

# NATIONAL BUREAU OF STANDARDS REPORT

9921

Progress Report

on

THE CRYSTAL STRUCTURES OF GAYLUSSITE,  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$   
AND PIRSSONITE,  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$



U.S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS

## THE NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards<sup>1</sup> provides measurement and technical information services essential to the efficiency and effectiveness of the work of the Nation's scientists and engineers. The Bureau serves also as a focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To accomplish this mission, the Bureau is organized into three institutes covering broad program areas of research and services:

**THE INSTITUTE FOR BASIC STANDARDS . . .** provides the central basis within the United States for a complete and consistent system of physical measurements, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. This Institute comprises a series of divisions, each serving a classical subject matter area:

—Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic Physics—Physical Chemistry—Radiation Physics—Laboratory Astrophysics<sup>2</sup>—Radio Standards Laboratory,<sup>2</sup> which includes Radio Standards Physics and Radio Standards Engineering—Office of Standard Reference Data.

**THE INSTITUTE FOR MATERIALS RESEARCH . . .** conducts materials research and provides associated materials services including mainly reference materials and data on the properties of materials. Beyond its direct interest to the Nation's scientists and engineers, this Institute yields services which are essential to the advancement of technology in industry and commerce. This Institute is organized primarily by technical fields:

—Analytical Chemistry—Metallurgy—Reactor Radiations—Polymers—Inorganic Materials—Cryogenics<sup>2</sup>—Office of Standard Reference Materials.

**THE INSTITUTE FOR APPLIED TECHNOLOGY . . .** provides technical services to promote the use of available technology and to facilitate technological innovation in industry and government. The principal elements of this Institute are:

—Building Research—Electronic Instrumentation—Technical Analysis—Center for Computer Sciences and Technology—Textile and Apparel Technology Center—Office of Weights and Measures—Office of Engineering Standards Services—Office of Invention and Innovation—Office of Vehicle Systems Research—Clearinghouse for Federal Scientific and Technical Information<sup>3</sup>—Materials Evaluation Laboratory—NBS/GSA Testing Laboratory.

---

<sup>1</sup> Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C., 20234.

<sup>2</sup> Located at Boulder, Colorado, 80302.

<sup>3</sup> Located at 5285 Port Royal Road, Springfield, Virginia 22151.

# NATIONAL BUREAU OF STANDARDS REPORT

## NBS PROJECT

311.05-11-3110561

June 30, 1968

## NBS REPORT

9921

### Progress Report on

## THE CRYSTAL STRUCTURES OF GAYLUSSITE, $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ AND PIRSSONITE, $\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$

by

Brian Dickens\* and Walter E. Brown +

\* Research Chemist, Dental Research Section, National Bureau of Standards, Washington, D. C. 20234.

+ Director, Research Associate Program of the American Dental Association, Dental Research Section, National Bureau of Standards, Washington, D. C. 20234

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.

### IMPORTANT NOTICE

NATIONAL BUREAU OF STANDARDS  
for use within the Government. I  
and review. For this reason, the  
whole or in part, is not authorized  
Bureau of Standards, Washington  
the Report has been specifically p

Approved for public release by the  
Director of the National Institute of  
Standards and Technology (NIST)  
on October 9, 2015

s accounting documents intended  
subjected to additional evaluation  
listing of this Report, either in  
Office of the Director, National  
the Government agency for which  
pies for its own use.



U.S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS



The Crystal Structures of Gaylussite,  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$   
and Pirssonite,  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$

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  $a = 14.361 \pm .002$ ,  $b = 7.781 \pm .004$ ,  $c = 11.209 \pm .002\text{\AA}$ ,  $\beta = 127.84 \pm .01^\circ$ , and the space group is  $C2/c$ .  $R_w = (\sum (w|F_O| - |F_C|)^2) / \sum (w|F_O|)^2 = 0.043$ ,  $R = 0.054$ . The hydrogen atoms have been located. Two  $\text{CO}_3$  anions are coordinated to a Ca ion and form a dihedral angle of  $134.3^\circ$ . Each  $\text{CO}_3$  group is coordinated to four Na ions and four water molecules, but to only one Ca ion. Each Na is coordinated to four  $\text{CO}_3$  groups and two water molecules. Two water molecules form hydrogen bonds to neighboring  $\text{CO}_3$  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  $a = 11.340 \pm .004$ ,  $b = 20.096 \pm .005$ ,  $c = 6.034 \pm .002\text{\AA}$  and the space group is  $Fdd2$ .  $R_w = 0.029$ ,  $R = 0.044$ . The hydrogen atoms have been located. As in gaylussite, two  $\text{CO}_3$  anions are coordinated to a Ca ion but with a dihedral angle of  $95.5^\circ$ . In contrast to gaylussite, the  $\text{CO}_3$  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  $\text{CO}_3$  anions and loosely to two water molecules. The water molecules complete the coordination of Ca ions and form hydrogen bonds with neighboring  $\text{CO}_3$  anions.

## INTRODUCTION

In our studies<sup>1</sup> of hydrated salts which have potential importance in biological mineralization, the crystal synthetic structures of gaylussite<sup>2</sup>,  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ , and synthetic pirssonite<sup>3</sup>,  $\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ , have been determined and are reported here. Work on both these structures was completed before that of Corazza and Sabelli<sup>4</sup> 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  $\text{Na}_2\text{CO}_3$ , 10 g  $\text{CaCl}_2$  and 800 ppm of sodium polyphosphate, combining the procedures of Bury and Redd<sup>5</sup> and Brooks, Clark and Thurston.<sup>6</sup> The initial solid phase was mostly spherulites, probably of  $\text{CaCO}_3 \cdot \text{H}_2\text{O}$  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 ( $\mu_{\text{Mo}} = 9 \text{ cm}^{-1}$ ) was sealed in a borate glass capillary to prevent slow dehydration. The cell dimensions\* were refined from 25  $2\theta$  values observed on a diffractometer<sup>7</sup> to  $a = 14.361 \pm .002$ ,  $b = 7.781 \pm .001$ ,  $c = 11.209 \pm .002 \text{ \AA}$ ,  $\beta = 127.84 \pm .01^\circ$ , assuming  $\lambda(\text{Mo } K\alpha_1, \alpha_2) = 0.71069 \text{ \AA}$ , 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.<sup>8</sup> The space groups C2/c and Cc were chosen using the convention adopted in the International Tables for Crystallography<sup>8</sup>.

The intensities of reflections in a hemisphere of the reciprocal lattice were measured on a diffractometer<sup>7</sup> using Mo-K $\alpha$  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  $2\theta$  range,

---

\*The uncertainties quoted on cell dimensions are standard errors computed from least squares refinements of the cell dimensions to fit observed  $2\theta$  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  $F_{hkl}$  would be too small, any supposedly genuine and equivalent values of  $F_{hkl}$  which were not within 10 % of one another were not averaged. Instead, the larger of the two was taken as the observed  $F_{hkl}$ . 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<sup>9</sup> ( $\langle |E^2| \rangle$  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
	2.0	.0366	.046
	3.0	.0009	.003
			.368
			.018
			.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  $R_w = \sum (w|F_o| - |F_c|)^2$  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 ( $B_H = 1.0\text{\AA}^2$ ) 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  $\ell$ ,  $10F_O$ ,  $10F_C$

