

Crystallographic Studies of the Role of Mg as a Stabilizing Impurity in β - $\text{Ca}_3(\text{PO}_4)_2$

II. Refinement of Mg-Containing β - $\text{Ca}_3(\text{PO}_4)_2$ *

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The crystal structures of five samples of Mg-containing β -tricalcium orthophosphate, β - $\text{Ca}_3(\text{PO}_4)_2$, have been refined and the Mg-impurity distribution has been examined. Typically, ~7500 reflections were measured and merged into a unique set of ~2500. Least-squares refinements with anisotropic temperature factors (and third cumulants for some atoms) produced weighted residuals, $R_w(F)$, in the region of 0.02 to 0.04. Three of the five cation sites are always completely filled with calcium ions, a fourth site with Ca and Mg ions, and the fifth site contains Ca, Mg, and vacancies. Local order may exist because the sizes of the coordinations about the two Mg-containing cation sites are directly related by the orientation of phosphate group $\text{P}(2)\text{O}_4$ such that a small ion in one site favors the incorporation of a small ion in the other site.

Introduction

The background for the present investigation was given in our earlier paper on pure β - $\text{Ca}_3(\text{PO}_4)_2$ (1). Since then, the crystal structures of synthetic Mg-whitlockite, $\text{Ca}_{18}\text{Mg}_2\text{H}_2(\text{PO}_4)_{14}$ (2), and of the mineral whitlockite, $\text{Ca}_{18.19}\text{Mg}_{1.17}\text{Fe}_{0.83}\text{H}_{1.62}(\text{PO}_4)_{14}$ (3), from the Palermo quarry have been reported. Thus the relationship between whitlockite and synthetic β - $\text{Ca}_3(\text{PO}_4)_2$ has been clarified. β - $\text{Ca}_3(\text{PO}_4)_2$ is known to be stabilized by the presence of small amounts of Mg; this is amply corroborated by the fact that the

samples of β - $\text{Ca}_3(\text{PO}_4)_2$ used in this work were prepared in the stability range of pure β - $\text{Ca}_3(\text{PO}_4)_2$ (4).

Some insight into the stabilization of the β - $\text{Ca}_3(\text{PO}_4)_2$ structure is given by the relationship between the $\text{Ba}_3(\text{VO}_4)_2$ and β - $\text{Ca}_3(\text{PO}_4)_2$ structures. As mentioned in reference (1), in the unit cell of the β - $\text{Ca}_3(\text{PO}_4)_2$ structure both a and c are doubled relative to the $\text{Ba}_3(\text{VO}_4)_2$ cell. An isostructural relationship would yield 24 Ca ions and 16 PO_4 groups, allowing for the factor of 4 in cell volumes. The β - $\text{Ca}_3(\text{PO}_4)_2$ structure actually has 21 cations and 14 PO_4 groups in the rhombohedral unit cell which is 3 cations and 2 PO_4 groups less than in the $\text{Ba}_3(\text{VO}_4)_2$ structure. However, smaller cation coordination polyhedra are now evident (see Fig. 1) and, in particular cation site M(5) is nearly octahedral. Cation sites M(4) and M(5) are new sites relative to the $\text{Ba}_3(\text{VO}_4)_2$ structure.

There are 22 cation sites per cell (space-group R3c) but, as our previous results (1) have shown, two cation sites (of type M(4)) are only

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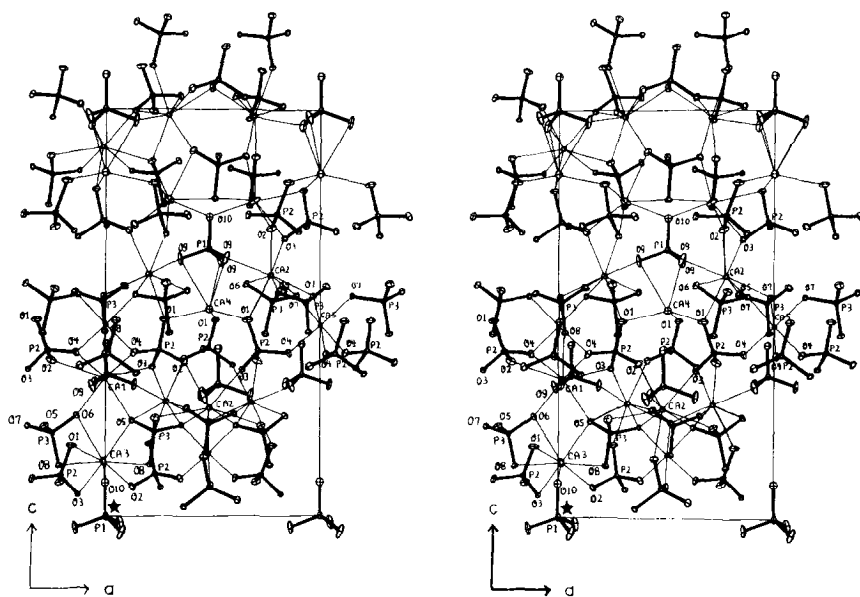


