American Mineralogist, Volume 63, pages 520–527, 1978

The crystal structure of synthetic calcium phosphate–sulfate hydrate, $Ca_2HPO_4SO_4{\cdot}4H_2O$, and its relation to brushite and gypsum

TOSHIRO SAKAE

Department of Oral Histology
Nihon University Matsudo School of Dentistry
Matsudo, Chiba, Japan

HIROSHI NAGATA

Geological and Mineralogical Institute
Faculty of Science, Tokyo University of Education
Otsuka, Bunkyo, Tokyo, Japan

AND TOSHIO SUDO

Miyasaka 3-20-7
Setagaya, Tokyo, Japan

Abstract

The synthetic calcium phosphate–sulfate hydrate, $Ca_2HPO_4SO_4 \cdot 4H_2O$, is monoclinic, space group *Cc*, $a = 5.721(5)$, $b = 30.992(5)$, $c = 6.250(4)$A, and $\beta = 117.26(6)°$, $Z = 4$. The structure has been determined by the Patterson method and refined by full-matrix least-squares method to a conventional $R = 0.068$, using 268 independent reflections. The structure possesses four sheet-structure units parallel to (010), in which Ca atoms are coordinated by six oxygen atoms belonging to $(P,S)O_4$ tetrahedra and two water molecules at the surface of the sheet. Each sheet unit is analogous to those of brushite and gypsum, but there is a different mode of sheet stacking from those in brushite and gypsum. The mean *T*–O bond lengths, 1.50A at *T*(1) site and 1.49A at *T*(2) site, are close to an average distance of P–O (1.54A) and S–O (1.46A) bond lengths. The distribution of P and S atoms in *T* sites seems to be random.

Introduction

Ardealite, $Ca_2HPO_4SO_4 \cdot 4H_2O$, is a rare phosphate–sulfate mineral first described by Schadler (1932) from Cioclovina cave, Transylvania. This original material is found in close association with gypsum, $CaSO_4 \cdot 2H_2O$, and brushite, $CaHPO_4 \cdot 2H_2O$. Recently, one of the authors (T. Sakae) found ardealite from the Onino-Iwaya limestone cave at Hiroshima Prefecture, Japan (in preparation).

Beevers (1958) and Hill and Hendricks (1936) pointed out that, because of a close similarity in their chemical compositions, ardealite may belong to a solid solution between brushite and gypsum. In the crystal structures of brushite (Jones and Smith, 1962) and gypsum (Atoji and Rundle, 1958), the corrugating sheets stack along the *b* axis. O'Daniel (1939) and Baynham and Raistrick (1960), however, reported that X-ray powder diffraction patterns of ardealite, brushite, and gypsum are considerably different from each other. Ferraris (1969) insisted that brushite and gypsum are not in a strict isostructural relation because of the different space groups: *Ia* for brushite and *I*2/*a* for gypsum. Recent X-ray and neutron-diffraction analyses have revealed that the configuration of water molecules in brushite (Curry and Jones, 1971) is quite different from that of gypsum (Cole and Lancucki, 1974). The crystal–chemical relation among ardealite, brushite, and gypsum is a matter for further research.

The study of the crystal structure of ardealite is significant and interesting. It was difficult, however, to obtain a single crystal of ardealite for structural determination. Single crystals obtained from synthetic material have been used in this structure deter-

0003-004X/78/0506-0520$02.00

mination. These synthetic crystals almost agree with natural ardealite in various properties, but are slightly different from ardealite in their X-ray powder patterns.

Experimental

Material

$Ca(OH)_2$, $Na_2HPO_4 \cdot 12H_2O$, and Na_2SO_4 were used as starting materials. Each of these were made up in water solutions with the same mole concentrations. These solutions were mixed with each other in the mole ratio of $Ca/(P + S) = 1$. The pH values of the mixed solutions were controlled by adding dilute hydrochloric acid. Varying the conditions from pH 2 to 5; P/S, 0/10 to 10/0; mole conc., 0.25 to 0.5; temperatures, 0°C to 50°C, three-component mixtures of brushite, ardealite-like material, and gypsum were not found in precipitates although two-component mixtures were found. In the series of syntheses at pH 4, precipitates are brushite plus ardealite-like material (P/S = 6/4), ardealite-like material plus gypsum (P/S = 5/5), and gypsum (P/S = 4/6), as revealed by X-ray powder diffraction analysis. A crystalline precipitate from a solution with P/S = 9/1 and pH = 3, after standing for 43 days at 20°C, consisted of the ardealite-like material free from brushite and gypsum, as revealed by X-rays. This crystalline precipitate was used for the present study.

Chemical composition of the product is as follows: CaO, 32.5; P_2O_5, 20.9; SO_3, 23.2; ignition loss (below 600°C), 22.9; total, 99.5 (weight percent). Several crystals in the product were analyzed semi-quantitatively by the point-analysis method employing HITACHI-KEVEX SEM. Each of them had the mole ratio of Ca:P:S = 2:1:1. Although the chemical compositions of the crystals are uniform, Weissenberg photographs of the crystals show some differences. Throughout the photographs the cell dimensions are the same but the extinctions are different. Among them a crystal showing the extinctions set out below was used for the data collection. Crystals with other extinctions are also being studied. Further, the single crystal was analyzed by the point analysis method, which confirmed that it had the mole ratio of Ca:P:S = 2:1:1. The chemical formula was therefore assumed to be $Ca_2HPO_4SO_4 \cdot 4H_2O$.

