$KNaSO_4$ are 2·340 (16) and 2·349 (15) Å (mean 2·345 Å), and the Na—O distance in $K_3Na(SO_4)_2$ is 2·386 (2) Å. The $M(2)$ sites of $KNaSO_4$ are occupied by K and Na atoms, while those of $K_3Na(SO_4)_2$ are occupied only by K atoms. The Na(2)—O distances range from 2·419 (21) to 2·994 (19) Å (mean 2·829 Å) and the K(2)—O distances range from 2·537 (29) to 3·213 (17) Å (mean 2·909 Å) in $KNaSO_4$. The K(2)—O distances of $K_3Na(SO_4)_2$ range from 2·547 (6) to 3·112 (3) Å (mean 2·901 Å). There are fairly short Na—O and K—O distances in each $M(2)O_{10}$ polyhedron. The $M(3)$ sites of both substances are occupied by K atoms. The K(3)—O distances of $KNaSO_4$ range from 2·761 (12) to 3·253 (3) Å (mean 3·054 Å), while those of $K_3Na(SO_4)_2$ are 2·908 (2) and 3·288 (1) Å (mean 3·098 Å).

The crystal structure of glaserite has been postulated by many workers. Moore (1973) considered that the formal composition of glaserite could be written as $M(3)^{[12]}M(2)_2^{[10]}M(1)^{[6]}[T^{[4]}O_4]_2$ and that K atoms occupy the $M(2)$ sites and Na atoms the $M(1)$ and $M(3)$ sites in $KNaSO_4$. Eysel (1973), however, considered that K atoms first fill the $M(3)$ and then the $M(2)$ sites. Our structure determinations of $KNaSO_4$ and $K_3Na(SO_4)_2$ show that K atoms first fill the $M(3)$ and then go into the $M(2)$ sites while Na atoms first fill the $M(1)$ and then the $M(2)$ sites. This result is in line with the propositions of Eysel (1973) but not with those of Moore (1973). As the Na and K atoms in the $M(2)$ sites in $KNaSO_4$ are ordered, the space group of $KNaSO_4$ must be $P3m1$ and not $P\bar{3}m1$. Therefore, the formal composition of $KNaSO_4$ is written as $M(3)^{[12]}M(2)^{[10]}M(2')^{[10]}M(1)^{[6]}[T^{[4]}O_4]_2$. It can be considered that the structure of $KNaSO_4$ is an ordered derivative of glaserite and that there is a slight discontinuity between the structure of $KNaSO_4$ and that of $K_3Na(SO_4)_2$.

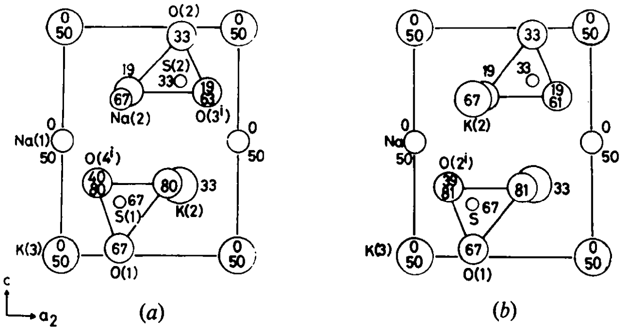

Fig. 2. The crystal structures of (*a*) $KNaSO_4$ and (*b*) $K_3Na(SO_4)_2$ viewed along the *a* axis. The numbers give the heights of atoms ($\times 10^2$) in decimal fractions of the *a* length. The atoms are depicted as in Fig. 1.

We are grateful to Professor M. Kato for allowing us to use an automated diffractometer at the Tokyo Institute of Technology. Computations were carried out on an M-180 computer at the Computer Centre of the Tokyo Institute of Technology.

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α-Calcium Disodium Pyrophosphate Tetrahydrate

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(*Received* 11 *September* 1979; *accepted* 10 *January* 1980)

Abstract. α-$CaNa_2P_2O_7.4H_2O$, $M_r = 332·0$, monoclinic, Pc, $a = 5·689$ (6), $b = 8·586$ (8), $c = 10·565$ (9) Å, $\beta = 106·3$ (1)°, $Z = 2$, $D_c = 2·08$ Mg m^{-3} (not measured), μ(Cu $K\alpha$) = 9·09 mm^{-1}. The structure reported is one of three known polymorphs. The α and β structures contain almost identical parallel Ca^{2+}...