$0,0,L$	-16 245 -240	0 347 -514	4 130 130	-7 779 -795	0 231 -236	-9 181 -176	-8 233 -233	9 158 131	-6 301 247	
-8 229 957	-8 30 16	3 230 308	7 80 81	-1 411 396	2 129 -136	-3 131 -147	-6 66 -63	17,3,L	-3 830 889	
-6 459 477	-8 53 57	4 152 -145	2 246 246	4 233 -242	-1 162 139	-5 227 -231	-1 150 -3	-1 247 473		
-4 135 413	-8 53 57	5 150 151	19,1,L	1 150 153	-1 153 -163	-5 64 -64	-1 150 -150	-1 247 473		
-16 121 125	-2 293 -309	6 216 -221	19,1,L	4 266 -368	6 304 290	-2 139 -132	-17 220 -264	2 376 -393		
-12 484 479	0 71 51	7 179 183	-28 42 18	5 668 -704	7 205 198	22,2,L	-1 166 -162	-16 40 126		
-14 181 -181	2 289 -213	9 229 -227	-1 181 180	6 260 -276	8 153 -145	0 166 -162	-16 40 126	3 118 126		
-16 249 227	4 105 112	16 82 67	-17 159 161	5 511 -557	-9 276 -18	-10 87 93	1 36 32	-14 279 284		
	16,6,L	11 89 -85	-16 147 -139	11 34 -19	-19 136 -128	-17 76 78	2 750 754	-13 97 -95	6 35 -16	
-16 57 57	-28 147 157	12 52 36	-16 147 -139	7 121 127	9 276 -18	-17 76 78	2 750 754	-13 97 -95	6 35 -16	
-16 164 -175	-21 231 -210	13 89 -85	-16 147 -139	11 34 -19	-19 136 -128	-14 172 188	5 289 -289	-1 18 376	9 381 383	
-12 118 125	-15 125 126	7,1,L	-13 47 56	12 175 -179	-10 76 68	-13 117 109	6 285 193	-9 101 -101	1 148 -159	
-10 120 125	-15 125 127	8 111 -105	-11 111 114	14 52 71	-12 120 -212	-12 120 -212	7 195 -186	-8 189 -189	11 260 -16	
-8 810 120	-12 368 363	-10 106 -93	-10 446 -440	15 141 -166	-10 69 56	9 212 204	-6 262 252	13 146 152	13 146 152	
-6 589 -621	-18 269 -384	-17 213 198	-9 70 86	4,2,L	16 135 143	-9 153 154	18 264 -37	9 97 -97	-18 164 -164	
-4 173 -163	-16 163 -163	4 260 -276	-16 163 -163	11 147 -159	-16 177 179	11 79 -78	-14 179 180	1 182 182	6,4,L	
-2 344 -344	-6 341 -347	4 260 -276	-7 347 -408	-17 134 116	-12 94 -87	-7 150 -175	-3 246 -246	-3 246 -246	-3 246 -246	
0 644 -632	-12 113 118	-16 239 -8	-6 67 68	11 111 111	-11 104 -191	-6 183 195	9,3,L	-2 205 224	-17 267 -191	
2 207 212	-2 303 -330	-13 480 481	-5 189 192	-15 195 -192	-10 175 175	5 88 98	-1 284 -211	-16 189 -189	10 233 229	
-6 87 87	5 177 173	9 105 105	-11 105 105	14 53 53	-13 55 -55	-5 58 -58	-10 108 189	0 189 189	1 133 145	
8 329 325	-9 111 -111	-16 105 108	-3 324 -329	12 72 72	8 515 -517	3 295 -295	-17 167 169	2 281 210	1 116 116	
10 182 -202	-16 167 157	-2 88 -106	-13 36 -45	-7 552 -552	-5 566 -566	-13 151 151	3 99 -111	12 31 115	13 316 -295	
12 403 400	28,6,L	-9 388 388	-1 91 90	-11 96 96	-6 45 -45	-13 151 151	1 122 122	-16 122 122	1 122 122	
14 77 -94	-16 260 -276	12 300 -300	-12 120 120	-13 143 -143	-13 143 -143	-12 120 120	-16 122 122	-16 122 122	-16 122 122	
	4,0,L	-18 29 47	-7 339 345	1 229 -246	-9 173 -153	-6 432 -433	-16 77 -93	-13 249 -243	19,3,L	-18 136 138
-16 267 277	-6 545 -529	3 83 -77	-9 51 56	3 219 -219	15 44 -46	-12 418 -396	-9 308 -315			
-16 370 -383	-5 861 860	3 80 85	-9 578 -585	-2 241 -241	-18 218 -218	-18 176 176	-18 290 290	-18 290 290	-18 290 290	
-16 110 -118	-18 130 -137	-3 117 -117	9 182 184	3 259 -260	13 73 -73	-10 241 -241	-18 204 204	-18 204 204	-18 204 204	
-12 201 205	-25 298 299	3 252 -461	-10 237 -237	-2 246 -246	-11 225 -225	-23 508 -519	-16 228 -227	-5 499 -592	-10 233 229	
-10 111 -117	-15 117 -117	-1 122 122	7,1,L	-2 122 -122	-12 122 -122	-12 122 -122	-17 147 147	1 133 145	1 133 145	
-8 207 -207	-2 183 -186	1 81 -72	-28 298 -301	-1 31 -16	6 262 -262	-6 189 -189	-5 119 -118	-13 186 -186	-2 223 -226	
-6 87 -110	0 145 182	4 451 -451	-15 209 -15	6 632 -767	5 43 -33	-7 187 -187	-4 476 -476	-12 188 -188	1 485 -489	
8 513 -492	22,0,L	4 266 -266	-17 159 -157	2 122 122	3 200 -200	-1 248 -248	-1 188 -188	-1 188 -188	-1 188 -188	
2 1281 -1189	5 177 -173	-16 237 228	3 98 181	8 204 -209	4 675 -741	-1 57 74	-9 123 -134	2 378 300		
4 446 436	-18 159 -155	6 177 -174	-15 45 46	4 36 -43	-3 303 -303	0 432 -433	-8 112 -116	3 67 -67	-482	
-4 174 -174	-16 174 -174	6 174 -174	-16 46 -46	-1 46 -46	-1 46 -46	-1 46 -46	-18 194 -194	0 194 -194	-1 194 -194	
0 543 -556	-14 68 -31	6 165 159	13 321 545	6 127 125	-12 120 -120	-12 120 -120	-16 155 -155	1 155 -155	1 155 -155	
18 129 -136	-19 172 223	9 72 -67	-12 197 -192	7 198 -197	-19 55 -55	13 206 -167	-17 74 -74	1 155 -155	1 155 -155	
12 87 -81	-10 221 -254	18 257 -246	-11 188 -106	6 632 -632	4 197 -197	1 208 -108	-6 181 -181	4 218 -218	7 47 -47	
6,6,L	-6 88 -85	12 114 114	9 72 -70	9 219 -219	-17 259 -11	-12 120 -120	-8 256 -269	-8 172 -172	1 172 -172	
-10 307 -291	-7 275 309	-6 230 -236	11 75 75	7 185 -187	6 421 -452	7 71 -60	-1 56 -60	1 80 -80	-47	
-16 226 202	1,1,L	-6 260 -255	13 222 -212	1 181 181	8 216 -216	3 212 -212	0 111 -122	0 66 -66	-52 11 169 -117	
-14 411 -413	-19 149 -133	-5 303 310	-12 326 -345	7 308 -308	-6 602 -602	16 61 31	-5 53 -53	12 74 63		