Data collection

The crystal is a triangular plate (fragment) approximately 0.015 mm thick, 0.06 mm along the *a* axis and 0.09 mm along the *c* axis. The systematic extinctions hkl with $h + k = 2n + 1$ and $0k0$ with $k = 2n + 1$ lead to the space group of *Cc* or *C2/c*. The occurrence of $0k0$ reflections with $k = 4n$ only (040, 080, 0120, *etc.*) suggest that the periodicity along the *b* axis occurs at four times the elementary unit, as described later. Lattice parameters are determined and refined to a = 5.721(5), b = 30.992(5), c = 6.250(4)A, β = 117.26(6)° by least-squares method, using 16 reflections measured on a Phillips four-circle diffractometer (graphite-monochromatized Mo$K\alpha$ radiation).

For intensity measurement the ω-2θ scanning technique was employed (0.05° per second in ω). Scanning width was defined as $a + b(tan\theta)$ where $a = 1.5$ and $b = 0.5$. The crystal was so small that 400 reflections to $sin\theta/\lambda = 0.7$ were collected with monochromatized Mo$K\alpha$ radiation. Finally, 268 independent reflections of $|F_o|$ greater than $4|\sigma F_o|$ were used for the following structure determination. The data were corrected for Lorentz polarization factors, but not for absorption (μ = 15.35 cm^{-1}).

Structure analysis

The lattice parameters of the present crystal are similar to those of gypsum and brushite (Table 1), except the *b* dimension, which is nearly equal to the sum of the *b* dimensions of gypsum and brushite. One-dimensional Patterson synthesis along the *b* axis shows a similar pattern to those of gypsum and brushite, but with a repeat of one-fourth of the *b* dimension. The results lead to an assumption that the crystal has also a sheet structure, in which each sheet stacks along the *b* axis with a four-fold periodicity in contrast to a two-fold periodicity in gypsum and brushite.

The space group is *Cc* in brushite (*Ia* by Jones and Smith, 1962) and *C2/c* in gypsum (*I2/a* by Atoji and Rundle, 1958), and *Cc* or *C2/c* in the present crystal. If the structure is a sheet structure analogous to those of gypsum and brushite, a possible space group for the crystal is *Cc* rather than *C2/c*, because the symmetry of the structure may be reduced on account of the presence of H atoms, as in the case of brushite. Thus the space group *Cc* was examined in the first step of the crystal structure analysis[1].

A structure model having the space group *Cc* may be constructed in the following two ways: (1) one-sheet structure unit is located between *n* and *c* glide

---

[1] For the sake of the comparison of lattice parameters between the present crystal, brushite, and gypsum, *Cc* lattice was selected. When *Ia* lattice for the present crystal is selected, the lattice parameters are a = 6.248, c = 6.250A, and β = 125.52°.

Table 1. Crystallographic data for $Ca_2HPO_4SO_4 \cdot 4H_2O$, brushite, and gypsum

	$Ca_2HPO_4SO_4.4H_2O$	Brushite	Gypsum
	This study	Beevers (1958) Jones + Smith (1962)	Cole + Lancucki (1974)
a	5.721(5)* A	5.812±0.002 A	5.670±0.002 A
b	30.992(5)	15.180±0.003	15.201±0.002
c	6.250(4)	6.239±0.002	6.533±0.002
β	117.26°(6)	116.42°±0.03	118.60°±0.07
Cell volume	985.1(9) A^3	493 A^3	494.4 A^3
Chemical formula	$Ca_2HPO_4SO_4.4H_2O$	$CaHPO_4.2H_2O$	$CaSO_4.2H_2O$
Cell content	4	4	4
Space group	*Cc*	*Ia*	*I2/a*

**Estimated standard deviations are given in parentheses and refer to the last decimal place.*

planes, and the mode of sheet stacking is controlled by these symmetry operations; and (2) two-sheet structure units are located on *n* and *c* glide planes respectively; in this case the mode of sheet stacking is not affected by the symmetry operations. In the former, a strong peak should occur at (0,50,0), coordinates multiplied by 100, in three-dimensional Patterson synthesis, but such a peak could not be observed. A strong peak at (8,17,16) may indicate that the positions of Ca, P, or S atoms in the adjacent sheets have shifted to *a* and *c* directions. Such a shift cannot be expected in the former but favors the latter. At this stage of the three-dimensional Patterson synthesis, the structure model based on the space group *C2/c* was considered unlikely, because there were no 2-fold axis symmetry peaks of (8,17,16) and no related peaks on the Harker section at *b*/2.

Note that in brushite and gypsum the sheet structure units are located on the *c* glide plane, but those in the second proposed model for the present crystal are located both on the *c* and *n* glide planes. The sheet structure unit analogous to those of gypsum and brushite can be located both on *c* and *n* glide planes in the present cell, because of the similar cell dimensions (Fig. 1).

The mode of sheet stacking is not defined for the second proposed model, but Ca or (P,S) atoms in the adjacent sheets may shift in accordance with the (8,17,16) vector components found in the Patterson map. Through several trials concerning this shift, a structure reduced the conventional *R* rapidly to 0.178, whereas the other models hardly reduced *R* to less than 0.26 by a diagonal least-squares method. The positional parameters were refined by full-matrix least-squares method using UNICS program (Sakurai, 1967, after ORFLS written by Busing *et al.*, 1962). The neutral atomic scattering factors (*International Tables for X-ray Crystallography*, 1962) were used for Ca, P, S, and O atoms. Isotropic thermal factors were set at Ca, 1.4; P and S, 1.0; O, 2.0; H_2O, 2.5. In the successive refinements, an averaged factor of P and S was used for the atoms at the *T* sites.

The positional parameters were divided into several groups, because the number of variables were too many compared with the number of reflections. Each group of positional parameters was refined separately and resulted in a reduction of *R* to 0.070 (w*R*, 0.077). A further cycle of refinement of all positional parameters except for Ca(1) reduced *R* to 0.069 (w*R*, 0.077), and the refinement of isotropic temperature factors reduced *R* to 0.068 (w*R*, 0.077). Refinement with anisotropic temperature factors was not attempted, because of the prohibitive number of least-squares variables necessary for such a model. At the last stage of refinements, Fourier difference synthesis showed no peak except a ripple near the *T*(1) site, which seemed to be caused by the paucity of the data set.

