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Occurrence and crystal structure of Ca-free beusite in the El Sampal IIIA iron meteorite

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ABSTRACT

Euhedral, Ca-free beusite $(Mn_{1.5}Fe_{1.5})(PO_4)_2$ coexists with sarcopside and alkali-bearing phosphates within a troilite nodule in the El Sampal IIIA iron meteorite. From single-crystal X-ray data, the structure is monoclinic, $P2_1/c$ with $a = 8.757(3)$, $b = 11.381(4)$, $c = 6.136(1)$ Å, $\beta = 99.09(2)°$. Refinement ($R = 0.047$) showed the structure to be that of graftonite. The coordination of the M1 site, in contrast to Ca-rich beusite, is nearly sixfold coordinated, as two O atoms are displaced 2.86 and 2.97 Å from the M1 cation. A comparison of graftonite-type structures with different Ca contents in M1 shows a progressive change from eightfold to sixfold, tending to fivefold coordinated M1 as the M1 cation changes from Ca to Mn,Fe to Fe. This illustrates the extreme flexibility of this structure type.

INTRODUCTION

The beusite-graftonite series, $Mn_3(PO_4)_2$-$Fe_3(PO_4)_2$, is restricted on Earth to pegmatites where beusite is intergrown with other phosphates including triphylite (Wise and Černý, 1990) and lithiophilite (Hurlbut and Aristarain, 1968); it represents a breakdown of a high-temperature phase (Hurlbut and Aristarain, 1968). Graftonite occurs in pegmatites and in some iron meteorites (Olsen and Fredriksson, 1966), in the latter as euhedral single crystals. Below we report the first occurrence of beusite from a meteorite. Terrestrial samples of this mineral always contain at least several percent CaO and MgO, but the meteoritic samples almost always contain only trace Ca and Mg; thus they lie along the Mn-Fe compositional join (Fig. 1). Although the structures of natural Ca-bearing graftonite (Calvo, 1968) and beusite (Wise et al., 1990) are known, the structure of Ca, Mg-free samples has only been determined on synthetic phases (Kostiner and Rea, 1974; Nord and Ericsson, 1982). Nord and Ericsson (1982) determined the cation distribution among the several metal sites using Mössbauer spectroscopy and neutron diffraction for a series of synthetic compositions between graftonite and beusite. One of their samples matches almost exactly the composition reported here for the meteoritic occurrence. The graftonite-type structure is interesting in that the coordination about the metal ions is variable depending on the amount of Ca in the structure (Wise et al., 1990); in addition, there is observed ordering among these sites (Nord and Ericsson, 1982). The present structural work is thus meant to confirm that the meteoritic beusite has the graftonite structure and to provide a structural comparison of natural Ca-free with Ca-bearing beusite.

OCCURRENCE

In meteorites, the iron manganese orthophosphates occur primarily, but not exclusively, in the group of iron meteorites classified as IIIAB (Scott and Wasson, 1975). They most frequently occur as euhedral crystal inclusions within troilite nodules that in turn are surrounded by Fe-Ni metal. In rare cases they occur directly in metal. The phosphates form as a result of a small, late-stage increase in O partial pressure within the nodule volume that oxidizes some phosphorus alloyed in the Fe-Ni metal host (Olsen and Fredriksson, 1966). They appear to form as crystals within molten troilite nodules in the interval of approximately 500 °C between the crystallization of metal and sulfide (Kracher, 1983). The Mn content is derived from the surrounding sulfide, again as a result of the local increase in the O partial pressure that in turn results from the occlusion of trace amounts of O from the surrounding metal mass.