$0,0,L$	-13 125 -125	0 705 695	1 -16	7 69 -69	-22 213 213	5 204 -215	-15 215 215	11,3,L	21,3,L	0,4,L
-16 163 167	1 650 -648	1 557 552	13 317 323	-3 612 -615	6 296 -9	-1 54 54	-5 123 124	-3 43 -35	-3 265 256	
-14 244 -244	1 648 -648	1 557 552	13 317 323	-3 612 -615	6 296 -9	-1 54 54	-5 123 124	-3 43 -35	-3 265 256	
-12 108 115	3 416 424	1 559 -559	-11 239 -235	5 193 -193	-10 189 -189	-16 94 -93	-5 117 117	1 155 -155	1 155 -155	
-10 224 -236	4 428 452	2 328 -321	6 62 61	0 399 408	-7 183 -183	-7 183 179	-2 116 181	0 388 -388	0 388 -388	
-8 441 -441	2 282 -282	4 324 -324	9 61 -61	-1 360 -360	-1 360 -360	-1 360 -360	-1 360 -360	0 368 -368	0 368 -368	
-6 870 876	7 125 155	3 55 -55	-23 -23	7 239 239	3 91 -93	-10 82 82	-5 246 -246	-6 246 -246	-6 246 -246	
-2 2054 -1989	0 65 -61	6 38 -37	-6 155 -158	161 -161	-16 161 -161	-17 196 197	-3 313 -314	2 172 -175	2 111 99	
0 79 88	0 88 -98	7 186 191	-5 223 246	5 265 -266	-16 256 -256	-2 848 847	3 381 -434	9 634 -678	5 106 106	
2 383 -376	11 369 371	7 240 -240	-5 255 -255	-5 255 -255	4 85 -88	-12 61 -75	-7 62 62	-5 270 -270	2 281 281	0 76 -76
-10 303 -371	1 51 -51	11 216 216	-1 216 216	-1 216 216	1 83 -83	-10 280 292	4 124 133	9 159 168	0 149 -149	
8 193 200	-5 320 347	4 212 222	-7 65 -67	-15 155 -156	-15 155 -156	-15 155 -156	-15 155 -156	1 155 -156	1 155 -156	
	3,1,L	-19 146 -130	1 182 -183	11 84 83	-10 280 292	4 124 133	9 159 168	18 87 91	10,4,L	
-18 269 -31	0 726 727	-1 187 187	21,1,L	-7 156 -155	7 69 -69	-15 19 63	49 121 191	1 197 -18 284		
-16 342 347	-17 86 -87	16 133 108	-19 119 -118	-10 119 126	5 31 -22	9 46 -47	1 162 154	-9 171 134 -133		
-14 129 -136	-16 216 -215	15 315 -315	-11 181 -181	-17 181 -181	-1 153 155	13 279 -279	6 187 -187	14 92 -16 87	10 233 229	
-12 135 -140	-15 49 -54	-13 36 -36	-31 125 -125	-16 119 -119	-3 170 -183	11 105 -80	-10 110 117	15 289 -289	1 155 155	
-10 630 -643	-14 56 -63	-13 36 -36	-31 125 -125	-16 119 -119	-3 170 -183	-1 183 183	-1 183 183	-1 183 183	-1 183 183	
-8 136 -136	-12 153 -153	-12 192 -191	-12 126 -126	-12 126 -126	-2 191 206	12 316 -303	-14 243 247	-13 273 -273	-13 273 -273	
-6 580 -580	-7 242 -242	4 300 -300	-3 327 -327	-18 218 -218	-18 218 -218	-18 218 -218	-18 218 -218	-18 218 -218	-18 218 -218	
-4 295 -295	-6 76 -76	-5 86 -86	-5 327 -327	-19 200 -200	-15 156 -156	-5 156 -156	-5 156 -156	-5 156 -156	-5 156 -156	
-2 631 -631	-7 76 -76	-5 86 -86	-5 327 -327	-19 200 -200	-15 156 -156	-5 156 -156	-5 156 -156	-5 156 -156	-5 156 -156	
-16 148 -146	-6 63 -65	6 596 615	-2 290 -290	-3 479 -480	-16 172 -172	-16 172 -172	-16 172 -172	-16 172 -172	-16 172 -172	
-16 175 -175	-5 252 -252	9 216 -216	-1 157 172	-7 172 -172	-1 157 172	-7 172 -172	-7 172 -172	-7 172 -172	-7 172 -172	
-14 231 -237	1 825 136	1 292 192	-1 157 157	-1 157 157	-1 157 157	-1 157 157	-1 157 157	-1 157 157	-1 157 157	
-12 769 716	8 963 -945	9 222 210	0 244 -250	-16 188 186	176 176	-6 67 -67	9 70 69	-6 67 -67	2 132 285	
-10 138 -119	9 62 -65	2 65 -62	1 157 -157	1 157 -157	1 157 -157	1 157 -157	1 157 -157	1 157 -157	1 157 -157	
-8 204 -204	3 376 323	7 640 -634	-18 218 -218	-18 218 -218	-18 218 -218	-18 218 -218	-18 218 -218	-18 218 -218	-18 218 -218	
-6 305 -305	-15 364 -364	-15 320 -320	-15 320 -320	-15 320 -320	-15 320 -320	-15 320 -320	-15 320 -320	-15 320 -320	-15 320 -320	
-4 205 -205	-7 60 -60	7 155 140	-2 623 -693	4 99 -125	-10 291 290	-6 168 -168	-10 291 290	-6 168 -168	-10 291 290	
-2 78 100	7 188 284	8 270 -4	3 515 570	5 116 -114	-9 75 84	-3 646 656	6 270 4	2 78 7	2 286 -275	

$0,0,L$	0 621 633	8 95 96	9 121 -123	4 1500 -1500	8 358 345	-8 286 -221	-2 1071 1146	7 92 -49	3 113 116	8 46 -48
-8 229 -229	-9 210 -211	-10 189 -189	5 570 -521	7 99 -94	-12 123 -123	-10 173 -173	-1 153 153	-10 173 -173	-10 173 -173	-10 173 -173
-6 449 453	10 222 -228	13,1,L	6 570 -521	8 50 -52	-11 118 1					

-7a-

TABLE 2  
(continued)

-5	252	-249	-3	32	-0	3	124	130	-11	250	9	-1	54	-42	-14	67	64	6	166	177	-3	193	187					
-109	121	-17	29	-15	-3	108	100	5	552	531	-13	253	150	161	-13	40	-26	2	8,8,L	-2	17	28						
-3	345	339	-1	101	117	-2	234	-2	5	460	-460	-14	141	153	-153	-12	40	-26	12,8,L	-1	21	29						
-1	177	-131	-1	109	99	-2	102	82	-91	88	-104	-205	215	157	172	-10	27	-234	-14	94	92	29						
0	89	94	-2	132	-88	-2	1	45	64	8	206	180	-9	201	196	4	71	-71	9	73	62	-12	152					
243	256	-1	113	118	-2	103	103	-17	174	-174	-33	339	50	50	50	-9	204	-204	-15	205	-20	-2	2	153				
3	108	-112	-1	111	22	-2	3	259	33	10	-37	-54	-6	202	-2	7	263	269	-18	225	-10	120	123	116				
29	-10	-10	-1	110	360	-2	213	201	11	63	63	-2	142	142	76	252	-7	90	-5	53	-50	-12	110	-114				
9	-32	10	-1	97	100	-2	5	42	-1	12	61	49	-5	125	128	8	256	-237	-5	103	100	-8	105	-103				
29	-10	-10	-1	97	100	-2	6	210	-216	13	141	-141	-1	139	-167	9	170	-143	-1	143	141	-1	141	-140				
18,4,L	-7	89	-86	-6	217	-516	15,5,L	4,6,L	-2	3	45	-52	-10	115	105	-1	165	-150	-6	274	261	-9	99	-105				
-19	124	110	-5	136	120	-1	1	216	226	12	40	30	-1	136	139	-4	254	-42	-37	-7	23	20	10	26	12			
-1	19	49	-1	106	106	-1	183	-172	-16	59	53	-1	216	226	11	300	31	11	209	5	-1	136	139	-4	254			
-17	165	-172	-3	173	186	-17	1	41	17	-15	113	-112	1	160	-166	-1	113	-133	-2	122	124	-15	168	-175				
-15	57	31	-2	170	10	-1	16	105	105	99	-92	-29	2	49	-54	-3	7,L	-2	44	-44	-1	48	-44	-3	391	-409		
15	65	63	-1	107	107	-1	19	-15	24	-2	13	29	3	225	232	-1	132	-52	54	0	401	-414	-3	386	-394			
13	180	-103	1	141	145	-1	13	98	-88	-11	253	-240	5	167	-170	-14	164	156	5	93	-63	2	113	124				
12	24	23	-2	208	584	-12	228	-232	-10	283	283	6	29	-37	-11	73	36	6	106	107	1	71	77	0	166	-171		
-21	213	197	-1	108	108	-1	1	142	142	3	101	100	-1	142	142	5	58	-60	-1	137	137	4	222	-240				
-10	210	211	-4	108	108	-1	9	209	-317	-12	30	310	-1	140	-140	-1	111	-69	-1	137	137	4	222	-240				
-370	-383	5	119	122	-9	228	-226	-7	380	380	-1	300	-300	-10	23	-17	13,7,L	0	84	88	3	279	-5	0	80	59,L		
-8	87	-90	6	302	310	-9	113	115	6	461	-462	-18	29	-7	-9	22	-1	117	42	-3	7,123	-119	4	198	-194			
-17	178	174	-1	106	106	-1	134	-134	-9	5	116	-116	-1	144	-144	-1	139	-139	-3	116	-108	-6	52	-48				
-208	-106	0	268	270	-4	425	-420	-20	220	220	-1	568	-576	-7	144	-136	-15	195	-192	9	129	118	-1	148	-144			
-202	-217	9	46	-5	85	85	25	-3	584	-614	-15	195	-186	-6	266	256	-12	122	131	10	72	79	14,8,L	-243	261			
155	190	150	47	-55	-4	121	119	-12	246	-155	-16	174	-168	-5	146	-129	13	36	54	11	27	79	-1	142	140			
22	222	221	11	29	6	-2	276	-269	0	91	-103	12	56	-37	-3	397	-370	-11	200	-198	-1	162	-110	-1	142	140		
-2	20	-70	12	29	4	-2	276	-269	0	91	-103	12	56	-37	-3	397	-370	-11	200	-198	-1	150	-58	-1	253	-262		
-153	-165	-1	1	50	46	-1	6	87	-510	-11	83	-85	-2	271	273	-10	135	137	-1	144	144	-1	144	144				
0	69	79	7	75,L	0	38	-36	2	561	-569	-10	232	-227	-1	9	239	-31	-1	142	142	-1	142	142	-1	142	142		
1	102	111	-1	1	30	-2	4	561	-569	-10	232	-227	-1	9	239	-31	-1	142	142	-1	142	142	-1	142	142			
-17	72	-71	-2	217	-226	4	241	-240	-8	291	291	-1	342	-566	-7	325	-337	-13	52	-64	-11	92	99	3	222	-223		
20,4,L	-16	213	193	3	27	-14	5	309	-310	-7	205	-219	2	166	-162	-16	163	-161	-12	101	-88	-10	196	206	4	246	3	
15	61	-35	4	106	107	6	119	-120	-6	268	-264	3	112	-131	-15	122	-116	-11	40	-16	-28	105	-101	5	153	149		
18	96	87	-1	106	106	-1	131	-131	-6	268	-264	3	112	-131	-15	122	-116	-11	40	-16	-28	105	-101	5	153	149		
-17	154	-150	-1	123	9	17,5,L	0	108	100	-11	114	129	-6	142	-141	-3	173	-161	-7	68	62	-7	47	39	7	59	-53	
16	97	90	-12	159	156	-9	9	333	-319	-3	311	-304	6	67	-69	-2	136	144	-8	54	-60	-136	137	0	117	114		
17	187	182	-1	106	106	-1	106	207	-204	25	26	30	7	71	-71	-2	136	144	-8	54	-60	-136	137	0	117	114		
14	87	87	-10	281	270	-17	89	-71	11	103	103	63	-1	203	218	8	85	-72	74	340	335	-30	207	-208				
22	230	-230	-9	106	-166	-16	16	49	60	12	28	11	0	104	-97	9	114	-105	1	163	-176	-5	20	30	-3	69	-62	
12	54	48	-9	97	100	-15	142	44	4	219	-223	9	99	90	2	178	180	-4	56	-63	-2	150	154	-1	164	160		
13	14	13	-1	106	106	-1	106	207	-204	25	26	30	7	71	-71	3	103	103	3	93	-93	-1	164	160				
10	166	-213	-6	355	-340	-13	124	-120	-30	6	6,6,L	0	92	104	12	149	-145	5	138	-145	-1	31	-23	1	64	-50		
-109	106	-5	544	-251	-12	112	112	129	-16	270	6	230	234	-5	0	263	-202	2	122	130	-11	111	111	-1	101	102		
-3	71	62	-2	62	-67	-9	53	-61	13	179	176	-15	48	28	-17	65	77	3	105	-109	16,8,L	-1	164	160				
-202	-209	1	121	-121	-12	112	112	129	-16	46	47	-18	210	-167	-14	139	136	-17	65	77	3	105	-109	16,8,L	-1	164	160	
-103	-121	0	234	237	-23	23	23	-19	176	-176	17	137	136	-13	176	175	-20	284	287	3	110	-110	16,8,L	-1	164	160		
-2	72	76	2	19	15	-5	23	-14	9	237	-226	-15	45	-59	-11	239	-20	-14	156	152	6	200	193	-15	110	116		
-132	-146	3	34	32	-12	-22	221	223	9	201	-21	-13	129	-111	-10	59	61	-13	60	64	7	64	23	-21	19	215	-64	60
22,4,L	6	189	-185	-1	121	-60	-62	9	253	-256	-11	175	-186	-8	176	-175	-17	157	145	10	155	150	-11	73	66	-1	200	-194
-17	97	-89	2	74	-76	0	27	34	-6	178	172	-10	265	-290	-8	206	-201	-1	91	92	11	259	-13	171	171	0	110	107
1	15	15	-1	106	-106	-1	4	47	-51	10	270	-264	-10	270	-264	-1	91	92	11	259	-13	171	171	0	110	107		

