

THE CRYSTAL STRUCTURE OF GRAFTONITE

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ABSTRACT

The crystal structure of the mineral graftonite has been determined by single crystal X-ray diffraction methods. The lattice parameters for the crystal examined are $a=8.91(1)$ Å, $b=11.58(1)$ Å, $c=6.239(8)$ Å, $\beta=98.9(1)^\circ$ and $Z=4$. The space group is $P2_1/c$. The anions are slightly irregular PO_4^{3-} tetrahedra with individually averaged PO bond lengths of 1.55 Å for both anion groups. Three cation polyhedra are found, and in two the cations have five-fold coordination while for the third the coordination number is seven. The Ca^{2+} is found to be preferentially dissolved in the latter site. The structure is composed of chains of trigonal bipyramidal cation polyhedra running parallel to the c axis formed through edge-sharing. The seven coordinated cations occur in edge-shaped pairs which are corner-shared with similar groups to form sheets in the b - c plane while the remaining cation polyhedra join these sheets with the chains. This site has four-fold coordination in $\text{CdZn}_2(\text{PO}_4)_2$ which otherwise has essentially the same structure as graftonite. The major cationic species in graftonite are Fe^{2+} and Mn^{2+} whose orthophosphates can be crystallized with the graftonite structure.

INTRODUCTION

Graftonite is a phosphate mineral of wide occurrence whose composition can be expressed as $(\text{Fe}, \text{Mn}, \text{Ca}, \text{Mg})_3 (\text{PO}_4)_2$ (Lindberg, 1950). The cations have been ordered according to their relative abundance with the Ca and particularly the Mg as minor constituents. This structure type is also one which occurs in divalent orthophosphate mixed systems (Calvo and Stephens, 1968). Graftonite has been found naturally intergrown with sarcopside by Peacor and Garske (1964) and Hurlbut (1967) and these authors concluded that these structures resulted from precipitation from a common phase. Hurlbut reported the details of the crystallographic coherence in the intergrowth of the mixed system which in some cases shows lamellae alternation of each phase. Thus these structures appear to grow from supersaturated conditions with the growth direction parallel to the plane of the lamellae. Further, both investigations showed extensive preferred solubility of Ca in graftonite and that Fe had a somewhat greater preference for the sarcopside phase and Mn the graftonite phase.

The resolution of these characteristics of the system will probably require the resolution of the structures of the two precipitated phases and the parent phase. Mrose and Appleman (1961) reported that structure of sarcopside is closely related to that of lithiophilite, LiMnPO_4 , with the cations in the former occupying the same position as they do in the latter crystal. Since the cation to PO_4^{3-} ratio is 2:1 in lithiophilite and 1.5:1 in sarcopside, there apparently is some cationic disorder. Unfortunately, a full report of this work is not available.

The results presented below will indicate that the large cation, Ca^{2+} in this case, preferentially dissolves in the cation site having the highest coordination number. Further, since $\text{Mn}_3(\text{PO}_4)_2$ (Stephens 1967) and $\text{Fe}_3(\text{PO}_4)_2$ both can be produced synthetically with the graftonite structure, it is apparent that the major stabilization of this structure results from this site preference of Ca^{2+} and not the relative amounts of Mn^{2+} and Fe^{2+} .

EXPERIMENTS

A crystal of graftonite was selected from a sample, said to be intergrown with triphylite, which originated from Grafton, New Hampshire and was obtained through Ward's Nature Science Establishment. A crystal with dimensions $0.08 \text{ mm} \times 0.08 \text{ mm} \times 0.15 \text{ mm}$ was mounted parallel to the long direction which coincided with the c axis of the unit cell. Photographs containing reflections of the type $hk0$, $hk1$, and $hk2$ were taken with a Weissenberg camera using MoK_α radiation. Precession photographs of the $\{201\}$, $\{100\}$ and $\{010\}$ zones were obtained using the same radiation. Accurate parameters were determined from films calibrated with reflections from a TiO_2 single crystal whose lattice parameters were taken to be $a = 4.5929(5) \text{ \AA}$ and $c = 2.9591(3) \text{ \AA}$ (Cromer and Herrington, 1955) and the β angle was taken from direct measurements of an $h0l$ photograph. These parameters are listed in Table 1 along with other pertinent crystal data. The reported space group, $P2_1/c$, (Lindberg, 1950) was confirmed.

