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Crystallographic Studies of the Role of Mg as a Stabilizing Impurity in β-$Ca_3(PO_4)_2$

I. The Crystal Structure of Pure β-$Ca_3(PO_4)_2$

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β-$Ca_3(PO_4)_2$ crystallizes in the rhombohedral space group $R3c$ with unit cell parameters $a = 10.439(1)$, $c = 37.375(6)$ Å (hexagonal setting) and cell contents of 21 [$Ca_3(PO_4)_2$]. The structure was refined to $R_w = 0.026$, $R = 0.030$ using 1143 X-ray intensities collected from a single crystal by counter methods. Corrections were made for absorption, secondary extinction, and anomalous dispersion.

The structure is related to that of $Ba_3(VO_4)_2$, but has lower symmetry because of the widely different ionic sizes of Ca and Ba. Seven [$Ca_3(PO_4)_2$] units occupy a volume corresponding to eight [$Ba_3(PO_4)_2$] units. The requirement of the c glide in β-$Ca_3(PO_4)_2$ has been shown in the least squares refinements to be attained by disorder of one cation over two sites. This disorder has a far-reaching effect on the structure.

Introduction

We determined the structure of pure β-$Ca_3(PO_4)_2$ as part of a study of the effect of magnesium as an impurity in the β-$Ca_3(PO_4)_2$ structure. Our studies of Mg-containing β-$Ca_3(PO_4)_2$, which will be published in a separate paper, run the full range of magnesium incorporation in β-$Ca_3(PO_4)_2$.

Because a component of dental calculus of individuals in areas where the drinking water contains magnesium ions had been reported to be essentially whitlockite (*1*), we decided to determine the crystal structure of whitlockite. The material in dental calculus is too fine-grained for use in single crystal studies, so we had to seek more suitable material. In view of the known stabilization of whitlockites by Mg, and in view of our previous difficulties with multiple substitution of P, Si, and V in the same sites in

$$Ca_5(PO_4)_2SiO_4$$

(*2*), where only general conclusions could be drawn, we decided to synthesize material with known amounts of only one impurity, the dentally important magnesium ion, and to systematically study the location and role of this impurity in the crystal structure. The hydrothermal material proved difficult to grow and the various levels of impurity difficult to obtain. Mineral whitlockite seemed replete with impurities of various kinds which would mitigate the population analysis of the impurity sites. We therefore decided to grow samples of the supposedly identical material β-$Ca_3(PO_4)_2$ with various amounts of Mg as an impurity. Later, Gopal and Calvo (*3*) were to show that whitlockite is different from our material because it

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contains some HPO_4 groups, with a corresponding reduction in the number of cations. Pending the successful growth of a similar series of hydrothermal material, we continued our work on magnesium containing β-$Ca_3(PO_4)_2$ as a pilot study of the effects of impurities.

Background

The chemistry of "$Ca_3(PO_4)_2$" in its various forms has led to almost as much confusion as that of the apatites. Immediately below the melting point of 1800°C (*4*), $Ca_3(PO_4)_2$ exists as the phase $\bar{\alpha}$-$Ca_3(PO_4)_2$ (*5*), which forms a continuous solid solution with the highest temperature form, α, of Ca_2SiO_4. The continuous solid solution is believed to have a structure related to that of α-K_2SO_4 (*6*), with systematic cation vacancies in proportion to the PO_4/SiO_4 ratio. Structures such as $Ca_5(PO_4)_2SiO_4$ (*2*) are lower temperature distortions of the $\bar{\alpha}$-$Ca_3(PO_4)_2$/α-Ca_2SiO_4 solid solution.

The phase α-$Ca_3(PO_4)_2$ is stable between 1120°C and 1470°C (*4*) in the absence of impurities. The detailed structure of α-$Ca_3(PO_4)_2$ is unknown at present, but our preliminary results reveal that it too is related to the α-K_2SO_4 structure. The determination is complicated by the existence of a pseudocell (with $b' = b/3$) and by the large size of the real cell ($a = 12.887(2)$, $b = 27.280(4)$, $c = 15.219(2)$ Å, $\beta = 126.20(1)°$).

In the pure state, β-$Ca_3(PO_4)_2$ is the phase stable below 1120°C, although the inclusion of small cations as impurities stabilizes the β-$Ca_3(PO_4)_2$ structure to temperatures above 1350°C. β-$Ca_3(PO_4)_2$ then persists until near room temperature in a system free of moisture. Two further phase changes in β-$Ca_3(PO_4)_2$ have been suggested (*7*) to occur near and below room temperature. β-$Ca_3(PO_4)_2$ was long considered to be equivalent to the mineral whitlockite (*8, 9*) and to the material produced in an aqueous system. Mackay (*10*) considered the possibility of whitlockite (i.e., the mineral) having the idealized formula $Ca_{20}H_2(PO_4)_{14}$ when all cations were considered to be Ca. Keppler (*11*) stated from an examination of published analyses and densities that the formula should be considered to be $[6Ca_3(PO_4)_2 \cdot 2MHPO_4]$ where M is a small cation such as Mg, Mn, or Fe.

Legeros, Tranutz, and Klein (*12*) state that 'synthetic whitlockite' forms instead of $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ and $Ca_5(PO_4)_3OH$ in aqueous systems when as little as 3 mole% magnesium ions are present, and that magnesium-free 'synthetic whitlockite' never forms in aqueous systems because it decomposes to $CaHPO_4$ and $Ca_5(PO_4)_3OH$. [Note that the term whitlockite should be reserved for the mineral as described by Frondel (*8, 9*). Samples grown in aqueous systems *in vitro* are referred to here as 'synthetic whitlockite'.] The investigations of Gopal and Calvo (*3*) on the mineral whitlockite and Ito and Calvo (*13*) on synthetic whitlockite show when compared with this work that there are, indeed, differences between β-$Ca_3(PO_4)_2$ and the whitlockites and that for the whitlockites there must be at least part of the structure where there are two hydrogen atoms for every 14 PO_4 groups in accord with Keppler's suggestion. Although the extent of possible substitution of other cations for Ca is as yet unknown in whitlockite, Keppler's formula should at least be written $(Ca, M)_{20}H_2(PO_4)_{14}$ or, judging from our unpublished results on Mg-containing β-$Ca_3(PO_4)_2$, as

$$Ca_{18}(Ca, Mg)_2H_2(PO_4)_{14},$$

to show that most of the substitution of M for Ca occurs in two sites.

Experimental Methods and Data Processing

Samples of β-$Ca_3(PO_4)_2$ were made by heating pressed pellets of stoichiometric amounts of finely ground $CaHPO_4$ and $CaCO_3$ mixed with 1% by weight of cornstarch. Most of our preparations of pure β-$Ca_3(PO_4)_2$ were relatively fine-grained, but we were able to find crystals of adequate size in a sample kept at 1400°C for 2 days (i.e., in the stability range of α-$Ca_3(PO_4)_2$) and then at 1100 ± 10°C for 1 wk. Several crystals 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 unit cell dimensions were determined from thirty 2θ values obtained after the crystal selected for data collection was aligned on a Picker 4-circle[1] diffractometer equipped with Mo radiation and a highly oriented graphite monochromator. The 2θ values were determined automatically using a PDP 8/I computer program supplied by Lenhert (*14*). Two equivalent sets of data ($-h$, $+k$, $+l$) were collected using θ–2θ scans to a maximum 2θ of 60° at 0.125° min^{-1} for 2θ and with 40-sec background counts at each end of the scan range. The crystal data are: ideal formula: $Ca_3(PO_4)_2$; unit cell at 25°C: rhombohedral with $a = 10.439(1)$, $c = 37.375(6)$ Å in the hexagonal setting; wave-length assumed, $\lambda(\text{Mo}K\alpha) = 0.70926$ Å; cell volume $= 3526.9$ Å^3; space group $R3c$; Bragg angle for monochromator = 6.46°; crystal diameter 0.134(5) mm; approximate error in intensity due to assuming crystal is spherical, 1% in F; calculated density, 3.067 $\text{g}\cdot\text{cm}^{-3}$; $\mu(\text{Mo}) = 27.48$ cm^{-1}. 2513 reflections were measured and merged using the program DMERGE written by Dickens and Schroeder (unpublished) into a unique set of 1347, of which 1143 had $I > 2\sigma(I)$ and were used in the refinements. The R factor between the two equivalent sets was 0.041 measured over 905 reflections.