-19	172	176	9	65	69	2	90	-93	-2	549	-583	-8	65	-65	4	208	-213	-7	130	-132	8,0,L	-8	157	-149	2	165	175					
-10	60	-47	10	164	-155				-1	182	145	-7	200	-266	-3	312	-298	-1	160	145	-4	-1	41	-41	2	165	-175					
-13	135	-140			9,9,L					200	16	-6	93	-93	-2	344	-157	-5	35	29	-15	49	45	-6	214	219	4	68	47			
-12	24	-10							1	314	-320	-5	233	231	-1	40	31	-4	45	-3	-14	194	183	-3	141	142	3	75	65			
-11	153	176							16	26	51	-1	208	-13	-2	208	-13	0	139	-167	-2	244	-250	-13	73	55	-4	26	21	6	40	27
-10	10	-10	-10	-10	294	16	17	209	-23				200	-13	-2	200	-13	0	139	-167	-2	244	-250	-13	73	55	-4	26	21	6	40	27
-9	79	-84	-17	274	13	-16	157	151		4	199	-190	-2	202	-202	2	30	30	-1	45	-48	-11	60	66	-2	174	173	0	75	60		
-8	53	-47	-16	263	292	-19	45	42		5	319	-339	-1	26	-0	3	82	-82	0	81	-100	-349	360	-10	349	360	-10	121	-121			
-7	102	121	15	46	-26	16	189	-165		6	237	-241	0	94	-87	4	222	-224	1	91	-94	-9	23	1	0	163	-172	9,9,L				
-6	10	-10	-10	-10	294	16	17	209	-23				200	-13	-2	200	-13	0	139	-167	-2	244	-250	-13	73	55	-4	26	21	6	40	27
-5	167	-165	-13	125	-124	-12	210	213		8	142	139	2	147	-142	6	23	-13	3	29	21	-1	113	-113	1	113	124	-1	77	-77		
-4	29	-16	-12	231	268	-11	25	0		9	136	-116	-2	147	-142	7	19	11	-1	93	-94	-9	23	1	0	163	-172	9,9,L				
-3	11	-32	27	10	-101	-08	10	147	-139		10,6,L	8	37	-0	17,7,L		-6	257	262	10,8,L	-6	30	-3	15	20	31	-14	94	-77			
-2	1	-10	10	47	-49	11	49	40		9	136	-116	-2	147	-142	7	19	11	-1	93	-94	-9	23	1	0	163	-172	9,9,L				
1,5,L									-17	78	92	0	82	-17	12	162	156	-4	20	-16	-15	83	82	-6	14	142	-12	26	18			
-10	9	-132	-136	-132	-136	-23	247	0		-17	78	92	0	82	-17	12	162	156	-4	20	-16	-15	83	82	-6	14	142	-12	26	18		
-9	6	-515	932	-7	23	12	6,6,L		-16	111	105	11	86	66	-16	28*	-28	-2	431	446	-13	98	83	-10	24	25	-15					
-11	24	-227	34	-24	27	-102	-106		-15	121	-127				-15	28*	-12	-1	72	-12	-95	90	-4	245	227							
-12	50	-59	-145	-145	-145	-145	-145	-145	-17	130	120		141	-140	7,7,L	-15	141	141	0	31	-23	-11	56	-29	-8	84	-80					
-11	76	66	-145	-145	-145	-145	-145	-145	-17	130	120		141	-140	7,7,L	-15	141	141	0	31	-23	-11	56	-29	-8	84	-80					
-10	22	-27	-3	260	-305	-2	119	-126	-126	-11	179	-176	-11	209	-214	-5	15	27	-13	-11	42	-43	1	89	91	-16	173	-172	-1	161	-161	
-9	26	-254	-26	-254	-26	-1	290	-27	-27	-23	229	-227	-12	222	-22	-2	152	-151	-10	162	-160	4	110	-127	-9	109	114	-4	35	41		
-8	182	197	-1	12	293	0	184	207	-207	8	162	172	-158	160	-158	22	22	22	150	-150	-10	162	-160	4	110	-127	-9	109	114	-4	35	41
-7	49	22	-23	299	352	-1	116	-36	-36	-8	259	-22	-12	196	-186	-8	149	-105	8	184	161	-2	91	-90	8	101	-100	-3	23	23		
-6	262	-280	1	62	61	21,5,L	-10	42	-36	-7	147	-130	-11	45	-62	-7	79	-79	7	246	4	-127	-135	1	202	-192						
-5	66	36	-2	171	-170	-17	299	-22	-22	-22	240	-234	-22	251	-246	-8	25	64	-8	209	-49	-3	138	139	0	24	10					
-4	9	66	-2	171	-170	-17	299	-22	-22	-22	240	-234	-22	251	-246	-8	25	64	-8	209	-49	-3	138	139	0	24	10					
-3	292	342	6	111	110	-10	220	220	-22	-7	29	16	-9	159	158	-9	256	-256	-9	82	81	-9	170	165	1	62	92					

TABLE 2  
(continued)

The large correlation coefficients are 0.25 between the scale and the Ca  $\beta_{11}$  anisotropic temperature factor, 0.75 between the Ca  $\beta_{33}$  and  $\beta_{13}$  anisotropic temperature factors, 0.68 between the Na  $x$  and  $z$  parameters and 0.78 between the Na  $\beta_{33}$  and  $\beta_{13}$  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  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ , it is not surprising that both  $\text{CO}_3^{2-}$ -groups are coordinated (via O(2) and O(3)) to Ca, which lies on a two-fold axis, to form what may be considered/an ion triplet,  $\text{OCO}_2\text{-Ca-O}_2\text{EO}$ . 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	*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  $\text{Å}^2$ .