The intensity of the reflections was estimated by visual comparison and the results corrected for the effects of absorption in addition to Lorentz and polarization factors. Trial parameters were obtained from the structure resolution of a crystal having composition $\text{CdZn}_2(\text{PO}_4)_2$ whose powder pattern and lattice parameters closely resemble those of

TABLE 1. CRYSTAL DATA FOR GRAFTONITE

$a = 8.91(1) \text{ \AA}$	
$b = 11.58(1) \text{ \AA}$	
$c = 6.239(8) \text{ \AA}$	
$\beta = 98.9(1)^\circ$	
systematic extinctions, $h0l$, l -odd and $0k0$, k =odd	
space group $P2_1/c$	
ρ meas. = $3.775 \text{ (gm/cm}^3\text{)}^a$ ρ cal. = 3.66 gm/cm^3	
adsorption coeff. 76 cm^{-1}	
number of observed reflections	637
number of reflections used	917

^a Value of Lindberg (1950).

the mineral. Initially, all the cations were assumed to be Fe^{2+} . This trial structure was refined by least-squares methods using a program written by J. S. Stephens for an IBM 7040 computer. The effects of vibrational disorders were accounted for by using individual isotropic thermal parameters, B_j . A large discrepancy was noted between the B_j values of the three cations which indicated a preferred ordering of the cations among the available sites. These available cation sites are: site I, showing seven-fold coordination, site II and site III showing five-fold coordination. In $\text{CdZn}_2(\text{PO}_4)_2$, where site II shows four-fold coordination, Cd^{2+} has been found to preferentially dissolve into site I (Calvo and Stephens, 1967). Since Ca^{2+} has the largest radii among the cations found in graftonite, it was assumed that it preferentially dissolved into site I. The composition of the crystal graftonite was taken to be $\text{Fe}_{1.8}\text{Mn}_{0.8}\text{Ca}_{1.4}\text{P}_2\text{O}_2$ which corresponded to the results found by Hurlbut (1965) if one assumes the small amount of Mg^{2+} to be Ca^{2+} . These changes lead to a more uniform Debye-Waller factor for the cations in addition to better agreement with the measured data as determined by the lowered reliability index

$$R_1 = [\Sigma |F_o| - |F_o|] / \Sigma |F_o|.$$

The atomic scattering factors for Fe^{2+} , Ca^{2+} , P and O^- were obtained from Vol. III of the International Tables.

The final stages of refinement were pursued with weights for the reflections assigned as $w^{-1} = 1.0 + 0.5 F_o + 0.006 F_o^2$. The coefficients in this function were determined so that $\langle w \Delta F^2 \rangle$ should be independent of the magnitude of F_o . Unobserved reflections were given zero weight if their calculated structure factor was less than the minimum observable value. The final atomic parameters are listed in Table 2 and the calculated and observed structure factors are shown in Table 3.¹ An anisotropic model for the atomic motion was not considered since only a limited amount of data was taken up the c axis. This, together with the uncertainty concerning the composition, would probably result in parameters devoid of direct physical meaning. The final R value for all data is 0.115 and

$$R_2 \left(= \left\{ \frac{\Sigma w \left(|F_o|^2 - |F_c|^2 \right)}{\Sigma w |F_o|^2} \right\}^{1/2} \right)$$

is 0.145.