FIG. 1. The $\beta\text{-Ca}_3(\text{PO}_4)_2$ structure from sample (III). Only half of the cell is shown along c and two-thirds perpendicular to the ac plane. The origin of the coordinate system is marked by *.

half filled because of charge balance requirements. Meteoritic whitlockite ("merrillite") (6) appears to have a formula near $\text{Ca}_{18}(\text{Mg}, \text{Fe})_2\text{Na}_2(\text{PO}_4)_{14}$. These meteorites could have the $\beta\text{-Ca}_3(\text{PO}_4)_2$ structure with all cation sites filled and still be electroneutral.

The environment of site M(4) is shown in Fig. 2. This cation site is on the threefold axis

and has an unusual coordination to the O(9), O(9'), O(9'') face of the P(1)O₄ group. Electrostatic repulsion between the cation and the phosphorus atom is expected to be significant and long Ca(4) ··· O(9) distances are observed in pure $\beta\text{-Ca}_3(\text{PO}_4)_2$. The M(4) coordination is completed by three O(1) atoms from surrounding P(2)O₄ groups.

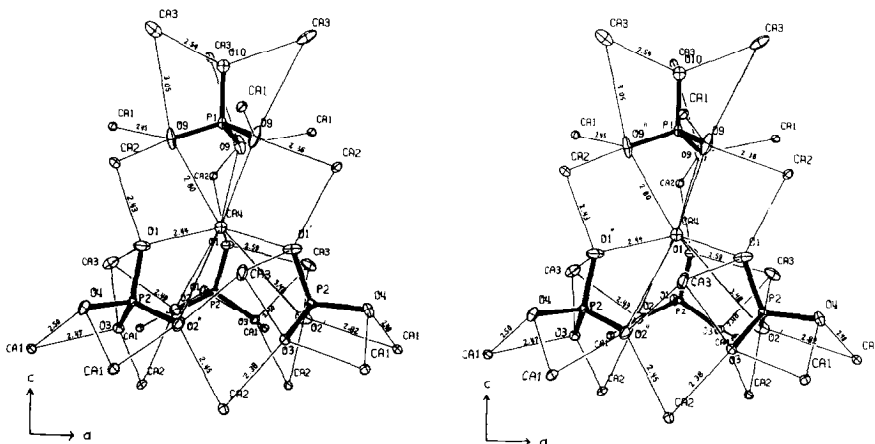


FIG. 2. The environment of cation site M(4) (labeled Ca4) and the P(1)O₄ group. Here the M(4) site is labeled Ca(4).

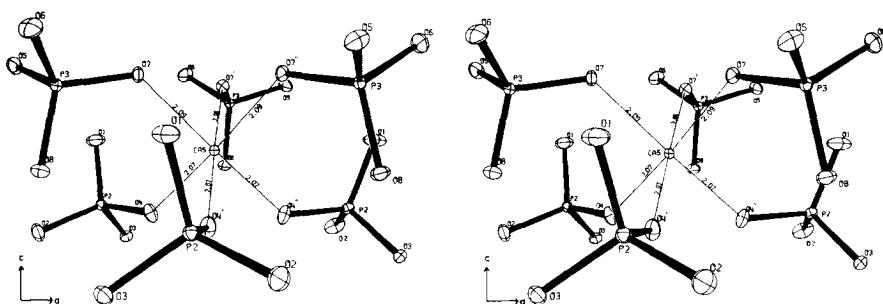


FIG. 3. The approximately octahedral cation site M(5) (labeled Ca5). This site is located on the trigonal axis.

Figure 3 shows the environment of site M(5), which is also located on the threefold axis. The coordination is essentially octahedral with no shared PO₄ edges, which allows the M(5)···oxygen distances to be small and uniform, and favors the incorporation of small impurity ions requiring a coordination number of 6.

We have synthesized five samples of β -Ca₃(PO₄)₂ containing amounts of Mg ranging from 4 to 14% of the cations and refined their

crystal structures in order to elucidate the manner by which Mg stabilized β -Ca₃(PO₄)₂. This paper gives details of the structures of three of these samples. The two others seemed to contain Fe as an additional impurity.

Experimental

We made our samples from a mortar-ground slurry in alcohol of CaCO₃ dried at 100°C, MgO (allowing for 2% weight loss on

TABLE I
SAMPLE PREPARATION AND COMPOSITION OF Ca_{3-x}Mg_x(PO₄)₂

Crystal I.D.	0	I, II	III ^b
Value of <i>x</i> in formula	0.00	0.11	0.29
Atom %, Mg	0.00	4.8	11.6
CaHPO ₄ · 2H ₂ O(g) ^a	1.9998	7.0010	10.0000
CaCO ₃ (g)	0.5820	1.7915	2.5750
MgO(g)	0.0000	0.1001	0.4530
Heating temp (°C)	1400	1350	1350
Heating time (hr)	24 ^c	24	5
Microprobe results, wt% ^d			
Ca		37.2 ^f	35.0
Mg		0.8	2.3
P		20.1	20.0
Sum ^e		99.7	98.3

^a Numbers in this row and following two rows are the amounts in grams of the reactants. 0.5–1.0 wt% cornstarch added to aid in formation of pellets.