The beusite reported here is the first known occurrence in a meteorite, the IIIA iron, El Sampal, found in 1973 near Nueva Lubuka, Chubut Province, Argentina (Graham et al., 1985). The composition is almost exactly 50 mol% graftonite and 50 mol% beusite (Table 1). The original definition of beusite is based on weight percent MnO and FeO (Hurlbut and Aristarain, 1968), which puts this composition in the beusite field. It occurs as a euhedral crystal, 680 μm × 270 μm, separated by about 18 μm from the nearest other phosphate crystal in the nodule within the plane of the polished section. The other phosphates in this nodule are mainly sarcopside (Table 1; verified by X-ray diffraction), although two grains of an as yet uncharacterized alkali-bearing phosphate are present.

The most frequently encountered graftonite-beusite se-

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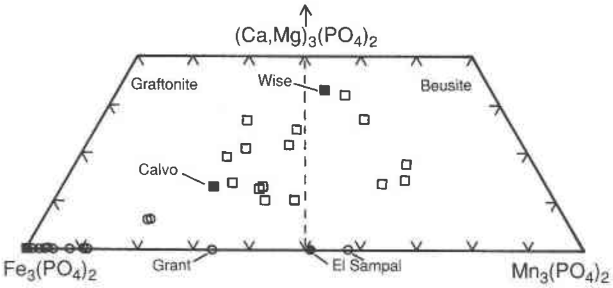

Fig. 1. Compositions (mole percent) of terrestrial (squares) and meteoritic (circles) graftonite and beusite samples. Compositions for which structures have been determined by X-ray diffraction are solid symbols (Wise = Wise et al., 1990; Calvo = Calvo, 1968; El Sampal = this work; synthetic $Fe_3(PO_4)_2$ = Kostiner and Rea, 1974). Terrestrial data from Hurlbut and Aristarain, 1968. Point labeled "Grant" is from Table 1.

ries composition in iron meteorites is graftonite with 3–5 mol% $Mn_3(PO_4)_2$. A range of other compositions has been found in rare instances. A graftonite composition of $Fe_{1.92}Mn_{0.98}P_{2.04}O_8$ (Table 1) has been found in the Grant IIIB iron meteorite. Because there are three cation sites, it is possible this is an ordered compound, although it would be difficult to prove. Other compositions encountered in a variety of other iron meteorites range from Mn-free $Fe_3(PO_4)_2$ to beusite samples with molar Mn > Fe, and a few with significant Ca or Mg or both. Pure $Fe_3(PO_4)_2$ always occurs entirely within metal, not within troilite.

STRUCTURE DETERMINATION

From the polished section, a small portion of the beusite grain was excavated for X-ray study. A minimal amount was removed to preserve as much material as possible for additional isotopic measurements of excess ^{53}Cr. From ^{53}Cr measurements it is possible to date the formation time of asteroid cores (Davis and Olsen, 1990; Birck and Allègre, 1988). The irregular fragment was oriented on a precession camera to obtain initial lattice parameters and then transferred to a four-circle automated diffractometer for intensity data measurement. Initial scans of diffraction peaks showed a full width at half maximum up to 1°, probably resulting from weak shock commonly seen in these meteorites. There was, however, no indication of multiple crystals. Cell parameters were obtained by least-squares refinement using 20 centered diffractions (29 < 2θ < 43), each the average of automatic centering of eight equivalent diffractions. Experimental details are given in Table 2. The absence of intensities for $h0l$, l = odd and $0k0$, k = odd diffractions confirms the $P2_1/c$ space group.