Details of the $Ca_3(AsO_4)_2$ structure, which had then just been determined, were supplied to us by Gopal and Calvo. To facilitate comparisons, their atomic labeling scheme has been retained here and in our Mg-containing β-$Ca_3(PO_4)_2$ studies. We redefined the anomalously high thermal parameters in $Ca_3(AsO_4)_2$ to be 1 Å^2, substituted P for As, and refined the structure except for the $P(1)O_4$ group, which was omitted because of the question of its orientation. The thermal parameters remained "normal", i.e., in the range 1–3 Å^2, and R_w decreased to 0.16, where R_w is defined as $[\sum w(|F_0| - |F_c|)^2/\sum w|F_0|^2]^{1/2}$, and $w = 1/\sigma^2$, where σ^2 is obtained from counting statistics. Throughout the investigation, the scattering factors used were those for the neutral atoms P and O and for the ion Ca^{2+} (Refs. *15* and *16*). The least-squares refinements were carried out using the program RFINE, which was written by L. W. Finger of the Carnegie Institute of Washington and augmented by Prince, Dickens, and Schroeder at NBS. We found the atoms Ca(4), P(1), O(9), and O(10) in a subsequent electron density synthesis. Ca(4) is a new site not present in the parameter set supplied for $Ca_3(AsO_4)_2$. The Ca(4) site contained a peak about half the height expected for Ca, consistent with the dictates of the stoichiometry that in the asymmetric unit (half the rhombohedral unit cell) there should be 10.5 Ca ions for 7 PO_4 ions. The $P(1)O_4$ group in β-$Ca_3(PO_4)_2$ had the same orientation as the AsO_4 group in $Ca_3(AsO_4)_2$.

The structure, with the Ca(4) site half occupied, was refined with isotropic thermal parameters and then with anisotropic thermal parameters to $R_w = 0.05$. Corrections were then made for isotropic secondary extinction and each cation site was allowed to be a mixture of Ca ions and vacancies. The results were occupancies of Ca(1), 0.995(4); Ca(2), 0.997(5); Ca(3), 0.979(4); Ca(4), 0.442(10); Ca(5), 0.987(7); with $R_w = 0.027$, $R = 0.033$. This is a total of 10.3 Ca ions in the asymmetric unit when the multiplicities are incorporated (the first three are in general positions, the last two are on a threefold axis), and shows an error of 2% from the theoretical value of 10.5 Ca ions. When the total Ca content was constrained to be 10.5, the resulting occupancies were: Ca(1), 1.000(4); Ca(2), 1.000(4); Ca(3), 1.011; Ca(4), 0.475(8); Ca(5), 0.991(7); with $R_w = 0.030$ and a value of 2.12 for the standard deviation of an observation of unit weight. The occupancies of Ca(1) and Ca(2) would have refined to 1.007(4) and 1.014(4), respectively, but were further constrained to be between 0 and 1 by the program. The occupancy of Ca(3) was determined by subtracting the sum of the other occupancies from the total Ca content of 10.5.

Stereo illustrations (similar to the final figures) of the apparent thermal motions showed that the effects of occupancy disorder of the Ca(4) site are far-reaching, e.g. in the

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[1] Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

Atomic Parameters in β-$Ca_3(PO_4)_2$[a]

Atom	Occupancy	x	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1)	1.004(4)	−0.2766(2)	−0.1421(1)	0.1658(1)	104(5)	109(5)	163(5)	53(4)	1(4)	1(5)
Ca(2)	1.009(3)	−0.3836(1)	−0.1775(1)	−0.0336(1)	131(6)	108(6)	164(5)	59(4)	−24(5)	−17(5)
Ca(3)	1.003	−0.2721(2)	−0.1482(2)	0.0606(1)	501(8)	208(6)	199(6)	250(6)	−108(5)	−71(5)
Ca(4)	0.491(8)	0.0	0.0	−0.0850(3)	205(17)	205	793(50)	103	0.0	0.0
Ca(5)	0.9990(7)	0.0	0.0	−0.2658(1)	184(6)	184	139(9)	92(5)	0.0	0.0
P(1)		0.0	0.0	0.0	89(6)	89	283(3)	45(4)	0.0	0.0
O(9)		0.007(1)	−0.1366(8)	−0.0136(3)	19(2)	16(2)	60(3)	10(2)	14(2)	0(2)
O(10)		0.0	0.0	0.0400(4)	32(3)	32	40(5)	16	0.0	0.0
P(2)		−0.3109(2)	−0.1365(2)	−0.1320(1)	155(6)	166(7)	160(7)	111(5)	42(6)	24(6)
O(1)		−0.2736(6)	−0.0900(6)	−0.0926(1)	63(3)	56(3)	15(2)	49(3)	7(2)	6(2)
O(2)		−0.2302(5)	−0.2171(5)	−0.1446(1)	45(3)	50(3)	23(2)	43(3)	12(2)	10(2)
O(3)		−0.2735(4)	0.0053(4)	−0.1523(1)	12(2)	11(2)	15(2)	2(1)	0(1)	−2(1)
O(4)		−0.4777(4)	−0.2392(4)	−0.1378(1)	20(2)	12(2)	43(2)	6(2)	12(2)	2(2)
P(3)		−0.3465(2)	−0.1537(1)	−0.2333(1)	81(5)	95(6)	162(6)	38(5)	4(5)	4(6)
O(5)		−0.4031(4)	−0.0489(4)	−0.2211(1)	14(2)	18(2)	17(2)	11(2)	−4(1)	−1(2)
O(6)		−0.4246(4)	−0.3056(4)	−0.2152(1)	20(2)	11(2)	21(2)	3(1)	3(2)	4(1)
O(7)		0.1814(4)	−0.0805(4)	−0.2233(1)	7(1)	10(2)	22(2)	4(1)	0(1)	0(1)
O(8)		−0.3696(5)	−0.1748(4)	−0.2735(1)	27(2)	21(2)	16(2)	16(2)	1(2)	2(2)

3rd cumulants where refined

	C_{111}[c]	C_{222}	C_{333}	C_{112}	C_{132}	C_{113}	C_{133}	C_{223}	C_{233}	C_{123}
Ca(1)	−2(1)−5	—	−5(4)−7	—	—	−5(2)−6	−13(6)−7	—	—	−3(2)−6
Ca(2)	—	—	−7(4)−7	—	—	—	—	3(2)−6	—	—
Ca(3)	33(4)−5	—	−9(4)−7	17(2)−5	−7(1)−5	31(4)−6	—	6(4)−6	—	13(3)−6
Ca(4)	—	—	13(4)−6	—	—	—	0.0	—	0.0	0.0
Ca(5)	−1(2)−5	—	—	—	1 −5	—	0.0	—	0.0	0.0
O(6)	—	—	—	—	—	−7(3)−6	0.0	−7 −6	0.0	0.0
O(9)	—	—	−7(2)−6	—	—	−2(2)−5	—	−4(1)−5	18(4)−6	−1(1)−5
O(10)	—	—	—	—	—	−6(2)−5	0.0	−6 −5	0.0	0.0

[a] Thermal parameters have the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$. Third cumulant parameters have the form $\exp[-i\sum\sum\sum_{klm} h_k h_l h_m c_{klm}]$.

Figures in parenthesis are standard errors in the last significant digits and were calculated in the final cycle of least squares refinement.

[b] × 10^4 for Ca and P; × 10^3 for O.

[c] Quantities are: cumulant value (error), exponent of 10.

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES FOR β-$Ca_3(PO_4)_2$[a]