^b 4 wt% cristobalite (SiO₂) added to act as a flux.

^c Followed by heating at 1100°C for 162 hr.

^d Four data points on each crystal, reproducibility 0.1–0.5%, systematic error ± 2% or less of the amount present.

^e Assuming all P present as PO₄.

^f Results for crystal II used in data collection were imprecise because of difficulty in preparing a flat surface. Results from another crystal were equal within experimental error to those for crystal I.

heating) and CaHPO_4 (prepared by heating $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ for two days at 80°C). The slurry was dried, heated to 1000°C for 5 hr, reground, pelletized with cornstarch, a few drops of water, and sometimes cristobalite (to act as a flux), and then heated in platinum foil. Details for individual cases (I–III) are given in Table I.

The crystals were made in a solid state reaction which included the evolution of CO_2 . Thus they contain many pores, and great care had to be taken to prepare a flat area on which to perform microprobe analyses. Typically, three to four points were taken on each crystal and three crystals were taken from each preparation. Each individual crystal appeared to be homogeneous. Single crystals of $\text{Mg}_3(\text{PO}_4)_2$ and $\alpha\text{-Ca}_3(\text{PO}_4)_2$ were used as standards. Table I gives the analysis for the actual crystal used in the data collection for all samples except II. Samples I and II are different crystals from the same preparation. They are similar chemically but were treated as independent cases so that various statistical tests could be made in the course of the investigation.

Crystals of all samples were ground into approximate spheres and mounted in random orientations on goniometer heads. Their quality and alignment were checked optically and by precession photography. The cell

determinations and data collections were performed on an automated 4-circle diffractometer equipped with Mo radiation and a graphite monochromator. The procedures in (I) were utilized with the following conditions: $2\theta \leq 80^\circ$; scan speed = $1^\circ/\text{min}$ in 2θ ; and backgrounds were counted for 20 sec. Crystal data and a summary of the results of data collections are given for each crystal in Table II.

Three equivalent members ($+h, +k, +l$) of each form were measured on the diffractometer. An equivalent reflection was included in the average if its magnitude and the magnitude of at least one other equivalent agreed within $4[\sigma_c^2(1) + \sigma_c^2(2)]$. The variance σ_c^2 is based on counting statistics and a propagation of an assumed 2% uncertainty in μr as an absorption correction was applied (see Table II). The value of σ for the mean $|F_0|$ was taken as the larger of $\bar{\sigma}$ and $(\bar{\sigma} + s/n^{1/2} + r/n^{1/2})/3$. Here $\bar{\sigma}^2 = 1/\Sigma \eta_i^2(1/\sigma_c^2(i))$, s^2 is the usual variance computed for the deviations from the mean, and r is the range estimate based on a normal distribution and equals 0.89 (range) and 0.59 (range) for two and three equivalents, respectively.

We incorporated the statistical procedures suggested by Abrahams and Keve (7) and other statistical procedures of our own into our program STATUS (8). STATUS was used

TABLE II
CRYSTAL DATA AND DATA COLLECTION STATISTICS FOR $\text{Ca}_{3-x}\text{Mg}_x(\text{PO}_4)_2$

Value of x in formula	0.00(0) ^{a,b}	0.11(I)	0.11(II)	0.29(III)
a (Å)	10.439(1)	10.401(1)	10.400(1)	10.337(1)
c (Å)	37.375(6)	37.316(2)	37.315(3)	37.068(4)
Volume (Å ³)	3527.2	3495.8	3495.3	3437.7
ρ_{calc} (g·cm ⁻³)	3.07	3.08	3.08	3.10
Reflections measured	2513	7633	7616	7501
No. of unique reflections with $I \geq 2\sigma$,	1143	2495	2461	2524
R for equivalent reflections	0.041	0.021	0.022	0.017
Number of equivalent reflections averaged	1810	6530	6431	6526
μR	0.18	0.37	0.35	0.42
Max/min transmission factor ^c	0.75/0.74	0.57/0.56	0.61/0.60	0.54/0.53

^a Data from reference (1).

^b Sample identification given in parentheses is the same as in Table I.

^c Equation (2) as given by K. D. Rouse and M. J. Cooper, *Acta Crystallogr.* **18**, 682–691 (1970) was used to calculate transmission factors.

to compare the $|F_0|$ values and associated $\sigma(F_0)$ values of samples I and II. We conclude the $\sigma(F_0)$ values assigned to samples I and II account satisfactorily for random error and such systematic errors as are detectable. Any remaining systematic errors, such as absorption (revealed in the d^* plots) or gross differences in secondary extinction or multiple diffraction (revealed in the $\log(|F_0|^2/\sin 2\theta)$ plots), are not larger than the uncertainties represented by the assigned $\sigma(F_0)$ values.