TABLE 2. Experimental details and crystallographic data for beusite

	Crystal-cell data	
a (Å)	8.757(3)	
b (Å)	11.381(4)	
c (Å)	6.136(1)	
β (°)	99.09(2)	
V (Å^3)	603.8(3)	
Space group	$P2_1/c$	
Z	4	
Formula	$(Mn_{0.5}Fe_{0.5})_3(PO_4)_2$	
D_{calc} (g·cm^{-3})	3.916	
μ (cm^{-1})	70.6	
	Intensity measurements	
Crystal size	Irregular, 0.07 × 0.08 × 0.14 mm	
Diffractometer	Picker, Krisel control	
Monochromator	Graphite	
Radiation	Mo$K\alpha_1$	
Scan type	θ-2θ	
2θ range	3.0–55.0	
Diffractions measured	1623 (80 systematically absent)	
Unique diffractions	1412	
	Refinement of the structure	
R	0.047	$R = \Sigma(\|\|F_0\| - \|F_c\|\|)/\Sigma\|F_0\|$
R_w	0.041	$R_w = [\Sigma w(\|F_0\| - \|F_c\|)^2/\Sigma w\|F_0\|^2]^{1/2}$, $w = \sigma^{-2}(F_0)$
Variable parameters	118	
Goodness of fit (GOF)	2.50	

TABLE 1. Electron microprobe analyses of beusite, sarcopside, and graftonite

Oxide	Beusite El Sampal	Sarcopside El Sampal	Graftonite Grant
P_2O_5	41.75 (2.06)	40.13 (2.02)	40.95 (2.04)
CaO	0.07 (0.004)	0.03 (0.002)	0.06 (0.004)
MnO	29.31 (1.44)	1.62 (0.082)	19.67 (0.980)
FeO	28.98 (1.41)	57.59 (2.86)	38.96 (1.92)
Sum	100.11 (4.92)	99.37 (4.97)	99.64 (4.95)

Note: All analyses done on Cameca SX50 electron microprobe with 15-kV accelerating potential and 25-nA beam current. Standards include P, Ca = synthetic $Ca_2P_2O_7$; Fe = natural manganese hortonolite; Mn = Mn metal. Matrix corrections were made using manufacturer supplied PAP correction procedure. Values in parentheses are atoms based on a total of eight O atoms. Na_2O, MgO, and SiO_2 less than 0.02 wt%.

Initial parameters were those of Calvo (1968), and the refinement with isotropic temperature factors converged to R near 0.07. The occupancy of each of the three metal sites was fixed at 0.5Fe + 0.5Mn. An additional six cycles with anisotropic thermal parameters yielded the final R values given in Table 2. No attempt was made to refine occupancy of Fe and Mn among the three sites. Final positional and thermal parameters for Ca-free beusite are given in Table 3 and bond distances in Table 4. A copy of the observed and calculated structure factors, Table 5, is available.[1]

DISCUSSION

The general description of the graftonite structure has been given (Calvo, 1968; Wise et al., 1990). A most interesting aspect of this structure is the unusual coordination of the three sites occupied by Fe, Mn, and Ca. This refinement of Ca-free beusite provides a basis for comparison with the recent data of Wise et al. (1990) for Ca-rich beusite and the earlier determination by Calvo (1968) of graftonite with intermediate Ca as well as the

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[1] A copy of Table 5 may be ordered as Document AM-91-479 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 3. Positional and isotropic displacement parameters for beusite

Atom	x	y	z	U_{eq}*
P1	0.0911(2)	0.1372(1)	0.3932(2)	0.0109(4)
P2	0.6065(2)	0.0878(1)	0.8070(2)	0.0114(4)
M1	0.9457(1)	0.1165(1)	0.8441(2)	0.0194(3)
M2	0.7218(1)	0.0799(1)	0.3297(1)	0.0174(3)
M3	0.3639(1)	0.1918(1)	0.1260(1)	0.0140(2)
O1	0.0760(4)	0.0675(3)	0.1766(6)	0.015(1)
O2	0.4818(4)	0.1783(3)	0.8303(7)	0.016(1)
O3	0.9402(4)	0.2031(3)	0.4067(7)	0.016(1)
O4	0.7001(4)	0.1250(3)	0.6281(6)	0.015(1)
O5	0.2204(4)	0.2268(4)	0.3791(7)	0.019(1)
O6	0.7276(4)	0.0844(3)	0.0159(6)	0.014(1)
O7	0.1299(5)	0.0627(3)	0.6004(7)	0.017(1)
O8	0.5335(4)	−0.0343(3)	0.7588(7)	0.015(1)