The final positional parameters and isotropic temperature factors are shown in Table 2, along with their estimated standard deviations. The observed and calculated *F* values are given in Table 3, and the interatomic distances and angles in Table 4.

Discussion and description of the crystal structure

The crystal structure is shown in Figure 2(3), where a unit cell is projected along the *c* axis and compared with the crystal structures of gypsum and brushite [Fig. 2(1) and 2(2)]. The sheets on the *c* glide planes are similar to each other. The sheet on the *n* glide plane in the present structure was assumed to be identical to that on the *c* glide plane, and the refined structure does not differ significantly from the assumed one (Fig. 1). The main difference among the three crystal structures is in the mode of sheet stackings. In the crystal structures of gypsum and brushite, the mode of sheet stackings is controlled by the *a* glide symmetry, but in the present crystal structure it is not defined by such a symmetry operation. This difference causes the different configurations of the water molecules described later.

T–O bond lengths at *T*(1) site range from 1.47 to 1.54A with a mean of 1.50A, and at *T*(2) site from 1.47 to 1.53A with a mean of 1.49A. There are no significant differences between the two. The mean distances are close to an average value of 1.50A between the mean P–O bond length, 1.540A in brushite, and the mean S–O bond length, 1.459A in gypsum.

Calculation of structure factor multiplicities for *T*(1) and *T*(2) gave the values of 1.008 and 0.984 respectively, which are near unity. These values ought to be 1.033 and 0.967 respectively in a structure having a completely ordered distribution of P and S atoms in the *T* sites. On the other hand, the isotropic temperature factor of *T*(2) is three times that of *T*(1), as shown in Table 2. The result suggests that there is a ordering of P and S atoms in the *T* sites. Refinement based on the ordered structure model did not reduce *R* to less than 0.071. These facts, with the result of the Fourier difference synthesis, suggest that at this stage there seems to be no ordering in the distribution of P and S atoms in the *T* sites.

Table 2. Positional and isotropic thermal atomic parameters for $Ca_2HPO_4SO_4 \cdot 4H_2O$

Atom	x	y	z	B
Ca(1)	0.500	0.0383	0.250	1.5(2)
Ca(2)	.590(3)	.2120(3)	.428(4)	1.1(2)
T(1)	.999(4)	.0388(4)	.747(5)	0.6(2)
T(2)	.592(4)	.2111(4)	.937(4)	1.6(2)
O(1)	.942(7)	.0700(10)	.549(7)	1.7(6)
O(2)	.038(6)	.0632(11)	.976(7)	1.8(5)
O(3)	.771(7)	.0098(10)	.676(7)	2.0(5)
O(4)	.257(7)	.0151(10)	.828(8)	2.0(6)
O(5)	.412(6)	.1852(11)	.714(7)	3.1(6)
O(6)	.735(7)	.1809(11)	.140(7)	2.0(5)
O(7)	.775(7)	.2354(11)	.872(7)	2.2(5)
O(8)	.432(6)	.2399(10)	.001(7)	1.5(5)
W(1)	.373(7)	.0875(14)	.493(9)	2.6(6)
W(2)	.614(7)	.0931(12)	.019(8)	2.0(6)
W(3)	.227(7)	.1620(14)	.200(9)	3.1(6)
W(4)	.940(7)	.1554(13)	.654(8)	3.1(6)

* *Estimated standard deviations are given in parentheses and refer to the last decimal place.*

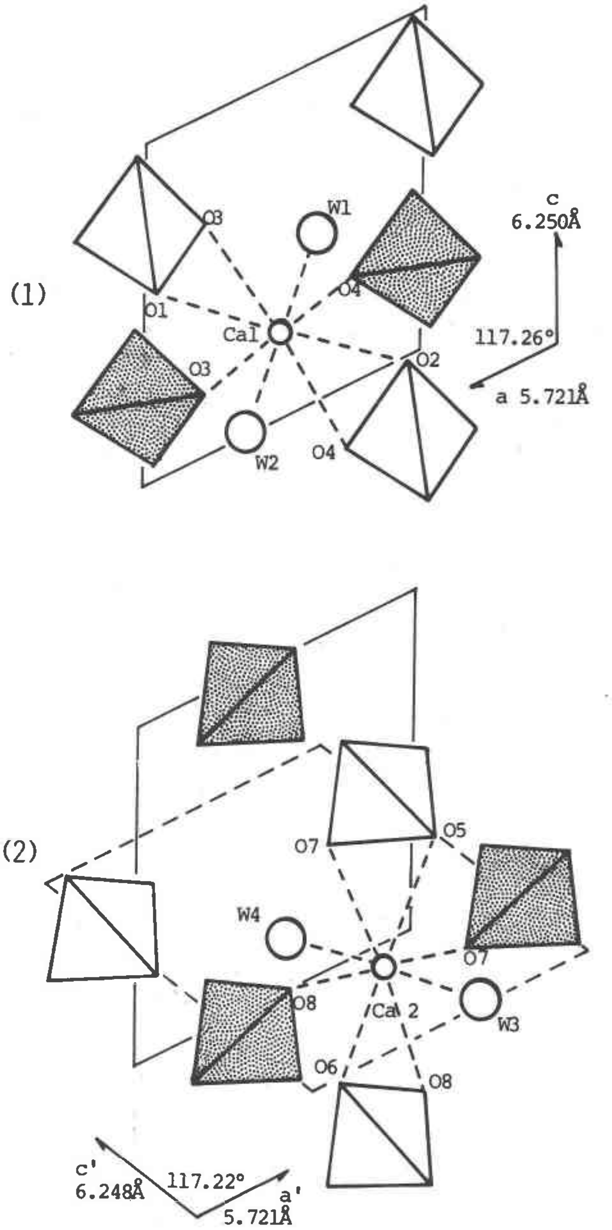

Fig. 1. Projection of the crystal structure onto (1) *c* glide plane and (2) *n* glide plane along the *b* axis. The sheet structure on *c* glide plane (1) also appears in (2), as is easily shown by selecting *a'* and *c'* axes. The dark tetrahedra lie below the planes.