¹ Deposited as Document No. 9821 with the American Documentation Institute, Library of Congress. Copies may be secured by citing the Document number, and remitting \$1.25 for photoprints or microfilm, in advance to the Chief. Photoduplication Service, Library of Congress, Washington, D. C. 20540.

TABLE 2. ATOMIC PARAMETERS FOR GRAFTONITE
(esd's are enclosed in parentheses)

M(1)	0.9472(4)	0.1208(3)	0.8355(10)	1.00(7)
M(2)	0.7144(4)	0.0790(3)	0.3255(9)	1.44(7)
M(3)	0.3619(3)	0.1915(2)	0.1295(7)	0.58(6)
P(1)	0.0959(5)	0.1338(4)	0.3956(13)	0.22(7)
O(1)	0.0826(16)	0.0702(11)	0.1787(39)	0.98(26)
O(3)	0.9390(16)	0.1915(12)	0.4237(38)	1.02(26)
O(5)	0.2165(1)	0.2299(13)	0.3889(35)	1.32(28)
O(7)	0.1451(14)	0.0586(11)	0.5961(34)	0.47(23)
P(2)	0.6011(5)	0.0891(4)	0.8024(12)	0.21(8)
O(2)	0.4705(17)	0.1742(12)	0.8241(37)	1.10(26)
O(4)	0.6888(15)	0.1271(11)	0.6235(35)	0.63(23)
O(6)	0.7242(18)	0.0905(13)	0.0070(39)	1.32(28)
O(8)	0.5357(15)	-0.0368(12)	0.7623(33)	0.72(23)

O(\bar{n}) are generated from O(n) by inversion and O(n') by the c glide plane operation.

DESCRIPTION OF STRUCTURE

The structure of graftonite consists of three different cation polyhedra bonded through edge and corner sharing of oxygen atoms contributed by the two PO_4^{3-} tetrahedral groups. These latter groups have average PO bond lengths of 1.549 Å for P(1) and for P(2) individually. The range of these distances is 1.529 Å to 1.584 Å around P(1) and 1.524 Å to 1.576 Å around P(2) and since the esd's on these distances are about 0.02 Å, these differences are probably not significant. The distribution of the angles O-P-O about the P atoms range from 106° to 115° to 103° and 112° in the two tetrahedra but with the magnitude of the errors the deviation of the tetrahedra from ideality is not significant. These angles and distances are recorded in Table 4.

The three cation sites, depicted in Figure 1, each show individual polyhedral geometries. Site I shows seven-fold coordination with O(3') and O(1) acting as the axial oxygen atoms of an irregular pentagonal bipyramid. These axial bonds nearly parallel the *b* axis. The remaining oxygen atoms, O(1), O(3), O(4), O(6) and O(7) lie roughly in a plane and in a distorted pentagonal arrangement. The average bond distance of these equatorial bond distances is 2.50 Å and all these are significantly longer than the axial bond lengths of 2.25 Å and 2.23 Å. All the Ca^{2+} has been assumed to repose in this site.

The oxygen atom arrangement about cation sites II are nearly arranged in a square pyramid. The axial cation oxygen bond length involving O(7) is 2.04 Å whereas the equatorial bonds range from 1.99 Å to 2.39 Å with a mean of 2.16 Å. The base of the pyramid is in fact of dia-

TABLE 4. BOND DISTANCES AND ANGLES IN GRAFTONITE
 (esd's are enclosed in parentheses)

