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The Crystal Structure of Crandallite

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Abstract

Crandallite, $CaAl_3(OH)_6[PO_3(O_{1/2}(OH)_{1/2})]_2$, has a structure analogous with that of alunite. Refinement of the structure was carried out to $R = 0.044$ for 182 reflections. The hexagonal structure ($a = 7.005$ Å and $c = 16.192$ Å) consists of corner-sharing Al octahedra which are linked into trigonal and hexagonal rings to form sheets perpendicular to the c axis. Ca ions, surrounded by twelve oxygen and hydroxyl ions, lie in large cavities between the sheets. Each phosphate tetrahedron shares three corners with three Al octahedra from a trigonal ring in the sheet. The unshared corner points away from the trigonal hole towards the adjacent sheet to which it is hydrogen bonded. The mineral "deltaite" has been found to be identical to crandallite, within the accuracy of the structural results.

Introduction

Crandallite, $CaAl_3(OH)_6[PO_3O_{1/2}(OH)_{1/2}]_2$, a mineral of little economic value, is found in considerable quantities in lateritic phosphate rock deposits. Since crandallite occurs only in massive form, an X-ray investigation was undertaken of "deltaite," a closely related mineral. Elberty and Greenberg (1960) had suggested that deltaite could be crandallite in the form of crystals. They explained the difference in the X-ray diffraction powder patterns of the two minerals as due to apatite being generally present in samples of crandallite. Deltaite was first named and described by Larsen and Shannon (1930) as crystals intergrown with whitish and yellowish crusts of crandallite in variscite nodules from Fairfield, Utah. Subsequently, Larsen (1942) derived the formula—$Ca_2Al_2(PO_4)_2(OH)_4H_2O$ for deltaite. From the similarity of the X-ray powder patterns, he concluded that pseudo-wavellite ($CaAl_3(PO_4)_2(OH)_5H_2O$) and deltaite are isostructural. Pseudowavellite is now considered to be a synonym for crandallite with perhaps some variation in composition (Palache, Berman, and Frondel, 1957).

Experimental

A sample of "deltaite," from the original material studied by Larsen and Shannon (1930), was kindly supplied for this structural determination by Dr. C. Frondel of Harvard University. The sample consisted of 2 × 2 mm of white crusty material covered by tiny pinkish prismatic crystals, each with a triangular cross section. Analysis of two crystals with an AMX microprobe indicated 18.29 percent Al, 14.22 percent P, 9.11 percent Ca, and 0.08 percent Sr. Careful checks for S, F, and C proved negative. The standards used were wollastonite, apatite, and $SrSO_4$. Water was not determined. The formula $CaAl_3(PO_4)_2(OH)_5(H_2O)$, used for the preliminary structural determination, was later modified to $CaAl_3(OH)_6[PO_3(O_{1/2}(OH)_{1/2})]_2$ to agree with X-ray and infrared results, as will be explained subsequently.

Weissenberg photographs revealed the mineral to belong to class $R3$, $R\bar{3}$, $R32$, $R\bar{3}m$. Unit cell dimensions determined by least-squares from diffractometer measurements were: $a = 7.005 \pm 0.015$ Å and $c = 16.192 \pm 0.032$ Å (λ Cu = 1.5418 Å). For a 0.2 × 0.06 × 0.06 mm crystal mounted about the z axis on a Hilger-Watts model Y290 four circle diffractometer, 1630 reflections were measured with Cu radiation and an $\omega/2\theta$ scan. Reflections with an intensity less than 2.5 times the standard deviation of I were considered unobserved. The data were corrected for Lp and absorption. Symmetrically related reflections were averaged.[2]

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[2] The crystal used in this investigation has been deposited in the Museum of the Department of Geology and Geophysics, University of Wisconsin, Madison, Wisconsin, number UW1538/1.

TABLE 1. Final Positional Parameters and Their Standard Deviations

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Ca*	.0440	.0134	.0000		.0000	
Ca**	.0490	.0007	.0000		.0000	
P	.0000		.0000		.3137	.0002
Al	.5000		.0000		.5000	
O(1)	.0000		.0000		.4076	.0004
O(2)	.2142	.0003	−.2142		.9471	.0002
O(3)	.1237	.0003	−.1237		.1353	

**Parameters for Ca with anisotropic temperature factor.*
***Parameters for Ca with isotropic temperature factor.*

Crandallite was thought to have an alunite-type structure; thus, the initial parameters used were those for alunite (Wang, Bradley, and Steinfink, 1965). The structure was refined using the program ORFLS (Busing, Martin and Levy, 1963) and the scattering factors for Ca^{2+}, P^0, $Al^{1.5+}$ and O^{1-} obtained from the *International Tables for X-ray Crystallography*. The unit cell contains three formula units. The *E* test (Karle, Hauptman, and Christ, 1958) indicated the structure was centrosymmetric, and thus the refinement was carried out in space group $R\bar{3}m$.