The structures were refined using the crystallographic least-squares program RFINE4 (9). The quantity minimized was $\sum w(|F_0| - |F_c|)^2$, where $w = [\sigma(F_0)]^{-2}$. Scattering factors were taken from references (10, 11).¹ Starting parameters were obtained from β -Ca₃(PO₄)₂ (I). Cation sites were allowed to be a mixture of Ca and Mg. The total occupancy of each site is 1 except for that of site M(4), which is $\frac{1}{2}$. Difference syntheses calculated after uneventful refinement to $R_w = \{w(|F_0| - |F_c|)^2/\sum w(F_0)^2\}^{1/2} \sim 0.02$ to 0.04 with anisotropic temperature factors for all atoms and third cumulant parameters for some atoms showed extra peaks corresponding to one-half to two electrons on the threefold axis (at $x = 0, y = 0$). After examination of the crystal structure and consideration of the method of preparation, we considered that a possible interpretation of these extra peaks is that "extra" CaO and/or MgO had been incorporated into the structures and that space for the "extra" atoms had been generated by reflection of about 10% of the P(1)O₄ groups through the O(9), O(9'), O(9'') triangle. However, during attempts to incorporate these extra peaks into the refinement, the R_w indices increased slightly and the reflected P(1)O₄ group became very distorted. Refinements in which the reflected PO₄ group

was constrained to have reasonable geometry led to higher R_w values. The extra peaks were therefore ignored in the final refinements. Fortunately, the main items of interest in the structure, the distribution of Ca and Mg over the cation sites, remained invariant during the extra peak refinements, consistently with the fact that the extra peaks comprise a very small part of the structure.

Refinements were also carried out with and without a constraint on the overall Ca content. The results reported here are from refinements in which the total Ca content was constrained to be compatible with the microprobe analyses. Occupancy parameters were constrained to be in the range 0.0 to 1.0; those which refined to values (≤ 1.007) outside these limits were set to the appropriate limit and fixed. Differences in the atomic parameters from I and II relative to the standard errors assigned in the least-squares refinements were compared with those expected for a normal distribution using our program STATUS. The plot derived from the differences in positional parameters in samples I and II was linear with a slope of 1.28 and an intercept of -0.08 . This suggests that the standard deviation of the positional parameters of each sample should be 15% larger since samples I and II are chemically similar. In contrast, the plot of differences in anisotropic thermal parameters in I and II had a nominal linear slope of 1.26 but showed some curvature indicative of some systematic differences in cation sites M(3), M(4), and M(5).

Results

Atomic parameters for the Mg containing samples of β -Ca₃(PO₄)₂ are given in Table III. A listing of observed and calculated structure amplitudes and third cumulants is available.²

¹ During the final stages of the preparation of this paper we noticed that we had inadvertently introduced anomalous dispersion factors early in the refinements although the data had been averaged over Friedel pairs. The anomalous dispersion factors are about 1% of the scattering for MoK α radiation. Thus, their contribution to the calculated structure factors is not deemed significant for the purpose of this study.

² Supplementary material has been deposited as Document No. 03056 with the National Auxiliary Publication Service, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N. Y. 10017. A copy may be secured by citing the document number and by remitting \$9.75 for photocopy or \$1.50 for microfiche. Advance payment is required. Make check or money order payable to Microfiche Publications.

TABLE III
 ATOMIC PARAMETERS ($\times 10^4$) FOR $\text{Ca}_{3-x}\text{Mg}_x(\text{PO}_4)_2$