Cation Groups			
M(1)-O(1)	2.363(22) Å	O(3)-M(1)-O(3'')	86.7(7)°
O(3)	2.687(24)	-O(1)	151.2(5)
O(4)	2.473(12)	-O(1')	106.2(7)
O(6)	2.425(21)	-O(7)	56.8(5)
O(7)	2.584(9)	-O(4)	66.0(6)
O(3'')	2.246(15)	-O(6)	124.3(6)
O(1')	2.228(13)	(O3')-M(1)-O(1)	92.8(7)
		-O(1')	164.2(8)
		-O(7)	117.5(6)
		-O(4)	92.2(5)
		-O(6)	88.4(6)
		O(1)-M(1)-O(1')	80.3(7)°
		-O(7)	99.0(6)
		-O(4)	143.6(7)
		-O(6)	84.4(7)
		O(1')-M(1)-O(7)	77.8(6)
		-O(4)	85.0(5)
		-O(6)	76.9(6)
		O(7)-M(1)-O(4)	111.2(6)
		-O(6)	153.4(5)
		O(4)-M(1)-O(6)	58.7(7)
M(2)-O(7)	2.040(13)	O(8)-M(2)-O(7)	115.8(5)°
-O(3)	2.388(14)	-O(6)	88.1(8)
O(4)	1.987(22)	-O(4)	92.1(7)
O(6)	2.007(25)	O(7)-M(2)-O(6)	99.8(8)
O(8)	2.264(14)	-O(4)	98.6(7)
		O(6)-M(2)-O(4)	159.5(6)°
		O(3)-M(2)-O(8)	159.2(5)
		-O(7)	84.6(5)
		-O(6)	93.1(7)
		-O(4)	79.6(7)
M(3)-O(5'')	2.039(19)	O(5)-M(3)-O(2)	168.1(6)°
O(2'')	2.113(12)	-O(5')	94.0(7)
O(8')	2.075(14)	-O(8)	102.0(7)
O(5)	2.276(19)	-O(2')	73.0(7)
O(2)	2.268(19)	O(2)-M(3)-O(5')	74.1(7)
		O(2)-M(3)-O(8)'	88.5(7)°
		-O(2')	109.2(7)
		O(5')-M(3)-O(8)	145.3(7)
		-O(2')	106.1(6)
		O(8)-M(3)-O(2')	108.0(7)
Anion Groups			
P(1)-O(1)	1.529(23) Å	O(1)-P(1)-O(3)	110.6(1.0)°
O(3)	1.584(15) Å	-O(5)	106.3(1.1)
O(5)	1.553(14) Å	-O(7)	115.0(0.9)
O(7)	1.531(19) Å	O(3)-P(1)-O(5)	109.1(0.8)°
p(2)-O(2)	1.548(15) Å	-O(7)	107.2(1.1)
O(4)	1.524(21) Å	O(5)-P(1)-O(7)	108.5 (.9)
O(6)	1.549(21) Å	O(2)-P(2)-O(4)	111.0(1.0)°
O(8)	1.576(15) Å	-O(6)	111.6(1.1)
		-O(8)	109.7(1.8)
		O(4)-P(2)-O(6)	102.9(1.0)°
		-O(8)	113.7(1.0)
		O(6)-P(2)-O(8)	109.8(0.9)

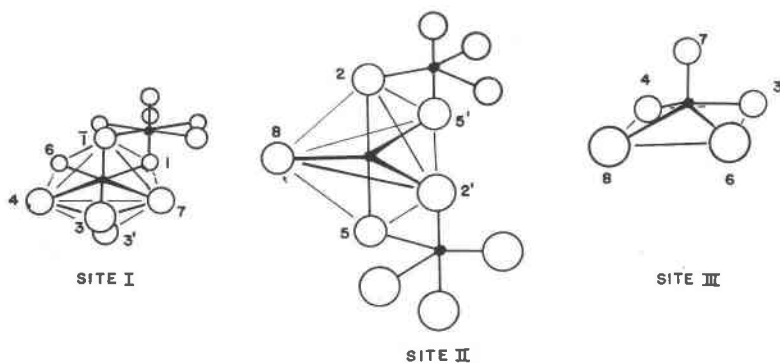


FIG. 1. Coordination of the cation sites in graftonite. The circles represent oxygen atoms.

mond shape with the O(3)-O(8) length the longer diagonal while the O(6)-O(4) length the shorter one. These lengths also mirror the cation oxygen bond distances in that those to O(3) and O(8) are 2.39 Å and 2.26 Å long respectively and those to O(6) and O(4) are 2.01 Å and 1.99 Å long.

