NATIONAL BUREAU OF STANDARDS REPORT

9921

Progress Report

on

THE CRYSTAL STRUCTURES OF GAYLUSSITE, $CaNa_2(CO_3)_2 \cdot 5H_2O$ AND PIRSSONITE, $CaNa_2(CO_3)_2 \cdot 2H_2O$

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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NBS PROJECT 311.05-11-3110561

June 30, 1968

NBS REPORT 9921

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by

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This investigation is part of the dental research program conducted by the National Bureau of Standards, in cooperation with the Council on Dental Research of the American Dental Association; the National Institute for Dental Research; the Dental Research Division of the U. S. Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

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The Crystal Structures of Gaylussite, $CaNa_2(CO_3)_2 \cdot 5H_2O$ and Pirssonite, $CaNa_2(CO_3)_2 \cdot 2H_2O$

Brian Dickens and Walter E. Brown

Abstract

The crystal structure of synthetic gaylussite has been determined from single-crystal x-ray diffraction data. The unit cell is $\underline{a}$ = 14.361 ± .002, $\underline{b}$ = 7.781 ± .004, $\underline{c}$ = 11.209 ± .002Å, β = 127.84 ± .01°, and the space group is C2/c. $R_w = (\Sigma(w||F_o| - |F_c||)^2)/\Sigma(w|F_o|)^2$ = 0.043, R = 0.054. The hydrogen atoms have been located. Two CO_3 anions are coordinated to a Ca ion and form a dihedral angle of 134.3°. Each CO_3 group is coordinated to four Na ions and four water molecules, but to only one Ca ion. Each Na is coordinated to four CO_3 groups and two water molecules. Two water molecules form hydrogen bonds to neighboring CO_3 anions. The remaining water forms hydrogen bonds with the oxygens of two other water molecules.

The crystal structure of synthetic pirssonite has also been determined from single-crystal x-ray diffraction data. The unit cell is $\underline{a}$ = 11.340 ± .004, $\underline{b}$ = 20.096 ± .005, $\underline{c}$ = 6.034 ± .002A and the space group is Fdd2. R_w = 0.029, R = 0.044. The hydrogen atoms have been located. As in gaylussite, two CO_3 anions are coordinated to a Ca ion but with a dihedral angle of 95.5°. In contrast to gaylussite, the CO_3 anions are also coordinated to a second Ca ion, as well as to four Na ions and two water molecules. Each Na ion is coordinated to four CO_3 anions and loosely to two water molecules. The water molecules complete the coordination of Ca ions and form hydrogen bonds with neighboring CO_3 anions.

INTRODUCTION

In our studies[1] of hydrated salts which have potential importance in biological mineralization, the crystal structures of synthetic gaylussite[2], $CaNa_2(CO_3)_2 \cdot 5H_2O$, and synthetic pirssonite[3], $CaNa_2(CO_3)_2 \cdot 2H_2O$, have been determined and are reported here. Work on both these structures was completed before that of Corazza and Sabelli[4] on pirssonite came to our attention.

Determination of the Structure of Gaylussite

Crystals of gaylussite were grown in beakers containing 100 ml water, 18 g Na_2CO_3, 10 g $CaCl_2$ and 800 ppm of sodium polyphosphate, combining the procedures of Bury and Redd[5] and Brooks, Clark and Thurston.[6] The initial solid phase was mostly spherulites, probably of $CaCO_3 \cdot H_2O$ or vaterite. On standing, these dissolved and good single crystals of gaylussite were formed.

A single crystal of gaylussite about 0.2 mm in cross-section (μ_{Mo} = 9 cm^{-1}) was sealed in a borate glass capillary to prevent slow dehydration. The cell dimensions* were refined from 25 2θ values observed on a diffractometer[7] to $\underline{a}$ = 14.361 ± .002, $\underline{b}$ = 7.781 ± .001, $\underline{c}$ = 11.209 ± .002 Å, β = 127.84 ± .01°, assuming λ(Mo $K\alpha_{1},\alpha_{2}$) = 0.71069 Å, for the cell with space group C2/c or Cc and z = 4. The most obvious cell is body centered, with axial ratios which correspond to those given in Dana[2]. The space groups C2/c and Cc were chosen using the convention adopted in the International Tables for Crystallography[8].

The intensities of reflections in a hemisphere of the reciprocal lattice were measured on a diffractometer[7] using Mo-Kα radiation, an 0.001 inch Nb filter, and the peak-height method. The peak-to-intensity curve was established from 48 suitable reflections, spread uniformly over the 2θ range,

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*The uncertainties quoted on cell dimensions are standard errors computed from least squares refinements of the cell dimensions to fit observed 2θ values.

which were measured both by peak heights and by scanning. The data were merged into 2988 unique reflections, of which 2632 were of observable intensity. Since serious errors in peak height measurements are usually caused by measuring the background too near an adjacent peak, by slight misalignment of the crystal, or by absorption, in all of which cases the observed $F_{hk\ell}$ would be too small, any supposedly genuine and equivalent values of $F_{hk\ell}$ which were not within 10 % of one another were not averaged. Instead, the larger of the two was taken as the observed $F_{hk\ell}$. The discrepancy value, $\Sigma||F_i|-|F_i'||/\Sigma|F_i|$, between reflections accepted as equivalent was 0.045, based on F's. (Although the anisotropy of the mosaic spread of the crystal affects the peak heights, in this case the peak height method provided data of sufficient accuracy.) No corrections for absorption were made.

The subsequent calculations were all performed using the crystallographic computing system (X-ray 63) assembled under the editorship of J. M. Stewart at the University of Maryland. The quasi-unitary structure factors[9] ($\langle|E^2|\rangle$ made equal to 1) indicate (see Table 1) that the space group is

TABLE 1

Quasi-Unitary Structure Factor Statistics for Gaylussite

	$\langle\|E\|\rangle$	$\langle\|E^2\|\rangle$	$\langle\|E^2-1\|\rangle$
All reflections	.816	1.000	.922
3-dimensional reflections only	.803	.957	.887
Theoretical, centric	.798	1.000	.968
Theoretical, acentric	.886	1.000	.736

		obs.	centric	acentric
Fraction of E's	> 1.0	.341	.317	.368
	2.0	.0366	.046	.018
	3.0	.0009	.003	.0001

Number of reflections 2988

Suggested overall temperature factor 1.28

centrosymmetric, C2/c, instead of non-centrosymmetric, Cc. This choice was subsequently verified by the structure determination. The atomic scattering factors used were taken from reference 10, except for those of hydrogen, which were taken from reference 11. The quantity $R_w = \Sigma(w||F_o|-|F_c||)^2$ was minimized in the full matrix least squares refinements using a weighting scheme based on the counting statistics.

The structure was solved from the sharpened Patterson function, calculated from the (E^2-1) coefficients, and from subsequent F_o Fourier syntheses. It was refined isotropically to $R_w = 0.079$ allowing the scale factor, the positional parameters and the thermal parameters to vary. The structure was then refined anisotropically to $R_w = 0.061$. The hydrogens were located from a difference synthesis. Inclusion of these hydrogens with fixed thermal parameters ($B_H = 1.0\text{Å}^2$) in the refinement decreased R_w to 0.043. The observed and calculated structure factors are given in Table 2.