\*\*All hydrogen thermal parameters were kept constant at B (isotropic) =  $1.0 \text{ Å}^2$ . 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  $\text{CO}_3$  group is essentially planar with an average C-to-O distance of  $1.288\text{\AA}$ . Its dimensions and environment are summarized in Table 5 and Figure 2. Oxygen O(1) is bonded electrostatically to Na ( $2.314\text{\AA}$ ) and is hydrogen bonded to water oxygens O(5) ( $2.847\text{\AA}$ ) via H(3) ( $\sim 2.0\text{\AA}$ ) and O(6) ( $2.667\text{\AA}$ ) via H(5) ( $\sim 2.0\text{\AA}$ ). Oxygen O(2) is bonded electrostatically to Ca ( $2.573\text{\AA}$ ), Na ( $2.400\text{\AA}$ ), and Na ( $2.610\text{\AA}$ ) and is hydrogen bonded to O(5) ( $2.852\text{\AA}$ ) via H(2) ( $\sim 2.1\text{\AA}$ ). Oxygen O(3) is electrostatically bonded to Ca ( $2.385\text{\AA}$ ) and Na ( $2.331\text{\AA}$ ) and is hydrogen bonded to O(6) ( $2.666\text{\AA}$ ) via H(4) ( $\sim 1.8\text{\AA}$ ). 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,  $118.1^\circ$ , is less than  $120^\circ$  because coordination with the Ca pulls these oxygens together.

The two  $\text{CO}_3$  groups coordinated to Ca are also coordinated to two Na ions (Figure 1) which cause a dihedral angle of  $134.3^\circ$  between the planes of the two  $\text{CO}_3$  groups instead of the expected  $180^\circ$ . This coordination is instrumental in making the O(2)-to-O(3) vector in one  $\text{CO}_3$  group very nearly parallel to the O(2')-to-O(3') vector in the other  $\text{CO}_3$  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)
<u>O(1) Environment</u>	
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)
<u>O(2) Environment</u>	
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  $0.69\text{\AA}$  below the intersection of the planes of these  $\text{CO}_3$  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  $\text{CO}_3$  groups, and by the O(4) and O(5) waters. The repulsion arising from the Ca-to-Na closest approach of  $3.626\text{\AA}^\circ$  is reduced by their sharing O(2) and O(3') (Figure 1). These atoms are in the two  $\text{CO}_3$  groups bonded to the Ca. The next closest Ca-to-Na approach,  $3.831\text{\AA}$ , is stabilized by the intervening pair O(2) and O(5'). The Na-to-Na approaches are  $3.903\text{\AA}$  and  $4.305\text{\AA}$ , 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  $\text{CO}_3$  group via a hydrogen bond H(5) to O(1), where H(5) to O(1)  $\sim 2.0\text{\AA}$ , O(6) to O(1) =  $2.667\text{\AA}^\circ$ , and to O(3) of the next  $\text{CO}_3$  group (generated by the c glide) by a hydrogen bond H(4) to O(3), where H(4) to O(3)  $\sim 1.8\text{\AA}$ , O(6) to O(3) =  $2.666\text{\AA}^\circ$ . O(6) is in the coordination octahedron of the Ca

TABLE 6

The Sodium Environment in Gaylussite

Atoms	distance, $\text{\AA}$
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       $\begin{array}{c} \text{H}(1) \\ \diagdown \\ \text{O}(4) \\ \diagup \\ \text{H}(1') \end{array}$

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       $\begin{array}{c} \text{H}(3) \\ \diagdown \\ \text{O}(5) \\ \diagup \\ \text{H}(2) \end{array}$

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		H(4) O(6) H(5)
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) ~2.0 $\text{\AA}$ , O(4)-to-O(6) = 2.774 $^{\circ}\text{\AA}$ . 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<sub>3</sub> group to O(2) in the CO<sub>3</sub> 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) ~2.0 $\text{\AA}$ , O(5)-to-O(1) = 2.847 $\text{\AA}$ , and O(5)-H(2)....O(2), where H(2)-to-O(2) ~2.1 $\text{\AA}$  and O(5)-to-O(2) = 2.852 $\text{\AA}$ . 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<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>•2H<sub>2</sub>O, before the recent work of Corazza and Sabelli<sup>4</sup> 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 micro-densitometer, corrected for absorption, and refined using block-diagonal least squares.

In the present work, good crystals of synthetic pirsso-nite were grown at 50°C from a solution of 27% by weight of  $\text{Na}_2\text{CO}_3$  and 5% NaOH in water in contact with powdered calcite.<sup>5</sup> A small crystal, maximum dimension 0.20 mm ( $\mu_{\text{MO}} = 10.6 \text{ cm}^{-1}$ ) was selected. The cell dimensions\* were determined to be  $a = 11.340 \pm .004$ ,  $b = 20.096 \pm .005$  and  $c = 6.034 \pm .002 \text{ \AA}$  from 2 $\theta$  values of axial reflections observed on a diffractometer. Evans<sup>1,2</sup> reported the dimensions  $a = 11.32 \pm .02$ ,  $b = 20.06 \pm .02$  and  $c = 6.00 \pm .02 \text{ \AA}$ , and that the space group is Fdd2. Our values, which were calculated using the weighted mean value for  $\text{M}_0\text{K}\alpha_1$ ,  $\alpha_2$  radiation ( $\lambda = .71069 \text{ \AA}$ ) are systematically larger than these reported by Evans.

Over 2200 reflections from two octants of the reciprocal lattice were measured on a diffractometer<sup>7</sup> 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

---

\*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

	$\langle  E  \rangle$	$\langle  E^2  \rangle$	$\langle  E^2 - 1  \rangle$
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 pirs<sup>s</sup>sonite.

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  $F_0$  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 ( $B_H = 1.0\text{\AA}^2$ ). 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 Pirossonite  
Columns are  $\ell$ ,  $10F_0$ ,  $10F_c$  and phase in millicycles

TABLE 9  
(continued)

	14x4,0	6 28 27 372 7 74 73 71 5 97 97 53 22 16 21 0	16x4,6	
18 19 11 500	6 18 135 10 9 10 10 281 7 69 69 9 22 16 21 0	16x4,2	2 66 66 29 11 77 73 94 2 33 36 467	19x4,3
18 159 161 0	3 30 18 525 11 68 70 85% 9 11 40 36 933	16x4,2	4 15% 13 575 13 77 76 44 6 106 109 970	
20 13+ 2 300	10 69 63 65 13 78 78 86 11 40 36 933	16x4,2	4 15% 13 575 13 77 76 44 6 106 109 970	1 59 56 1
22 31 78 0	12 52 50 97 15 69 43 980 13 89 81 129 2 86 89 981 8 65 66 12 15 39 38 843 8 23 26 108	15x4,2	1 59 56 1	
24 15+ 16 500	16 43 39 493 19 38 29 797 17 16+ 19 21 6 74 73 35 10 135 127 681	15x4,2	17 53 44 302 8 23 26 108	31 71 901
26 90 79 0	18 96 81 15 21 50 76 52 0 32 30 572	15x4,2	10 23 23 679 5 83 35 736	
20 61 56 970	20 61 56 970 23 51 46 821	15x4,7	17 79 82 0 7 63 55 306	
22 92 84 27	22 92 84 27	15x4,3	12 79 82 0 7 63 55 306	
14x4,2	14x4,0	15x4,3	1 42 39 942 14 67 42 133 9 53 47 978	
0 127 130 993	1 26 26 912 3 128 121 139	1 56 55 890 14 33 35 937 1 56 49 834	1 42 39 942 16 76 71 34	20x4,0
2 60 62 77	2 35 34 177 5 162 166 678	3 70 69 207 18 12+ 11 698 3 82 83 94 3 130 116 871	18x4,6	0 50 48 0
4 52 56 725 0	156 157 953 3 128 121 139	7 45 37 86 20 38 30 12.7	7 39 43 223 2 81 76 948 2 33 23 500	
6 31 33 143 2	2 35 34 177 5 162 166 678	9 66 68 874 11 80 86 93	4 13+ 20 892 4 83 84 0	
8 157 153 9	4 62 38 49 7 79 78 104	16x4,0	11 87 83 69	
10 13 11 673 9	6 65 40 159 9 21 15 115	16x4,4	13 87 75 754	
12 79 32 866 0	173 166 950 11 70 63+3 0 219 228 0 0 63 59 8 13 75 76 155	16x4,4		
14 33 32 592 10	26 25 467 13 126 122 806 2 70 71 500 2 13+ 8 208 17 46 48 880	16x4,4		
16 46 82 37 12 64 77 38 19 98 95 152 4 20 0 0 4 96 100 986 19 46 40 70	16x4,4			
18 24 22 14 27 17 56 51 51 42 96 0 0 8 32 29 0	16x4,4			
20 60 60 908 16	98 94 934 14 36 37 66 8 126 128 0 0 52 20 26	17x4,3	6 63 36 953 6 13+ 0 0	
22 15+ 19 911 21	64 78 910 10 33 30 500 10 31 25 391 1 13+ 3 733	16x4,0	8 16+ 9 580 8 83 80 0	
24 58 54 3	15x4,1	15x4,5	10 121 111 958	20x4,2
14x4,4	1 45 48 220 3 90 88 824 1 13+ 14 163 18 16+ 3 0 18 32 28 340	14x4,4	1 31 37 157 4 15+ 11 711	
2 115 113 45	5 77 78 104 J. 61 58 783 20 100 98 0	9 47 43 610 8 39 56 0	12 109 93 9 5 71 71 994	
		2 39 42 0	12 73 73 500 5 71 71 994	
		14 13+ 10 0	14 23 13 0	7 30 56 766
		16 23 13 0	11 43 42 80	
		18x4,2	13 30 36 42	
		0	0 117 119 90	

The atomic parameters obtained by us, as well as those of Corazza and Sabelli,<sup>4</sup> 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  $2\sigma$  when our estimated standard errors are used; four of the 18 parameters differ by more than  $2\sigma$  when the estimates of Corazza and Sabelli<sup>4</sup> 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  $108.7 \pm .4^\circ$ .