The calcium atoms at Ca(1) and Ca(2) sites are eight-coordinated: six to the oxygens belonging to tetrahedra and two to water molecules at the surface of the sheet. Thus structural environments of the calcium atoms are similar to those in gypsum and brushite. It is found that the Ca–*W* bond lengths are

Table 3. $Ca_2HPO_4SO_4 \cdot 4H_2O$, structure factors ($h$, k, $\lvert F_{obs}\rvert$, $\lvert F_{calc}\rvert$, A_{calc}, B_{calc})

h	k	$\lvert F_{obs}\rvert$	$\lvert F_{calc}\rvert$	A_{calc}	B_{calc}
			l = 0		
2	0	114.24	114.88	108.33	38.25
4	0	53.26	50.96	42.30	28.41
3	1	40.03	34.89	24.08	-25.25
5	1	28.79	24.90	23.93	-6.91
2	2	73.92	71.85	51.94	-49.64
4	2	100.49	89.23	88.95	-7.13
6	2	76.73	66.87	64.44	17.86
1	3	85.68	91.62	79.41	45.70
3	3	49.57	40.70	-18.77	36.11
0	4	147.13	173.67	173.67	0.00
2	4	44.48	41.97	30.41	28.92
4	4	56.48	50.21	34.67	36.38
-3	5	45.53	42.34	-19.04	37.81
1	5	124.54	123.98	-102.18	-70.22
2	6	74.68	66.92	-66.01	-10.98
4	6	48.52	44.59	43.34	-10.47
1	7	128.58	128.88	105.06	74.65
3	7	54.19	52.46	-36.28	37.89
5	7	53.38	50.42	-49.81	7.80
0	8	107.69	112.47	-112.47	0.00
2	8	98.91	94.32	-86.79	-36.93
-3	9	41.79	37.82	-4.35	37.57
1	9	149.06	144.74	-126.69	-70.00
5	9	46.70	40.94	40.93	-0.37
2	10	104.06	98.25	-76.19	62.05
4	10	99.55	89.74	-82.28	35.83
6	10	65.78	50.79	-49.05	-13.18
3	11	43.95	37.85	14.72	34.88
-4	12	60.63	50.12	-7.58	49.55
2	12	162.70	158.41	-124.00	-98.58
1	13	51.33	45.19	45.09	-3.11
2	14	67.13	67.42	-26.73	61.90
4	14	99.55	87.12	-78.92	36.90
6	14	63.56	59.22	-56.44	-17.92
-1	15	33.71	30.13	24.06	18.13
0	16	99.49	102.65	-102.65	0.00
2	16	90.36	88.74	-62.50	-63.00
1	17	70.17	70.81	69.33	14.39
3	17	95.22	87.48	-19.82	85.21
2	18	47.76	43.03	-25.68	34.53
1	19	34.53	34.73	-21.00	-27.66
3	19	96.92	84.58	14.66	-83.30
3	21	85.62	74.38	-13.72	73.10
1	23	63.44	65.40	-59.16	-27.88
0	24	80.18	80.68	80.68	0.00
2	24	78.66	75.14	59.51	45.88
2	26	68.83	68.56	38.10	-57.00
4	26	74.85	72.97	66.65	-29.72
0	28	64.38	71.10	71.10	0.00
2	28	81.82	78.86	68.48	39.11
-1	33	50.92	51.30	-42.75	28.37
-2	36	29.97	36.80	-32.29	17.65
0	36	86.50	81.96	-81.96	0.00
0	40	80.30	81.52	-81.52	0.00
			l = 1		
-3	1	72.69	71.21	60.63	-37.34
1	1	58.64	58.25	52.21	-25.81
-2	2	117.52	107.80	106.96	13.42
2	2	62.27	55.03	-16.85	-52.38
-5	3	55.60	48.53	48.53	-0.59
-3	3	37.92	40.12	27.41	29.30
-1	3	75.26	90.58	90.51	3.76
1	3	97.97	90.67	90.11	9.99
3	3	80.06	77.19	77.16	-1.95
-4	4	42.96	43.83	40.64	-16.41
2	4	112.25	102.14	-90.24	47.85
-5	5	75.26	67.36	67.29	-2.99
-3	5	97.50	91.49	90.18	-15.43
-1	5	109.56	124.16	124.15	-1.42
1	5	96.57	95.39	95.36	2.33
3	5	33.83	30.69	30.21	5.40
-2	6	56.07	46.46	-43.99	14.95
-5	7	59.46	50.19	45.34	-21.53
-3	7	90.71	85.99	85.23	11.36
-1	7	119.04	128.78	128.64	-5.86
1	7	70.11	73.37	57.05	46.14
3	7	80.18	69.40	68.89	8.43
-3	9	71.75	71.10	70.96	-4.41
-1	9	143.04	145.86	145.46	10.86
1	9	79.36	75.40	51.69	-54.89
3	9	47.29	44.58	44.49	-2.89
-2	10	147.48	145.37	-145.31	4.29
1	11	68.12	63.79	21.95	59.89
3	11	52.32	47.64	46.19	11.66
-3	13	35.47	35.24	-35.22	-1.30
-1	13	50.10	53.68	-42.24	-33.12
1	13	30.67	31.26	13.30	-28.28
-3	15	49.40	46.70	-46.65	-2.10
1	15	31.49	30.26	-25.15	-16.83
5	15	48.34	36.20	-33.36	-14.06
0	16	56.30	60.76	32.64	-51.25
-3	17	51.97	51.40	-50.02	11.86
-1	17	70.70	73.48	-67.04	-30.07
1	17	75.73	79.36	-78.73	10.02
3	17	54.08	51.47	-50.89	-7.75
0	18	50.57	58.79	46.75	35.64
1	19	86.62	89.04	-88.68	7.92
3	19	73.62	65.43	-65.42	0.64
-3	21	41.79	42.50	-41.32	9.96
1	21	79.95	80.59	-77.74	-21.23
0	22	51.03	58.37	45.68	36.33
-3	23	56.54	53.17	-51.93	11.41
-1	23	64.50	64.36	-63.72	-9.08
1	23	42.02	37.55	-34.06	15.80
			l = 2		
-6	0	65.20	65.87	-53.83	37.97
-4	0	198.87	192.57	-192.02	14.50
-2	0	96.22	106.08	-75.96	-74.05
2	0	61.57	58.20	49.55	30.54
4	0	71.28	60.19	-44.46	40.57
-3	1	65.20	68.88	68.79	3.55
-1	1	58.06	61.05	-34.96	50.05
1	1	39.80	38.48	34.90	16.20
-6	2	53.02	49.52	-35.66	-34.35
-2	2	62.51	70.19	-27.00	64.78
0	2	113.66	135.75	-122.20	59.11
2	2	100.08	100.02	-98.24	-18.80
4	2	83.34	68.79	-54.93	-41.41
-5	3	28.79	36.25	-27.73	23.35
-3	3	34.53	45.16	-8.96	-44.26
-1	3	83.22	92.96	-1.88	-92.94
1	3	92.12	95.66	95.65	0.86
-6	4	50.92	40.80	-27.08	30.52
-4	4	64.61	63.17	-61.42	14.76
0	4	89.31	97.94	-36.18	-91.02
-3	5	89.43	85.92	80.03	31.26
-1	5	86.38	94.59	-15.45	93.32
3	5	84.86	74.19	-62.22	-40.42