TABLE 2

Observed and Calculated Structure Factors for Gaylussite

Columns are ℓ, $10F_o$, $10F_c$

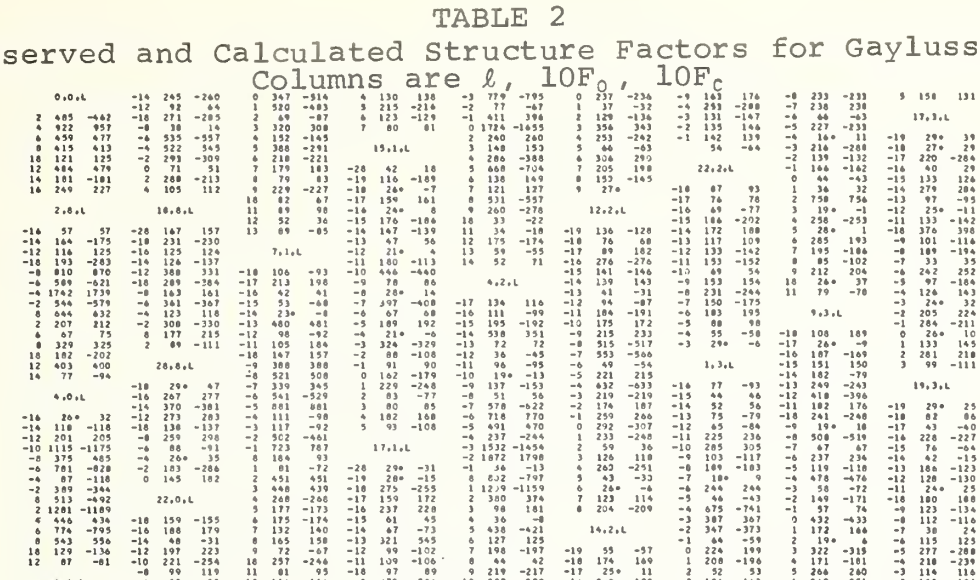


TABLE 2
(continued)

TABLE 2
(continued)

The large correlation coefficients are 0.25 between the scale and the Ca β_{11} anistropic temperature factor, 0.75 between the Ca β_{33} and β_{13} anisotropic temperature factors, 0.68 between the Na x and z parameters and 0.78 between the Na β_{33} and β_{13} thermal parameters. Most coefficients are, however, much less than 0.04.

The atomic parameters are given in Table 3. The hydrogen positions are those from the final least-squares refinement and are recognized as being only approximate.

Discussion of the Structure of Gaylussite

The calcium environment.--The immediate Ca environment is summarized in Table 4 and in Figure 1. Since the strongest electrostatic attraction in the crystal is between Ca^{2+} and CO_3^{2-}, it is not surprising that both CO_3^{2-} groups are coordinated (via O(2) and O(3)) to Ca, which lies on a two-fold axis, to form what may be considered to be an ion triplet, OCO_2-Ca-O_2CO. The coordination of Ca is completed by four water molecules, O(5), O(5'), O(6) and O(6'). The Ca-to-O distances are within the normal range. The strongest possible electrostatic repulsion in the structure, the Ca-Ca interaction, is minimized by the Ca ions being widely separated from one another (Ca-to-Ca>4.5 Å).

TABLE 3
Atomic Parameters of Gaylussite

Atom	x	y	z	B_{11}*	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	.0000	.1929(1)	.2500	.59(1)	1.27(2)	.86(2)	-.06(3)	.41(1)	-.16(3)
Na	.0881(1)	.1822(1)	-.0107(1)	1.56(3)	1.92(3)	1.67(3)	.01(5)	1.12(3)	.11(5)
C	.1853(2)	-.0286(2)	.3161(2)	.94(6)	1.18(6)	1.18(6)	.96(4)	.65(5)	.67(5)
O(1)	.2852(1)	-.0906(2)	.3633(2)	1.26(5)	2.88(6)	1.85(6)	.01(4)	1.13(5)	-.01(4)
O(2)	.1033(1)	.0031(2)	.1749(1)	1.07(4)	2.09(5)	.90(5)	.10(4)	.44(4)	.00(4)
O(3)	.1658(1)	.0095(2)	.4113(1)	.94(4)	1.97(5)	.99(5)		.67(4)	
O(4)	.0000	.6791(3)	.2500	1.84(8)	1.90(8)	2.22(9)		1.16(8)	
H(1)**	.05(2)	.60(3)	.27(3)	1.00	1.00	1.00			
O(5)	.0696(1)	.2935(2)	.5029(2)	1.44(5)	2.02(6)	1.50(5)	.13(5)	.83(5)	-.06(5)
H(2)	.10(2)	.21(3)	.55(3)	1.00	1.00	1.00			
H(3)	.11(2)	.38(3)	.54(3)	1.00	1.00	1.00			
O(6)	.1467(1)	.4048(2)	.3109(2)	1.12(5)	2.60(6)	1.27(5)	-.47(5)	.76(4)	-.22(5)
H(4)	.20(2)	.44(3)	.40(3)	1.00	1.00	1.00			
H(5)	.16(2)	.39(3)	.27(3)	1.00	1.00	1.00			

computed

*Figures in parentheses are/standard errors in last significant figures quoted and were obtained in the full matrix least squares refinements.
Average shift/error for last cycle = 0.23.
Units of thermal parameters are $Å^2$.

**All hydrogen thermal parameters were kept constant at B (isotropic) = 1.0 $Å^2$. The hydrogen positional parameters are only approximate.

TABLE 4

The Calcium Environment in Gaylussite

atoms	distance, Å
Ca,O(2)	2.573(2)*
Ca,O(3)	2.385(1)
Ca,O(5)	2.484(2)
Ca,O(6)	2.420(2)
Ca,O(4)	3.783(2)
Ca,O(4)	3.997(2)

*In all distances and angles quoted in this paper the values computed in parentheses are the standard errors in the last significant figures.

The carbonate group.--The CO_3 group is essentially planar with an average C-to-O distance of 1.288Å. Its dimensions and environment are summarized in Table 5 and Figure 2. Oxygen O(1) is bonded electrostatically to Na (2.314Å) and is hydrogen bonded to water oxygens O(5) (2.847Å) via H(3) (~2.0Å) and O(6) (2.667Å) via H(5) (~2.0Å). Oxygen O(2) is bonded electrostatically to Ca (2.573Å), Na (2.400Å), and Na (2.610Å) and is hydrogen bonded to O(5) (2.852Å) via H(2) (~2.1Å). Oxygen O(3) is electrostatically bonded to Ca (2.385Å) and Na (2.331Å) and is hydrogen bonded to O(6) (2.666Å) via H(4) (~1.8Å). The observed C-to-O bond distances correlate qualitatively with the oxygen environments. Oxygens O(2) and O(3), which are under strong anisotropic cationic attraction, have longer bond distances to the carbon than does O(1). Similarly, the O(2)-C-O(3) bond angle, 118.1°, is less than 120° because coordination with the Ca pulls these oxygens together.

The two CO_3 groups coordinated to Ca are also coordinated to two Na ions (Figure 1) which cause a dihedral angle of 134.3° between the planes of the two CO_3 groups instead of the expected 180°. This coordination is instrumental in making the O(2)-to-O(3) vector in one CO_3 group very nearly parallel to the O(2')-to-O(3') vector in the other CO_3 group.

TABLE 5

The Carbonate Anion and Environment in Gaylussite

Atoms	distance, Å
C,O(1)	1.280(3)
C,O(2)	1.291(2)
C,O(3)	1.293(3)
O(1),O(2)	2.247(2)
O(1),O(3)	2.229(3)
O(2),O(3)	2.216(2)
Coordinated atoms	**angle, deg**
O(1),C,O(2)	121.8(2)
O(1),C,O(3)	120.1(2)
O(2),C,O(3)	118.1(2)

O(1) Environment

Atoms	distance, Å
O(1),O(5)	2.847(2)
O(1),H(3)	2.05(2)
O(1),Na	2.341(2)
O(1),O(6)	2.667(3)
O(1),H(5)	2.02(4)

O(2) Environment

Atoms	distance, Å
O(2),Ca	2.573(2)
O(2),Na	2.400(2)
O(2),Na'	2.610(2)
O(2),O(5)	2.852(2)
O(2),O(6)	3.364(2)
O(2),O(4)	3.285(2)
O(2),H(2)	2.11(3)

TABLE 5
(continued)

O(3) Environment

Atoms	distance, Å
O(3),Ca	2.385(1)
O(3),O(5)	3.096(3)
O(3),O(4)	3.204(2)
O(3),Na	2.331(2)
O(3),O(6)	2.666(2)
O(3),H(4)	1.83(2)

The Ca ion is 0.69Å below the intersection of the planes of these CO_3 groups.