The structure was refined initially to $R = 0.07$. At this stage the Ca ion showed an anomalously high temperature factor, its isotropic temperature factor being 3.6 and its anisotropic factors B_{11}, B_{22}, and B_{12} being ten times larger than those for the other ions in the structure. An electron-density difference map was calculated including all the ions in the structure except Ca. The resulting peak at the Ca position was an ellipsoid with a circular cross section in the *xy* plane and the shortest dimension along *z*. A refinement attempted with Ca in the *x*, 0, 0 position and 1/6 occupancy, instead of a single atom at the origin, yielded an unweighted $R = 0.067$. For refinements with Ca in the *x*, *y*, 0 and *x*, *y*, *z* positions, the parameters proved too highly correlated, but with Ca in the *x*, 0, 0 position the temperature factors dropped to reasonable values.

Secondary extinction corrections were applied to the data as suggested by Zachariasen (1963). The final *R* value was 0.044 if isotropic and 0.046 if anisotropic temperature factors were applied to Ca in the *x*, 0, 0 position. The final positional and thermal parameters are listed in Tables 1 and 2. The observed and calculated structure factors are contained in Table 3.

TABLE 2. Final Vibrational Parameters and Their Estimated Standard Deviations*

	β_{11}	σ	β_{22}	σ	β_{33}	σ	β_{12}	σ	β_{13}	σ	β_{23}	σ
Ca	60	178	167	338	3.0	1.0	83		.3		.7	9.0
P	40	5	40		4.5	1.0	20					
Al	28	5	23	6	5.0	1.0	12		.5			
O(1)	61	11	61		8.0	3.0	31					
O(2)	95	9	95		6.0	1.0	78	10	.3	2.0	−.3	
O(3)	36	7	36		6.0	2.0	19	8	1.0	1.0	−1.0	
	B											
Ca	.56	.13										

**Anisotropic temperature factor:* $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. *The anistropic temperature parameters have been multiplied by* 10^4.

Identity of Deltaite with Crandallite

Seven samples labeled "deltaite" and "crandallite" from Fairfield, Utah, were obtained from the Harvard Geological Museum. In addition, Dr. Frondel kindly supplied four diffractometer tracings of crandallite and deltaite samples. Powder film patterns of the seven samples, obtained using the Guinier-de-Wolff camera with Cr radiation and a quartz standard

