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THE CRYSTAL STRUCTURE OF CAHNITE,* $Ca_2BAsO_4(OH)_4$

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ABSTRACT

Cahnite is one of the few crystals assigned to crystal class $\bar{4}$. A precession study showed that its diffraction symbol is $4/mI\text{-}/\text{-}$, which contains space groups $I4$, $I\bar{4}$, and $I4/m$. Because of the known $\bar{4}$ morphology, it must be assigned to space group $I\bar{4}$. The unit cell, whose dimensions are $a=7.11$ Å, $c=6.20$ Å, contains $2Ca_2BAsO_4(OH)_4$. The structure was studied with the aid of intensity measurements made with a single-crystal diffractometer. Patterson syntheses were made for projections along the c, a, and [110] directions. The atomic numbers of the atoms are in the ratio As:Ca:O:B:H=33:20:8:5:1, so that the Patterson peaks are dominated by the atom pairs containing As as one member of the pair. Since there are only two As in a body-centered cell, one As can be arbitrarily assigned to the origin. Then the major peaks of the Patterson syntheses are at locations of atoms in the structure. The structure, determined approximately in this manner, was refined by least-squares and by two-dimensional difference maps.

The structure consists of As tetrahedrally surrounded by O_1 at a distance of 1.68 Å, and B tetrahedrally surrounded by O_2 at a distance of 1.47 Å. Ca_1 is surrounded by four O_1 at a distance of 2.44 Å, and by four O_2 at 2.55 Å, while Ca_2 is surrounded by four O_1 at 2.38 Å and four O_2 at 2.54 Å. The structure of cahnite is somewhat similar to that of zircon and its numerous isomorphs, but more specifically, it is a derivative structure based upon KH_2AsO_4, so that its formula can be written $CaH_2B_{\frac{1}{2}}As_{\frac{1}{2}}O_4$.

INTRODUCTION

Cahnite, $Ca_2BAsO_4(OH)_4$, is a rare mineral found originally in the mines at Franklin, New Jersey. This paper contains the results of an investigation of its crystal structure, using single-crystal x-ray diffraction methods.

Cahnite was first mentioned in the literature by Palache (1921) in a paper read by title only at a meeting of the Mineralogical Society of America. Subsequently, Palache and Bauer (1927) published a paper describing the occurrence, morphology, chemistry, and physical properties of Franklin cahnite. Palache (1941) gave additional morphological information. Bügge (1952) reported an occurrence of cahnite in the Klodeborg mine, Arendal, Norway.

PREVIOUS WORK

Palache and Bauer (1927) published three analyses of cahnite. These are given in Table 1 along with the composition calculated from the

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* Presented at the Fifth Congress of the International Union of Crystallography, Cambridge, England, August 17, 1960, and at the 41st Meeting of the Mineralogical Society of America, Denver, Colorado, October 31, 1960.

TABLE 1. CHEMICAL ANALYSES OF CAHNITE, AFTER PALACHE AND BAUER (1927)

	1	2	3 very pure material	4 calculated
CaO	38.27	37.13	37.62	37.64
B_2O_3	10.14	11.64	11.86	11.74
As_2O_5	36.79	37.47	38.05	38.54
H_2O	11.75	11.78	12.42	12.08
PbO	1.15	trace	—	
MgO	0.24	—	—	
ZnO	trace	1.58	—	
CO_2	trace	—	—	

formula $Ca_2BAsO_4(OH)_4$. According to these authors, analysis 3 in Table 1 came from a very pure sample. From these figures it is evident that there is little likelihood that much substitution exists in cahnite, nor is there any doubt that the formula is correct. According to Palache and Bauer, the density of cahnite is 3.156 and the hardness is 3; cahnite is uniaxial positive with $n_O = 1.662$ and $n_E = 1.663$.

Palache (1941) assigned cahnite to the crystal class $\bar{4}$ on the basis of the development of the form $\{311\}$. Cahnite is one of the few minerals in this class.