The Na environment.--The sodium ion is coordinated (Table 6 and Figure 3) approximately octahedrally by O(1), O(2), O(2'), O(3), all in different CO_3 groups, and by the O(4) and O(5) waters. The repulsion arising from the Ca-to-Na closest approach of 3.626Å is reduced by their sharing O(2) and O(3') (Figure 1). These atoms are in the two CO_3 groups bonded to the Ca. The next closest Ca-to-Na approach, 3.831Å, is stabilized by the intervening pair O(2) and O(5'). The Na-to-Na approaches are 3.903Å and 4.305Å, and the small stabilization required is provided by the intervening octahedral edges O(2)-O(5) and O(2)-O(2').

The water environments.--The water environments are summarized in Table 7 and Figure 4. The O(6) water is bonded to O(1) of one CO_3 group via a hydrogen bond H(5) to O(1), where H(5) to O(1) ~2.0Å, O(6) to O(1) = 2.667Å, and to O(3) of the next CO_3 group (generated by the c glide) by a hydrogen bond H(4) to O(3), where H(4) to O(3) ~1.8Å, O(6) to O(3) = 2.666Å. O(6) is in the coordination octahedron of the Ca

TABLE 6

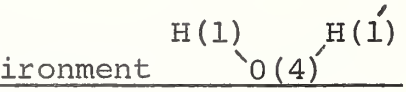
The Sodium Environment in Gaylussite

Atoms	distance, Å
Na,O(2')	2.400(2)
Na,O(2)	2.610(2)
Na,O(3')	2.331(2)
Na,O(4)	2.408(1)
Na,O(5)	2.475(2)
Na,O(1)	2.341(2)

TABLE 7

The Water Environments in Gaylussite

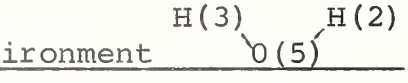
1) the O(4) water environment



Atoms	distance, Å
O(4),H(1)	0.82(3)
O(4),O(6)	2.774(2)
O(4),Na	2.408(1)
H(1),O(6)	1.96(3)
H(1),H(1)	1.14(4)

Coordinated atoms	angle, deg
H(1),O(4),H(1')	88.(3)
O(6),O(4),O(6')	79.37(8)
O(4),H(1),O(6)	174.(2)

2) the O(5) water environment

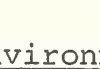


Atoms	distance, Å
O(5),H(2)	0.81(3)
O(5),H(3)	0.81(2)
O(5),Ca	2.484(2)
O(5),O(1)	2.847(2)
O(5),O(2)	2.852(2)
O(5),Na	2.475(2)
H(2),H(3)	1.35(4)
H(2),O(2)	2.11(3)
H(3),O(1)	2.05(2)

Coordinated atoms	angle, deg
H(2),O(5),H(3)	113.(2)
O(1),O(5),O(2)	122.36(6)
O(5),H(2),O(2)	152.(4)
O(5),H(3),O(1)	172.(4)

TABLE 7
(continued)

3) the O(6) water environment



Atoms	distance, Å
O(6),H(4)	0.84(2)
O(6),H(5)	0.67(4)
O(6),Ca	2.420(2)
O(6),O(4)	2.774(2)
O(6),H(1)	1.96(3)
O(6),O(3)	2.666(2)
O(6),O(1)	2.667(3)
H(4),H(5)	1.28(4)
H(4),O(3)	1.83(2)
H(5),O(1)	2.02(4)
Coordinated atoms	**angle, deg**
H(4),O(6),H(5)	115.(3)
O(3),O(6),O(1)	106.87(8)
O(6),H(4),O(3)	171.(4)
O(6),H(5),O(1)	162.(3)

ion and is the oxygen acceptor of a hydrogen bond from the water molecule O(4) on the two-fold axis. The distances in these hydrogen bonds are H(1)-to-O(6) ~2.0Å, O(4)-to-O(6) = 2.774Å. Besides linking two O(6) waters to each other, the O(4) water serves to separate two Na ions (Figures 1 and 4). The O(5) water connects O(1) in one CO_3 group to O(2) in the CO_3 group related by a two-fold screw axis. The hydrogen bonds thus used are O(5)—H(3).....O(1), where H(3)-to-O(1) ~2.0Å, O(5)-to-O(1) = 2.847Å, and O(5)-H(2).....O(2), where H(2)-to-O(2) ~2.1Å and O(5)-to-O(2) = 2.852Å. Also O(5) is in an edge which is shared between neighboring Na coordination octahedra.

Determination of the Crystal Structure of Pirssonite

We determined the crystal structure of synthetic pirssonite, $CaNa_2(CO_3)_2 \cdot 2H_2O$, before the recent work of Corazza and Sabelli[4] came to our attention. There are enough differences in the two procedures to warrant a brief description of our determination. They used a mineral specimen ground to a sphere of 0.616 mm diameter, measured 481 reflections of observable intensity from integrated films with a microdensitometer, corrected for absorption, and refined using block-diagonal least squares.

In the present work, good crystals of synthetic pirssonite were grown at 50°C from a solution of 27% by weight of Na_2CO_3 and 5% NaOH in water in contact with powdered calcite.[5] A small crystal, maximum dimension 0.20 mm (μ_{Mo} = 10.6 cm^{-1}) was selected. The cell dimensions* were determined to be $\underline{a}$ = 11.340 ± .004, $\underline{b}$ = 20.096 ± .005 and $\underline{c}$ = 6.034 ± .002 Å from 2θ values of axial reflections observed on a diffractometer. Evans[12] reported the dimensions $\underline{a}$ = 11.32 ± .02, $\underline{b}$ = 20.06 ± .02 and $\underline{c}$ = 6.00 ± .02Å, and that the space group is Fdd2. Our values, which were calculated using the weighted mean value for $M_o K\alpha_1$, α_2 radiation (λ = .71069 Å) are systematically larger than these reported by Evans.

Over 2200 reflections from two octants of the reciprocal lattice were measured on a diffractometer[7] with the peak height procedure used for gaylussite. These data were merged into a unique set of 1141 reflections, 1079 of which were of observable intensity. The R value between reflections accepted as equivalent was 0.027 based on F's. The quasi-unitary structure-factor statistics are given in Table 8 and confirm that the space group is acentric. Weights based on the counting statistics were used in the full-matrix least-squares refinements. The atomic scattering

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*The uncertainties quoted on cell dimensions are estimates based on experience with the technique used for measurement and in the authors' opinion may be treated as standard errors.

TABLE 8

Quasi-Unitary Structure-Factor Statistics for Pirssonite

	$\langle \lvert E \rvert \rangle$	$\langle \lvert E^2 \rvert \rangle$	$\langle \lvert E^2-1 \rvert \rangle$
all reflections	.879	1.000	.731
3-dimensional reflections only	.875	.968	.694
Theoretical centric	.798	1.000	.968
Theoretical acentric	.886	1.000	.736

		obs.	centric	acentric
Fraction of E's >	1.0	.394	.317	.368
	2.0	.014	.046	.018
	3.0	.0002	.003	.0001

Number of reflections 1140

Suggested overall temperature factor 0.65

factors used for gaylussite were also used for pirssonite. No corrections for absorption were made.

All atoms other than the water molecule were found from the sharpened Patterson map. The oxygen of the water molecule was found from an F_o Fourier synthesis. The structure was refined isotropically to $R_w = 0.059$ and then anisotropically to $R_w = 0.042$. These hydrogens were found from a difference synthesis and were included with fixed thermal parameters ($B_H = 1.0\text{Å}^2$). The structure was then refined anisotropically to $R_w = 0.029$, $R = 0.044$. The largest correlation coefficients are about 0.2 and are between the scale factor and some of the anisotropic temperature factors, between some of the anisotropic factors themselves, and between the x and y parameters of most atoms. Most of the remaining coefficients are less than 0.05. The observed and calculated structure factors are given in Table 9.