Atom	U_{11}**	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P1	0.0127(6)	0.0113(7)	0.0085(6)	−0.0006(5)	0.0012(5)	0.0003(5)
P2	0.0134(6)	0.0134(7)	0.0074(6)	0.0001(5)	0.0021(5)	0.0002(6)
M1	0.0215(5)	0.0141(4)	0.0208(5)	0.0000(3)	−0.0019(4)	−0.0019(4)
M2	0.0206(4)	0.0259(5)	0.0057(4)	0.0069(4)	0.0018(3)	0.0001(4)
M3	0.0173(4)	0.0143(4)	0.0100(4)	0.0021(3)	0.0009(3)	0.0003(3)
O1	0.018(2)	0.015(2)	0.010(2)	0.003(2)	0.001(2)	−0.002(2)
O2	0.018(2)	0.018(2)	0.013(2)	0.006(2)	0.002(2)	0.002(2)
O3	0.017(2)	0.015(2)	0.018(2)	0.003(2)	0.004(2)	−0.001(2)
O4	0.015(2)	0.019(2)	0.011(2)	−0.003(2)	0.004(2)	0.002(2)
O5	0.018(2)	0.025(2)	0.014(2)	−0.009(2)	0.003(2)	−0.002(2)
O6	0.007(2)	0.021(2)	0.012(2)	0.001(1)	0.001(1)	0.000(2)
O7	0.021(2)	0.016(2)	0.011(2)	−0.002(2)	−0.002(2)	0.004(2)
O8	0.018(2)	0.012(2)	0.015(2)	−0.003(2)	0.002(2)	−0.001(2)

Note: Estimated standard errors in parentheses refer to the last digit.

* U_{eq} is defined as $\frac{1}{3}\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

** Anisotropic displacement parameters U_{ij} are defined as $\exp(-2\pi^2\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}U_{ij}a_i^*a_j^*h_ih_j)$.

ferrous phosphate structure (Kostiner and Rea, 1974). The M1 site of the graftonite-type structure has been described as sixfold, sevenfold, or eightfold coordinated; the M2 site as fivefold coordinated; and the M3 site as fivefold or sixfold coordinated. For Ca-bearing samples, the Ca occupies the larger M1 site. Neutron diffraction (Nord and Ericsson, 1982) has shown that Mn prefers the M1 and M3 sites in Ca-free synthetic samples of graftonite-beusite.

Table 6 provides a comparison of the M-O distances for the four structures, and Figure 2 illustrates the variation in M1-O distances of the eight nearest atoms. For the sample with Ca occupancy of M1 equal to 0.98, seven Ca-O distances are between 2.31 and 2.55; one (O5) is 2.80 Å. Although Wise et al. (1990) consider this sevenfold coordinated, the 2.80 Å distance is within the range for eightfold-coordinated Ca (Baur, 1970). The situation becomes more complex as the occupancy of Ca in M1 decreases, as shown on Figure 2. With decreasing Ca, the O5 and O3 distances increase. Some of the increase will result from the different Fe/Mn ratios in each of these structures, but the longest M1-O distance is 2.975 Å in the Ca-free beusite structure. The effect of increasing the Fe/Mn ratio is shown dramatically by comparing the ferrous phosphate structure to the Ca-free beusite structure: the O5 and O3 distances increase to 3.19 and 3.11 Å, respectively, in ferrous phosphate. An important observation is that if M1 is considered eightfold coordinated in all four structures, the average M1-O distance is nearly constant, ranging only from 2.43 to 2.49 Å. This small range results because as M1-O3 and M1-O5 become longer with decreasing Ca, the other M1-O distances all decrease to maintain a nearly constant average distance.