SPACE GROUP AND UNIT CELL

X-ray photographs were taken with the Weissenberg and precession cameras using CuKα and MoKα radiations. Precession photographs lead to a tetragonal unit cell with

$$a = 7.11 \text{ Å},$$
$$c = 6.20 \text{ Å}.$$

The diffraction symbol, $4/mI\text{-}/\text{-}$, contains space groups $I4$, $I\bar{4}$, and $I4/m$. Because of the morphological symmetry, it must be assigned to the space group $I\bar{4}$.

There are two formula weights per body-centered cell. Palache and Bauer's (1927) c/a ratio corresponds to the face-centered cell. If the diffraction results are referred to a face-centered cell, the axial ratio is

$$c/a = 6.20/(7.11 \times 1.414) = 0.616$$

as compared to the morphological value of 0.615. This relation must be considered when aligning cahnite crystals for *x*-ray analysis using Palache's indexing.

It is interesting to note that, to our knowledge, no other terrestrial minerals have been reported in space group $I\bar{4}$. The only minerals assigned to this space group by Donnay and Nowacki (1954) are the meteoric phosphides of the schreibersite (Fe_3P) type.

COLLECTION OF INTENSITIES

Collection of three-dimensional diffraction intensities was carried out using an equi-inclination single-crystal diffractometer with a Geiger counter as a detector. Several small splinters were cleaved from the original crystals and checked for twinning with the polarizing microscope and by Weissenberg photographs. The crystal chosen was untwinned and had the following dimensions: $0.061 \times 0.064 \times 0.3$ mm., with the longest dimension in the direction of the *c* axis.

All intensities were collected using CuKα radiation. An absorption correction was made by assuming that the crystal approximated a cylinder after the method of Buerger and Niizeki (1958).

PATTERSON PROJECTIONS

Patterson syntheses were computed for the projections along *c*, *a* and [110]. The projection along *c*, given in Fig. 1, turned out to be the most useful because its plane group, *p*4, is the same as that of the electron-density projection along *c*. Because of the relatively small number of Fourier coefficients available for each computation, the Patterson maps show large series-termination effects. Any attempt to interpret the Patterson, or, for that matter, the electron-density maps, must take these effects into account when determining atom locations.

The atomic numbers of the atoms in cahnite are in the ratio As:Ca:O:

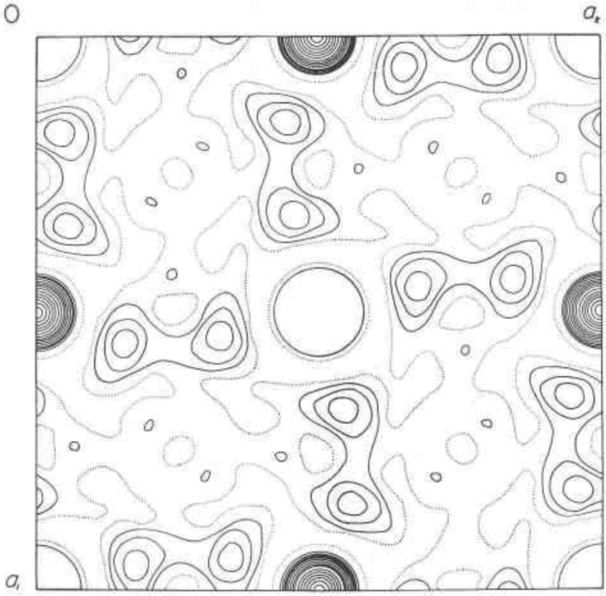

FIG. 1. Patterson projection of cahnite along *c*.

B:H=33:20:8:5:1 so that the Patterson peaks are dominated by atom pairs containing As as one member of the pair. Since the body-centered unit cell contains 2 $Ca_2BAsO_4(OH)_4$, there are 2 As, 2 B, 4 Ca, and 16 O to be distributed among the equivalent positions of the space group. Table 2 gives the equipoints for space group $I\bar{4}$. It is obvious that As must be assigned to position 2*a*, 2*b*, 2*c* or 2*d*, which are indistinguishable. If As is arbitrarily assigned to the origin, equipoint 2*a*, the major peaks of the Patterson projections can be expected to lie at locations of atoms in the structure.