TABLE 10

Atomic Parameters of Pirssonite

Atom D+B*	C+S*	X	Y	Z	B <sub>11</sub> **	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Ca		.0000	.0000	.0000	.73(8)	.63(8)	.50(8)	.00(1)	-	-
Ca	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	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	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)	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)	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)	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)
H(1)***		.56(1)	.27(1)	.07(3)	1.0	1.0		-	-	-
H(2)	H(2)	.527	.265	.034	5.00					
H(2)	H(1)	.62(1)	.21(1)	.20(3)	1.0	1.0		-	-	-
H(1)	H(1)	.611	.227	.220	5.00					

\*D+B, this work; C+S Corazza and Sabelli<sup>4</sup>

\*\*Values of B given by Corazza and Sabelli

\*\*\*All hydrogen thermal parameters were kept constant at B (isotropic) = 1.0A<sup>2</sup>. 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  $\text{CaCO}_3 \cdot$

$6\text{H}_2\text{O}$ ,<sup>13</sup> 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  $\text{CO}_3$  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  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  forces the formation of  $\text{OCO}_2-\text{Ca}-\text{O}_2\text{CO}$  ion triplets as in gaylussite, but, since there are only two water molecules present, further coordination of  $\text{CO}_3^{2-}$ -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  $\text{CO}_3$  group is coordinated to two/different Ca ions/and the coordination of Ca is octahedral. In calcite and aragonite, no  $\text{CO}_3$  group has two oxygens bonded to the same Ca. In gaylussite and pirssonite, however, the Ca coordination comprises two  $\text{CO}_3$  edges and four other oxygens. In pirssonite only two of the latter are water molecules; the other two are  $\text{CO}_3$  apexes (Figure 5). The two  $\text{CO}_3$  groups coordinated to Ca by their

TABLE 11  
Ca Environment in Pirs sonite

Atoms	distance, $\text{\AA}$
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  $95.5^\circ$  to one another, and have twisted around to allow the close approach to Ca of the apexes of the other  $\text{CO}_3$  groups. The Ca lies  $0.1\text{\AA}$  away from the intersection of the planes of the  $\text{CO}_3$  groups coordinated edgewise.

The carbonate group.--The  $\text{CO}_3$  group is planar and trigonal within experimental error with an average C-to-O distance of  $1.286\text{\AA}$ . Its dimensions and environment are summarized in Figure 6 and Table 12. Oxygen O(1) is bonded electrostatically to Ca ( $2.428\text{\AA}$ ) and forms two hydrogen bonds, O(1)-to-H(1)  $\sim 2.2\text{\AA}$ , O(1)-to-O(4) =  $2.716\text{\AA}$ , and O(1)-to-H(2)  $\sim 1.8\text{\AA}$ , O(1)-to-O(4) =  $2.865\text{\AA}$ , with neighboring water molecules. Oxygen O(1) is too far from Na ( $2.945\text{\AA}$ ) for Na to be its primary coordination. Oxygen O(2) may form a very weak hydrogen bond with H(1) ( $2.4\text{\AA}$ ) but its primary coordination is electrostatically to Ca ( $2.461\text{\AA}$ ) and to the 'chain' of Na ions ( $2.299\text{\AA}$ ,  $2.302\text{\AA}$ ) formed above it by the d glide (Figure 7). Oxygen O(3) is not hydrogen bonded but is electrostatically bonded to Ca ( $2.536\text{\AA}$ ) and to a 'chain' of Na ions ( $2.351$ ,  $2.392\text{\AA}$ ) formed below it by the d glide. The C-to-O(2) and C-to-O(3) distances are shorter ( $1.28\text{\AA}$ ) and C-to-O(1)

TABLE 12

Carbonate Group Dimensions and Environment in Pirssonite

Atoms	distance, $\text{\AA}$
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, $\text{\AA}$
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, $\text{\AA}$
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

( $1.30\text{\AA}$ ), the reverse of that in gaylussite, and the O(2)-C-O(3) angle is essentially  $120^\circ$ . 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  $3.255\text{\AA}$  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  $2.722\text{\AA}$ , where, other things being equal,  $2.3\text{\AA}$  is expected.

TABLE 13

The Na Environment in Pирssonite

Atoms	distance, $\text{\AA}$
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<sub>3</sub> groups together (Figure 6) and is also coordinated electrostatically (2.483 $\text{\AA}$ ) to Ca. The water molecule is also coordinated to two Na ions (2.722 $\text{\AA}$ , 2.751 $\text{\AA}$ ), and reduces their mutual repulsion. It appears in the coordination of Na twice (Figure 7). In forming hydrogen bonds in the pирssonite 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.

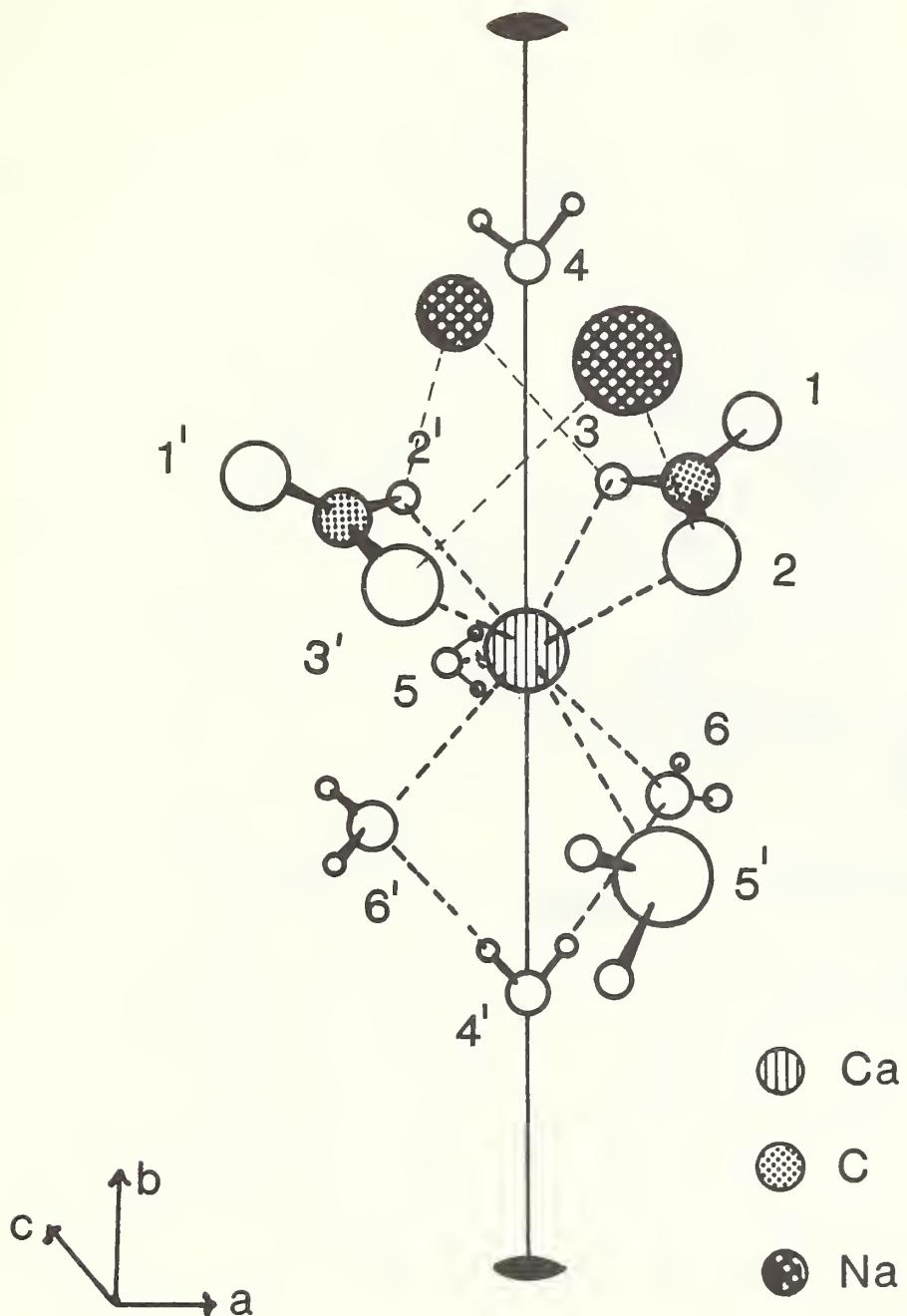


Fig. 1. The calcium ion environment in gaylussite. Primed atoms are related to unprimed atoms by the two-fold axis.