Site ^a	x	y	z	u_{11}^b	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ca(1)	-2749(1)	-1423(1)	1666(1)	84(2)	84(2)	93(2)	46(1)	-1(1)	-12(1)
	-2749(1)	-1423(1)	1664(1)	85(2)	87(2)	92(2)	46(1)	0(1)	-11(1)
	-2730(1)	-1420(1)	1665(1)	75(1)	76(1)	70(1)	41(1)	-3(1)	-11(1)
Ca(2)	-3833(1)	-1772(1)	-339(1)	94(2)	76(2)	86(2)	37(1)	-16(1)	-2(2)
	-3833(1)	-1772(1)	-340(1)	96(2)	78(2)	86(2)	38(1)	-19(1)	-5(2)
	-3840(1)	-1769(1)	-348(1)	87(1)	66(1)	75(1)	34(1)	-24(1)	-5(1)
Ca(3)	-2737(2)	-1483(1)	604(1)	407(1)	171(1)	134(1)	210(1)	-98(2)	-76(2)
	-2733(1)	-1481(1)	602(1)	398(1)	173(1)	135(1)	206(1)	-95(2)	-75(2)
	-2738(1)	-1480(1)	595(1)	307(1)	149(1)	140(1)	174(1)	-103(1)	-79(1)
M(4) ^c	0	0	804(1)	117(1)	117	186(1)	59	0	0
	0	0	809(1)	178	178	288(1)	89	0	0
	0	0	780(1)	127(1)	127	134(1)	64	0	0
M(5) ^c	0	0	2653(1)	168(2)	168	101(3)	84	0	0
	0	0	2655(1)	147(2)	147	83(3)	74	0	0
	0	0	2652(1)	42(2)	42	44(3)	21	0	0
P(1)	0	0	0	69(2)	69	199(5)	35	0	0
	0	0	0	69(2)	69	201(5)	35	0	0
	0	0	0	56(1)	56	120(3)	28	0	0
O(9)	61(3)	-1363(3)	-128(1)	179(8)	104(8)	512(14)	83(8)	149(9)	0(9)
	62(3)	-1364(3)	-128(1)	172(8)	109(9)	521(15)	84(8)	143(9)	3(9)
	47(2)	-1378(2)	-135(1)	145(5)	82(5)	371(8)	68(5)	102(5)	-3(5)
O(10)	0	0	407(2)	286(2)	286	200(20)	143	0	0
	0	0	403(2)	255(2)	255	234(19)	178	0	0
	0	0	414(2)	131(6)	131	141(9)	66	0	0
P(2)	-3124(1)	-1379(1)	-1312(1)	104(2)	113(3)	88(2)	74(2)	15(2)	12(2)
	-3124(1)	-1378(1)	-1314(1)	106(2)	116(3)	87(4)	74(2)	13(2)	12(2)
	-3133(1)	-1389(1)	-1310(1)	73(1)	75(2)	59(1)	46(1)	9(1)	8(1)
O(1)	-2673(3)	-863(3)	-922(1)	481(15)	378(13)	81(7)	319(13)	14(9)	11(8)
	-2670(3)	-861(3)	-924(1)	493(16)	382(13)	81(8)	320(13)	20(8)	19(8)
	-2606(2)	-820(2)	-924(1)	289(7)	215(6)	69(4)	162(6)	-17(4)	-8(4)
O(2)	-2383(3)	-2240(3)	-1445(1)	368(12)	362(13)	150(8)	324(11)	80(8)	64(8)
	-2376(3)	-2233(3)	-1446(1)	378(13)	379(13)	151(9)	339(12)	82(8)	66(9)
	-2430(2)	-2287(2)	-1450(1)	206(6)	201(6)	137(5)	169(5)	58(4)	36(4)
O(3)	-2745(2)	-38(2)	-1525(1)	107(7)	94(7)	85(6)	30(6)	10(5)	8(6)
	-2744(2)	-39(2)	-1527(1)	104(7)	102(7)	84(6)	35(6)	8(5)	9(5)
	-2766(1)	-2(1)	-1537(1)	81(4)	71(4)	75(4)	25(3)	4(3)	17(3)
O(4)	-4817(2)	-2394(2)	-1356(1)	138(9)	75(7)	415(13)	38(7)	19(9)	14(8)
	-4816(2)	-2395(2)	-1358(2)	138(9)	87(8)	411(13)	40(7)	24(9)	18(8)
	-4857(1)	-2404(1)	-1333(1)	89(4)	74(4)	150(5)	34(4)	45(4)	15(4)
P(3)	-3457(1)	-1529(1)	-2334(1)	63(2)	70(2)	67(2)	30(2)	-4(2)	3(2)
	-3456(1)	-1529(1)	-2336(1)	64(2)	70(2)	70(2)	29(2)	-2(2)	4(2)
	-3439(1)	-1514(1)	-2347(1)	48(1)	59(1)	55(1)	24(1)	1(1)	2(1)
O(5)	-3997(2)	-468(2)	-2211(1)	139(7)	184(8)	102(7)	120(7)	-22(6)	-30(6)
	-3997(2)	-466(2)	-2213(1)	142(7)	186(8)	103(7)	121(7)	-19(6)	-31(6)
	-3964(1)	-434(1)	-2222(1)	107(4)	153(5)	100(4)	95(4)	-19(3)	-34(4)
O(6)	-4227(2)	-3038(2)	-2146(1)	207(9)	106(8)	137(8)	29(7)	32(7)	51(6)
	-4224(2)	-3038(2)	-2148(1)	212(9)	108(8)	140(8)	30(7)	28(7)	47(6)
	-4200(1)	-3004(1)	-2145(1)	127(5)	90(4)	114(5)	13(4)	20(4)	41(4)
O(7)	-1787(2)	-786(2)	-2251(1)	70(6)	97(7)	242(9)	42(6)	-39(6)	-30(6)
	-1787(2)	-789(2)	-2252(1)	74(7)	97(7)	236(9)	45(6)	-44(6)	-27(7)
	-1741(1)	-767(1)	-2279(1)	48(4)	84(4)	85(4)	33(3)	-2(3)	-3(3)
O(8)	-3748(3)	-1785(2)	-2736(1)	255(10)	201(9)	69(6)	155(8)	-6(6)	-9(6)
	-3747(3)	-1784(2)	-2738(1)	246(10)	200(9)	70(6)	149(8)	-5(6)	-7(6)
	-3789(1)	-1821(1)	-2748(6)	112(4)	117(4)	58(4)	56(4)	-15(3)	-12(3)

^a The three lines with each site are parameters for crystals I, II ($x=0.11$) and III ($x=0.29$).