TABLE 2. ASSIGNMENT OF ATOMS IN CAHNITE TO EQUIVALENT POSITIONS OF $I\bar{4}$

Equipoint	Point Symmetry	Equivalent Positions $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2})+$	Atom Assignment
2*a*	$\bar{4}$	000	As
2*b*	$\bar{4}$	$00\frac{1}{2}$	Ca_1
2*c*	$\bar{4}$	$0\frac{1}{2}\frac{1}{4}$	B
2*d*	$\bar{4}$	$0\frac{1}{2}\frac{3}{4}$	Ca_2
4*e*	2	$00z, 00\bar{z}$	—
4*f*	2	$0\frac{1}{2}z, \frac{1}{2}0z$	—
8*g*	1	$xyz, \bar{x}\bar{y}z, y\bar{x}\bar{z}, \bar{y}x\bar{z}$	O_1, O_2

With As assigned to position 2*a*, then 2 B and 4 Ca must occupy either two or three of the positions 2*b* through 4*f*. Examination of Fig. 1 shows that the strongest peaks occur at the origin and at $0\frac{1}{2}$. These peaks represent the usual origin peak plus peaks due to the atoms in special positions. Since the projection along *a* and [110] showed only peaks which could be due to atoms in equipoints 2*b*, 2*c* and 2*d*, equipoints 4*e* and 4*f* were eliminated as possible Ca locations.

Two additional sets of peaks in Fig. 1 are in fourfold coordination around the origin and $0\frac{1}{2}$. From the formula of cahnite and from the results of other structure analyses, it is reasonable to assume that As and B are tetrahedrally surrounded by oxygen. If this is true in cahnite, each of the two additional peaks represents superposed images of oxygen as seen from As and Ca. The peaks, therefore, determine the approximate oxygen locations. The distribution of oxygen atoms, as well as B and Ca, is then as given in the right-hand column of Table 2. It does not matter whether B is assigned to equipoint 2*c* or 2*d* until the signs of the *z* coordinates of the oxygens are established.

If the positions of the four cations are fixed, the relative positions of the the oxygens can be obtained by taking the *x* and *y* coordinates from Fig. 1 and assuming regular tetrahedral coordination around the As and B. The orientation of each tetrahedron with respect to two positions which differ from each other by a 90° rotation around the $\bar{4}$ axis cannot be determined from the Patterson projections. Calculation of the closest O_1-O_2* distance for each of the four possible combinations of orientations gives 1.95 Å, 1.21 Å, 2.77 Å, and 1.97 Å. The only acceptable O_1-O_2 distance is 2.77 Å which uniquely determines the oxygen locations.

REFINEMENT

The structure, established as described in the preceding section, was refined by least-squares and two-dimensional difference maps. The parameters varied during least-squares refinement were the scale factor, the coordinates of O_1 and O_2, and individual isotropic temperature factors. Computations were carried out on the IBM 704 digital computer using a two-dimensional Fourier program and the crystallographic least-squares program written by Busing and Levy (1959).

The oxygen parameters converged in three cycles to the values given in stage 4 of Table 3. However, the temperature factors of As and Ca refined to negative values. Further cycles were run in which different conditions were imposed on the refinement to try to determine the cause of the negative temperature factors. When reflections with $\sin\theta < 0.2$ were not included and the cation temperature factors were set to 0.4, the results in stage 5 of Table 3 were obtained. When the temperature factors were refined they again became negative. The coordinates in stage 6 resulted from a cycle of refinement in which a separate scale factor was assigned to each level. An interesting result of this was that, when the temperature factors were allowed to vary, all of them refined to positive quantities. This suggests that the data for the separate levels differed in some way not taken into account. Since the temperature factors obtained are thus not considered to be reliable they have not been included in Table 3. It can be seen from the table, however, that changes in temperature factors and number of reflections used in refinement, as well as changes in scale factors, have very little effect on the oxygen coordinates.

In order to test the refinement results, and at the same time to detect any possible anomaly due to hydrogen, two-dimensional difference maps were computed for the projection along *c*. These confirmed the least-squares results. The hydrogen locations are discussed in the next section.