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     0,K,2
1 1198 1102 37
4 1360 1319 42
7 850 826 9
10 2262 2239 20
     0,K,4
2 2414 2359 66
5 4886 4589167
8 305 275 19
11 1792 1771 16
     0,K,6
0 1320 1380 6
3 1719 1748 33
6 577 560 14
9 1048 1037 11
12 1071 1041 17
     0,K,8
1 762 809 13
4 4254 4092 82
7 2152 2051 75
10 1143 1145 13
     0,K,10
2 9711 9602295
5 2658 2612 45
8 1396 1363 23
11 597 605 20
     0,K,12
0 1009 998 7
3 1662 1576 47
6 998 1001 11
9 869 842 12
12 1754 1674 18
     0,K,14
1 1928 1927 7
4 1132 1155 22
7 2251 2219 25
10 375 419 27
     0,K,16
2 1991 1936 8
5 802 802 9
8 2991 3004 13
11 658 660 20
     0,K,18
0 3964 4005 17
3 2500 2448 68
6 618 594 11
9 1098 1085 13
     0,K,20
1 3097 3161 29
4 3409 3464 11
7 1783 1796 11
10 1193 1199 15
     0,K,22
2 1985 2009 9
5 1556 1571 10
8 1538 1501 32
11 698 692 40
     0,K,24
0 1846 1860 12
3 1309 1311 22
6 221 260 37
9 1801 1773 22
     0,K,26
1 892 897 19
4 2142 2195 27
7 1364 1357 20
10 2065 2009 48
     0,K,28
2 1044 1058 14
5 2468 2441 79
8 774 798 46
     0,K,30
0 5297 5266 23
3 1858 1826 46
6 2720 2718 36
9 678 669 20
     0,K,32
1 397 368 16
4 657 649 14
7 231 285 38
10 1210 1099 91
     0,K,34
2 1212 1247 28
5 2376 2310133
8 1046 1007 58
     0,K,36
0 1522 1478 17
3 629 677 34
6 1014 1047 33
9 772 765 59
     0,K,38
1 669 665 15
4 342 339 26
7 1635 1634 48
     0,K,40
2 3345 3270111
5 1676 1582 92
8 1138 1143 70
     0,K,42
0 1265 1294 21
3 922 857 48
6 283 279 65
     0,K,44
1 820 801 20
4 664 648 26
7 1605 1578 70
     0,K,46
2 498 505 27
5 1018 867102
     0,K,48
0 1152 1051 29
3 751 780 25
     0,K,50
1 888 869 25
4 2370 2234159
     0,K,52
2 626 555 26
     1,K,0
1 2444 2349 49
4 879 893 12
7 2616 2582 14
10 1284 1294 13
     1,K,1
3 1590 1554 50
6 2028 1997 23
9 1176 1166 26
12 1274 1279 18
     1,K,2
2 1685 1636 50
5 538 516 10
8 407 406 22
11 1148 1212 17
     1,K,3
1 513 512 4
4 1389 1376 16
7 1133 1082 39
10 336 264 33
     1,K,4
0 1709 1673 7
3 656 636 15
6 1137 1120 17
9 427 405 19
12 247 323 60
     1,K,5
2 513 533 8
5 879 873 19
8 1718 1651 41
11 942 927 17
     1,K,6
1 655 631 10
4 3176 3143 45
7 963 961 14
10 183X 217 68
     1,K,7
3 269 265 17
6 1204 1167 46
9 1490 1508 28
12 1164 1188 32
     1,K,8
2 5278 3275 14
5 2402 2362 50
8 999 965 25
11 453 435 25
     1,K,9
1 1118 1107 25
4 1075 1060 10
7 401 415 23
10 344 358 27
     1,K,10
0 3896 3946 16
3 1899 1853 22
6 353 352 15
9 1002 954 14
     1,K,11
2 1008 965 8
5 1092 1096 15
8 1901 1857 22
11 1436 1457 37
     1,K,12
1 1802 1814 16
4 1299 1371 15
7 2184 2130 24
10 803 775 16
     1,K,13
3 531 520 18
6 708 710 18
9 388 377 27
     1,K,14
2 1006 1009 9
5 375 403 13
8 815 781 13
11 810 808 20
     1,K,15
1 1413 1411 8
4 868 878 10
7 1142 1142 10
10 719 717 20
     1,K,16
0 4121 4111 17
3 1589 1563 50
6 1928 1925 27
9 242 160 45
     1,K,17
2 284 275 20
5 249 274 20
8 1226 1238 13
11 1063 1060 18
     1,K,18
1 466 443 8
4 1934 1959 16
7 2028 2018 17
10 195X 109 72
     1,K,19
3 489 506 17
6 984 993 15
9 391 353 33
     1,K,20
2 1645 1658 10
5 986 999 20
8 294 226 34
11 686 687 23
     1,K,21
1 513 500 10
4 1326 1361 18
7 1933 1943 12
10 1289 1278 16
     1,K,22
0 759 918 22
3 491 505 17
6 856 832 11
9 1565 1562 15
     1,K,23
2 203 99 11
5 1141 1167 17
8 321 352 28
     1,K,24
1 999 996 9
4 1403 1422 10
7 1330 1345 18
10 649 637 22
     1,K,25
3 1086 1117 19
6 1114 1087 26
9 1164 1118 31
     1,K,26
2 2304 2308 24
5 793 801 30
8 603 621 20
     1,K,27
1 534 575 14
4 588 605 17
7 955 966 21
10 843 822 28
     1,K,28
0 2038 2069 13
3 1413 1423 25
6 1140 1093 30
9 293 288 37
     1,K,29
2 576 546 21
5 786 813 16
8 388 394 23
     1,K,30
1 623 612 22
4 537 519 22
7 529 573 22
     1,K,31
3 495 503 15
6 921 883 14
9 1358 1322 31
     1,K,32
2 473 506 16
5 830 835 32
8 680 670 33
     1,K,33
1 519 518 14
4 318 317 23
7 478 500 23
     1,K,34
0 1181 1131 15
3 972 1037 39
6 592 599 20
9 721 708 22
     1,K,35
2 852 842 17
5 669 717 43
8 934 858 98
     1,K,36
1 293 263 27
4 1053 1082 38
7 264 293 57
     1,K,37
3 167X 25 62
6 182X 109 68
     1,K,38
2 2270 2200 61
5 1427 1450 46
8 610 630 42
     1,K,39
1 433 390 24
4 578 550 37
7 432 449 32
     1,K,40
0 804 735 22
3 389 348 41
6 202X 167 75
     1,K,41
2 431 432 24
5 919 927 23
     1,K,42
1 681 650 50
4 536 545 25
7 798 816 25
     1,K,43
3 196X 222 73
6 559 590 56
     1,K,44
2 185X 9 69
5 512 533 35
     1,K,45
1 357 339 59
4 534 511 54
     1,K,46
0 1213 1221 27
3 383 229 38
     1,K,47
2 200X 83 74
5 210X 144 78
     1,K,48
1 786 748 29
4 1163 1130 51
     1,K,49
3 666 625 32
     1,K,50
2 434 499 43
     1,K,51
1 329 267 37
     1,K,52
0 595 575 45
     2,K,0
2 9204 9036215
5 1817 1801 13
8 866 884 17
11 597 621 25
     2,K,1
1 1106 1083 13
4 428 393 10
7 542 542 13
10 541 591 21
     2,K,2
0 1471 1480 7
3 2263 2266 16
6 2880 2902 32
9 382 364 21
     2,K,3
2 2077 1933 10
5 652 415105
8 539 568 15
11 325 257 49
     2,K,4
1 4663 4452104
4 1614 1603 23
7 3601 3591 26
10 862 851 16
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3 786 794 7
6 576 568 19
9 503 470 16
     2,K,6
2 2425 2298 36
5 1831 1816 26
8 1817 1796 12
11 457 466 26
     2,K,7
1 175 179 12
4 775 778 8
7 369 295 16
10 493 460 22
     2,K,8
0 1132 1092 7
3 4143 4191 12
6 1501 1552 13
9 302 285 27
     2,K,9
2 605 589 13
5 1002 1005 18
8 485 503 17
11 241 139 58
     2,K,10
1 2724 2735 61
4 3578 3703 27
7 1600 1615 29
10 526 513 37
     2,K,11
3 954 951 9
6 738 757 10
9 227 241 52
     2,K,12
2 2837 2671 70
5 1418 1395 14
8 1467 1459 12
11 533 477 25
     2,K,13
1 882 828 14
4 226 202 22
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1 1106 1065 29
4 273 238 52
     9,K,21
3 408 405 31
     9,K,22
2 696 705 22
     9,K,23
1 798 766 31
     9,K,24
0 945 909 20
3 1040 1041 23
     9,K,25
2 279 314 40
     9,K,26
1 381 309 26
     9,K,27
3 607 530 25
     9,K,28
2 498 504 31
     9,K,29
1 1445 1446 18
     9,K,30
0 325 258 44
     9,K,31
2 202X 101 75
     9,K,32
1 489 467 27
     9,K,36
0 1479 1414 28
     10,K,0
1 1267 1284 14
4 300 289 36
     10,K,1
3 426 475 30
     10,K,2
2 806 829 19
     10,K,3
1 1447 1489 14
4 390 458 45
     10,K,4
0 1571 1601 18
3 643 657 21
     10,K,5
2 432 468 25
     10,K,6
1 263 227 34
4 685 649 29
     10,K,7
3 201X 124 74
     10,K,8
2 1956 1989 31
     10,K,9
1 1566 1576 14
4 832 834 29
     10,K,10
0 1285 1307 20
3 516 545 27
     10,K,11
2 408 389 29
     10,K,12
1 534 556 20
     10,K,13
3 912 926 25
     10,K,14
2 1059 1041 34
     10,K,15
1 1021 1029 47
     10,K,16
0 443 359 29
3 299 219 48
     10,K,17
2 699 696 40
     10,K,18
1 1191 1214 16
     10,K,19
3 941 918 24
     10,K,20
2 651 654 23
     10,K,21
1 729 702 35
     10,K,22
0 894 694 23
     10,K,23
2 214X 73 79
     10,K,24
1 440 437 26
     10,K,27
1 285 76 39
     10,K,28
0 1980 1927 24
     11,K,0
2 619 605 24
     11,K,1
1 324 306 34
     11,K,2
0 757 762 24
     11,K,3
2 305 182 32
     11,K,4
1 303 260 34
     11,K,6
2 908 919 19
     11,K,7
1 560 507 24
     11,K,8
0 776 787 25
     11,K,9
2 419 409 41
     11,K,10
1 574 507 21
     11,K,12
2 787 760 29
     11,K,13
1 1386 1392 17
     11,K,14
0 625 615 27
     11,K,15
2 208X 203 77
     11,K,16
1 494 452 23
     11,K,19
1 749 720 34
     11,K,20
0 433 434 38
     11,K,22
1 641 590 24
     11,K,26
0 1628 1565 28
     12,K,0
0 451 489 20
     12,K,2
1 851 843 26
     12,K,5
1 1038 1022 35
     12,K,6
0 278 344 59
     12,K,8
1 1125 1136 20
     12,K,12
0 738 730 30
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[a] The columns are *k*, $10F_o$, $10F_c$ and $10\sigma(F_o)$. Reflections which were less than $2\sigma(I)$ were given intensity $\sigma(I)$; none of these reflections is included here.