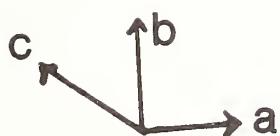
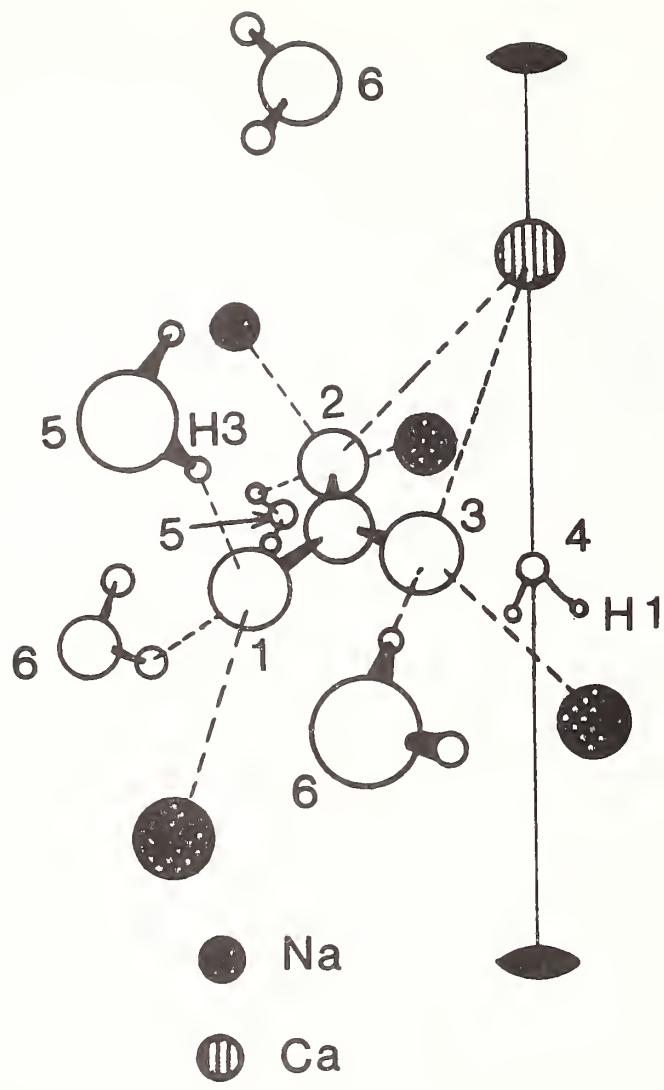


Fig. 2. The carbonate anion environment in gaylussite.

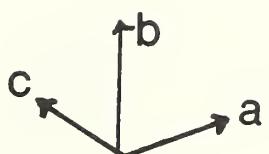
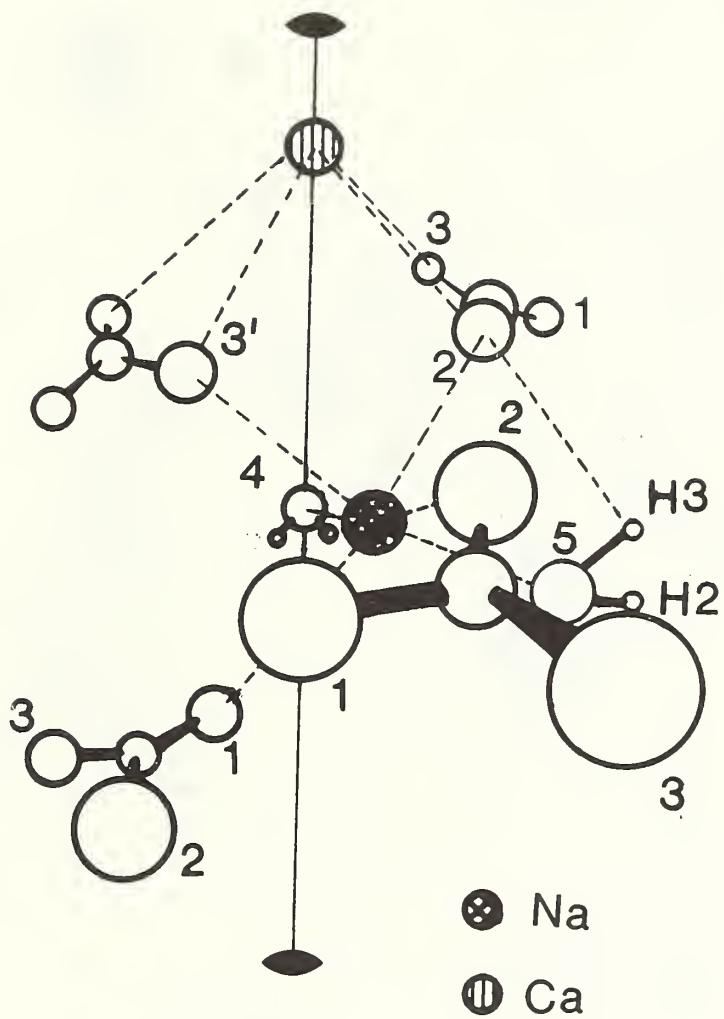


Fig. 3. The sodium ion environment in gaylussite.

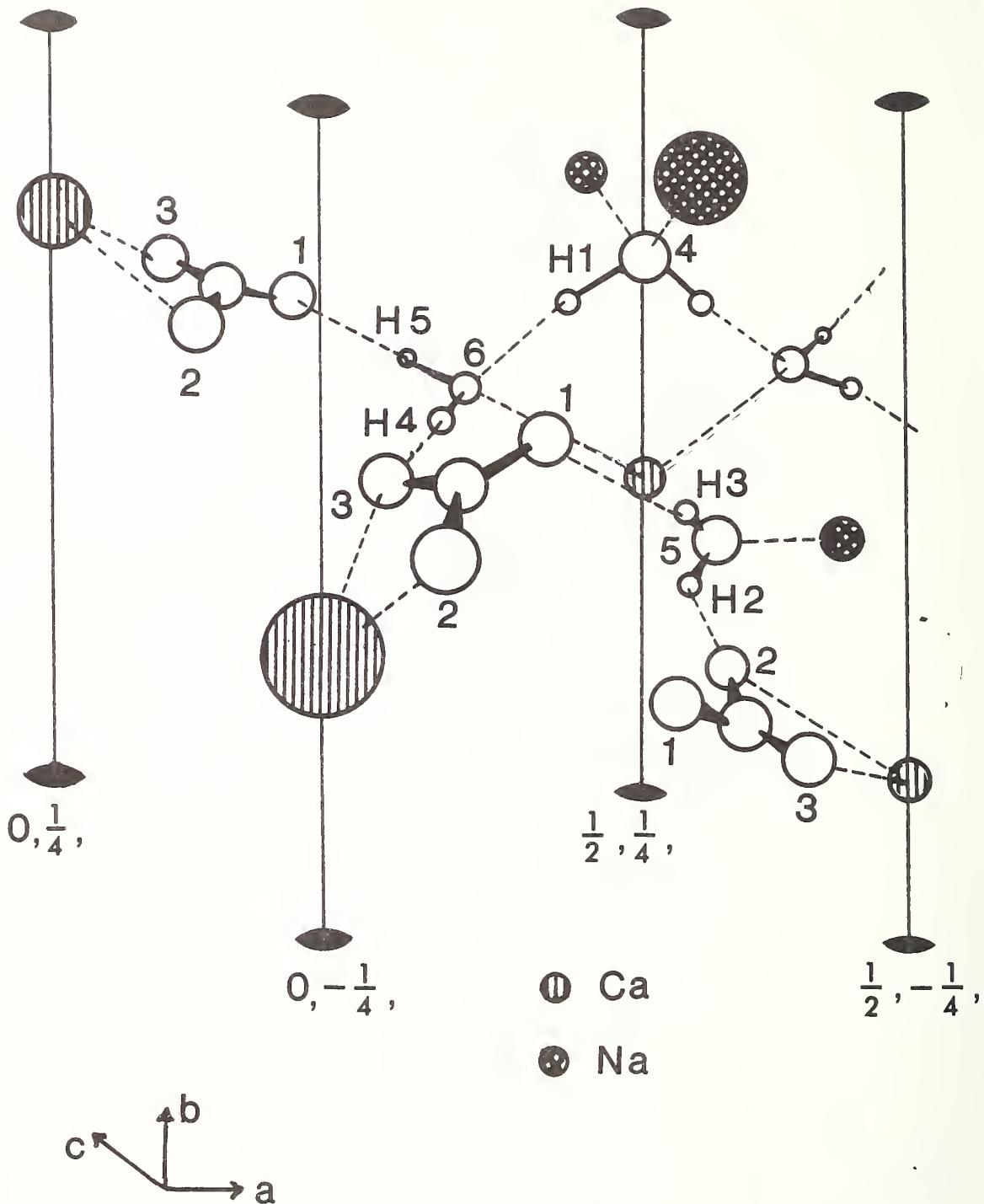


Fig. 4. The water environments and hydrogen bonding in gaylussite.