FINAL STRUCTURE

The final structure is shown in Fig. 2. The cahnite structure is similar to that of zircon and its numerous isomorphs (Durif-Varambon, 1959), the main difference being that cahnite contains hydrogen. The Ca atoms in cahnite are in the same position as Zr, and the B and As are in the same

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* O_1 is the oxygen neighbor of As, and O_2 is the neighbor of B.

TABLE 3. RESULTS OF LEAST-SQUARES REFINEMENT

Atom	Parameter	Stage of Refinement 1	2	3	4	5	6
O_1	x	.169	.174	.179	.178	.178	.178
	y	.031	.043	.054	.053	.054	.055
	z	.137	.154	.165	.167	.167	.167
O_2	x	.160	.159	.159	.159	.159	.160
	y	.454	.448	.444	.445	.444	.444
	z	.114	.110	.112	.113	.112	.113
$R=\frac{\Sigma\|\|F_o\|-\|F_c\|\|}{\Sigma\|F_o\|}$		—	.127	.105	.076	.075	.059

Stage	
1	Original coordinates from Patterson maps.
2	End of 1st cycle.
3	End of 2nd cycle.
4	End of 3rd cycle (including all reflections except 002 which was greatly affected by extinction). Temperature factors of As and Ca_2 set to .01; other temperature factors allowed to vary.
5	Reflection with $\sin\theta<0.2$ removed. Temperature factors of cations set to 0.4.
6	Separate scale factors assigned to each level. Other conditions same as stage 5.

position as Si in zircon. But the structure of cahnite is more closely related to that of KH_2AsO_4, and can be regarded as a derivative of it in which half the arsenic is replaced by boron, and neutrality is maintained by substituting Ca for K. From this point of view the formula of cahnite can be written $CaH_2B_{\frac{1}{2}}As_{\frac{1}{2}}O_4$. Accordingly, cahnite may be expected to act as a piezoelectric, and, possibly, as a ferroelectric at low temperatures.

On the basis of least-squares refinement and difference maps, the oxygen coordinates, $O_1=.178, .054, .167$, and $O_2=.160, .444, .114$, were regarded as the best set. Interatomic distances computed using these coordinates are given in Table 4. As is surrounded by 4 O_1 at a distance of 1.68 Å in a tetrahedron elongated along the c axis. B is surrounded by 4 O_2 at a distance of 1.47 Å in a nearly regular tetrahedron. The O_1-O_1 distance is 2.56 Å along the two horizontal edges of the AsO_4 tetrahedron and 2.79 Å along the other two edges. The edges of the BO_4 tetrahedra are all about 2.40 Å. Ca_1 is surrounded by 4 O_1 at a distance of 2.44 Å and by 4 O_2 at 2.55 Å. Ca_2 is surrounded by 4 O_1 at a distance of 2.38 Å and 4 O_2 at a distance of 2.54 Å.

The most probable location for the hydrogen bond is between the two oxygens connected with dotted line A in Fig. 2. This O_1-O_2 distance is