-2	6	61.92	62.86	-33.50	-53.19
0	6	176.28	180.19	-166.36	69.23
-5	7	73.62	69.64	-55.19	42.27
-3	7	82.87	84.69	-65.91	-53.19
-1	7	68.83	76.38	-38.45	-66.00
1	7	80.41	85.17	83.73	-15.59
-4	8	42.02	43.11	42.83	4.94
-2	8	87.09	88.98	59.26	66.38
-5	9	57.71	52.35	45.17	-26.45
-3	9	65.90	64.34	57.15	29.56
-1	9	71.05	78.65	-66.32	42.27
1	9	106.63	103.37	-102.24	15.24
3	9	60.87	55.60	-37.48	-41.07
-2	10	89.43	99.07	26.27	-95.52
0	10	97.04	103.32	93.52	-43.93
2	10	82.17	79.91	77.85	18.02
-5	11	56.30	43.38	-26.17	34.59
-1	11	67.30	66.10	-56.70	-33.98
1	11	61.69	65.38	60.55	-24.66
-6	12	60.75	62.15	47.13	-40.51
-4	12	80.30	75.56	75.52	2.34
-2	12	149.83	160.06	142.24	73.40
0	12	92.35	97.79	43.35	87.66
1	13	34.30	34.60	-27.88	20.49
-6	14	36.87	31.01	18.40	24.97
-2	14	62.27	66.07	44.22	-49.09
0	14	144.32	148.52	137.07	-57.19
2	14	136.83	131.59	128.81	26.89
4	14	62.51	58.13	43.68	38.36
-3	15	46.70	48.55	42.61	23.26
3	15	48.93	38.24	-17.19	-34.16
-4	16	101.37	97.49	97.49	0.66
-2	16	88.37	90.56	85.80	28.97
0	16	41.67	46.31	18.80	42.33
-5	17	47.05	38.02	-36.69	9.96
-1	17	75.03	80.59	30.52	-74.59
1	17	64.50	67.55	65.65	-15.91
-2	18	42.49	43.75	21.93	-37.86
2	18	40.27	46.48	46.14	5.66
-3	19	40.50	41.64	38.96	14.69
-1	19	78.89	82.37	-11.68	81.54
1	19	57.24	58.62	-55.80	17.97
-1	21	77.37	78.33	-14.63	-76.95
0	22	55.95	58.33	-53.31	23.68
2	22	76.90	71.39	-70.36	-12.10
-1	23	36.29	37.52	-23.03	29.62
-4	24	81.47	78.07	-76.29	16.56
-2	24	73.98	77.36	-69.26	-34.45
4	24	54.31	45.84	-38.34	25.12
-2	26	71.64	71.29	-40.16	58.91
0	26	91.30	101.49	-92.80	41.09
2	26	87.20	84.63	-83.61	-13.10
-2	28	77.14	79.93	-67.30	-43.13
			l = 3		
-1	1	37.69	36.48	31.80	-17.88
-2	2	50.92	60.56	27.56	53.92
-3	3	42.84	45.96	-40.39	21.94
-1	3	87.91	99.98	-96.39	26.57
3	3	31.02	25.93	-24.55	-8.36
-2	4	94.81	99.61	94.81	-30.55
1	5	62.51	64.21	-59.09	-25.13
3	5	60.28	56.43	-56.21	4.91
5	5	50.68	40.49	-40.32	-3.79
-5	7	71.87	68.65	-68.48	4.78
-3	7	48.81	56.10	-44.52	34.13
-1	7	77.96	79.55	-78.88	10.34
1	7	61.33	59.78	-54.32	24.97
3	7	60.52	53.57	-51.87	-13.38
-5	9	50.92	51.43	-51.42	1.15
-1	9	92.47	100.84	-100.29	10.51
1	9	66.72	64.47	-64.13	-6.59
3	9	51.97	51.76	-51.72	1.93
-1	11	59.93	67.08	-66.15	-11.10
1	15	71.28	76.43	73.96	19.30
-5	17	40.27	47.73	46.39	11.19
-3	17	78.19	84.54	84.48	-3.03
-1	17	55.48	61.40	61.36	2.07
1	17	47.05	47.37	44.45	-16.38
-3	19	84.28	90.72	90.67	-3.05
-1	19	60.40	67.53	67.44	3.43
1	19	55.37	61.38	60.40	10.93
-3	21	77.25	80.25	80.25	-0.11
1	21	65.78	65.88	65.12	10.02
-1	27	41.44	39.83	-38.56	9.99
			l = 4		
-6	0	58.76	60.49	54.48	26.30
-4	0	43.89	42.42	-8.94	41.47
-2	0	55.01	59.69	59.13	-8.12
0	0	110.38	108.64	73.91	-79.63
2	0	117.40	110.81	109.45	-17.27
-6	2	54.55	50.30	18.82	-48.65
-4	2	87.67	90.09	67.41	-59.76
-2	2	96.92	105.12	105.12	-0.14
0	2	99.73	103.60	76.15	70.24
-3	3	62.04	63.75	-61.52	16.73
1	3	60.16	51.65	9.43	-50.78
-4	4	50.92	52.00	5.44	51.71
-5	5	68.83	64.40	7.48	-63.97
-1	5	61.80	67.55	61.81	27.25
1	5	67.30	69.70	-41.44	56.04
-4	6	41.90	41.83	35.42	-22.25
-5	7	52.44	46.83	9.74	45.80
-3	7	65.43	69.86	-65.56	24.13
1	7	61.10	62.30	6.18	-61.99
0	8	43.19	44.10	-33.21	29.01
-3	9	43.31	42.75	42.22	-6.71
-1	9	58.41	60.34	42.09	43.23
-4	10	87.67	89.06	-81.23	36.52
-2	10	71.87	80.88	-80.76	-4.40
0	10	59.34	58.78	-46.01	-36.58
-3	11	41.90	48.85	-41.80	25.27
-6	12	67.89	66.45	-62.09	-23.66
2	12	77.96	74.68	-71.14	22.73
-4	14	85.68	87.49	-80.44	34.43
-2	14	119.98	130.35	-129.22	-17.12
0	14	70.58	72.82	-58.16	-43.83
-1	15	65.67	68.83	54.76	41.71
0	16	54.43	49.63	-34.06	36.10
-3	17	56.18	53.12	-50.36	16.91
-3	19	59.34	60.04	57.40	-17.62
-1	21	64.85	65.63	-46.43	-46.39
-2	22	65.20	71.32	70.66	9.69
0	24	53.84	53.72	38.02	-37.96
-4	26	68.83	70.15	64.44	-27.74
-2	26	79.71	80.98	79.82	13.71
0	26	50.92	50.71	38.47	33.03
			l = 5		
-3	5	67.30	72.88	70.24	19.41
-1	5	69.06	76.52	75.02	-15.09
-3	7	25.75	49.06	44.59	-20.46
-1	7	58.88	62.00	56.41	25.72
-3	9	51.39	56.86	56.81	2.39
-5	19	39.45	36.64	-36.03	6.67
1	19	39.45	42.64	-42.64	0.83
			l = 6		
-4	0	58.06	57.02	-35.02	45.00
-2	0	103.24	103.51	-98.90	30.56
-6	2	64.85	66.80	-66.80	-0.78
-4	2	72.10	73.67	-52.30	-51.90
-2	4	62.39	65.18	-62.44	18.70
-3	9	41.20	41.83	23.51	-34.60
-2	12	68.36	76.17	73.04	-21.60
0	12	92.82	88.84	85.17	25.25
-6	14	67.89	61.65	61.55	-3.40
2	16	49.40	32.74	23.32	22.98
-5	21	56.54	39.11	28.95	26.29