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$P_2O_7^{4-}\cdots Ca^{2+}$ chains. The differences in the structures concern the coordination of Na^+ and H_2O between the chains.

Introduction. In the course of our studies of pyrophosphate crystal deposition disease (Pritzker, Cheng, Adams & Nyburg, 1978) we have made hydrogels containing sodium pyrophosphate over which was layered calcium chloride solution. Diffusion of this upper layer into the gel gives, from both microscopic examination and X-ray powder diagrams, two different deposits at different levels. At one level there were a few crystals large enough for single-crystal X-ray analysis but at the other they were too small. Powder diagrams showed the crystals in the two layers to differ. We now know they are polymorphs of $CaNa_2P_2O_7.4H_2O$ and the structure of one such polymorph (β) obtained from the gel has been reported elsewhere (Cheng, Nyburg, Adams & Pritzker, 1979). We have now prepared larger crystals of the second (α) and yet a third polymorph (γ) from suitable aqueous solutions. (For references to earlier preparative work, see *Gmelins Handbuch der Anorganischen Chemie*, 1961.) We report here the crystal structure of the α polymorph.

The α form is obtained by adding 0·1 *M* $Na_4P_2O_7.10H_2O$, first neutralized with hydrochloric acid, to 1 m*M* $CaCl_2$ at room temperature. (The γ polymorph is obtained by adding acidified 0·1 *M* sodium pyrophosphate solution, pH 5·5, to 1 m*M* $CaCl_2$. Its structure is presently under investigation and will be reported later.) The crystal used for data collection was a fine needle *ca* 0·03 × 0·03 × 0·15 mm. It was mounted about the *z* axis, parallel to its longest dimension. The cell parameters and standard deviations were obtained from the diffractometer angle settings of twelve well centered reflections, $\sin\theta \geq 0{\cdot}3$, using Cu *Kα* radiation. Intensities were collected on a computer-controlled Picker four-circle diffractometer fitted with a pulse-height analyzer using Ni-filtered Cu *Kα* radiation. Scanning was in the θ–2θ mode at 1° min^{-1}, for $\sin\theta \leq 0{\cdot}9$. Background was determined for 60 s at each end of the scan range of 2° adjusted for α splitting. The take-off angle was 3°. During the course of data collection there was a random deviation of <3% from the mean in the intensity of the standard reflection measured every 30 reflections. Counting statistics and a Bernstein factor (Abrahams & Bernstein, 1965) of 0·01 were used to calculate $\sigma(I)$. Of the 832 independent reflections measured, 830 were considered significant on the criterion $|F_o| > \sigma(F_o)$. Absorption corrections were not applied.

The positions of the Ca^{2+} ion and two P atoms were inferred from the Patterson function and the remaining non-hydrogen atoms from Fourier maps. Refinement was by *ORXFLS*3 (Busing, Martin & Levy, 1971) using $[\sigma(F_o)]^{-2}$ as weights and Hartree–Fock scattering factors (Cromer & Mann, 1968) with appropriate corrections for anomalous dispersion applied for Ca^{2+}, Na^+ and P. Scattering factors were from *International Tables for X-ray Crystallography* (1962). Three cycles of anisotropic refinement gave a final conventional, unweighted *R* of 0·048.* No H atoms were revealed on the ΔF map. Table 1 lists the atomic coordinates.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and temperature factors* ($Å^2 \times 10^4$) *where* $U = (1/6\pi^2) \times (\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{13}ac\cos\beta)$

(β_{ij} values have been deposited.)

	x	*y*	*z*	*U*
Ca	0	−122 (2)	5000	114
Na(1)	−2614 (8)	3667 (4)	4638 (4)	250
Na(2)	2246 (8)	−3993 (5)	4580 (5)	260
P(1)	3877 (5)	−736 (2)	3071 (3)	110
P(2)	1782 (5)	2414 (2)	2906 (3)	117
O(11)	3301 (11)	−966 (7)	1592 (6)	131
O(12)	3979 (12)	1120 (7)	3368 (6)	163
O(13)	6410 (10)	−1290 (7)	3788 (6)	174
O(14)	1878 (12)	−1432 (7)	3586 (7)	182
O(22)	707 (13)	2246 (7)	1425 (6)	157
O(23)	3185 (13)	3919 (7)	3275 (6)	172
O(24)	−36 (12)	2063 (7)	3661 (6)	196
O(*W*1)	−2257 (13)	−1484 (7)	1117 (6)	194
O(*W*2)	8058 (14)	4156 (7)	8426 (8)	253
O(*W*3)	1472 (14)	4169 (7)	6104 (8)	268
O(*W*4)	−3768 (15)	3907 (10)	1092 (9)	359