^b The form of the thermal parameter is $\exp[-2\pi^2(\sum_{ij} U_{ij} h_i h_j a_i^* a_j^*)]$. Numbers in parenthesis are estimated standard deviations from the final cycle of least-squares refinement. Normal probability plots suggest these standard deviations should be increased by 15%.

^c Occupancies of Mg in M(4) are I-0.195(7), II-0.079(7) & III-0.000(7). Corresponding occupancies of Ca are 0.5 - occupancy of Mg. Table V gives Mg occupancies for M(5).

TABLE IV

CATION-OXYGEN DISTANCES (Å) IN Ca_{3-x}Mg_x(PO₄)₂

Crystal I.D. atoms	I(0.11) ^a	II(0.11)	III(0.29)
Ca(1)			
0(6)	2.315(2) ^b	2.315(2)	2.308(1)
0(5)	2.431(2)	2.430(2)	2.462(1)
0(8)	2.408(2)	2.409(2)	2.375(1)
0(4)	2.461(3)	2.459(2)	2.478(1)
0(9)	2.458(3)	2.456(3)	2.446(2)
0(4)'	2.494(2)	2.494(2)	2.499(1)
0(3)	2.499(2)	2.499(2)	2.475(1)
0(2)	2.897(3)	2.904(3)	2.824(2)
Ca(2)			
0(9)	2.367(3)	2.368(3)	2.363(2)
0(3)	2.377(2)	2.375(2)	2.377(1)
0(7)	2.404(2)	2.406(2)	2.413(1)
0(7)'	2.434(2)	2.432(2)	2.433(1)
0(2)	2.452(2)	2.453(2)	2.451(1)
0(1)	2.438(3)	2.440(3)	2.426(2)
0(5)	2.664(2)	2.663(2)	2.625(1)
0(6)	2.723(2)	2.721(2)	2.681(1)
Ca(3)			
0(3)	2.387(2)	2.388(2)	2.404(1)
0(5)	2.393(2)	2.394(2)	2.381(1)
0(8)	2.523(2)	2.524(2)	2.480(1)
0(6)	2.593(2)	2.594(2)	2.626(2)
0(2)	2.530(2)	2.532(2)	2.491(2)
0(10)	2.574(3)	2.574(3)	2.544(2)
0(8)'	2.582(2)	2.580(2)	2.556(1)
0(1)	2.622(3)	2.625(3)	2.593(2)
M(4)			
0(1), (1)'(1)''	2.497(3)	2.491(3)	2.444(2)
0(9), (9)'(9)''	2.907(6)	2.927(6)	2.796(4)
0(2), (2)'(2)''	3.394(4)	3.378(4)	3.482(3)

^a Numbers indicate values of x.^b Estimated standard deviations given in parenthesis.

Table IV lists the cation-anion distances for four cation sites in each of the preparations.

A summary of the geometry of the three phosphate groups for the three preparations is given in Table V. The ranges and means compare well with those reported by Baur in his survey of orthophosphate groups (12). The variation of distances and angles within a given phosphate group was at least as large as the variation for that phosphate group as a function of Mg content. Within their precision, the dimensions of the phosphate groups remained invariant to the extent of Mg substitution except for distances P(3)-O(7) and P(2)-O(4) which increased by 0.01 (precision of bond distance ~0.002 Å) as the Mg occupancy in site M(5) quadrupled.

Several structural parameters which show a correlation with the occupancy of site M(5) by Mg are given in Table VI. Structural parameters associated with site M(4) suggest somewhat similar trends although the average occupancy of M(4) is limited to one-half and the effects of the vacancy and the Mg occupancy are confounded. Table II shows that the cell constants *a* and *c* decrease with increasing Mg content.

Discussion

(a) Comparison of Refined Model with Random Model

The major effects of the inclusion of Mg are associated with cation site M(5) (Fig. 3), the

TABLE V

SUMMARY OF THE GEOMETRY OF THE PO₄ GROUPS

<i>d</i> (P-O) (Å)		∠ O-P-O (°)	
Range	Mean	Range	Mean
P(1)O ₄			
1.505(3)-1.533(3) ^a	1.530(7)	108.2(2)-110.7(2)	109.4(2)
P(2)O ₄			
1.527(3)-1.554(3)	1.539(5)	105.4(2)-115.5(2)	109.5(2)
P(3)O ₄			
1.525(3)-1.544(3)	1.534(5)	107.4(2)-114.1(2)	109.5(2)

^a Numbers in parenthesis are estimated standard deviations.