TABLE 9

Observed and Calculated Structure Factors for Pirssonite

Columns are ℓ, $10F_o$, $10F_c$ and phase in millicyles

TABLE 9
(continued)

		14,K,0			4	24	27	372	7	74	73	71	5	97	97	53	22	16*	21	0			16,K,6													
					6	101	103	58	9	98	101	278	7	69	65	849																				
16	19	11	500		3	30	18	525	11	68	70	854	9	44	37	362			10,K,2			2	84	84	29	11	77	73	944	2	33	36	487		19,K,3	
18	159	141	0	10	49	63	65	13	78	78	84	11	40	34	933						4	15*	13	575	13	77	74	44	4	106	109	970			
20	13*	2	300	12	52	50	997	15	49	43	980	13	89	81	129	2	86	89	981		8	45	44	12	15	39	38	843	8	23	24	108	1	59	56	1
22	81	79	0	14	88	90	51	17	80	72	243	15	70	70	778	4	23	19	470		8	16*	3	417	17	53	44	302	8	79	79	93	3	81	71	981
24	15*	14	500	16	43	39	493	19	38	29	797	17	16*	19	21	6	74	75	35		10	135	127	981					10	23	23	679	5	83	35	734
26	90	79	0	18	96	81	15	21	80	74	52					8	32	30	572								17,K,3		12	79	82	0	7	63	55	304
				20	61	56	978	23	51	46	821			15,K,7		10	139	139	972				17,K,1						14	47	42	133	9	53	47	978
		14,K,2		22	92	84	27									12	26	16	861							1	42	39	942	16	76	71	34			
										15,K,3			1	54	55	890	14	33	35	957		1	54	49	834	3	77	72	100						20,K,0	
0	127	138	993			14,K,8							3	70	69	207	16	12*	11	498		3	82	83	94	3	130	116	871			18,K,6				
2	60	65	777						1	26	24	912	5	63	56	978	18	109	98	39		5	96	92	831	7	39	43	223					0	50	48	0
4	52	56	725	0	156	157	953	3	128	121	139	7	45	37	88	20	38	30	757		7	26	28	112	9	29	28	753	2	81	74	948	2	33	23	500
6	31	33	143	2	35	34	177	5	162	166	878										9	66	68	874	11	88	86	93	4	13*	20	892	4	83	84	0
8	157	153	9	4	42	38	49	7	79	78	104			16,K,0				16,K,4			11	87	83	69												
10	17	11	493	6	45	40	819	9	21	15	715										13	44	43	754												
12	79	82	866	8	173	164	950	11	70	68	993	0	219	228	0	0	63	59	8		15	75	76	143												
14	33	32	592	10	26	25	467	13	124	122	806	2	70	71	500	2	13*	8	208		17	46	48	880												
16	46	83	37	12	84	77	38	15	98	95	152	4	20	0	0	4	96	100	984		19	44	40	70												
18	24	22	316	14	27	17	137	17	54	61	942	6	96	96	0	6	32	29	0																	
20	60	60	904	16	98	94	938	19	34	37	66	8	124	128	0	8	52	50	24				17,K,3						6	63	36	953	6	13*	0	0
22	13*	19	911					21	84	78	910	10	33	30	500	10	31	25	391								18,K,0		8	16*	9	580	8	83	80	0
24	58	54	3			15,K,1						12	55	64	0	12	61	62	37		1	13*	3	733					10	121	111	958				
										15,K,5		14	13*	14	0	14	14*	10	180		3	84	79	952	2	39	42	0						20,K,2	
		14,K,4			1	45	48	220				16	91	85	0	16	86	77	979		5	117	118	104	4	30	29	300			19,K,1				
					3	90	88	824	1	13*	14	163	18	14*	3	0	18	32	28	380		7	24	20	659	6	40	40	0					2	67	62	12
2	115	113	45	5	77	78	104	21	61	58	783	20	100	98	0						9	47	43	410	8	39	54	0	1	31	37	157	4	15*	11	711
																									10	101	93	0	3	73	71	896				
																									12	72	73	500	5	71	71	93				
																									14	13*	10	0	7	30	54	768				
																									16	23	13	0	9	43	42	80				
																													11	72	66	901				
																							18,K,2						13	30	34	42				
																					0	117	119	90												

The atomic parameters obtained by us, as well as those of Corazza and Sabelli,[4] are given in Table 10. The agreement between the two sets of parameters is excellent. All positional parameters for atoms other than hydrogens are within 2σ when our estimated standard errors are used; four of the 18 parameters differ by more than 2σ when the estimates of Corazza and Sabelli[4] are used. Their estimates of errors, which are about 60% as large as ours, were derived from the block-diagonal least-squares approximation using only 481 observed reflections and are probably too small. The placement of the hydrogen atoms from our refinements is recognized as being only approximate. Corazza and Sabelli apparently assumed that the O(4)-H(1).....O(1) and O(4)-H(2) .....O(1') hydrogen bonds are linear in placing the hydrogen atoms. This is reasonable since the O(1)-O(4)-O(1') angle is 108.7 ± .4°.

TABLE 10

Atomic Parameters of Pirrsonite

Atom D+B*	Atom C+S*	x	y	z	B_{11}**	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca		.0000	.0000	.0000	.73(8)	.63(8)	.50(8)	.00(1)	-	-
	Ca	.0000	.0000	.0000	.52(2)					
Na		.5653(4)	.1118(3)	-.0073(12)	1.09(16)	2.89(23)	.82(16)	.00(2)	.10(19)	.00(2)
	Na	.5653(3)	.1124(1)	-.0073(7)	1.51(4)					
C		.0841(8)	.1355(5)	-.0072(24)	.84(33)	1.05(36)	.55(30)	.00(2)	-.41(36)	.00(4)
	C	.0834(5)	.1362(2)	-.0090(13)	.63(1)					
O(1)		.1169(7)	.1975(4)	-.0121(18)	1.76(29)	.81(26)	1.24(31)	-.04(2)	-.43(34)	.02(3)
	O(3)	.1171(4)	.1982(2)	-.0119(10)	.98(6)					
O(2)		.0052(6)	.1161(4)	.1291(15)	.87(25)	1.45(29)	.73(27)	-.01(2)	.23(26)	.00(3)
	O(1)	.0052(4)	.1161(2)	.1294(10)	.94(6)					
O(3)		.1297(6)	.0935(4)	-.1420(15)	1.08(27)	1.29(27)	1.05(33)	.01(2)	.30(28)	-.02(3)
	O(2)	.1291(4)	.0934(2)	-.1419(9)	1.05(7)					
O(4)		.6093(7)	.2432(4)	.0645(18)	1.26(28)	1.99(34)	1.62(36)	.06(2)	.63(29)	.07(3)
	O(4)	.6088(5)	.2437(2)	.0625(10)	1.39(7)					
H(1)***		.56(1)	.27(1)	.07(3)	1.0	1.0	1.0	-	-	-
	H(2)	.527	.265	.034	5.00					
H(2)		.62(1)	.21(1)	.20(3)	1.0	1.0	1.0	-	-	-
	H(1)	.611	.227	.220	5.00					

*D+B, this work; C+S Corazza and Sabelli[4]

**Values of B given by Corazza and Sabelli

***All hydrogen thermal parameters were kept constant at B (isotropic) = 1.0A^2. The hydrogen parameters are only approximate. Average shift/error for last cycle = .22.

Discussion of the Structure of Pirssonite

The calcium environment--As in gaylussite and $CaCO_3 \cdot 6H_2O$,[13] the Ca ions lie on two-fold axes. Their immediate environment in pirssonite is summarized in Table 11 and Figure 5. In these tables we have numbered the atoms in the CO_3 group to correspond to gaylussite. The correspondence between our numbering scheme and that of Corazza and Sabelli is shown in Table 10. The strong electrostatic attraction between Ca^{2+} and CO_3^{2-} forces the formation of OCO_2-Ca-O_2CO ion triplets as in gaylussite, but, since there are only two water molecules present, further coordination of CO_3^{2-} groups to neighboring triplets is necessary to complete the Ca environment. This is a step towards the coordination in calcite and aragonite where each oxygen in a CO_3 group is coordinated to two/different and three respectively Ca ions/and the coordination of Ca is octahedral. In calcite and aragonite, no CO_3 group has two oxygens bonded to the same Ca. In gaylussite and pirssonite, however, the Ca coordination comprises two CO_3 edges and four other oxygens. In pirssonite only two of the latter are water molecules; the other two are CO_3 apexes (Figure 5). The two CO_3 groups coordinated to Ca by their

TABLE 11

Ca Environment in Pirssonite

Atoms	distance, Å
Ca,O(1)	2.428(9)
Ca,O(2)	2.461(7)
Ca,O(3)	2.536(7)
Ca,O(4)	2.483(10)

edges are at a dihedral angle of 95.5° to one another, and have twisted around to allow the close approach to Ca of the apexes of the other CO_3 groups. The Ca lies 0.1Å away from the intersection of the planes of the CO_3 groups coordinated edgewise.