Site III has a trigonal bipyramidal environment of oxygen atoms. The oxygen atoms in the plane O(5'), O(2') and O(8), average 2.08 Å in their cation oxygen bond distance while the axial bond lengths are 2.27 Å for O(5) and 2.28 Å for O(2).

The cations in site I edge share in pairs across a center of symmetry. This edge is indicated by "a" in Figure 2 where a portion of the structure is shown in projection down the *b* axis. Only one group in each pair is shown however. These groups then corner-shared through O(3) with each of four similar pairs that are related to the first pair by the *c* glide plane operation. Sheets parallel to the *b*-*c* plane are generated from this grouping by the translational symmetry of the crystal. The cations in site III share nonequatorial edges, called "c" in Figure 2, with neighbors related by the *c* glide plane and thus result in chains of trigonal bipyramids running parallel to the *c* axis. These chains do not share any oxygen

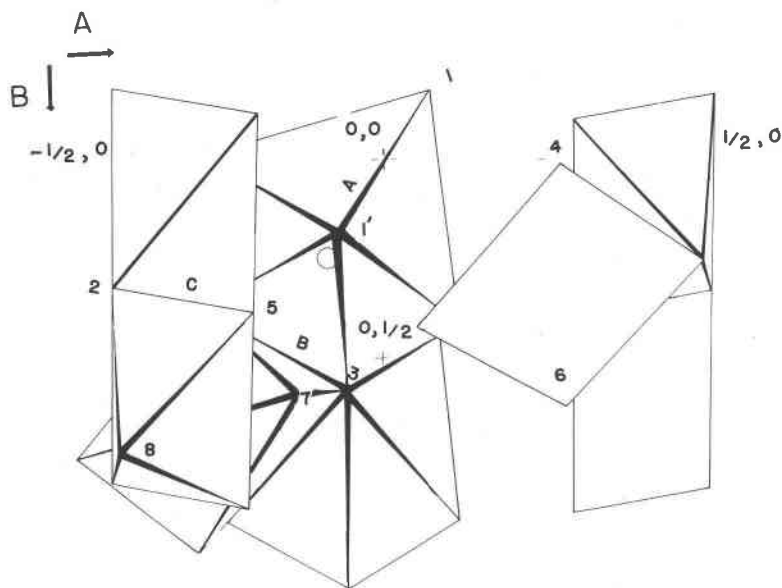


FIG. 2. Part of the structure of graftonite is shown projected onto the *x*, *y* plane. The corners of the polyhedra represent oxygen atoms which surround the cations. The phosphorus atoms are represented by circles.

atoms with cations of type I but share O(8) with cations of type II. These in turn share the O(3)-O(4) edge with one of edge shared site I pair and O(7) with the similar group but removed by one unit cell translation along the *c* axis. The shared edge is designated by "b" in Figure 2. Further bonding between these cation polyhedra is provided through the PO_4^{3-} groups. The positions of the phosphorus atoms are shown as circles in Figure 2.

DISCUSSION

The most interesting features of this structure are the preferred solubility of cations with large radii in site 1 and the variable coordination number of site 2. In each of the graftonite structures studied to date the cation with the largest radii, Cd^{2+} in $\text{CdZn}_2(\text{PO}_4)_2$, and Ca^{2+} here, is found in this site.