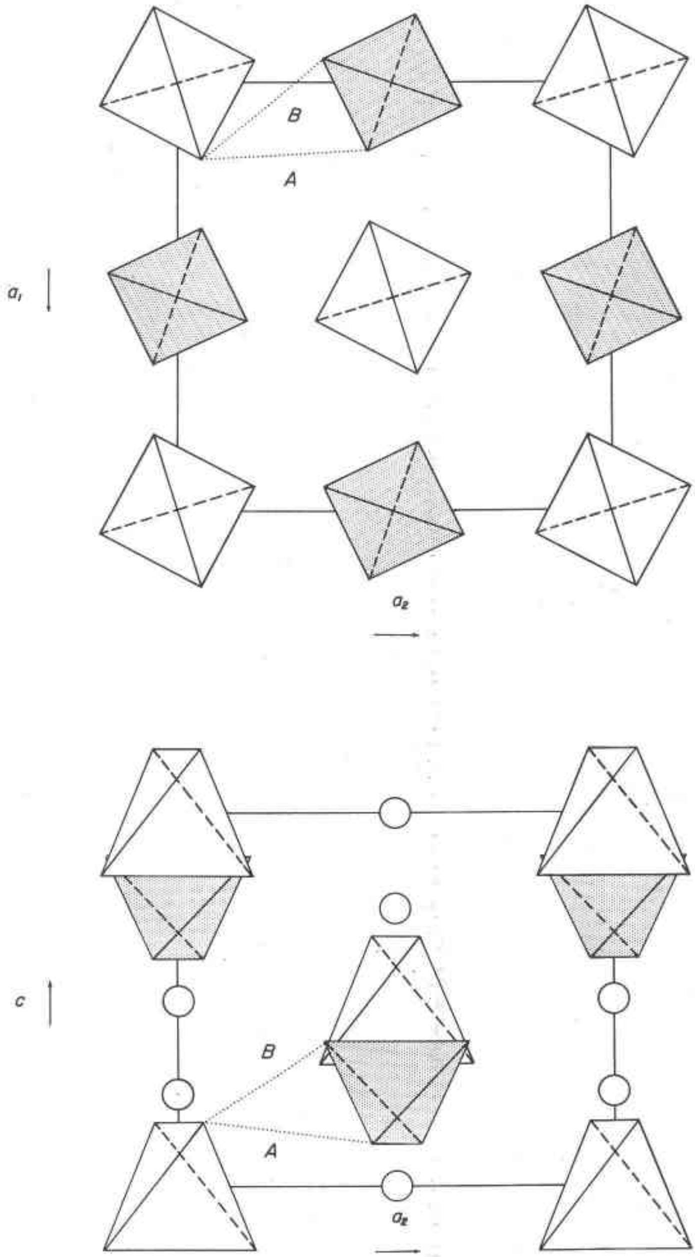

FIG. 2. Projections of the model of the cahnite structure along *c* (top) and along *a* (bottom). The unshaded tetrahedra are AsO_4 and the shaded ones are BO_4. Ca is shown by circles. Dotted lines *A* and *B* indicate possible hydrogen bonds.

TABLE 4. INTERATOMIC DISTANCES IN CAHNITE

Atom	Coordinate	Neighbor	Coordinate	Distance (Å)	Number of Neighbors
As	000	O_1	xyz	1.68	4
B	$0\frac{1}{2}\frac{1}{4}$	O_2	xyz	1.47	4
Ca_1	$00\frac{1}{2}$	O_1	xyz	2.44	4
		O_2	xyz	2.55	4
Ca_2	$0\frac{1}{2}\frac{3}{4}$	O_1	xyz	2.38	4
		O_2	xyz	2.54	4
O_1	xyz	O_1	$\bar{x}\bar{y}z$	2.56	1
			$y\bar{x}\bar{z}$	2.79	2
		O_2	xyz	2.80	1
			$y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z$	2.96	1
			$\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2}$	2.98	1
			$y\bar{x}\bar{z}$	3.65	1
O_2	xyz	O_2	$\bar{x}\bar{y}z$	2.40	1
			$y\bar{x}\bar{z}$	2.40	2

2.80 Å, the closest approach of O_1 to O_2. The two-dimensional difference maps, however, show a peak between the oxygens connected by dotted line *B* in Fig. 2. This latter distance is 2.96 Å. It is felt that nothing furthur can be said about the location of the hydrogen without further intensity data.

ACKNOWLEDGMENTS

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ADDITIONAL NOTE

P. Embrey (1960) has kindly sent to us the proof sheets of a forthcoming paper concerning a new occurrence of cahnite and his suggestions for a structure based on a comparison of the powder *x*-ray photographs of cahnite and xenotime. The occurrence is at Capo di Bove, near Rome, Italy. Embrey determined cell dimensions from a modified Nelson-Riley extrapolation of powder data and found

$$a = 7.0952 \pm 0.0015 \text{ Å}$$
$$c = 6.1904 \pm 0.003 \text{ Å}$$

These values are probably more accurate than ours. We are in agreement as to the similarity of the cahnite structure to that of xenotime and zircon.

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