P(1)O_4 group, O(10) was not undergoing motions consistent with those of P(1) and O(9). There was obviously appreciable positional disorder of this PO_4 group and also of Ca(3) which is bonded to O(10). A difference electron density synthesis showed, by the presence of abnormal asymmetry in the vicinity of Ca(3), Ca(4), Ca(5) and the P(1)O_4 group, that the scattering from these atoms was not satisfactorily represented by the usual formulations for thermal motion. This inadequacy was further reflected in the occupancy parameters, where the refinements persisted in placing slightly more than one ion in the Ca(1), Ca(2), and Ca(3) sites. The asymmetry in the difference synthesis suggested that introduction and refinement of third cumulant parameters was needed. Accordingly, the structure was refined with third cumulant parameters added for all cations and the P(1)O_4 group, making a total of 199 parameters. The final refinements extended over all atoms and included those third cumulant parameters which earlier refinements had shown to be significantly nonzero; in all 166 parameters were refined. The resultant occupancies were: Ca(1), 1.000(4); Ca(2), 1.000(4); Ca(3), 1.002; Ca(4), 0.493(8); Ca(5), 1.000(7); with $R_w = 0.025$, $R = 0.033$. Without the occupancy constraint, Ca(1) would have refined to 1.004(4) and Ca(2) to 1.007(4). The standard deviation of an observation of unit weight in this refinement was 2.02. The R_w factor ratio, 1.07, for refinements without and with third cumulants, was highly significant at the 0.5% level as determined by R factor ratio test (*17*). The isotropic secondary extinction parameter, r in the notation of Zachariasen (*18*), refined to the reasonable value $13(5) \times 10^{-5}$ cm. The subsequent difference synthesis showed some reduction in asymmetry around the atomic positions, as expected, and no peaks greater than 0.5 electrons/Å^3 (a reduction factor of 2–4 from previous refinements). It is now known that the positional parameters (first cumulants) are appreciably correlated with the third cumulants, as are the thermal parameters (second cumulants) with the fourth cumulants. The occupancies are correlated with the thermal parameters and hence with the fourth cumulants. In view of the relatively small amount of data (1118 observed reflections with maximum $2\theta = 60°$) and the reasonable values obtained for the occupancies, refinement of the fourth cumulant parameters for β-$Ca_3(PO_4)_2$ was not undertaken. Retention of significantly nonzero third cumulant parameters in the refinements resulted in statistically nonsignificant effects on the positional parameters. The atomic parameters from the final refinement are given in Table I, including those third cumulants which were significantly nonzero. It is obvious that statistically significant absences in the cation sites are confined to Ca(4). The observed and calculated structure factors from the third cumulant refinement are given in Table II. In the final refinement, which included third cumulant parameters, the 12 correlation coefficients above 0.826 were all between z parameters of atoms in the Ca(1), Ca(2), Ca(3), P(2), P(3) column. Each of the occupancies of the cations was correlated with a coefficient of less than 0.60 to one of the U_{ii} thermal parameters. There was essentially zero correlation of these parameters with the extinction parameter and less than 0.20 with the scale factor. The maximum correlation coefficient between positional and third cumulant parameters was 0.70.

Description of the Structure

Mackay (*10*) pointed out that the structures of β-$Ca_3(PO_4)_2$ and whitlockite are related to those of $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ (*19*). We can best describe the general features of β-$Ca_3(PO_4)_2$ in terms of its similarity to the $Ba_3(VO_4)_2$ structure (*20*) shown in Fig. 1. This structure has been more precisely determined than the isostructural $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ structures; the cell dimensions, $a' = 5.762$ Å, $c' = 21.29$ Å, show it to be a subcell of the β-$Ca_3(PO_4)_2$ structure with $a' \simeq a/2$, $c' \simeq c/2$, where a and c are the unit cell dimensions of β-$Ca_3(PO_4)_2$. The regularity of the $Ba_3(VO_4)_2$ structure can be seen from Fig. 1; all atoms are in special crystallographic positions so that the site symmetry is generally high.

Although the $Ba_3(VO_4)_2$ structure has been described by Susse and Buerger (*20*) and

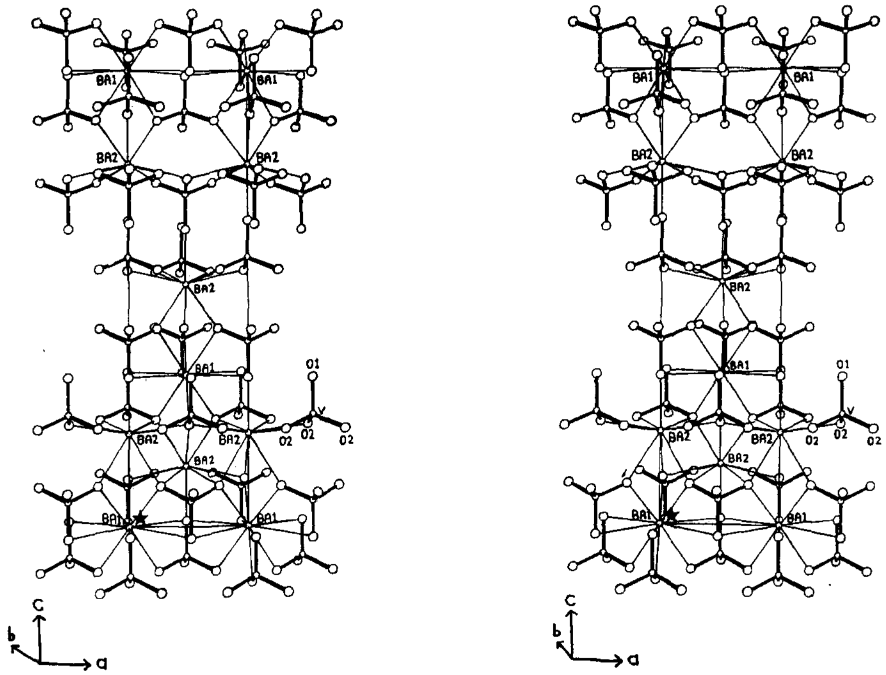

FIG. 1. A stereo illustration of the $Ba_3(VO_4)_2$ structure with positional parameters taken from Süsse anc Buerger (*20*). The origin of the coordinate system is marked by ★.

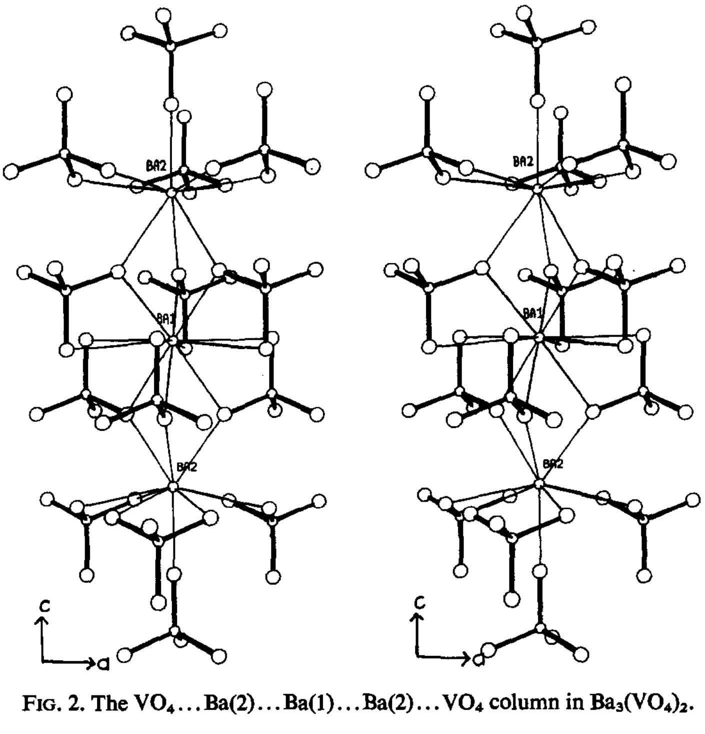

FIG. 2. The VO_4...Ba(2)...Ba(1)...Ba(2)...VO_4 column in $Ba_3(VO_4)_2$.

related to $Ca_3(AsO_4)_2$ by Gopal and Calvo (*3*), for completeness we include a brief description here. The $Ba_3(VO_4)_2$ structure may be thought of as containing layers of VO_4 groups. Each layer has the VO_4 groups on one surface oriented with one V–O vector along [0001] and the VO_4 groups on the other surface oriented with one V–O vector along [000$\bar{1}$]. V–O vectors from adjacent layers are meshed together. Ba(1) ions with 12 coordinated oxygens lie in the centers of these layers, and Ba(2) ions with 10 coordinated oxygens lie between layers. The motiv VO_4...Ba(1)...Ba(2)...Ba(1)...VO_4 lies parallel to [0001] and is shown in Fig. 2.