Bond valence calculations as described by Baur (1970) show only a slightly better agreement of sixfold compared with eightfold coordination of M1. For sixfold coordination, the largest deviation of the electrostatic bond-strength sum compared with the anion valence is +0.05 to −0.08; for eightfold coordination, the maximum deviations are +0.16 to −0.10 valence units. These values are within the ranges observed for Ca-O and Fe-O in mineral structures (Baur, 1970).

These bond distance data are illustrated in Figure 3 by

TABLE 4. Bond lengths for beusite

P1-O1	1.536(2)	P2-O2	1.523(4)	M1-O1	2.105(1)
-O3	1.533(4)	-O4	1.530(4)	-O1	2.245(1)
-O5	1.536(4)	-O6	1.530(4)	-O3	2.091(4)
-O7	1.521(4)	-O8	1.539(4)	-O3	2.852(4)
Mean	1.532	Mean	1.531	-O4	2.343(4)
				-O5	2.975(4)
M2-O3	2.358(4)	M3-O1	2.950(2)	-O6	2.352(4)
-O4	1.940(4)	-O2	2.230(4)	-O7	2.445(4)
-O6	1.935(4)	-O2	2.102(4)	Mean	2.426
-O7	2.081(4)	-O5	2.033(4)		
-O8	2.275(4)	-O5	2.183(4)		
Mean	2.118	-O8	2.078(4)		
		Mean	2.263		

TABLE 6. Comparison of M-O distances and site occupancies for graftonite-type structures

	1	2	3	4
M1-O1a	2.187	2.245	2.363	2.383
-O1b	2.019	2.105	2.228	2.310
-O3	3.118	2.852	2.687	2.547
-O3c	1.983	2.091	2.246	2.330
-O4	2.332	2.343	2.473	2.457
-O5	3.195	2.975	2.934	2.788
-O6	2.182	2.352	2.424	2.477
-O7	2.682	2.445	2.583	2.525
Mean	2.462	2.426	2.492	2.477
M2-O3	2.421	2.358	2.387	2.340
-O4	1.938	1.940	1.988	1.965
-O6	1.942	1.935	2.007	1.962
-O7	2.062	2.081	2.039	2.048
-O8	2.309	2.275	2.264	2.209
Mean	2.134	2.118	2.137	2.105
M3-O1	3.004	2.950	2.915	2.850
-O2	2.230	2.230	2.275	2.251
-O2	2.078	2.102	2.113	2.146
-O5	1.996	2.033	2.039	2.075
-O5	2.158	2.183	2.268	2.261
-O8	2.042	2.078	2.075	2.142
Mean	2.251	2.263	2.281	2.286
		Site occupancy		
M1-	$Fe_{1.0}$	$Fe_{0.5}Mn_{0.5}$	$Ca_{0.4}Fe_{0.4}Mn_{0.2}$	$Ca_{0.98}Mn_{0.02}$
M2-	$Fe_{1.0}$	$Fe_{0.5}Mn_{0.5}$	$Fe_{0.7}Mn_{0.3}$	$Fe_{0.92}Mn_{0.08}$
M3-	$Fe_{1.0}$	$Fe_{0.5}Mn_{0.5}$	$Fe_{0.7}Mn_{0.3}$	$Mn_{1.0}$

Note: Column 1—$Fe_3(PO_4)_2$ (Kostiner and Rea, 1974); column 2—Ca-free beusite, present study; column 3—Graftonite (Calvo, 1968); column 4—Ca-rich beusite (Wise et al., 1990).