TABLE 3. Observed and Calculated Structure Factors, for the Anisotropic Case*

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
0	0	3	15.3	3.9	2	1	1	6.4	3.2	5	2	0	11.4	12.9
0	0	6	138.6	137.3	2	1	4	25.1	26.6	5	2	3	40.3	40.3
0	0	9	84.7	84.3	2	1	7	36.4	35.3	5	2	6	7.7	8.0
0	0	12	30.9	31.6	2	1	10	9.6	7.7	5	2	9	11.9	13.1
0	0	15	21.2	22.1	2	1	13	74.6	76.7	6	2	1	58.9	60.0
1	0	1	49.9	44.6	2	1	16	18.7	18.2	6	2	4	46.5	48.0
1	0	4	13.2	12.3	3	1	2	59.6	57.2	0	3	3	197.8	207.1
1	0	7	191.7	187.9	3	1	5	60.1	56.5	0	3	6	21.7	16.8
1	0	10	40.2	37.1	3	1	8	34.7	34.3	0	3	9	115.7	120.8
1	0	13	64.3	62.8	3	1	11	13.7	12.1	0	3	12	8.5	9.0
1	0	16	17.4	16.3	3	1	14	32.9	30.9	0	3	15	12.9	13.0
2	0	2	26.3	30.0	3	1	17	5.8	4.5	0	3	18	17.2	17.8
2	0	5	68.0	55.9	4	1	0	54.0	54.9	1	3	1	7.4	3.0
2	0	8	48.4	46.5	4	1	3	88.6	92.5	1	3	4	47.5	44.0
2	0	11	75.8	74.0	4	1	6	9.0	3.2	1	3	7	57.7	57.1
2	0	14	23.1	21.2	4	1	9	47.8	47.9	1	3	10	65.3	64.2
3	0	0	7.3	3.9	4	1	12	10.0	9.1	1	3	13	58.4	56.4
3	0	3	26.8	23.3	4	1	15	15.1	15.4	1	3	16	28.0	29.3
3	0	6	18.1	18.1	5	1	1	14.1	14.7	2	3	2	70.1	69.7
3	0	9	21.3	21.7	5	1	4	36.1	34.2	2	3	5	37.3	36.6
3	0	12	87.3	90.7	5	1	7	16.6	17.1	2	3	8	16.4	15.9
3	0	15	29.0	29.8	5	1	10	52.1	50.8	2	3	11	25.7	25.6
3	0	18	22.7	21.5	6	1	2	19.4	19.7	2	3	14	8.1	8.1
4	0	1	83.5	83.7	6	1	5	5.4	2.9	3	3	0	109.6	117.4
4	0	4	80.8	79.7	6	1	8	48.1	48.0	3	3	3	52.5	53.2
4	0	7	53.6	49.3	0	2	1	127.9	133.5	3	3	6	12.5	4.1
4	0	10	94.2	95.2	0	2	4	49.7	45.4	3	3	9	10.1	8.5
4	0	16	65.8	68.4	0	2	7	65.6	58.7	3	3	12	33.7	33.1
5	0	2	36.8	33.9	0	2	10	190.1	202.3	4	3	1	7.5	6.9
5	0	5	23.5	21.5	0	2	16	100.7	105.4	4	3	4	12.1	11.3
5	0	8	67.7	69.0	1	2	2	78.5	72.1	4	3	7	41.6	41.5
5	0	11	25.9	23.4	1	2	5	15.1	12.4	4	3	10	6.4	5.7
5	0	14	54.0	53.8	1	2	8	77.0	77.6	5	3	2	47.6	48.1
6	0	0	68.0	66.5	1	2	11	24.9	23.8	5	3	5	42.4	41.2
6	0	3	27.3	27.2	1	2	14	55.9	54.2	0	4	2	83.1	83.1
6	0	6	60.9	61.1	2	2	0	188.1	200.9	0	4	5	54.0	54.5
6	0	9	6.2	6.5	2	2	3	13.2	9.4	0	4	8	7.6	5.9
7	0	4	32.8	32.9	2	2	6	101.1	102.3	0	4	11	83.4	82.1
0	1	2	63.1	69.1	2	2	9	36.6	33.8	0	4	14	10.1	10.0
0	1	5	45.0	43.6	2	2	12	63.8	64.2	1	4	0	54.0	54.8
0	1	8	10.8	12.1	2	2	15	22.0	18.5	1	4	3	57.1	56.2
0	1	11	17.4	17.5	3	2	1	25.1	25.2	1	4	6	13.0	11.4
0	1	14	9.1	5.0	3	2	4	34.1	32.3	1	4	9	21.8	21.1
0	1	17	31.5	31.8	3	2	7	111.3	116.9	1	4	12	18.8	17.3
1	1	0	93.9	98.4	3	2	10	18.8	18.5	1	4	15	21.0	23.1
1	1	3	141.6	144.0	3	2	13	35.4	36.1	2	4	1	61.6	61.6
1	1	6	24.2	22.4	4	2	2	22.7	22.5	2	4	4	51.5	50.1
1	1	9	66.8	66.8	4	2	5	87.1	89.6	2	4	7	10.1	5.4
1	1	12	28.8	28.4	4	2	8	27.4	25.6	2	4	10	71.8	71.6
1	1	15	30.6	29.0	4	2	11	76.5	75.4	2	4	13	18.6	18.4