The moiety in the β-$Ca_3(PO_4)_2$ structure (Fig. 3) corresponding to VO_4...Ba(1)...Ba(2)...Ba(1)...VO_4 in $Ba_3(VO_4)_2$ is

$$P(3)O_4...Ca(1)...Ca(3)...Ca(2)...P(2)O_4$$

(Fig. 4), but it is an obviously distorted version of the Ba/VO_4 column. The PO_4 group layers are disrupted in the β-$Ca_3(PO_4)_2$ structure and there are no P–O vectors parallel to [0001]. The obvious reason for this is the smaller coordination polyhedra of Ca in β-$Ca_3(PO_4)_2$ relative to the Ba coordination polyhedra in $Ba_3(VO_4)_2$. The net result of this distortion from the $Ba_3(VO_4)_2$ structure has been a loss of much of the edge-type coordination and the ejection of one PO_4 group and $1\frac{1}{2}$ Ca ions to form the β-$Ca_3(PO_4)_2$ structure.

The Ca Environments

Ca(1). The environment of Ca(1) in the β-$Ca_3(PO_4)_2$ structure is shown in Figs. 4 and 5 and detailed in Table III. Ca(1) is coordinated strongly to seven oxygens (2 PO_4 edges, and 3 apexes). Strong coordination of Ca to seven oxygens (including one PO_4 edge) is common in calcium phosphates. The small size and resultant inability of Ca to coordinate to more than eight oxygens simultaneously have obviously affected the $P(1)O_4$ groups on the threefold axis. The thermal ellipsoid of Ca(1) is approximately isotropic.

Ca(2). The environment of Ca(2), given in Table III and shown in Figs. 4 and 5, is like that of Ca(1) because Ca(1) and Ca(2) are opposite (but crystallographically non-

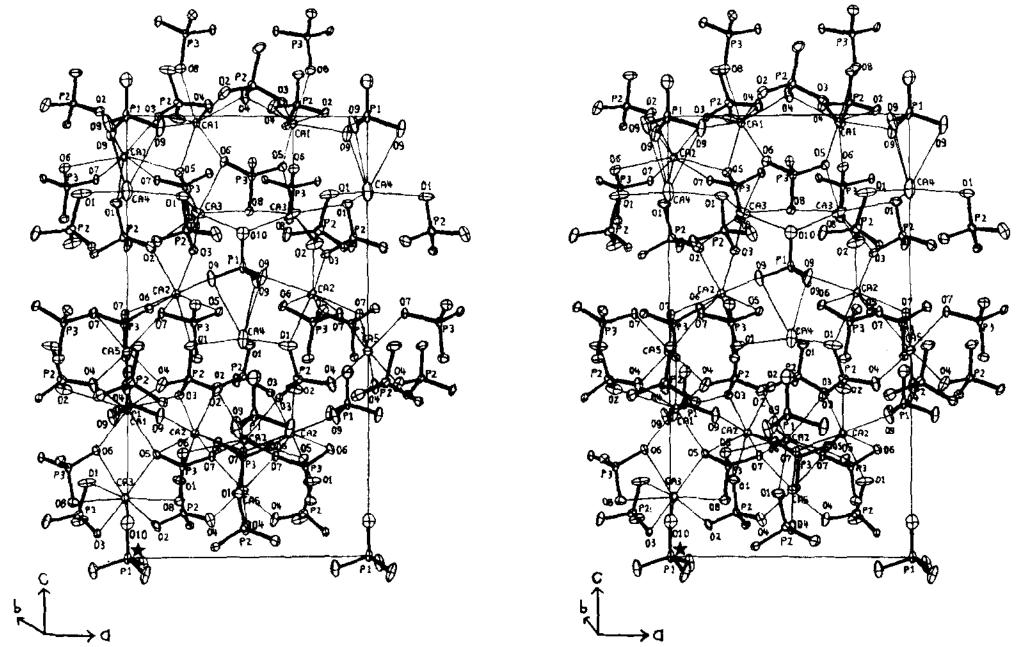

FIG. 3. The β-$Ca_3(PO_4)_2$ structure. Only half of the cell is shown along *c* and two-thirds perpendicular to the *ac* plane. The origin of the coordinate system is marked by *.

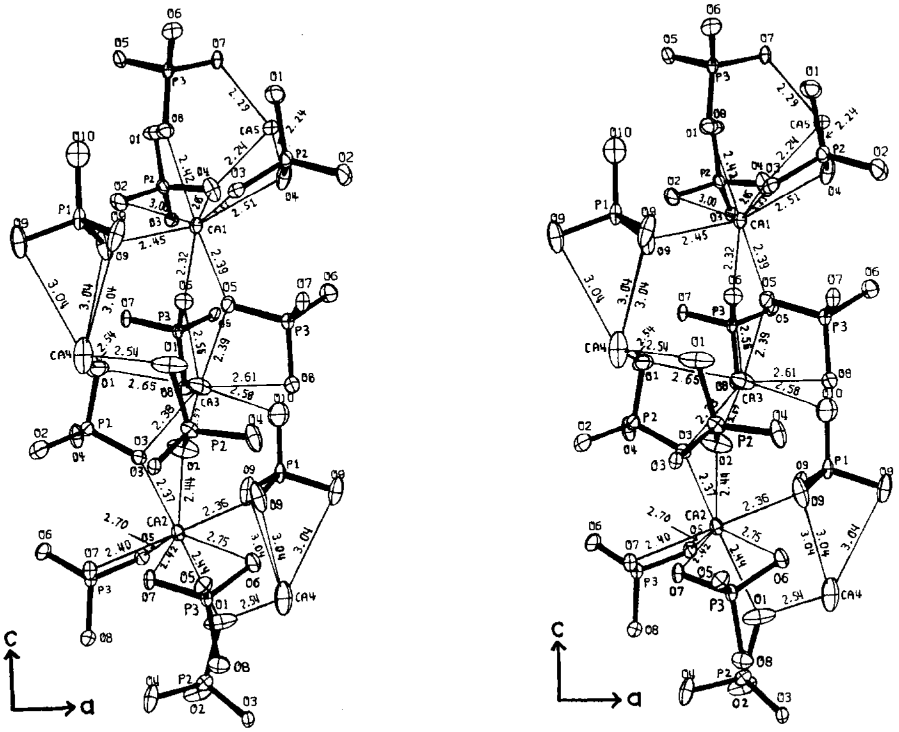

FIG. 4. The P(2)O$_4$...Ca(1)...Ca(3)...Ca(2)...P(3)O$_4$ column in β-Ca$_3$(PO$_4$)$_2$.

equivalent) ends of the cation sequence in the moiety P(3)O$_4$...Ca(1)...Ca(3)...Ca(2)... P(2)O$_4$. On the basis of Ca...O distances, Ca(2) is coordinated strongly to six oxygens and less strongly to two others, O(5) and O(6), of the shared PO$_4$ edges [O(6), O(7)] and [O(5′), O(7″)]. The apparent thermal parameters of Ca(2) are less isotropic than those of Ca(1).

Ca(3). The environment of Ca(3) is given in Figs. 4 and 6 and Table III. Ca(3) is coordinated to eight oxygens, including the PO$_4$ edges [O(5), O(8)], [O(1), O(3)], and [O(6), O(8)]. The maximum rms amplitude of Ca(3) is toward O(10) of the P(1)O$_4$ group and suggests that Ca(3) is in two or more different positions depending on the position of the P(1)O$_4$ group, which in turn depends on the occupancy of the Ca(4) site. Some of the coordinated oxygens have apparent thermal parameters which correspond to large displacements (e.g., O(10), 0.23 Å; O(1), 0.19 Å; O(9), 0.18 Å) parallel to the Ca(3)...O bonds. This suggests that the effect of the occupancy of Ca(4) is transmitted through several neighbor-neighbor interactions.

Ca(4). The environment of Ca(4) is shown in Fig. 7 and is given in Table III. Ca(4) has an unusual coordination to the O(9), O(9′), O(9″) face of the P(1)O$_4$ group. The Ca...O(9) bonds are long (3.041(1) Å) in accord with Pauling's rule (*21*) because of repulsion between Ca and P(1). Symmetry, site multiplicity and stoichiometric considerations require that there be some cation vacancies in the structure, and the occupancy refinements convincingly showed that these vacancies may be considered to be only in the Ca(4) site. Partial occupancy of this site is in accord with the Ca...O distances, all of which are greater than normal values of ~2.4 Å. The apparent thermal parameters of Ca(4) give an rms amplitude of 0.14 Å perpendicular to *c* and 0.28 Å along *c*. The value of 0.14 Å is comparable with values from other structures, but an rms amplitude of 0.28 Å suggests