TABLE VI
 OCCUPANCY OF Mg IN M(5) AND ASSOCIATED STRUCTURAL PARAMETERS

Crystal I.D.	O^a	I	II	III
x^b	0.0	0.11	0.11	0.29
O_{Mg}	0.0	0.190(7)	0.304(7)	1.000(7)
$R1^c$	0.0	0.285	0.285	0.677
$R2^d$	0.0	0.047	0.047	0.100
$d(\text{\AA})M(5)-O(4)$	2.238(2)	2.162(3)	2.163(3)	2.070(1)
$d(\text{\AA})M(5)-O(7)$	2.287(2)	2.205(2)	2.206(2)	2.084(1)
$\angle^\circ O(4)-M(5)-O(4)$	82.7(1)	83.8(1)	83.7(1)	85.4(1)
$\angle^\circ O(7)-M(5)-O(7)$	77.1(1)	78.6(1)	78.6(1)	79.1(1)
$\angle^\circ O(7)-M(5)-O(4)$	102.0(1)	100.5(1)	100.5(1)	98.4(1)
rms $\parallel c$, (\AA) M(5)	0.118(2)	0.100(1)	0.091(2)	0.066(2)
rms $\perp c$ (\AA) M(5)	0.136(2)	0.130(1)	0.121(2)	0.065(2)

^a Data from reference (1).

^b Values of x in $Ca_{3-x}Mg_x(PO_4)_2$.

^c R1 is a model in which Ca and Mg are randomly distributed over sites M(4) and M(5); the total occupancy of M(4) is one-half.

^d R2 is a model in which Ca and Mg are randomly distributed over all five cation sites allowing for the fact that the total occupancy of M(4) is one-half.

approximately octahedral site located on the threefold axis. Table VI shows how the details change as the Mg content is increased. Random distribution of Mg over all cation sites (model R2) is excluded by the results of the structural refinements.

Comparison of the observed occupancies, O_{Mg} , with those of random model R1 shows that although at low total Mg content the Mg distribution is essentially randomized over sites M(4) and M(5), additional Mg preferentially enters (M5). One reason is the short $M(5)\cdots O$ distances. A second reason may be that at low total Mg content the contribution of configurational entropy to the free energy is more important than the energy term. Table VI shows that the two cation-oxygen distances $M(5)\cdots O(7)$ and $M(5)\cdots O(4)$ become shorter and more nearly equal in compound III, which has M(5) filled with Mg. These distances of 2.084 Å and 2.070 Å agree well with reported (13) $Mg\cdots O$ values. The approach of $O\cdots M(5)\cdots O$ angles toward 90° with increasing Mg content provides further confirmation of the trend toward a more ideal octahedral configuration. The effective rms amplitudes of vibration for M(5)

also become smaller and more nearly equal in compound III, probably reflecting tighter binding and a more symmetrical local environment as M(5) is progressively filled with more Mg. We found during the course of this investigation that preparations containing more than ~14% of the cations as Mg contained both Mg-containing β - $Ca_3(PO_4)_2$ (sample III) and $Ca_7Mg_9(Ca, Mg)_2(PO_4)_{14}$ (14). This is in good agreement with Ando's phase diagram (4).

(b) Possibility of Coupled Substitution

Examination of the behavior of cation to oxygen distances as a function of Mg content provides insight into possible modes of coupled impurity substitution. Focusing on the $P(2)O_4$ environment (Tables IV, VI), one sees how the average structure changes as the Mg contents of sites M(4) and M(5) increase. Distances $M(5)\cdots O(4)$ and $M(4)\cdots O(1)$ decrease while $Ca(2)\cdots O(3)$, $Ca(2)\cdots O(2)$, and $Ca(2)\cdots O(1)$ remain essentially constant. A small cation such as Mg in M(5) would shorten the $M(5)\cdots O(4)$ distance and turn the $P(2)O_4$ group. It can be seen from Fig. 1 that if the $P(2)O_4$ rotates about $P(2)-O(3)$, the

M(4)···O(1) distance would also shorten. Thus there may be a tendency toward having a small cation in M(4) when one is occupying M(5). This in turn suggests that other sites related by the *a* lattice translations would also be preferentially occupied by a small cation because of the action of the other P(2)O₄ groups coordinated to M(4). This provides a mechanism for local ordering, the extent of which would be terminated where M(4) is unoccupied. Non-electrostatic repulsions between sites M(4) and M(5) are probably not very important because they are separated by more than 5 Å. To the extent that the above mechanism is effective in determining the size of adjacent coordination polyhedra, a Ca···Mg configuration for nearest neighbor sites M(4) and M(5) seems less likely than Mg···Mg, Mg···□, Ca···Ca, or Ca···□ configurations where □ denotes a vacancy.