The carbonate group.--The CO_3 group is planar and trigonal within experimental error with an average C-to-O distance of 1.286Å. Its dimensions and environment are summarized in Figure 6 and Table 12. Oxygen O(1) is bonded electrostatically to Ca (2.428Å) and forms two hydrogen bonds, O(1)-to-H(1) ~2.2Å, O(1)-to-O(4) = 2.716Å, and O(1)-to-H(2) ~1.8Å, O(1)-to-O(4) = 2.865Å, with neighboring water molecules. Oxygen O(1) is too far from Na (2.945Å) for Na to be its primary coordination. Oxygen O(2) may form a very weak hydrogen bond with H(1) (2.4Å) but its primary coordination is electrostatically to Ca (2.461Å) and to the 'chain' of Na ions (2.299Å, 2.302Å) formed above it by the d glide (Figure 7). Oxygen O(3) is not hydrogen bonded but is electrostatically bonded to Ca (2.536Å) and to a 'chain' of Na ions (2.351, 2.392Å) formed below it by the d glide. The C-to-O(2) and C-to-O(3) distances are shorter (1.28Å) and C-to-O(1)

TABLE 12

Carbonate Group Dimensions and Environment in Pirssonite

Atoms	distance, Å
C-O(1)	1.300(12)
C-O(2)	1.276(14)
C-O(3)	1.281(14)
Coordinated atoms	**angle, deg**
O(1),O(2)	120.5(1.1)
O(1),O(3)	120.1(1.1)
O(2),O(3)	119.4(.9)

O(1) Environment

Atoms	distance, Å
O(1),Ca	2.428(9)
O(1),O(4)	2.716(15)
O(1),H(2)	1.8(2)
O(1),O(4')	2.865(11)
O(1),H(1)	2.2(1)
O(1),Na	2.945(10)

O(2) Environment

Atoms	distance, Å
O(2),Ca	2.461(7)
O(2),H(1)	2.4(1)
O(2),O(4)	3.118(11)
O(2),Na	2.299(12)
O(2),Na'	2.302(9)

TABLE 12
(continued)

O(3) Environment

Atoms	distance, Å
O(3),Ca	2.536(7)
O(3),Na	2.351(12)
O(3),Na'	2.392(9)
O(3),O(1')*	3.023(10)
O(3),O(1")**	3.177(10)

*both coordinated to same Ca

**separated by d glide

(1.30Å), the reverse of that in gaylussite, and the O(2)-C-O(3) angle is essentially 120°. Presumably this, if a real difference, is due to the moderating influence of the coordinated 'chain' of Na ions, producing forces at right angles to those produced by the Ca ion, and to the fact that O(1) is coordinated to a Ca ion at a Ca-to-O distance slightly less than those of O(2) and O(3).

The Na environment.--The Na ion is coordinated approximately octahedrally. Its coordination is summarized in Table 13 and Figure 7. The repulsion associated with the Na-Na" and Na-Na' closest approaches of 3.255Å is reduced by the intervening 'octahedral' edges O(2')-O(4) and O(2)-O(3'), which are the most closely coordinated oxygens of the Na octahedron. Na, Na' and Na" are all related by the d glide. The water molecules, which complete the coordination of Na, are primarily coordinated to Ca.

The low charges of the Na and the atoms in the water molecule, together with the $\frac{1}{r}$ dependence of electrostatic energy, allow the water molecule to coordinate to Na with the large Na-to-O distance of 2.722Å, where, other things being equal, 2.3Å is expected.

TABLE 13

The Na Environment in Pirssonite

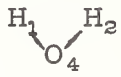
Atoms	distance, Å
Na,O(3)	2.351(12)
Na,O(2)	2.299(12)
Na,O(2')	2.302(9)
Na,O(3')	2.392(9)
Na,O(4)	2.722(10)
Na,O(4')	2.751(10)
Na,Na'	3.255(8)
Na,Na"	3.255(8)

The water environment.--The geometry of the unique water molecule and its environment are summarized in Table 14. Through its two hydrogens, the water molecule links two CO_3 groups together (Figure 6) and is also coordinated electrostatically (2.483Å) to Ca. The water molecule is also coordinated to two Na ions (2.722Å, 2.751Å), and reduces their mutual repulsion. It appears in the coordination of Na twice (Figure 7). In forming hydrogen bonds in the pirssonite structure, the hydrogens of the water define a plane which is approximately perpendicular to the configuration Na-O(4)-Na (angle = 164°), using the two Na's mentioned above.

Acknowledgement.--Collection of the diffractometer data was made possible with the advice and help of F. A. Mauer and the cooperation of E. C. Prince in using the SDS 921 computer. We acknowledge the extensive cooperation of J. M. Stewart in using the x-ray 63 system of crystallographic computing programs.

TABLE 14

The Water Environment in Pirssonite



Atoms	distance, Å
O(4),H(1)	.8(1)
O(4),H(2)	1.0(2)
H(1),H(2)	1.5(2)
O(4),O(1)	2.716(15)
O(4),O(1')	2.865(11)
O(4),Ca	2.483(10)
O(4),Na	2.722(10)
O(4),Na'	2.751(10)

Coordinated atoms	angle, deg
H(1),O(4),H(2)	118.(15)
O(1),O(4),O(1)	108.7(4)
O(4),H(1),O(1')	147.(13)
O(4),H(2),O(1)	153.(11)

References

1. W. E. Brown and B. Dickens, submitted to Science.

2. C. Palache, H. Berman and C. Frondel, Dana's System of Mineralogy, 7th ed., Vol. II, p. 234, (1951).

3. Reference 2, p. 232

4. E. Corazza and C. Sabelli, Acta Cryst., 23, 763 (1967).

5. C. R. Bury and R. Redd, J. Chem. Soc., 1160 (1933).

6. R. Brooks, L. M. Clark and E. F. Thurston, Phil. Trans. Roy. Soc., A243, 145 (1951).

7. F. A. Mauer and A. L. Koenig, paper #10, Summer meeting of American Crystallographic Association, August 1967, University of Minnesota, Minneapolis, Minnesota.

8. International Tables for Crystallography, The Kynoch Press (1962).

9. See C. Dickinson, J. M. Stewart and J. R. Holden, Acta, Cryst., 21, 663 (1966) for the method used in estimating the quasi-normalized structure factors.