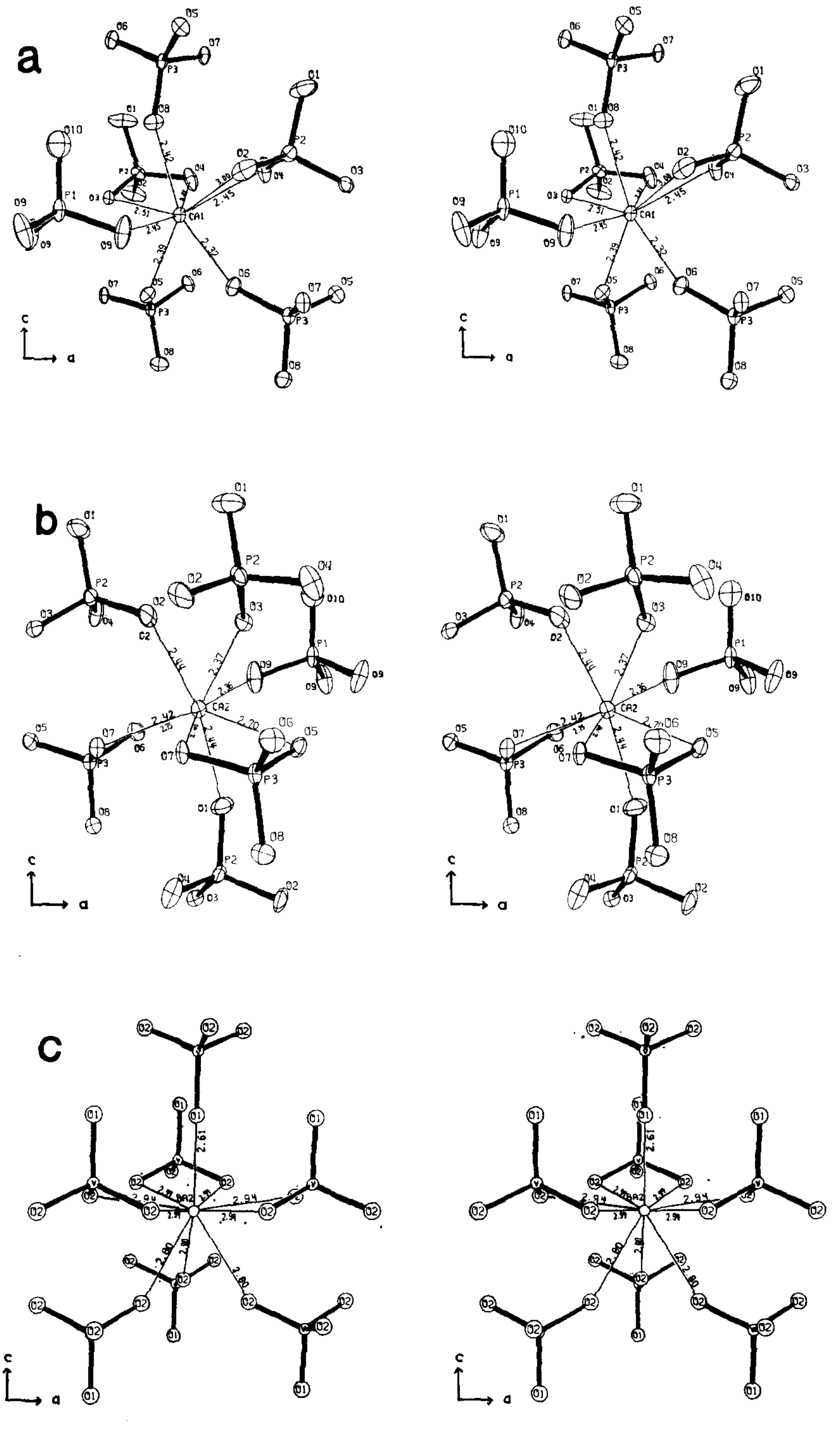

FIG. 5. Comparisons of the environments of (a) Ca(1) and (b) Ca(2) in β-$Ca_3(PO_4)_2$ and (c) Ba(2) in $Ba_3(VO_4)_2$

TABLE III

INTERATOMIC DISTANCES AND ANGLES IN β-$Ca_3(PO_4)_2$[a]

Cation environments	
Ca(1), O(6)	2.316(4) Å
O(5)	2.393(4)
O(8)	2.421(4)
O(4)	2.449(5)
O(9)	2.456(5)
O(4′)	2.503(4)
O(3)	2.507(4)
O(2)	2.997(5)
Ca(2), O(3)	2.369(4)
O(9)	2.371(5)
O(7)	2.398(4)
O(7′)	2.419(4)
O(2)	2.437(4)
O(1)	2.444(5)
O(5)	2.704(4)
O(6)	2.752(4)
Ca(3), O(5)	2.384(4)
O(3)	2.388(4)
O(8)	2.554(4)
O(6)	2.558(4)
O(2)	2.568(5)
O(10)	2.580(4)
O(8′)	2.611(4)
O(1)	2.650(5)
O(9)	3.115(8)
Ca(4), O(1, 1′, 1″)	2.538(5)
O(9, 9′, 9″)	3.041(11)
O(2, 2′, 2″)	3.228(9)
Ca(5), O(4, 4′, 4″)	2.238(4)
O(7, 7′, 7″)	2.287(4)
PO_4 group details	
P(1), O(9, 9′, 9″)	1.536(5) Å
O(10)	1.498(12)
O(9), O(9′)	2.512(7)
O(9), O(10)	2.473(12)
O(9), P(1), O(9′)	109.8(4)°
O(9), P(1), O(10)	109.2(4)
P(2), O(1)	1.539(4) Å
O(2)	1.532(4)
O(3)	1.530(4)
O(4)	1.537(4)
O(1), O(2)	2.518(5)
O(3)	2.442(5)
O(4)	2.550(7)
O(2), O(3)	2.594(5)
O(4)	2.490(6)
O(3), O(4)	2.431(5)
O(1), P(2), O(2)	110.2(2)°
O(3)	105.5(2)
O(4)	112.0(3)
O(2), P(2), O(3)	115.9(2)
O(4)	108.5(3)
O(3), P(2), O(4)	104.9(2)
P(3), O(5)	1.548(4) Å
O(6)	1.532(4)
O(7)	1.542(4)
O(8)	1.518(4)
O(5), O(6)	2.584(6)
O(7)	2.496(5)
O(8)	2.477(5)
O(6), O(7)	2.467(6)
O(8)	2.481(5)
O(7), O(8)	2.533(5)
O(5), P(3), O(6)	114.0(2)°
O(7)	107.7(2)
O(8)	107.8(2)
O(6), P(3), O(7)	106.8(2)
O(8)	108.9(2)
O(7), P(3), O(8)	111.7(2)
PO_4 group environments	
$P(1)O_4$:	
O(9), Ca(2)	2.358(9) Å
Ca(1)	2.454(8)
Ca(4)	3.041(12)
Ca(3)	3.111(9)
O(10), Ca(3, 3′, 3″)	2.581(6)
$P(2)O_4$:	
O(1), Ca(2)	2.444(5)
Ca(4)	2.538(5)
Ca(3)	2.650(5)
O(2), Ca(2)	2.437(4)
Ca(3)	2.568(4)
Ca(1)	2.997(5)
Ca(4)	3.228(9)
O(3), Ca(2)	2.369(4)
Ca(3)	2.388(4)
Ca(1)	2.507(4)
O(4), Ca(5)	2.238(4)
Ca(1)	2.449(5)
Ca(1′)	2.503(4)
$P(3)O_4$:	
O(5), Ca(3)	2.384(4)
Ca(1)	2.393(4)
Ca(2)	2.704(4)
O(6), Ca(1)	2.316(4)
Ca(3)	2.558(4)
Ca(2)	2.752(5)
O(7), Ca(5)	2.287(4)
Ca(2)	2.398(4)
Ca(2′)	2.419(4)
O(8), Ca(1)	2.421(4)
Ca(3)	2.554(4)
Ca(3′)	2.611(4)

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[a] The number in parentheses is the standard error in the last digit as estimated in the final cycle of full-matrix least squares refinements. It does not include the standard deviations of the cell parameters.

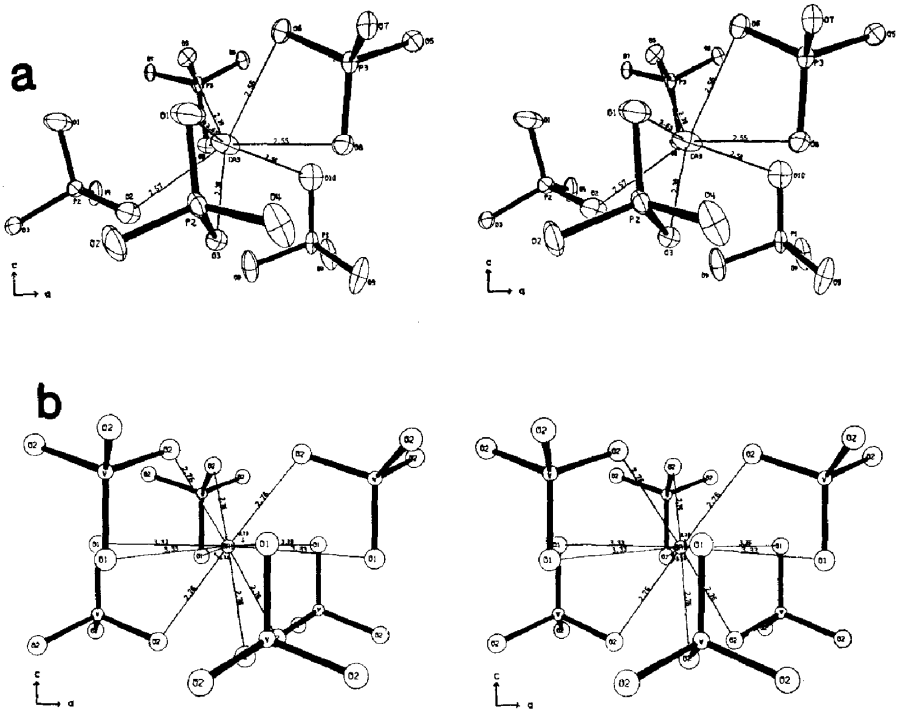

FIG. 6. Comparison of the environments of (a) Ca(3) in β-$Ca_3(PO_4)_2$ and (b) Ba(1) in $Ba_3(VO_4)_2$.