TABLE 5. LATTICE PARAMETERS OF COMPOUNDS WITH THE GRAFTONITE STRUCTURE

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β°
$\text{CdZn}_2(\text{PO}_4)_2$	9.032(4)	11.417(5)	5.952(6)	98.8(2)
$\text{Cd}_2\text{Zn}(\text{PO}_4)_2$	9.056(8)	11.86(1)	6.190(8)	100.1(2)
grafonite	8.91(1)	11.581(10)	6.239(6)	98.9(1)
$\text{Mn}_3(\text{PO}_4)_2$	8.80(1)	11.45(2)	6.25(5)	98.3(2)
$\text{Fe}_3(\text{PO}_4)_2$	8.8	11.5	6.25	99

The graftonite structure also seems to be found for the two pure end members $\text{Mn}_3(\text{PO}_4)_2$ and $\text{Fe}_3(\text{PO}_4)_2$. In Table 5 are listed the lattice parameters for those systems showing the graftonite structure. The lattice parameters of $\text{Mn}_3(\text{PO}_4)_2$ were determined from a crystal prepared by Stephens (1967) and those of $\text{Fe}_3(\text{PO}_4)_2$ were derived from the powder pattern reported by Korinth and Royen (1961). The latter pattern is compared to that of Lindberg (1950) in Table 6. Single crystal photographs of the graftonite polymorph of $\text{Mn}_3(\text{PO}_4)_2$ are very similar to those of the mineral and thus its structure should be nearly the same. Unfortunately without detailed intensity measurements it can not be ascertained whether site 2 has five-fold coordination as in the mineral and $\text{CdZn}_2(\text{PO}_4)_2$ or four-fold coordination as in $\text{CdZn}_2(\text{PO}_4)_2$ or whether some of the longer bonds found in the mineral about site 1 might be lost in forming $\text{Mn}_3(\text{PO}_4)_2$.

The results of the detailed crystal structure investigation of the two Zn, Cd orthophosphate phases and the mineral make it appear that the coordination number of site II can be changed homogeneously from four to five by altering the chemical composition. In $\text{CdZn}_2(\text{PO}_4)_2$ the coordi-

TABLE 6. A COMPARISON OF THE POWDER PATTERNS OF GRAFTONITE AND $\text{Fe}_3(\text{PO}_4)_2$

Graftonite ^a		$\text{Fe}_3(\text{PO}_4)_2$ ^b	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
2	4.31	14	4.277
1	3.61	8	3.640
9	3.50	90	3.420
1	3.36		
1	3.17	14	3.168
1	3.08	6	3.070
4	3.02	46	3.018
4	2.956	6	2.947
2	2.902	56	2.910
10	2.860	100	2.838
1	2.810	26	2.789
7	2.715	66	2.727
		10	2.705
		24	2.654
		6	2.627
1	2.510	14	2.512
3	2.412	40	2.419
2	2.377	14	2.346
1	2.311	18	2.295

^a Data of Lindberg (1950).

^b Data of Korinth and Royen (1961).

nation number is 4 with the M(2)-O(3) distance in excess of 2.9 Å whereas in $\text{Cd}_2\text{Zn}(\text{PO}_4)_2$ this distance is 2.6 Å. Although this length is significantly larger than the other bonds to this cation its change must be regarded as significant. It should be noted that Zn^{2+} occupies this site in this phase and further that there is a miscibility gap between these two compositions. In the mineral the fifth bond (M(2)-O(3)) is further shortened to 2.39 Å which is now just barely significantly longer than the next longest bond.

Since the two major components of graftonite, $\text{Mn}_3(\text{PO}_4)_2$ and $\text{Fe}_3(\text{PO}_4)_2$, crystallize with this structure, the fact that the sarcopside structure forms at all is curious. Either Mn^{2+} or Fe^{3+} in the seven-fold coordinated site would be expected to be somewhat unstable so that the free energy of this phase would be lowered by the addition of an ion of large radii to this site. In lieu of this some other structure such as sarcopside could be expected to be stable. If this were the case at some intermediate composition it would be expected to hold *a fortiori* for pure $\text{Fe}_3(\text{PO}_4)_2$. The fact that it is not true suggests that perhaps Mg^{2+} is playing a crucial role in the stabilization of the sarcopside structure. Since the detailed cation

distribution in this structure is not known we can not speculate further on this point.

ACKNOWLEDGEMENT

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