10. Reference 8, Vol. III, p. 202.

11. R. McWeeney, Acta Cryst., 4, 513 (1951).

12. H. T. Evans, Amer. Min., 33, 261 (1948).

13. B. Dickens and W. E. Brown, in preparation.

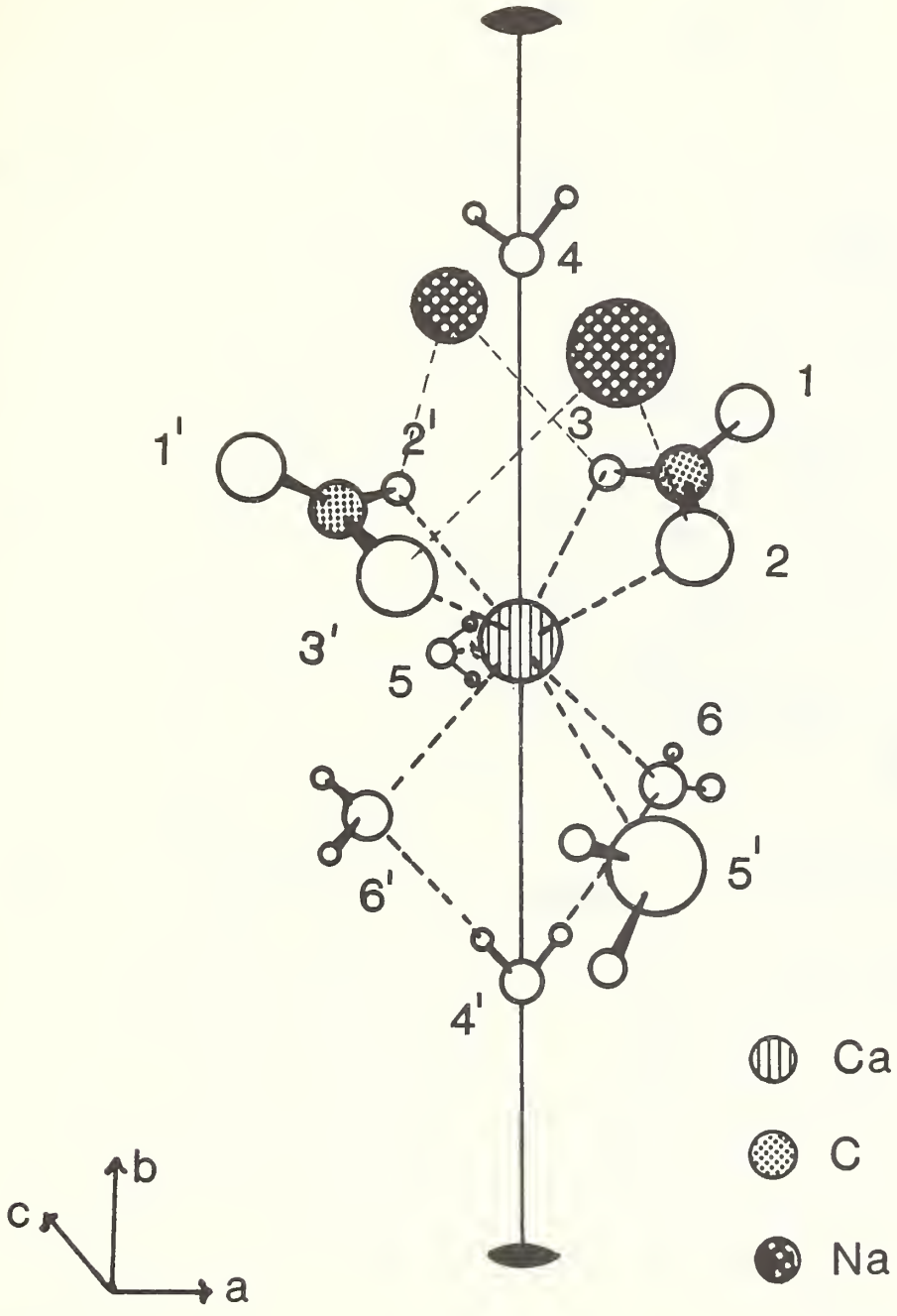
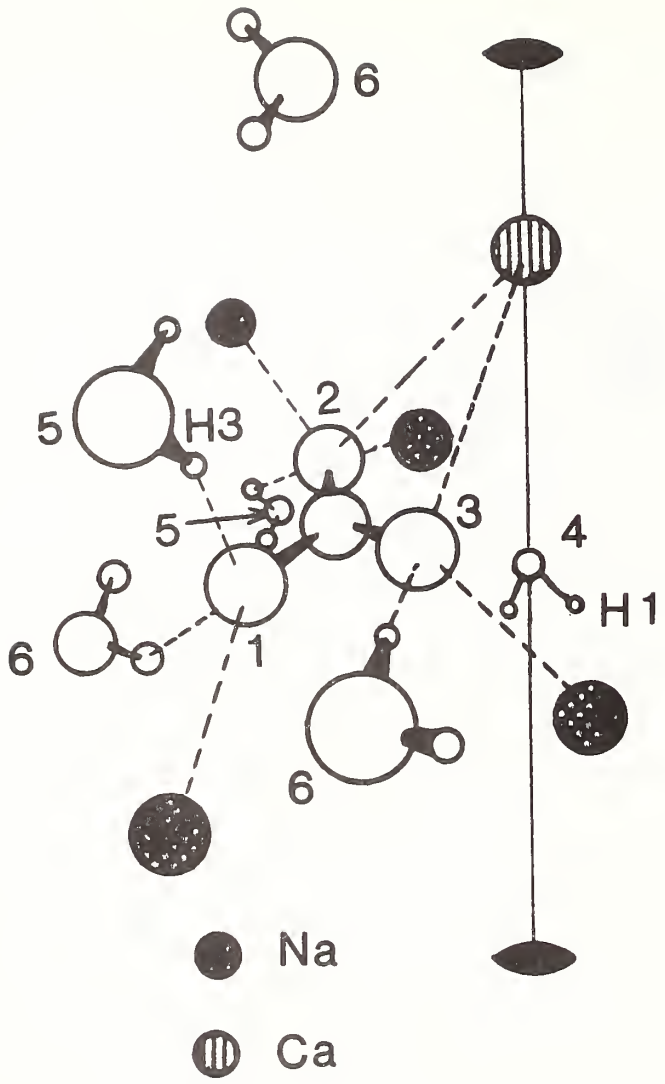


Fig. 1. The calcium ion environment in gaylussite. Primed atoms are related to unprimed atoms by the two-fold axis.



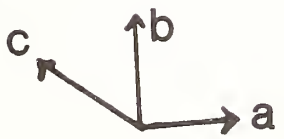


Fig. 2. The carbonate anion environment in gaylussite.

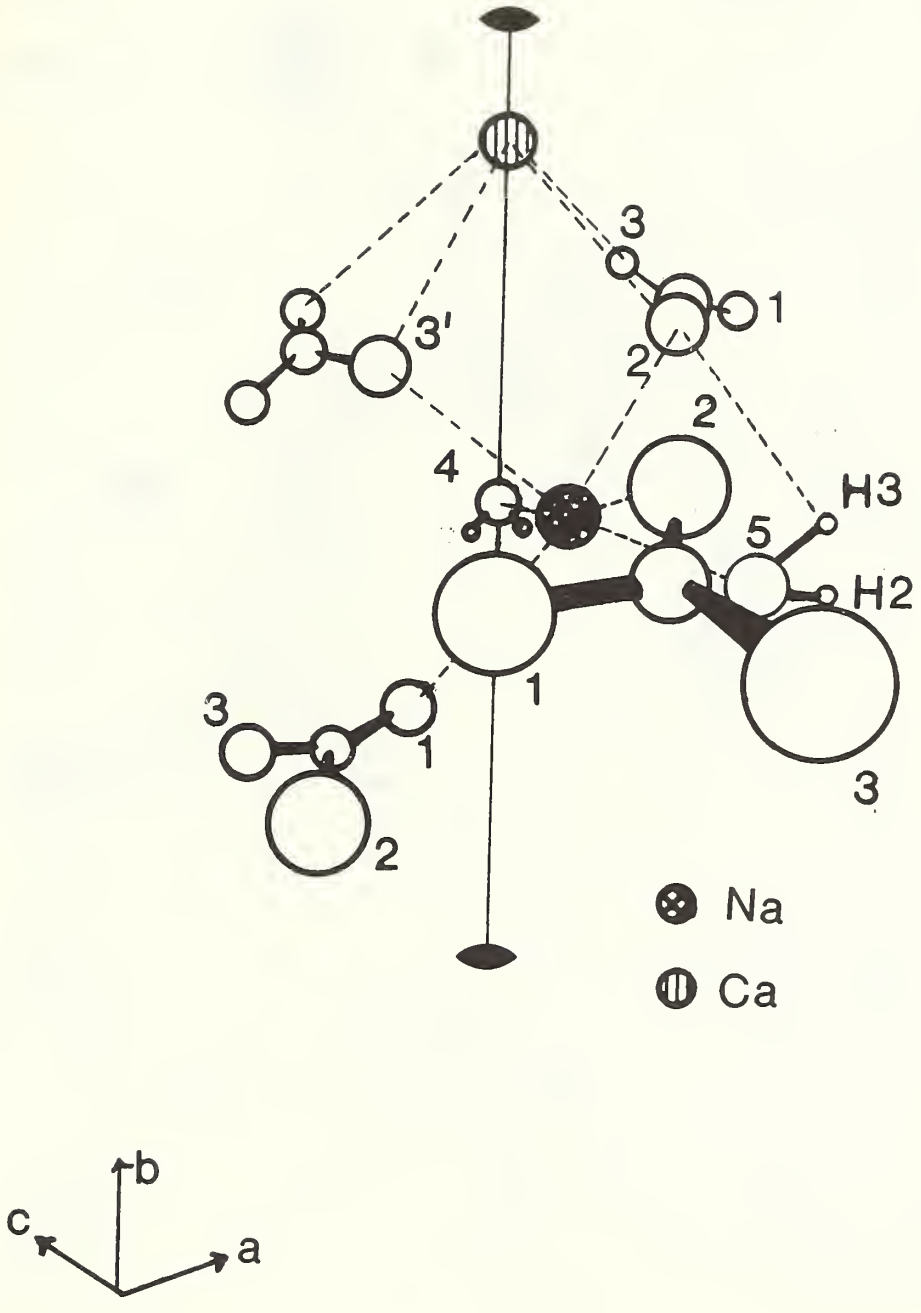


Fig. 3. The sodium ion environment in gaylussite.