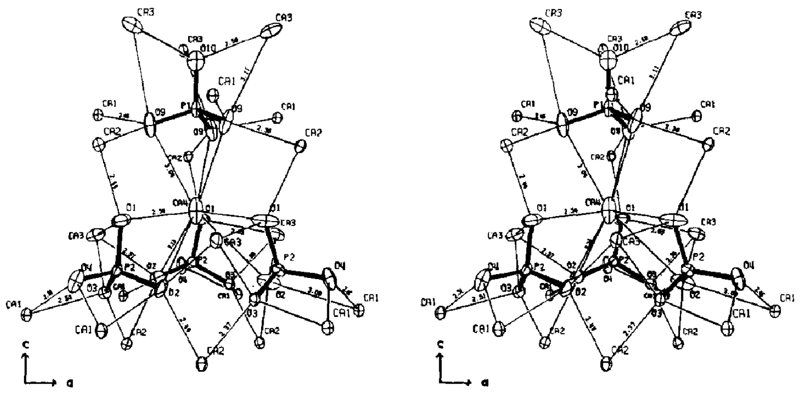

FIG. 7. The environments of Ca(4) and the $P(1)O_4$ group in β-$Ca_3(PO_4)_2$. The apparent thermal motions as revealed by the dimensions of the ellipses reveal that statistical occupancy of only half of the Ca(4) sites imposes positional disorder on the $P(2)O_4$ groups and propagates similar disorders through the $P(1)O_4$ groups to the Ca(3) ions.

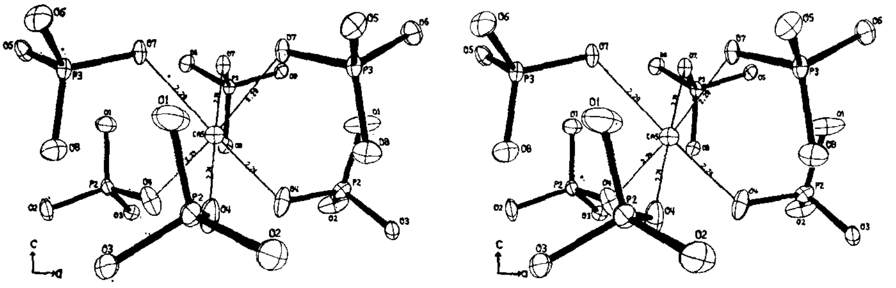

FIG. 8. The approximately octahedral coordination of Ca(5). The average Ca(5)...O distance is 2.263 Å.

that Ca(4) is slightly disordered along *c* and/or weakly bound.

Ca(5). The environment of the Ca(5) site is given in Fig. 8 and Table III. The Ca(5) coordination is essentially octahedral with no shared PO_4 edges, and all six Ca...O distances are relatively short, falling into the range 2.238–2.287 Å. The oxygen atoms in the environment have small thermal parameters. The thermal parameters of Ca(5) may be ascribed to normal thermal motion.

The PO_4 Ions and Their Environments

The environments of the PO_4 ions are given in Table III and are shown in Figs. 7 and 9.

P(1)O₄. The average P–O bond length in the $P(1)O_4$ group (Fig. 7) is 1.534 Å, and the angles are essentially all tetrahedral. That the P(1)–O(10) distance (1.547 Å) appears to be shorter than the P(1)–O(9) distance probably arises from the inability of the usual expressions for thermal motion to account for the behavior of this ion. This is complicated by the coordination of the Ca(4) ion to the O(9, 9′, 9″) face of $P(1)O_4$ since the Ca(4) site is only partially occupied. Analysis of the apparent thermal tensors of $P(1)O_4$ via the TLS model (*22*) indicated they were incompatible with PO_4 group translations and librations. This suggests positional disorder of $P(1)O_4$ that is very likely correlated with the occupancy of the Ca(4) site.

P(2)O₄. The environment of the $P(2)O_4$ group is shown in Fig. 9a. Each oxygen in the $P(2)O_4$ group is coordinated to three cations. Because O(4) is the only $P(2)O_4$ oxygen closely coordinated to Ca, the P(2)–O(4) bond is the longest, as expected. From the other O...cation distances, P(2)–O(3) would be expected to be the next longest, but this is not the case. However, O(2) does have the weakest association with cations and forms the shortest P(2)–O bond. Three edges, [O(1), O(3)], [O(3), O(4)], and [O(2), O(4)] are coordinated to Ca ions; all the associated O–P(2)–O angles are less than the tetrahedral angle, as expected. The largest angle, O(2)–P(2)–O(3), seems to be a resultant of edge sharing coordination in that O(2) and O(3) have been pulled toward Ca(1) and Ca(1′), respectively.

P(3)O₄. Four edges, [O(5), O(7)], [O(5), O(8)], [O(6), O(7)], and [O(6), O(8)], in the $P(3)O_4$ group are coordinated to cations (Fig. 9b), and have associated O–P(3)–O angles of less than the tetrahedral angle, and conversely, the remaining two O–P(3)–O angles are larger than the tetrahedral angle. To facilitate comparison between the PO_4 groups in β-$Ca_3(PO_4)_2$ and the VO_4 group in $Ba_3(VO_4)_2$, the environment of the VO_4 group is given in Fig. 9.

Discussion

Figures 1–4 show the correspondence between the $Ba_3(VO_4)_2$ and β-$Ca_3(PO_4)_2$ structures. Ba(1) is coordinated to 12 oxygen atoms, which comprise six VO_4 edges; the corresponding ion, Ca(3), in β-$Ca_3(PO_4)_2$ is coordinated to 8 oxygen atoms, including three PO_4 edges. Ba(2) is coordinated to 10 oxygen atoms including three VO_4 edges; both Ca(1) and Ca(2) are bonded to eight oxygen atoms, including two PO_4 edges. The distortions of the Ca coordination polyhedra relative to those of Ba are obvious from the figures.

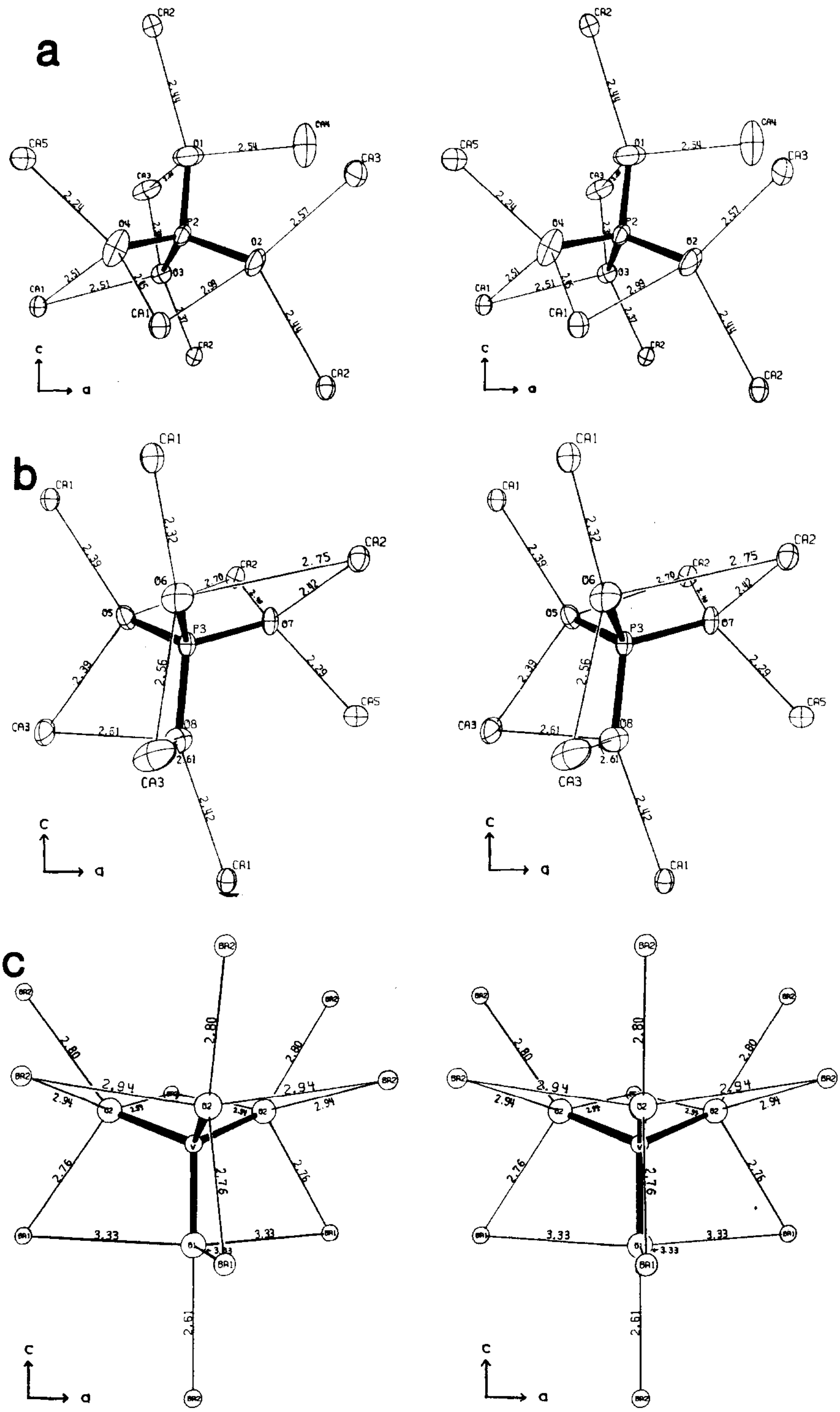

Fig. 9. Comparison of the environments of (a) $P(2)O_4$, (b) $P(3)O_4$ in β-$Ca_3(PO_4)_2$, and (c) VO_4 in $Ba(VO_4)_2$.