* *For crandallite UW1538/1 from Fairfield, Utah.*

TABLE 4. *d* Values and Relative Intensities of Seven Samples of Possible Crandallites and an Apatite*

crandallites								non-crandallites										
UW1538/3		UW1538/4		UW1538/8		UW1538/5		UW1538/6		UW1538/2		UW1538/7		Apatite		Deltaite (calc)		
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	hkl
						6.64												
5.69	37	5.70	35	5.69	30	5.69	41	5.68	32	5.69	30	5.69	36			5.68	31	101
						5.00												
4.87	37	4.87	35	4.87	27	4.87	36			4.88						4.85	36	012
						4.74												
3.51	37	3.52	35	3.52	38	3.51	37	3.50	24	3.51	25	3.51	30			3.51	38	110
		3.46				3.46				3.45		3.45		3.45	50			
						3.13												
						3.10								3.07	18			
						3.04												
						3.00	37											
2.99	45	2.99	45	2.99	38	2.98	39	2.98	18	2.99	14	2.99	18			2.98	45	021
2.94	100	2.95	100	2.94	100	2.94	100	2.94	100	2.94	100	2.94	100			2.94	100	113
						2.83		2.84		2.85		2.85				2.86	7	015
2.80		2.81		2.80		2.80		2.79		2.80		2.80		2.80	100			
2.78		2.78				2.78		2.77		2.78				2.78	43			
								2.74		2.74		2.75						
2.70		2.71		2.70		2.70		2.69		2.70		2.70		2.70	86	2.70	14	202
		2.63				2.63				2.63				2.63	36			
						2.60				2.59								
								2.44		2.45		2.45				2.43	6	024
								2.27		2.28		2.28				2.27	-	211
								2.23		2.24		2.24						
2.21		2.22		2.22		2.22		2.21		2.22		2.22				2.21	28	205
						2.19		2.19		2.20		2.20						
2.17		2.17		2.17				2.16		2.18		2.17				2.16	44	107
						2.12												
								2.01		2.01		2.01				1.99	-	214
		1.95												1.94				
1.90	30	1.90		1.90	30	1.90		1.90	31	1.91	30	1.91	30	1.89		1.89	37	033,303
		1.85				1.78				1.85								
1.76		1.76		1.76		1.76				1.76		1.74				1.75	28	220

**From powder diffraction photographs obtained on a Guinier-de Wolff camera with Cr radiation. The right column contains the calculated deltaite pattern and intensity values from single crystal work.*

Intensity values for all patterns except deltaite should be considered only approximate. The intensities were derived by comparison with a photographic intensity scale and from powder patterns which were not specifically prepared for intensity purposes.

***The apatite sample is from Raburn Co., Georgia.*

(Table 4) were compared with the powder pattern calculated for deltaite from F_0 values obtained from single crystal work and corrected for Lp and absorption.

The work of Owens, Altschuler, and Berman (1960) and of Cowgill, Hutchinson, and Joensuu (1963) indicate that crandallite has its most intense peak at 2.94 Å with three lesser peaks of intensities around 40 at 2.99, 4.87, and 3.51 Å. The diffractometer tracings contributed by Dr. Frondel substantiate this. Of the presently prepared powder patterns (Table 4), four (UW1538/5, UW1538/3, UW1538/4, and UW1538/8) appear to be crandallite whereas the other three (UW1538/2, UW1538/7, and UW1538/6) appear not to be, the 4.87 Å line being absent or nearly so and a 2.45 Å peak appearing. These three patterns thus resemble that reported by Cowgill *et al* (1963) for a "triclinic dimorph of crandallite" which contained significant amounts of Sr and Pb. Moreover,

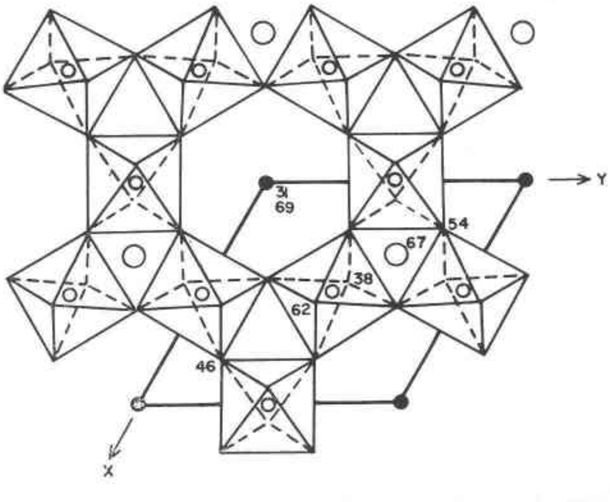

FIG. 1 *xy* projection of crandallite down the *z* axis. This shows primarily the octahedral sheet in which the Al lies at 0.50 along the *z* axis, and oxygens are located at the corners of the octahedra. ● = P; ◯ = Ca; ○ = Al.

