron			
P	—O(1)	1.5295 Å	±0.0029 Å
P	—O(2)	1.5356	0.0028
P	—O(3)	1.5059	0.0028 (×2)
O(1)	—O(2)	2.4819	0.0039
O(1)	—O(3)	2.5129	0.0035 (×2)
O(2)	—O(3)	2.4353	0.0040 (×2)
O(3)	—O(3) ³	2.4977	0.0051
Al(1)—octahedron			
Al(1)	—O(3) ⁶	1.8264 Å	±0.0030 Å (×2)
Al(1)	—OH(1)	1.9830	0.0029 (×2)
Al(1)	—OH(2)	1.8639	0.0021 (×2)
O(3) ⁶	—O(3) ⁷	2.8277	0.0047
O(3) ⁶	—OH(1)	2.7853	0.0030 (×2)
O(3) ⁶	—OH(2)	2.7244	0.0031 (×2)
O(3) ⁶	—OH(2) ⁴	2.6168	0.0038 (×2)
OH(1)	—OH(1) ⁴	2.3732	0.0056
OH(1)	—OH(2)	2.4087	0.0031 (×2)
OH(1)	—OH(2) ⁴	2.8491	0.0037 (×2)
Al(2)—polyhedron			
Al(2)	—O(1)	1.7984 Å	±0.0028 Å
Al(2)	—O(2)	1.7504	0.0032
Al(2)	—OH(1)	2.0544	0.0029
Al(2)	—OH(2)	1.7788	0.0029 (×2)
O(1)	—O(2)	2.7076	0.0037
O(1)	—OH(2)	2.6750	0.0035 (×2)
O(2)	—OH(1)	2.7152	0.0045
OH(1)	—OH(2)	2.4087	0.0031 (×2)
OH(2)	—OH(2) ³	2.8965	0.0046

Superscripts identify symmetrical equivalent positions (superscript 1 is omitted in the table):

- | | |
|--------------------------------------|---------------------------------------|
| 1. x, y, z | 2. $-x, -y, -z$ |
| 3. $x, -y, z$ | 4. $-x, y, -z$ |
| 5. $\frac{1}{2}+x, \frac{1}{2}+y, z$ | 6. $\frac{1}{2}-x, \frac{1}{2}-y, -z$ |
| 7. $\frac{1}{2}+x, \frac{1}{2}-y, z$ | 8. $\frac{1}{2}-x, \frac{1}{2}+y, -z$ |

shown in Figure 3. The most significant bond distances and angles are tabulated in Tables 3 and 4 respectively.

In the augelite structure there are two different types of coordination polyhedra of the Al atoms. Al (1) is octahedrally coordinated with four OH groups and two O atoms, the cation-anion distances within a polyhedron range from 1.826 to 1.983 Å and average 1.891 Å. The other aluminum, Al(2), is surrounded by five neighbors, two O atoms and one OH group located within a plane and two other OH groups nearly perpen-

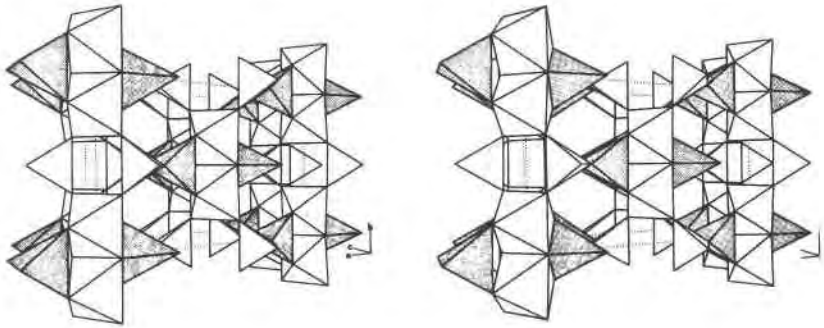


FIG. 3. Stereoscopic drawing of the polyhedral model of the augelite structure.
 Shaded polyhedra represent five-fold coordinated Al(2).

TABLE 4. SELECTED BOND ANGLES AND THEIR STANDARD DEVIATIONS

O(3) ⁶	—Al(1)	—O(3) ⁷	101.5°	±0.2°	
O(3) ⁶		—OH(1)	93.9	0.1	(×2)
O(3) ⁶		—OH(2) ⁴	90.3	0.1	(×2)
O(3) ⁶		—OH(2)	95.2	0.1	(×2)
OH(1)		—OH(1) ⁴	73.5	0.2	
OH(1)		—OH(2)	77.5	0.1	(×2)
OH(1)		—OH(2) ⁴	95.5	0.1	
O(3) ⁶		—OH(1) ⁴	161.2	0.4	(×2)
OH(2)		—OH(2) ⁴	171.4	0.7	
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O(1)	—Al(2)	—O(2)	99.4°	±0.2	
O(1)		—OH(2)	96.8	0.1	(×2)
O(2)		—OH(1)	90.7	0.1	
OH(1)		—OH(2)	77.5	0.1	(×2)
OH(2)		—OH(2) ³	109.0	0.2	
O(1)		—OH(1)	170.0	0.6	
O(2)		—OH(2)	122.8	0.1	(×2)
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O(1)	—P	—O(2)	108.1°	±0.2	
O(1)		—O(3)	111.8	0.1	(×2)
O(2)		—O(3)	106.4	0.1	(×2)
O(3)		—O(3) ³	112.1	0.2	
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P	—O(1)	—Al(2)	158.6°	±0.3	
P	—O(2)	—Al(2)	149.9	0.3	
P	—O(3)	—Al(1)	148.9	0.2	(×2)
Al(1)	—OH(1)	—Al(1) ³	106.5	0.2	(×2)
Al(1)	—OH(1)	—Al(2)	95.1	0.1	(×2)
Al(1)	—OH(2)	—Al(2)	109.8	0.1	(×2)

dicular to that plane. The cation-anion distances in the Al(2) polyhedron range from 1.750 to 2.054 Å, and average 1.833 Å.

Two Al(1) and two Al(2) polyhedra are linked together by sharing OH-OH edges and are concentrated in layers parallel with the 00 l plane and are separated by $d(001)$. These groups of aluminum polyhedra are connected with each other by phosphate tetrahedra sharing corner oxygen atoms thus linking the polyhedra into a continuous network.

There are no similar crystal structures known in mineralogy. The five-fold coordination of aluminum has been observed in andalusite by Taylor (1929) and by Burnham and Buerger (1960). As in andalusite, these five-fold Al coordination polyhedra are linked to other Al polyhedra by sharing edges. In a remote way the augelite structure resembles that of lazulite (Lindberg and Christ, 1959). That is, in both structures high density groups of Al- (and Mg-) polyhedra are connected by P-tetrahedra. That group in lazulite is composed of two Al- and one Mg-octahedra.

The perfect (110) cleavage of augelite can be explained by the relatively weak Al-OH bonds across that plane. The less perfect cleavages in the (201) and (001) planes on the other hand require the breakage of several Al-OH and Al-O bonds.

The authors wish to acknowledge the support of the National Science Foundation for this investigation.

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Manuscript received, December 26, 1967; accepted for publication, February 3, 1968.