The oxygens of the P(2)O_4 and P(3)O_4 ions in β-$Ca_3(PO_4)_2$ (Fig. 9) are each coordinated to three cations instead of the four cations (not counting V) to which the oxygens of the VO_4 group in $Ba_3(VO_4)_2$ are coordinated (Fig. 9c). The tilts of the P(2)O_4 ion near the threefold axis are such that there is no room for another PO_4 group, and instead a new cation site, Ca(4) (Fig. 7), is created in β-$Ca_3(PO_4)_2$. This cation is then bonded in an unusual coordination to the face of the P(1)O_4 group (see Fig. 7). Thus, Ca(4) occupies essentially the site of a VO_4 group in $Ba_3(VO_4)_2$. This situation, repeated by the *c* glide, serves to make the β-$Ca_3(PO_4)_2$ structure omit two PO_4 groups per comparable $Ba_3(VO_4)_2$ volume, i.e. 8 $Ba_3(VO_4)_2$ unit cells. For charge balance, three cations must also be omitted; the resulting spaces along the threefold axis where two Ca ions have been omitted are obvious in Fig. 3. The third cation is omitted from one-half of the Ca(4) sites, leaving one Ca(4) ion for every two Ca(4) sites. The Ca(5) ion (Fig. 8) is in another cation site not found in the $Ba_3(VO_4)_2$ structure. Its small, essentially octahedral, coordination polyhedron is very compatible with the distortions of the PO_4 group layers from the regularity of the $Ba_3(PO_4)_2$ structure. The remaining ion on the threefold axis, P(1)O_4, is in the center of the PO_4 layers, rather than on the surfaces as P(2)O_4 and P(3)O_4 are. Thus, the structures of $Ba_3(VO_4)_2$ and β-$Ca_3(PO_4)_2$ differ completely along the threefold axis.

As was remarked in the introduction, the assumption that the space group of

$$\beta\text{-}Ca_3(PO_4)_2$$

is *R*3*c* has posed the question of how the electroneutrality, the formula, and the even parity of the space-group requirements are to be reconciled. Refinement in space-group *R*3*c* occurred to the limit of the experimental data, so that the choice of this space-group is not contradicted. The electron-density syntheses and the least-squares refinements both point to the electroneutrality balance of the whole structure arising from partial occupancy of the Ca(4) cation site. That disorder should involve Ca(4) rather than some other cation is consistent with the fact that Ca(4) is coordinated to the face of the P(1)O_4 group in a configuration which is probably unstable relative to the other cation configurations. This instability is expected to arise from the Ca(4)...P(1) repulsion and from the low number (six) of oxygen atoms coordinated to Ca(4), which therefore undergoes less overall bonding. The above interpretation is corroborated by the essentially independent evidence of the apparent thermal motions in the environment of Ca(4). The largest apparent displacements of the coordinated oxygens are parallel to the direction of the strongest Ca(4)...O bonding, which would be highly improbable for true motion, and show that these oxygens are in two or more closely related positions depending on whether the Ca(4) site is occupied or not. Thus, the P(2)O_4 orientation is correlated with the occupancy of a given Ca(4) site. As may be seen from Fig. 7, Ca(4) has a considerable effect on the rest of the structure. When the Ca(4) site is occupied, the neighboring oxygen atoms will be drawn in towards that site. When the site is not occupied, the environment will relax in some complex way. The P(2)O_4 groups are obviously the averages of at least two positions and orientations. Their thermal ellipsoids do not yield sensible motions for the groups as rigid bodies. As judged from the anisotropies of the Ca(1) and Ca(2) ions, the positional disorder is not transmitted beyond the P(2)O_4 groups, presumably because the bonds from these Ca ions to the P(2)O_4 groups are 45° or more from the Ca(4)...O(1) vector. The P(2)O_4 group appears qualitatively to be undergoing rotations about the P(2)–O(3) vector, but this was not borne out in our quantitative rigid body analysis. The P(1)O_4 group is also undergoing positional disorder. The apparent motions of the P(1) and O(9) atoms are not consistent with the more isotropic motion of O(10). We suggest that configurations exist where the P(1)–O(10) vector tilts away from the *c* axis and that the PO_4 group is also displaced along *c*. The P(1)O_4 tilt is not transmitted through the Ca...O(9) bonds tangential to the tilt, but it *is* transmitted to Ca(3) via the Ca(3)...O(10) bonds. The tilting of the P(1)O_4 group means that the trigonal symmetry is not upheld at the local level, although deviations from average trigonal symmetry in the whole crystal are not discernible in the experimental data. Such effects might be discernible in the wings of the Bragg peaks and in the background between these peaks, and also in the infrared and Raman spectra, where the activities of the internal modes of $P(1)O_4$ would deviate from those expected for C_3 site symmetry. The apparent motion of Ca(4) along [001] probably arises because of local positional differences in the coordinated $P(1)O_4$ groups. On the basis of Ca...O distances, Ca(4) is weakly bound in this direction implying larger amplitudes of vibration along *c*. The $P(3)O_4$ groups are more remote from the Ca(4) site and are thus insulated from the effects of disorder. This is confirmed by their thermal parameters.

It is surprising at first sight that the β-$Ca_3(PO_4)_2$ phase, which is supposedly the stable phase between ~0°C and ~1000°C in the absence of hydrogen ions, should crystallize in an arrangement which has one formula unit missing from every unit cell. There has obviously been considerable loss of cation–oxygen bonds. This can be partly understood by relating β-$Ca_3(PO_4)_2$ to the $Ba_3(VO_4)_2$ type structure. Additional and necessary chemical context is supplied by considering the structure of the higher temperature form, α-$Ca_3(PO_4)_2$, which is metastable at room temperature. The detailed structure of α-$Ca_3(PO_4)_2$ is not yet known, although our unpublished determination of it has progressed to the point where we believe it to be closely related to $Ca_5(PO_4)_2SiO_4$ (*2*) and $Ca_7Mg_9(Ca, Mg)_2(PO_4)_{12}$ (*23*) and hence to crystallize in the glaserite-type structure [see Ref. (*24*) for a discussion of structural types in calcium phosphates]. Additional evidence for this view is the similarity (*25*) of the powder patterns of α-$Ca_3(PO_4)_2$ and $Ca_7Mg_9(Ca, Mg)_2(PO_4)_{12}$ [called $Ca_3Mg_3(PO_4)_4$ in Ref. (*25*) and $Ca_4Mg_5(PO_4)_6$ on ASTM card 11-231]. It therefore appears that α-$Ca_3(PO_4)_2$ is a superstructural variant of the $K_3Na(SO_4)_2$ and α-K_2SO_4 structures with systematic cation vacancies in α-$Ca_3(PO_4)_2$ similar to those found in the structures of $Ca_5(PO_4)_2SiO_4$ and $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$. All these compounds necessarily have cation vacancies because their cation-to-anion ratios are less than that of $K_3Na(SO_4)_2$. Both the α and β forms of $Ca_3(PO_4)_2$, therefore, seem to include vacancies, the former because it does not have the 2:1 stoichiometry required for complete emulation of the $K_3Na(SO_4)_2$ structure and the latter because it has the wrong cation size: anion size ratio to crystallize in the $Ba_3(VO_4)_2$ arrangement. It is not yet known which factors are significant in differentiating the energies of α- and β-$Ca_3(PO_4)_2$. One possible factor is that the α-$Ca_3(PO_4)_2$ structure has the larger percentage of ion vacancies (by any method of counting). Another is that the glaserite-type arrangement may not be stable at lower temperatures when all the cations are of similar size. Two such calcium phosphates (α-$Ca_3(PO_4)_2$ and $Ca_5(PO_4)_2SiO_4$) crystallizing in glaserite-type structures are only metastable below about 1000°C. $Ca_7Mg_9(Ca, Mg)_2(PO_4)_{12}$, which contains cations of widely differing sizes, is seen from Ando's phase diagram (*25*) to be stable at temperatures lower than 1175°C and to coexist with Mg-containing β-$Ca_3(PO_4)_2$ when the system contains enough magnesium.

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