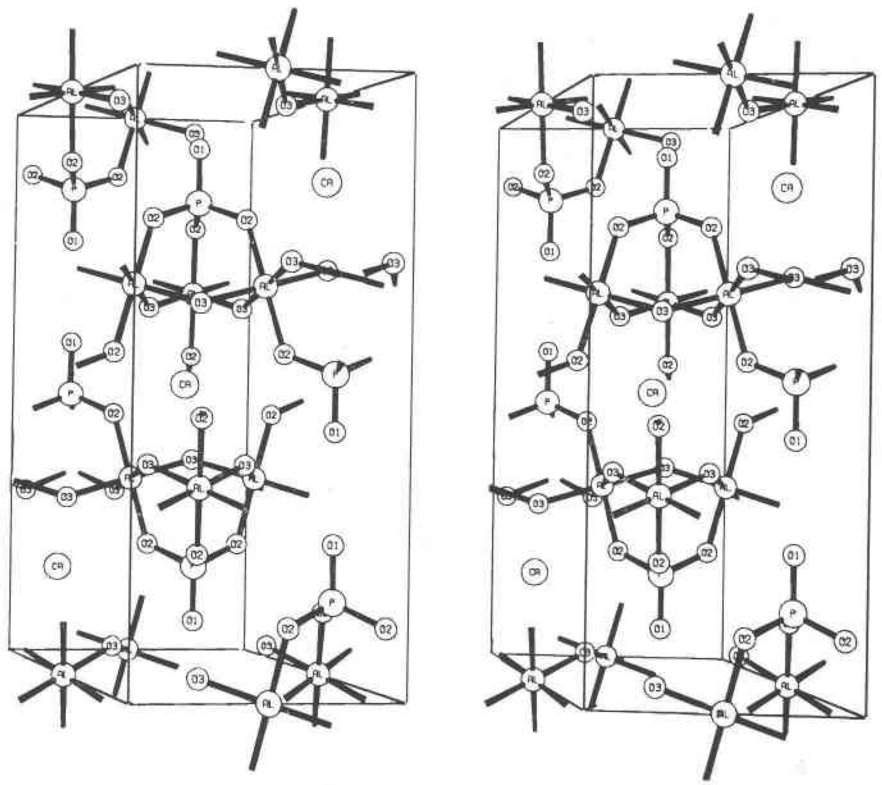

FIG. 2. Stereoscopic diagram of the crandallite structure. The outline indicates one unit cell with $x = 0$, $y = 0$, and $z = 0$ of Table 1 at the center.

X-ray spectrography revealed major amounts of Sr and traces of Fe in the three noncrandallite samples as well as Zn in sample UW 1538/5.

Except for some extra lines which have the correct *d* values for apatite, all observed crandallite patterns agree well with the calculated patterns for deltaite. The amount of apatite apparently varies from sample to sample, and other phosphate minerals may occur in some samples.

Discussion

Crandallite consists of sheets of Al octahedra each of which share four corners with four other octahedra to form large hexagonal and small trigonal rings (Fig.1). The sheets are perpendicular to the *z* axis, and Ca cations lie between the sheets in large cavities surrounded asymmetrically by twelve oxygen and hydroxyl ions (Fig. 2). Each phosphate tetrahedron shares three corners with the three Al octahedra common to a trigonal ring. The remaining unshared corner points away from the trigonal hole towards the adjacent sheet and is hydrogen bonded thereto.

Hydrogen bonding

The hydrogen atoms were not located during the X-ray structural determination, but the bond lengths (Table 5) along with *IR* data show that the OH groups are located at the O(3) sites and at one-half of the O(1) sites. The O(1)–O(1) distances are 2.992 Å, O(1)–O(3) distances are 2.729 Å, and the O(2)–O(2) distances are 3.112 Å. These distances are of proper size to be hydrogen bonds; however, the O(2)–O(2) distances are not likely to be hydrogen bonds because they form the edge of the Ca polyhedron. Assuming that the OH groups occupy the O(1) and O(3) sites, the formula would necessarily be modified from $CaAl_3(PO_4)_2(OH)_5H_2O$ to $CaAl_3(OH)_6[PO_3O_{1/2}(OH)_{1/2}]_2$ which corresponds more closely with the alunite formula, $KAl_3(SO_4)_2(OH)_6$. Both from structural considerations and from the formula, hydrogens can only be present at one half of the O(1) sites.