Table 4. Selected interatomic distances and angles for $Ca_2HPO_4SO_4 \cdot 4H_2O$

		Tetrahedral coordination				Calcium coordination	
		O(1)-O(2)	2.48(6) A	O(1)-T(1)-O(2)	109.7(2.1)°	Ca(1)-O(1)	2.56(3) A
T(1)-O(1)	1.49(5) A	-O(3)	2.40(6)	O(3)- -O(2)	108.3(2.3)	-O(2)	2.53(3)
-O(2)	1.54(5)	-O(4)	2.51(5)	O(4)- -O(2)	103.1(2.5)	-O(3)	2.55(4)
-O(3)	1.47(4)	O(2)-O(3)	2.44(4)	O(1)- -O(3)	108.6(2.3)	-O(3')	2.35(4)
-O(4)	1.52(4)	-O(4)	2.40(6)	O(1)- -O(4)	113.5(3.3)	-O(4)	2.46(4)
		O(3)-O(4)	2.50(5)	O(3)- -O(4)	113.4(1.9)	-O(4')	2.35(4)
						-W(1)	2.49(6)
						-W(2)	2.50(5)
MEAN	1.50 A	MEAN	2.45 A	MEAN	109.4°	MEAN	2.47 A
		O(5)-O(6)	2.45(5) A	O(5)-T(2)-O(6)	109.1(2.0)°	Ca(2)-O(5)	2.57(5) A
T(2)-O(5)	1.53(4) A	-O(7)	2.41(5)	O(5)- -O(7)	106.7(2.9)	-O(6)	2.49(5)
-O(6)	1.49(4)	-O(8)	2.43(6)	O(5)- -O(8)	108.8(2.1)	-O(7)	2.58(5)
-O(7)	1.48(5)	O(6)-O(7)	2.46(6)	O(6)- -O(7)	112.0(2.3)	-O(7')	2.34(4)
-O(8)	1.47(5)	-O(8)	2.39(5)	O(6)- -O(8)	108.3(3.0)	-O(8)	2.54(4)
		O(7)-O(8)	2.44(7)	O(7)- -O(8)	111.9(2.2)	-O(8')	2.33(4)
						-W(3)	2.46(4)
						-W(4)	2.55(4)
MEAN	1.49 A	MEAN	2.43 A	MEAN	109.5°	MEAN	2.48 A