The peculiar thermal ellipsoids of the P(1)O₄ group are common to all the structures of β -Ca₃(PO₄)₂ we have refined. It appears that vacancies in site M(4) allow the P(1)O₄ group on the same 3-fold axis to be mobile. Vacancies on neighboring 3-fold axes will reduce the local environment from trigonal symmetry and will allow the P(1)O₄ group to tilt away from the three-fold axis. The thermal ellipsoids indicate that this tilt is toward neighboring Ca(3) ions.

(c) *Structural Basis of the Stabilization of β -Ca₃(PO₄)₂ by Addition of Mg Ion*

Since Mg-containing β -Ca₃(PO₄)₂ is stable at temperatures above the $\beta \rightarrow \alpha$ phase transition temperature of 1180°C, its free energy must be less than that of pure α or β at least up to the 1350°C reached during the sample preparation.

The crystal energy (*E*) of Mg-containing β -Ca₃(PO₄)₂ contains terms proportional to

$$\sum_{\text{pairs}} \text{Mg} \cdots \text{O} + \sum_{\text{pairs}} \text{Ca} \cdots \text{O} + \\ \sum_{\text{pairs}} \text{Mg} \cdots \text{Ca} + \sum_{\text{pairs}} \text{Ca} \cdots \text{Ca}.$$

The total of pairs in the first two terms equals the total of Ca–O pairs in pure β -Ca₃(PO₄)₂. As regards the last two terms, cation sites are well separated so non-electrostatic repulsion is probably much the same whether the preparation contains Mg or not. Electrostatic repulsion would be similar if Ca and Mg ions have the same charge as is usually considered to be the case, and are at the same separations, which is approximately true. Crystal energy calculations on CaO and MgO which crystallize in the same structural type suggest that Mg···O interactions are stronger than Ca···O (15). It seems therefore likely that the internal energy for the Mg-containing salt is more negative because of increased electrostatic bonding. The net result is expected to be a lowering of internal energy of Mg-containing β -Ca₃(PO₄)₂ because the Mg···O distances are typically less than those of Ca···O, and the electrostatic energy is proportional to 1/*r*. Addition of Mg also increases the configurational entropy (*S*) because site M(4) contains Ca, Mg, or □ and site M(5) contains Ca or Mg. Since *S* (impure) > *S* (pure) and *E* (impure) < *E* (pure), substitution into the function *A* = *E* – *TS* shows that *A* (impure) < *A* (pure). Hence the impure material is stabilized over the pure.

(d) *Fe as an Additional Impurity*

Refinements on two additional samples of Mg-containing β -Ca₃(PO₄)₂ were discarded from final consideration because the results indicated the presence of an additional impurity. In particular, examination of the distances and angles indicated that the apparent Mg occupancy of M(5) was too low and that of M(4) was too high. A possible explanation is that M(5) also contains an element of higher atomic number than Ca or Mg but with a radius comparable to Mg ion. Findings (3) on the closely related mineral whitlockite suggest that Fe might be present here also. A rough estimate of the amount of Fe present was made assuming that all Fe is contained in site M(5). At zero scattering

angle the effective scattering is $O_{\text{Mg}}Z_{\text{Mg}} + (1 - O_{\text{Mg}})Z_{\text{Ca}}$ where O is the site occupancy and Z is the atomic number. The refinement estimated this effective scattering to be 13.2, but because $Z_{\text{Mg}} = 12$, total occupancy by Mg cannot provide enough scattering. If we now assume that this scattering comes only from Mg and Fe, then we have $O'_{\text{Mg}}Z_{\text{Mg}} + (1 - O'_{\text{Mg}})Z_{\text{Fe}} = 13.2$. Substitution of Z_{Mg} and Z_{Fe} leads to $O_{\text{Mg}} = 0.91$ and $O'_{\text{Fe}} \sim 0.09$, which gives a total of $2(0.09) = 0.18$ Fe atoms per rhombohedral cell (i.e., per 21 cations) or ~ 0.03 Fe cations per $\beta\text{-Ca}_3(\text{PO}_4)_2$ unit. Thus about 1% of the cations are Fe (about 4% of the 21 cations present in whitlockite are Fe). This reasoning prompted us to review the sample preparation and analysis. We found these samples, which were made last, were pelletized in a different and lower quality stainless steel die from that used in the preparation of the other samples.

The actual crystals used for collection of the data were then reexamined by microprobe analysis which indicated a Fe content of ~ 0.02 wt%. Regression analysis was used to fit a composition to the weight fractions of Ca, Mg, P, and Fe obtained from the microprobe analysis. At convergence a composition of $\text{Ca}_{2.63}\text{Mg}_{0.33}\text{Fe}_{0.04}(\text{PO}_4)_2$ was obtained which was approximately that deduced from the results of the structural refinement. This result should be considered only semiquantitative since the Fe component was ill determined (± 0.03). A similar analysis for the second crystal suggested it contained a little more Fe.

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