To check the surmise that O(3) is (OH) and that O(1) is $(OH_{1/2})$, an *IR* spectrum was made of massive crandallite in Nujol. Absorption bands at 3450 and 3290 cm^{-1} indicate O.H. . . . O bonds of 2.89 Å

TABLE 5. Bond Lengths (Å) and Bond Angles for Crandallite

P tetrahedra		
P-O(1)	1.520 (.007)	
-O(2)^{x}	1.543 (.004)	(X3)
av.	1.537	
O(2)-O(2)^{i}	2.504 (.004)	(X3)
O(1)-O(2)^{x}	2.516 (.007)	(X3)
av.	2.510	
O(2)^{i}-O(2)-O(2)^{ii}	66.0 (.0)	
O(2)^{x}-O(1)-O(2)^{ix}	59.7 (.2)	
O(2)^{i}-O(2)-O(1)^{ii}	60.1 (.1)	
O(1)-P-O(2)^{x}	110.4 (.1)	
O(2)^{x}-P-O(2)^{ix}	108.5 (.2)	
Al octahedra		
O(3)-O(3)^{i}	2.599 (.007)	(X2)
-O(3)^{xi}	2.739 (.004)	(X2)
O(2)-O(3)^{iv}	2.624 (.004)	(X4)
-O(3)^{vi}	2.775 (.004)	(X4)
av.	2.689	
Al-O(3)^{ix}	1.888 (.001)	(X4)
-O(2)^{xi}	1.931 (.004)	(X2)
av.	1.902	
O(3)^{v}-O(3)^{vi}-O(2)	56.8 (.1)	
O(3)^{xii}-O(3)^{iv}-O(2)	62.3 (.1)	
O(3)^{xii}-O(2)-O(3)^{iv}	60.9 (.1)	
O(2)-O(3)^{iv}-O(3)^{v}	60.3 (.1)	
O(3)^{iv}-O(2)-O(3)^{v}	59.4 (.1)	
O(3)^{xii}-O(2)-O(3)^{vi}	55.9 (.2)	
O(3)^{xii}-O(2)-O(3)^{v}	88.7 (.1)	
O(3)^{v}-O(3)^{vi}-O(3)^{xii}	90.0 (.0)	
O(2)^{x}-O(3)-O(2)^{v}	93.2	
O(3)^{xii}-O(3)^{iv}-O(3)^{v}	90.0 (.0)	
O(3)^{xii}-Al^{iii}-O(3)	93.0 (.2)	
-O(2)	93.2 (.1)	
O(3)^{iv}-Al^{iii}-O(3)^{v}	87.0 (.2)	
-O(2)	86.8 (.1)	
O(3)^{iv}-Al^{iii}-O(3)^{vi}	180.0 (.0)	
Ca polyhedra		
Ca-O(2)	2.461 (.005)	(X2)
-O(2)^{iii}	3.025 (.005)	(X2)
-O(2)^{i}	2.757 (.004)	(X2)
Ca-O(3)	2.506 (.004)	(X2)
-O(3)^{iii}	2.839 (.004)	(X2)
-O(3)^{i}	2.678 (.004)	(X2)
O(3)-O(3)^{i}	2.599 (.007)	
O(2)-O(2)^{iv}	3.112 (.005)	
-O(3)	3.239 (.005)	
-O(3)^{v}	2.624 (.004)	
O(3)-Ca-O(2)	81.4 (.2)	
O(3)^{i}-Ca-O(2)^{i}	73.1 (.1)	
O(3)^{iii}-Ca-O(2)^{iii}	67.0 (.1)	
O(3)-Ca-O(2)^{i}	127.0 (.1)	
O(3)-Ca-O(2)^{iii}	102.0 (.1)	
O(3)-Ca-O(3)^{v}	135.1 (.1)	
-O(2)^{v}	63.8 (.1)	
-O(3)^{i}	60.1 (.1)	
-O(2)^{i}	127.0 (.1)	
-O(3)^{iii}	167.1 (.2)	
-O(2)^{iii}	102.0 (.1)	
O(3)-Ca-O(3)^{ii}	57.8 (.1)	
-O(2)^{ii}	116.5 (.1)	
-O(3)^{iv}	126.6 (.1)	
-O(2)^{iv}	59.6 (.1)	
O(3)^{i}-Ca-O(3)^{iii}	114.1 (.2)	
-O(2)^{iii}	54.4 (.1)	
-O(3)^{ii}	56.1 (.1)	
-O(2)^{ii}	111.2 (.2)	
-O(3)^{iv}	165.3 (.2)	
-O(2)^{iv}	105.0 (.1)	
O(3)^{iii}-Ca-O(3)^{ii}	109.3 (.2)	
-O(2)^{ii}	53.1 (.1)	
O(2)-Ca-O(3)^{v}	63.8 (.1)	
-O(2)^{v}	78.4 (.2)	
-O(3)^{i}	132.8 (.2)	
-O(2)^{i}	119.1 (.1)	
-O(3)^{iii}	108.6 (.1)	
-O(2)^{iii}	171.7 (.1)	
-O(3)^{ii}	125.3 (.1)	
-O(2)^{ii}	109.8 (.1)	
-O(3)^{iv}	61.2 (.1)	
-O(2)^{iv}	73.0 (.1)	
O(2)^{i}-Ca-O(3)^{iii}	55.9 (.1)	
-O(2)^{iii}	64.9 (.1)	
-O(3)^{ii}	114.6 (.1)	
-O(2)^{ii}	102.1 (.1)	
-O(3)^{iv}	105.0 (.1)	
-O(2)^{iv}	165.7 (.2)	
O(2)^{iii}-Ca-O(3)^{ii}	53.1 (.1)	
-O(2)^{ii}	61.9 (.1)	