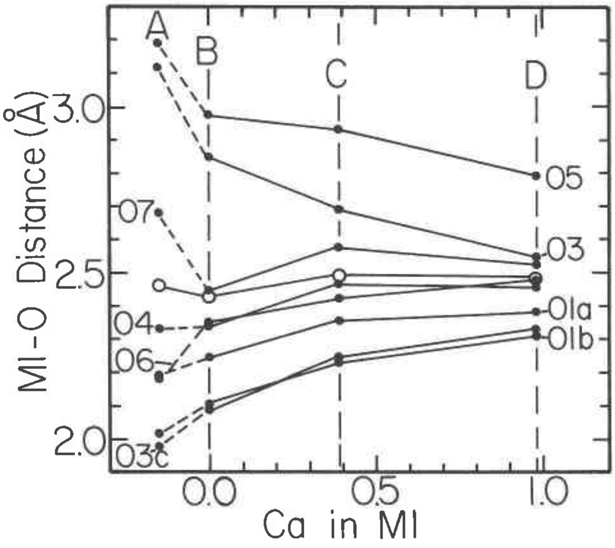

Fig. 2. Bond length variation of M1-O for eight nearest O atoms as a function of Ca atom fraction in M1. A = synthetic graftonite (Kostiner and Rea, 1974); B = low-Ca beusite (this work); C = Ca-bearing graftonite (Calvo, 1968); D = high-Ca beusite (Wise et al., 1990). The average distances of the eight M1-O distances are shown as open circles. Note that data for synthetic graftonite are displaced from Ca = 0.0 to illustrate the effect of pure Fe vs. mixed Fe-Mn in the M1 site.

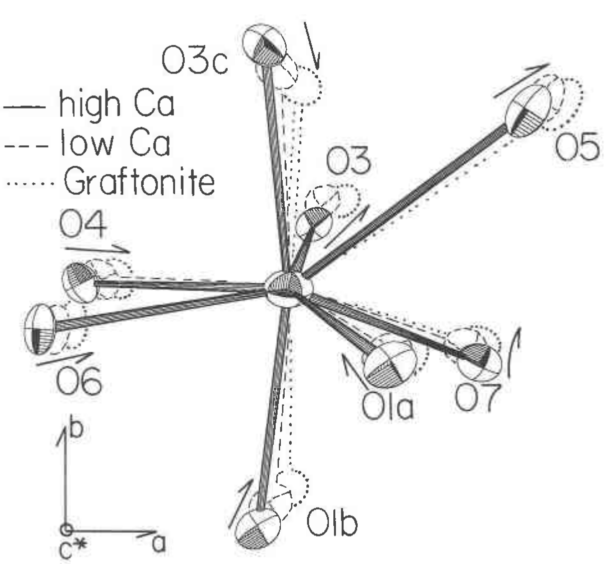

Fig. 3. Coordination about M1 for high-Ca beusite (solid lines), low-Ca beusite (dashed lines), and synthetic graftonite (dots). The position of M1 is fixed, and the relative position of the O atoms in the three structures is indicated. The O atoms adjacent to O3 and O5 (O3c, O1a, O1b, and O7) rotate toward O3 and O5 as Ca content decreases, and the O atoms O4 and O6 become shorter without significant angular displacement. The thermal ellipsoids are those for Ca-free beusite but are applied to all three structures only to show relative positions.

superimposing the eight O atoms around M1 for the three structures: high-Ca beusite, low-Ca beusite, and synthetic graftonite. As the Ca fraction decreases, O3 and O5 move away from M1, and the adjacent O atoms rotate toward the O3 and O5 bonds and show shorter M1-O distances. If all eight O atoms are considered, this represents a nominal change from eightfold coordination to sixfold coordination while maintaining a near-constant M1-O distance. When the Ca-free beusite is compared with the synthetic graftonite, the only chemical change is the Fe/Mn ratio. Whereas Mn and Fe are closer in size to each other than to Ca, the effect on the bond lengths is dimensionally greater as shown on Figure 2. The O3 and O5 distances increase beyond 3 Å, and M1-O7 also begins to increase, suggesting that the M1 site is itself tending to fivefold coordination as are the M2 and M3 sites. The structure of Ca-free beusite emphasizes the extreme flexibility of the graftonite structure in accommodating different sized cations in the M1 site without a change in the basic structure or space group symmetry.

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