Water molecule environment**

W(1)-O(1)	2.70(7) A	W(2)-O(6)	2.83(5) A	W(3)-W(1)	2.83(6) A	W(4)-O(5)	2.71(6) A
-O(2)	3.00(6)	-W(1)	2.93(7)	-O(6)	2.73(6)	-O(1)	2.73(5)

* *Estimated standard deviations are given in parentheses and refer to the last decimal place.*
** *The shortest two distances are selected.*

longer than the Ca–O bond lengths in the present crystal structure, whereas the Ca–*W* bond lengths are shorter than the Ca–O bond lengths in gypsum, brushite, and its arsenate analogue pharmacolite (Table 5).

The *W–W* bond lengths in a sheet in brushite and pharmacolite are shorter than in gypsum; this bond is termed an interwater hydrogen bond by Curry and Jones (1971). In the present crystal structure a short *W*(1)–*W*(2) bond length, 2.93A, seems to be due to the interwater hydrogen bond. On the other hand the *W*(3)–*W*(4) bond length, 3.04A, is not as short, but is still shorter than 3.09A of the interwater hydrogen bond length in brushite. The *W*–O bond lengths in the present crystal structure range from 2.70 to 2.83A. They are shorter than those in brushite (2.74–3.09A) and in gypsum (2.816–2.896A). Note that a short *W*(1)–*W*(3) bond length, 2.83A, making a bridge between the adjacent sheets, is unusual compared with similar bonds in the structures of gypsum, brushite, and pharmacolite.

Conclusion

Synthetic calcium phosphate–sulfate hydrate is identical to ardealite in chemical composition. The analyzed crystal structure has some interesting crystallographic properties, such as the cell dimensions being similar to gypsum and brushite but the *b* dimension of the present crystal being twice as long as those of the two minerals, and although the contrasting sheets are analogous to those in the two minerals the mode of sheet stacking is different. The result of synthesis suggests that this compound may occur in nature. X-ray powder diffraction data are calculated from the crystal structure, and most of the powder reflections agree with those of natural ardealite in spacings and intensities. But we note that several principal reflections usually observed in the pattern of natural ardealite are missing from the calculated pattern. It is not certain whether these additional reflections are due to impurities or to the structural

Table 5. Ca-O and Ca-*W* bond lengths for $Ca_2HPO_4SO_4 \cdot 4H_2O$, gypsum, brushite, and pharmacolite

$Ca_2HPO_4SO_4 \cdot 4H_2O$	Gypsum	Brushite	Pharmacolite
This study	Cole + Lancucki (1974)	Curry + Jones (1971)	Ferraris (1969)
Ca(1)-O 2.46 A Ca(2)-O 2.48	Ca-O 2.483 A	Ca-O 2.508 A	Ca-O 2.550 A
Ca(1)-W 2.49 Ca(2)-W 2.50	Ca-W 2.380	Ca-W 2.404	Ca-W 2.413