[a] Superscripts refer to the following positions:

for O(2) and O(3)

i	x	,2x	,z
ii	-2x	,-x	,z
iii	-x	,x	,-z
iv	-x	,-2x	,-z
v	2x	,x	,-z
vi	1/3+x	,2/3+2x	,2/3+z
vii	1/3-x	,2/3+x	,2/3-z
viii	1/3+2x	,2/3+x	,2/3-z
ix	2/3+x	,1/3-x	,1/3+z
x	2/3-2x	,1/3-x	,1/3+z
xi	2/3-x	,1/3-2x	,1/3-z
xii	1/3-2x	,2/3-x	,2/3+z

for O(1)

i	0	,0	,-z
ii	1/3+0	,2/3+0	,2/3-z

for Al

i	1/3+0	,2/3+1/2	,2/3+1/2
ii	1/3+1/2	,2/3+0	,2/3+1/2
iii	2/3+0	,1/3+1/2	,1/3+1/2

and 2.78 Å according to the graph of Nakamota, Margoshes, and Rundle (1955). The length of the proposed hydrogen bonds agree well with these values.

The method of Donnay and Allmann (1970) was also applied. The results are tabulated in Tables 6 and 7. The L_{max} used for phosphorus was 1.95 Å. Theoretically the total valence of the bonds reaching the anion is +1.0 if the anion is $(OH)^-$, +2.0 if the anion is O^{2-}, and +1.5 if the anion is $(OH_{1/2})$. The values in Table 6 are consistent with O(1) being $(OH_{1/2})$ and O(3) being $(OH)^-$. The total valence of the bonds to the O(1) corrected for hydrogen bonding is somewhat larger than expected. This discrepancy arises from the method's assumption that the shorter anion-cation distances have the stronger bond valence. In crandallite the P–O(1) bond is shorter than the three P–O(2) bonds.

The hydrogen bonding occurs between the layers

TABLE 6. Bond Lengths (Å) and Estimated Valences (in parentheses) for Crandallite

Anions	Al	P	Ca	C	Anion Chemistry	ΣC^v for H bonds
O(1)		1.52 (1.30)		1.30	OH	1.87
O(2)	1.93 (0.47)	1.54 (1.24)	2.46 (0.27) 3.03 (0.07) 2.76 (0.15)	1.87 ave.	O	1.87
O(3)	1.89 (0.53)		2.51 (0.25) 2.84 (0.13) 2.68 (0.18)	1.25 ave.	OH	1.06
ΣA^v	3.06	5.02	2.06			

ΣA^v = *valences of bonds emanating from cations summed over the bonded anions.*

ΣC^v = *valences of bonds reaching anion.*

TABLE 7. Short Oxygen-Oxygen Distances (Å) and Estimated Hydrogen-Bond Valences (in parentheses) for Crandallite

Donor / Acceptor	$O(1)H_{1/2}$	O(3)H	O(3)H	O(3)H	ΣH^v
$O(1)H_{1/2}$	2.99 (.100)	2.73 (1.90)	2.73 (1.90)	2.73 (1.90)	.67
ΣA^V	.100				

ΣH^V = sum of valences donated by hydrogen.
ΣA^V = sum of valences accepted by ions.

in such a way as to link together adjacent layers (O(1).H–O(3)) and every other layer (O(1).H–O(1)). Figure 4 illustrates how this occurs in crandallite. Each O(1) receives three hydrogen bonds from the hexagonal ring of Al octahedra in the adjacent layer so that the unshared apices of two PO_4 groups point towards one another through a hexagonal hole. These apical oxygens are bonded through a hydrogen so that alternate layers are bonded together by this mechanism. The structure is, thus, framework-like.