Discussion. Since the choice of (x,z) for the origin in *Pc* is arbitrary, Ca^{2+} ions were placed at $(0,y,0)$ and $(0,\bar{y},\frac{1}{2})$. The *y* coordinate is also found to be close to zero (Table 1) so that the Ca^{2+} ions lie virtually in straight lines parallel to the *z* axis, spaced *c*/2 apart (Fig. 1). Between these Ca^{2+} ions lie the glide-related pyrophosphate ions to which the Ca^{2+} ions are coordinated. The coordination, Fig. 2, is sixfold (two bidentate, one unidentate and one water molecule). The bond lengths and angles involved in the bidentate coordination of Ca^{2+} to pyrophosphate are closely similar in this structure, in the β polymorph and in triclinic calcium pyrophosphate dihydrate (Mandel, 1975). Table 2 sets out the dimensions in all three cases. Although there are significant differences, the geometry is similar in each case. This coordination doubtless governs the eclipsing of the $P_2O_7^{4-}$ ion. Viewed along the interphosphorus vector, the angle of eclipse is 12, 12 and 23·4° in these three cases.

Although the H positions could not be inferred from the ΔF map the crystal structure is clearly extensively hydrogen-bonded. However, as in the β polymorph,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35024 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bidentate coordination of* Ca^{2+} *to pyrophosphate in three crystal structures*

For crystal (*c*) the independent values have been averaged.

Bond lengths (Å)

Reference	Ca—O	P—O_T*	P(1)—O(12)	P(2)—O(12)
(*a*)	2·313–2·352 (6)	1·503–1·519 (7)	1·621 (6)	1·641 (7)
(*b*)	2·30 –2·39 (1)	1·50 –1·53 (1)	1·62 (1)	1·63 (1)
(*c*)	2·320–2·450 (1)	1·513–1·538 (1)	1·623 (1)	1·623 (1)

Internal angles (°) of the $CaP_2O_7^{2-}$ ring

Reference	O($^{11}_{14}$)—Ca—O($^{22}_{24}$)	Ca—O($^{11}_{14}$)—P(1)	Ca—O($^{22}_{24}$)—P(2)	O($^{11}_{14}$)—P(1)—O(12)	O($^{22}_{24}$)—P(2)—O(12)	P(1)—O(12)—P(2)
(*a*)	83·6 (2)	126·0 (4)	133·5 (4)	108·3 (3)	107·2 (4)	128·7 (4)
	85·9 (2)	124·0 (4)	126·1 (4)	107·9 (4)	106·6 (4)	
(*b*)	82·1 (4)	126·2 (9)	134·9 (9)	109·2 (8)	107·6 (8)	129·6 (8)
	86·3 (4)	126·4 (9)	127·2 (9)	104·5 (8)	105·0 (8)	
(*c*)	78·8 (1)	127·8 (1)	126·7 (1)	104·8 (1)	107·7 (1)	123·1 (1)
	77·4 (1)	126·8 (1)	126·9 (1)	108·6 (1)	107·6 (1)	

References: (*a*) this work; (*b*) β-$CaNa_2P_2O_7 \cdot 4H_2O$ (Cheng, Nyburg, Adams & Pritzker, 1979); (*c*) $Ca_2P_2O_7.2H_2O$, triclinic; atoms renumbered (Mandel, 1975).

* O_T: terminal oxygen atom.