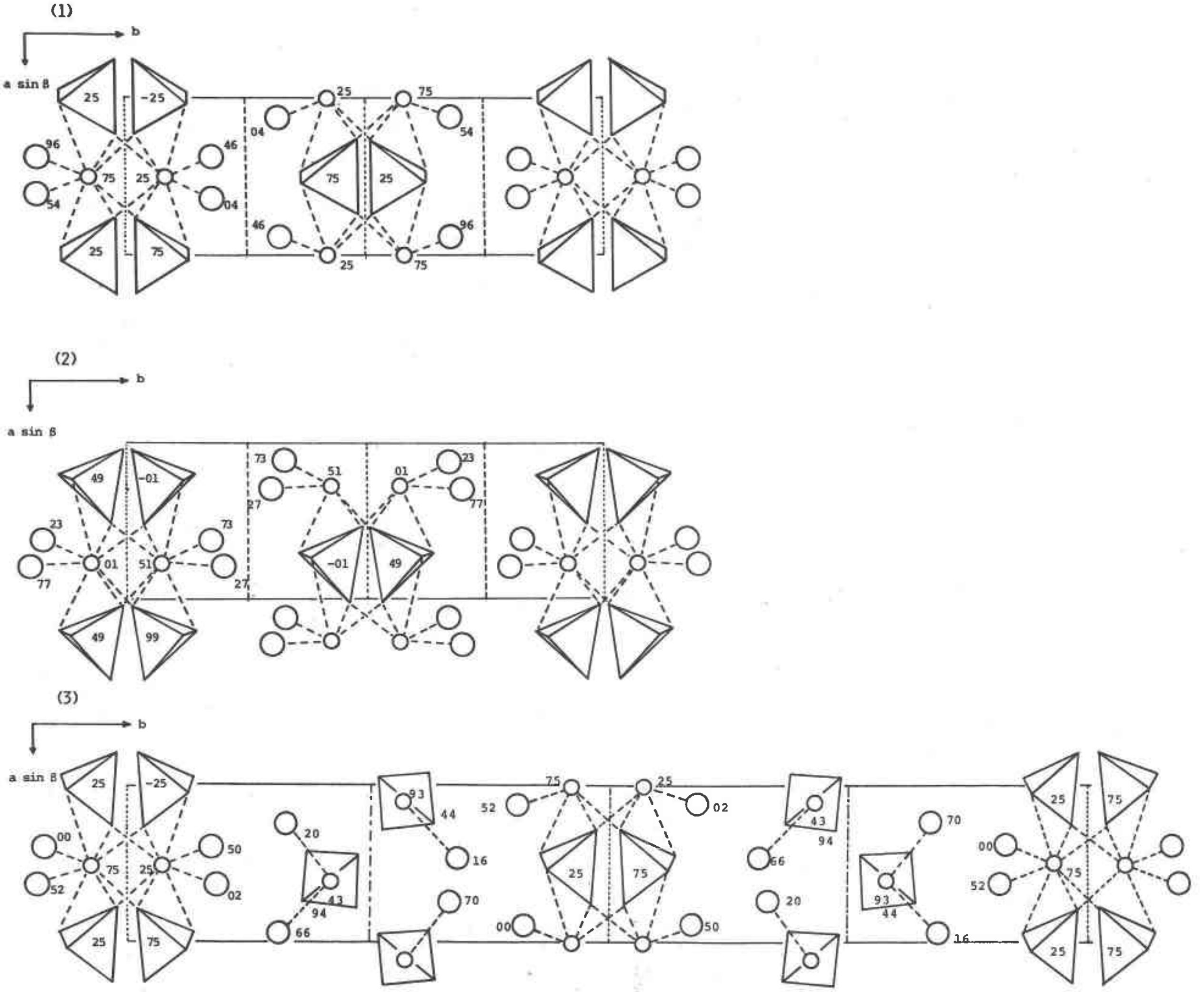

Fig. 2. Crystal structure of gypsum, brushite, and $Ca_2HPO_4SO_4 \cdot 4H_2O$ projected along the *c* axis; (1) gypsum (*I2/a*, Cole and Lancucki, 1974), (2) brushite (*Ia*, Curry and Jones, 1971), (3) $Ca_2HPO_4SO_4 \cdot 4H_2O$ (*Cc*, this study). Large circles represent water molecules and small circles represent calcium atoms. Numbers are the *z* coordinates of the tetrahedra, calcium, and water sites.

properties of ardealite, because we could not obtain a single crystal of ardealite for structural analysis. In this respect, we take care not to conclude that the present crystal structure is that of natural ardealite.

Acknowledgments

The authors thank Dr. K. Kihara of Kanazawa University for his helpful measurements and advice; Professor S. Shimoda and the members of the Mineralogical Institute, Tokyo University of Education, for their critical discussions; and Professor S. Sugiura of Kanazawa University for the opportunity to use the instrument, and Dr. N. Kohyama of Industrial Physics Institution for measurements on SEM. Computations were carried out on MELCOM 7500 at Tokyo University of Education and HITAC 8800/8700 at the University of Tokyo. A part of the expense was defrayed by a Grant-in-Aid for Science Research, Ministry of Education.

References

Atoji, M. and R. E. Rundle (1958) Neutron diffraction study of gypsum, $CaSO_4 \cdot 2H_2O$. *J. Chem. Phys., 29,* 1306–1311.

Baynham, J. W. and B. Raistrick (1960) Structural and X-ray data on chemical compounds found in fertilizers. In V. Sauchelli, Ed., *Chemistry and Technology of Fertilizers,* p. 538–575. Reinhold, New York.

Beevers, C. A. (1958) The crystal structure of dicalcium phosphate dihydrate, $CaHPO_4 \cdot 2H_2O$. *Acta Crystallogr., 11,* 273–277.

Busing, W. R., K. D. Martin and H. A. Levy (1962) ORFLS, a Fortran crystallographic least-squares program. *Oak Ridge National Laboratory, Report ORNL TM 305.*

Cole, W. F. and C. J. Lancucki (1974) A refinement of the crystal structure of gypsum, $CaSO_4 \cdot 2H_2O$. *Acta Crystallogr., B30,* 921–929.

Curry, N. A. and D. W. Jones (1971) Crystal structure of brushite, calcium orthophosphate dihydrate: A neutron diffraction investigation. *J. Chem. Soc. (A)*, 3725–3729.

Ferraris, G. (1969) The crystal structure of pharmacolite, $CaH(AsO_4)\cdot 2H_2O$. *Acta Crystallogr., B25*, 1544–1550.

Hill, W. L. and S. B. Hendricks (1936) Composition and properties of superphosphate. Calcium phosphate and calcium sulfate constituents as shown by chemical and X-ray diffraction analysis. *J. Ind. Eng. Chem., 28*, 440–447.

Jones, D. W. and J. A. S. Smith (1962) The crystal structure of brushite, $CaHPO_4\cdot 2H_2O$. *J. Chem. Soc.*, part I, 1414–1420.

O'Daniel, H. (1939) Die Gitterbeziehungen und Mischverhaltnisse zwischen $CaSO_4\cdot 2H_2O$ und $Ca(PO_4H)\cdot 2H_2O$. *Fortschr. Mineral., 23*, 108–110.

Sakurai, T. (1967) UNICS: *Universal Crystallographic Computation Program System*. Crystallographic Society, Japan.

Schadlar, J. (1932) Ardealite, ein neues Mineral $CaHPO_4\cdot CaSO_4 + 4H_2O$. *Centralbl. Mineral.*, Abt A, 40–41.

Manuscript received, March 14, 1977; accepted for publication, November 28, 1977.