The phosphate tetrahedron

The phosphate tetrahedron in crandallite is comparable to those found in other phosphate minerals. The PO_4 groups are isolated from one another as is the case for all known phosphate minerals. The bond between the phosphorus and the unshared apical oxygen (1.520 Å) is slightly shorter than between the phosphorus and the shared oxygen (1.543 Å).

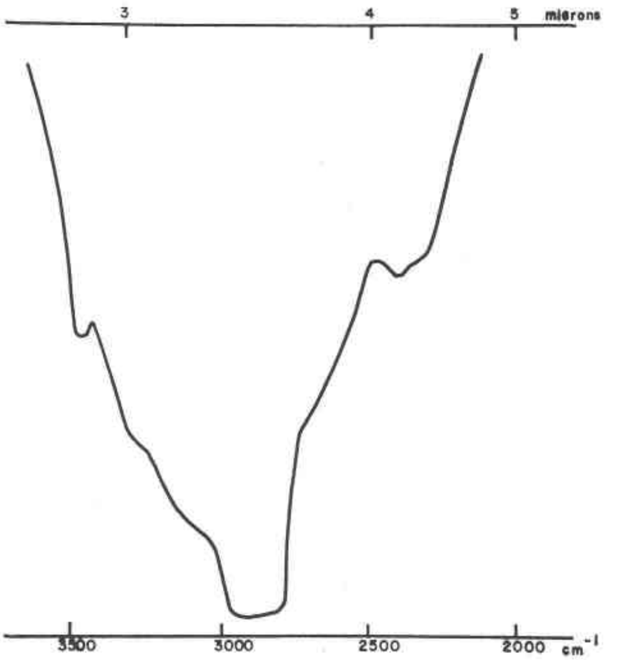

FIG. 3. Infrared absorption spectrum of powdered crandallite in Nujol.

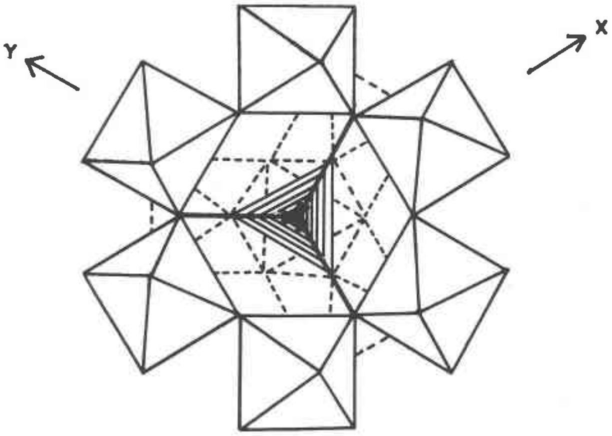

FIG. 4. The arrows illustrate the hydrogen bonding between OH(3) and $OH_{1/2}(1)$.

The Al octahedron

The Al octahedron is somewhat distorted. Two of its edges are much shorter (2.599 Å) than the other ten (av. 2.707 Å). This is due to Al–Al and Ca–Al repulsion, both of which tend to force the oxygens of these two edges towards one another. The Al–O bond length is 1.931 Å and the Al–OH bond is 1.888 Å. The shorter bond is probably due to the asymmetric charge on the OH which increases the negative charge towards the Al and thus tends to shorten the Al–O bond.

Ca coordination

The Ca cation is located in a cavity surrounded by six oxygens and six hydroxyls at 2.73 Å and 2.65 Å from the center of the cavity. The Ca cation is too small to be coordinated with all twelve anions. As explained previously, the refinement indicates that Ca is distorted. It is near four oxygens and four hydroxyls at distances of 2.46 Å to 2.75 Å. The position of the Ca statistically varies, and no particular position in the cavity seems to be preferred. This is supported by the fact that a Patterson map calculated with full (unaveraged) data showed almost ideal hexagonal symmetry.

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