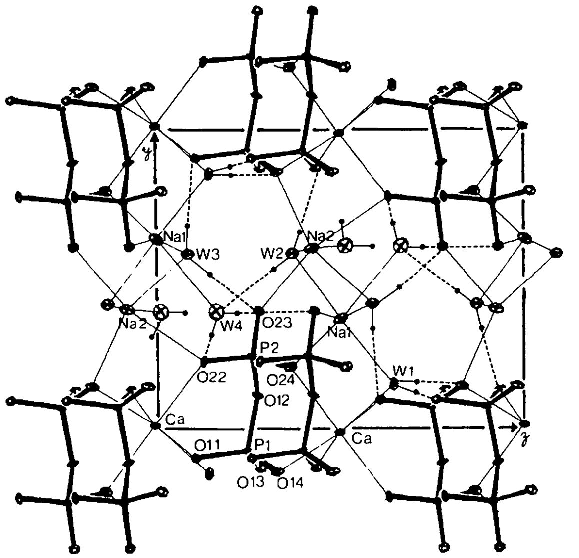

Fig. 1. Structure in x^* projection showing one set of possible H-atom positions (small black dots).

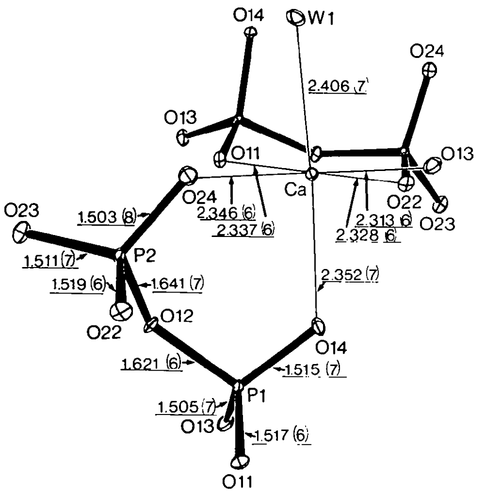

Fig. 2. Ca^{2+} coordination.

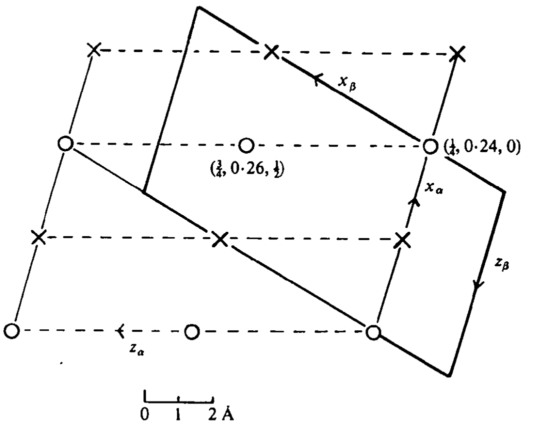

Fig. 3. Relation between α and β polymorphs. Broken lines are $Ca^{2+} \cdots P_2O_7^{4-} \cdots Ca^{2+}$ chains. Circles are Ca^{2+} ions common to both structures (numerical coordinates refer to the β cell). Crosses are Ca^{2+} ions at $y = \frac{1}{2}$ in the β structure only.

there are several ways of distributing the H atoms to satisfy the requirements of hydrogen bonding. (Possibly this is why no H peaks could be seen on the ΔF map.) One such scheme is shown in Fig. 1, indicating approximate H positions.

The structure is most simply described by reference to the $Ca^{2+} \cdots P_2O_7^{4-} \cdots Ca^{2+}$ chains along the z axis. These chains have Na^+ ions and water molecules coordinated between them. Both Na(1) and Na(2) are six-coordinate [three unidentate $P_2O_7^{4-}$ ions and three water molecules; Na—O distances range from

2·357–2·788 (8) Å]. The β polymorph also contains $Ca^{2+}\cdots P_2O_7^{4-}\cdots Ca^{2+}$ chains and this gives rise to a close connection between the two structures. In the α polymorph there is only one chain per cell but in the β polymorph there are two. The relation is shown in Fig. 3. The close connection in cell geometry (Fig. 3) should be noted: $a_\alpha = 5{\cdot}69$, $c_\beta = 5{\cdot}75$ Å; $[101]_\alpha = 10{\cdot}50$, $a_\beta = 10{\cdot}38$ Å; $2b_\alpha = 17{\cdot}17$, $b_\beta = 16{\cdot}89$ Å.

We thank Dr Mark Adams for his stimulating comments. We are grateful to the Canadian Arthritis Society, the Canadian Geriatrics Research Society, the Ontario Provincial Lottery Health Awards Program and the Natural Sciences and Engineering Research Council of Canada for financial support.

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