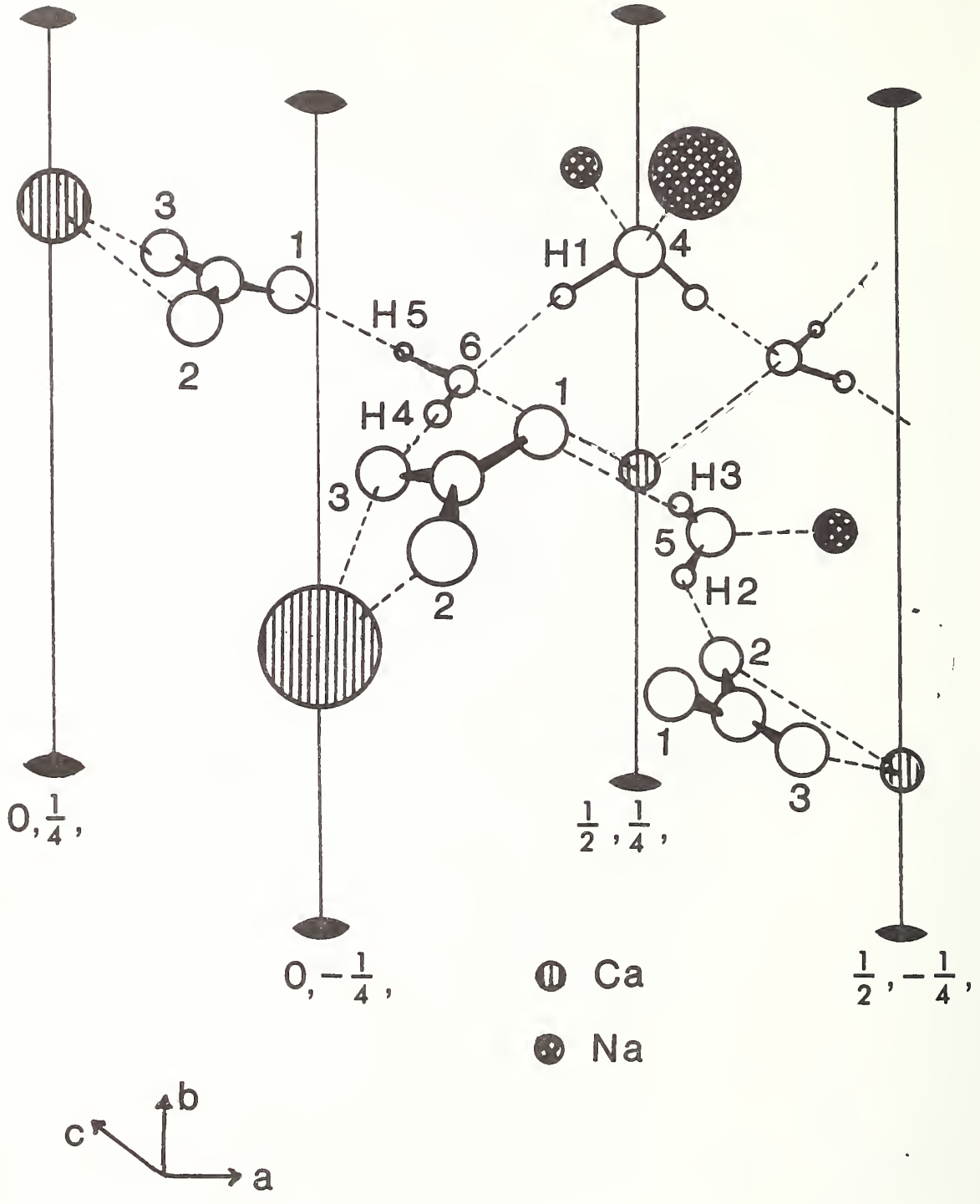


Fig. 4. The water environments and hydrogen bonding in gaylussite.

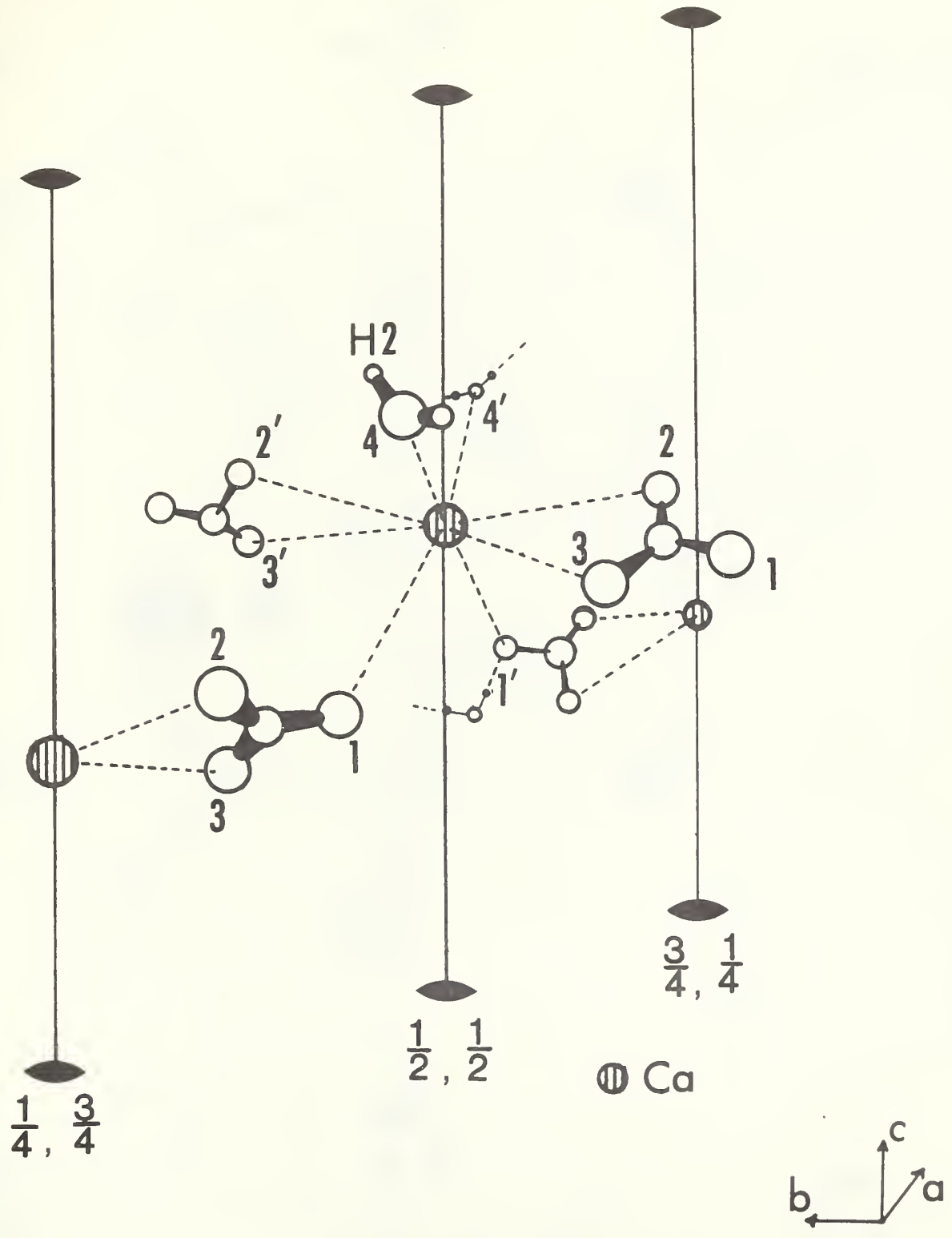


Fig. 5. The calcium ion environment in pirssonite.

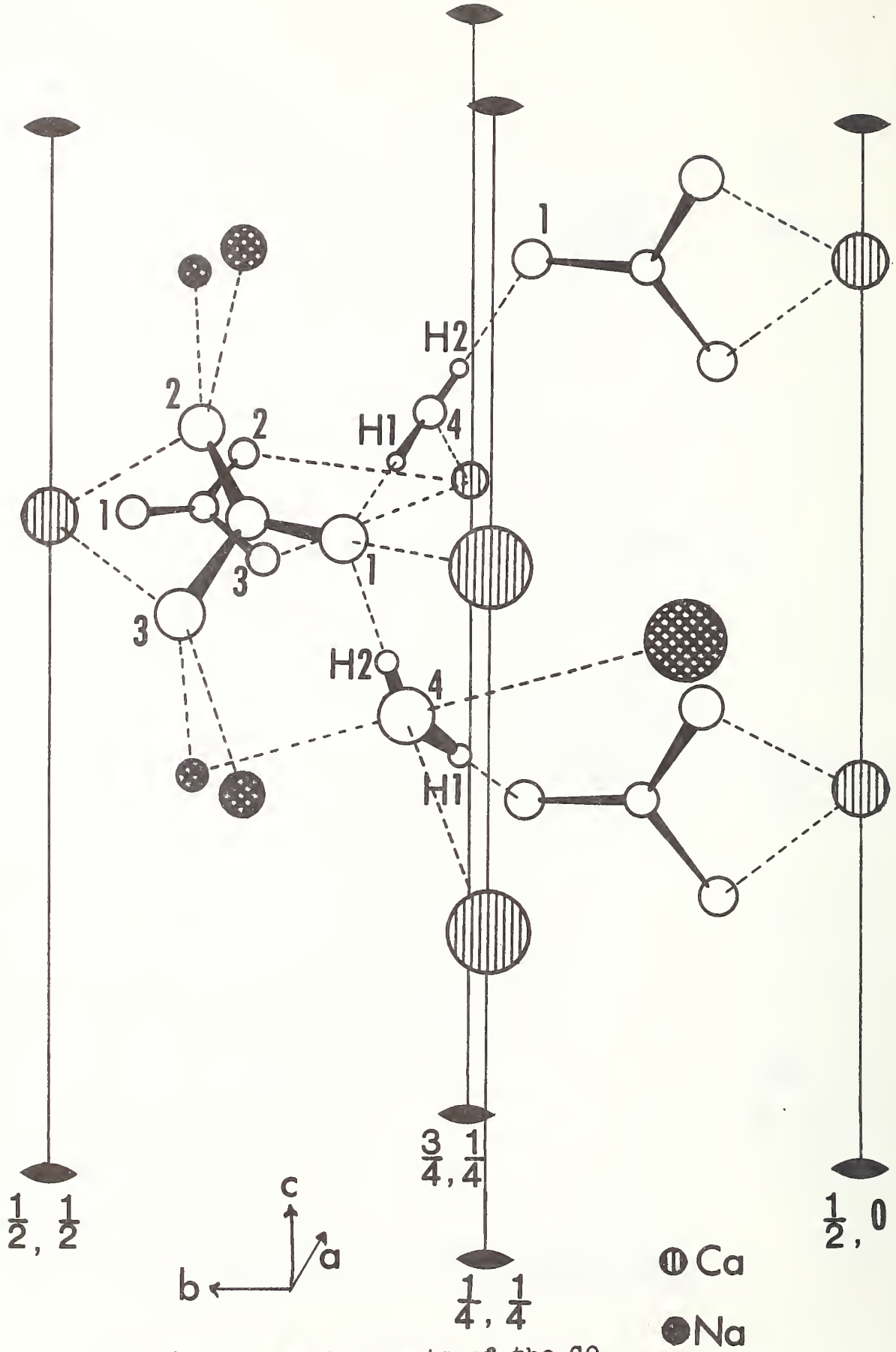


Fig. 6. The environments of the CO_3 anion and water molecule in pirssonite.

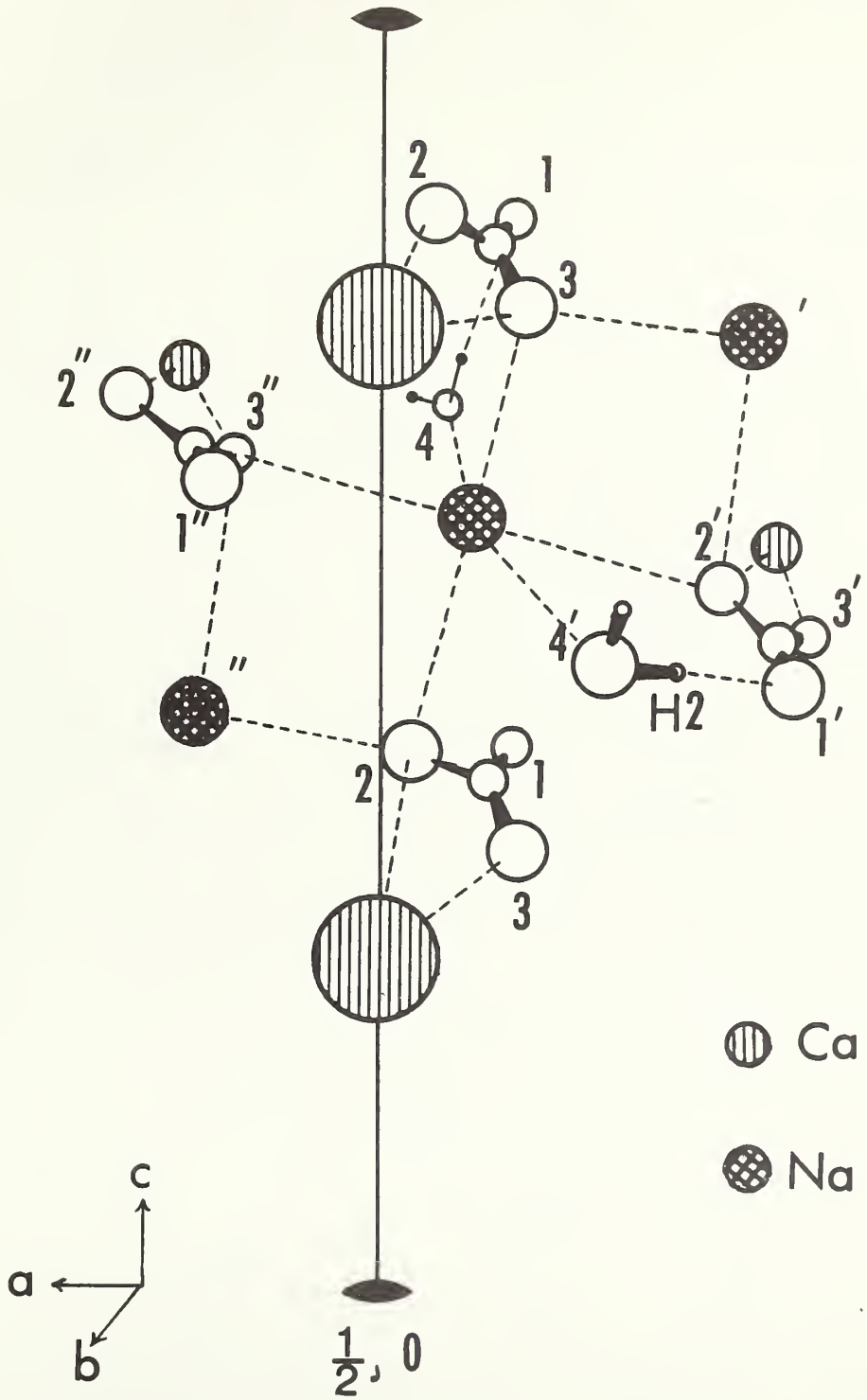


Fig. 7. The sodium ion environment in pirssonite.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