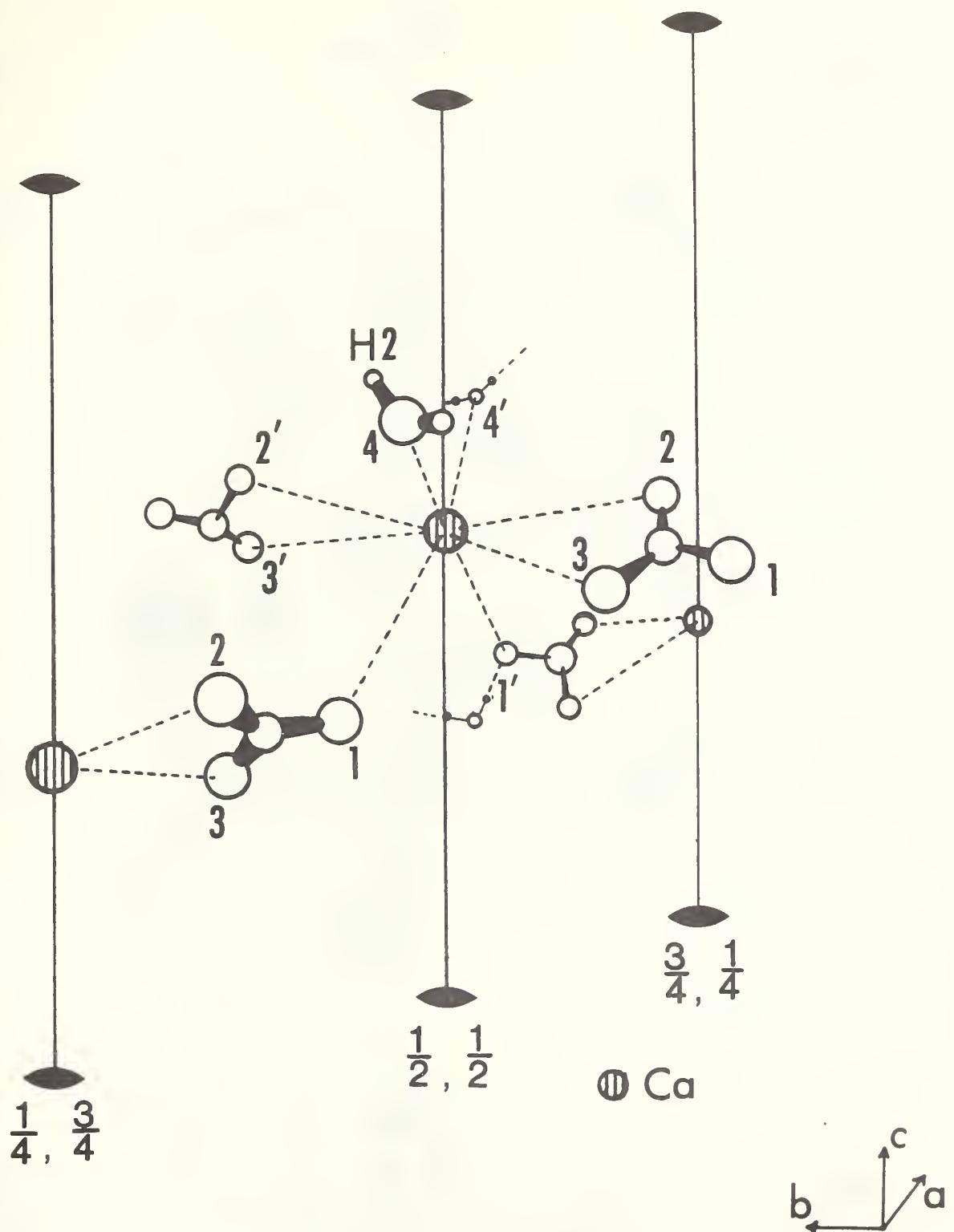


Fig. 5. The calcium ion environment in pirssonite.

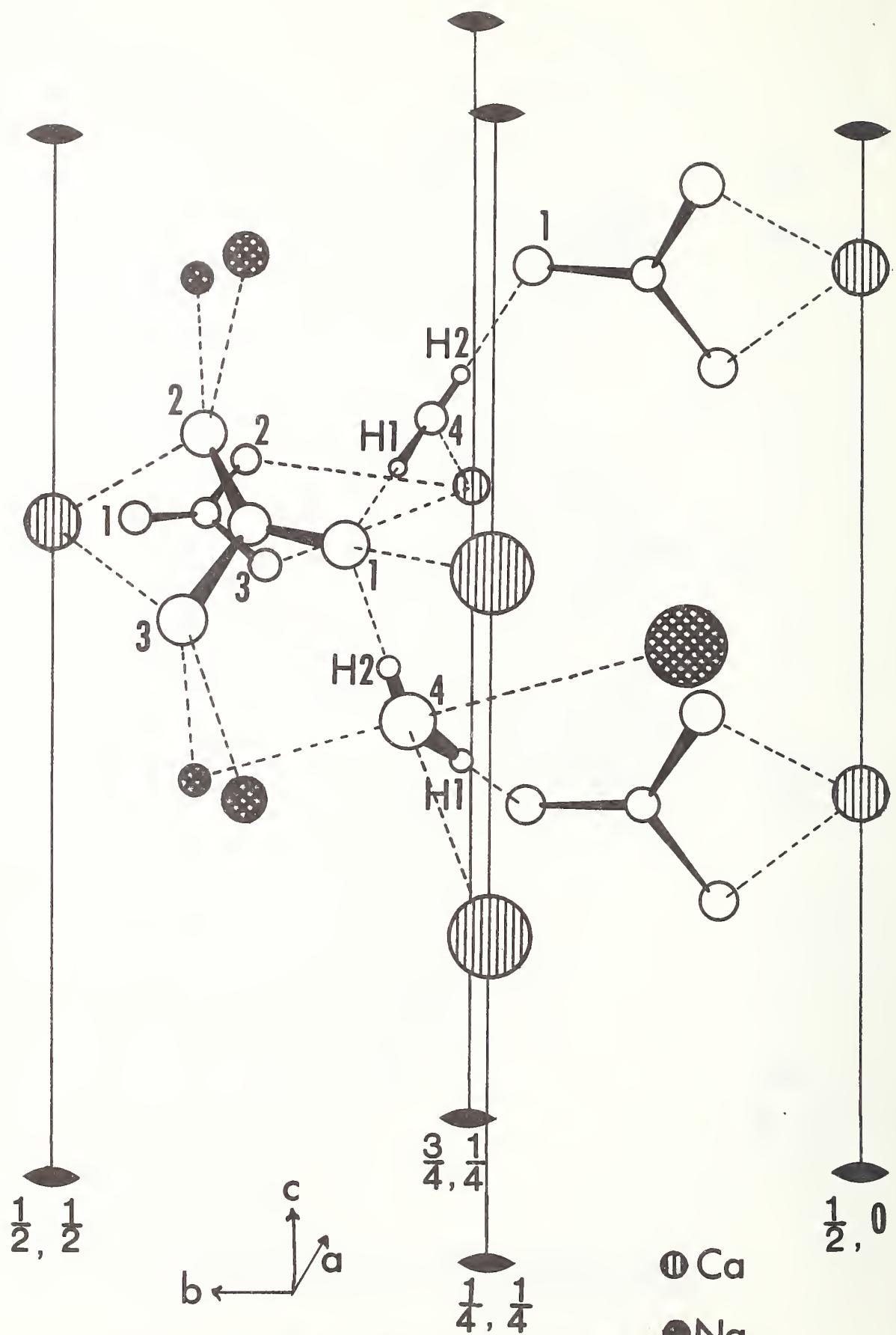


Fig. 6. The environments of the  $\text{CO}_3$  anion and water molecule in pirssonite.

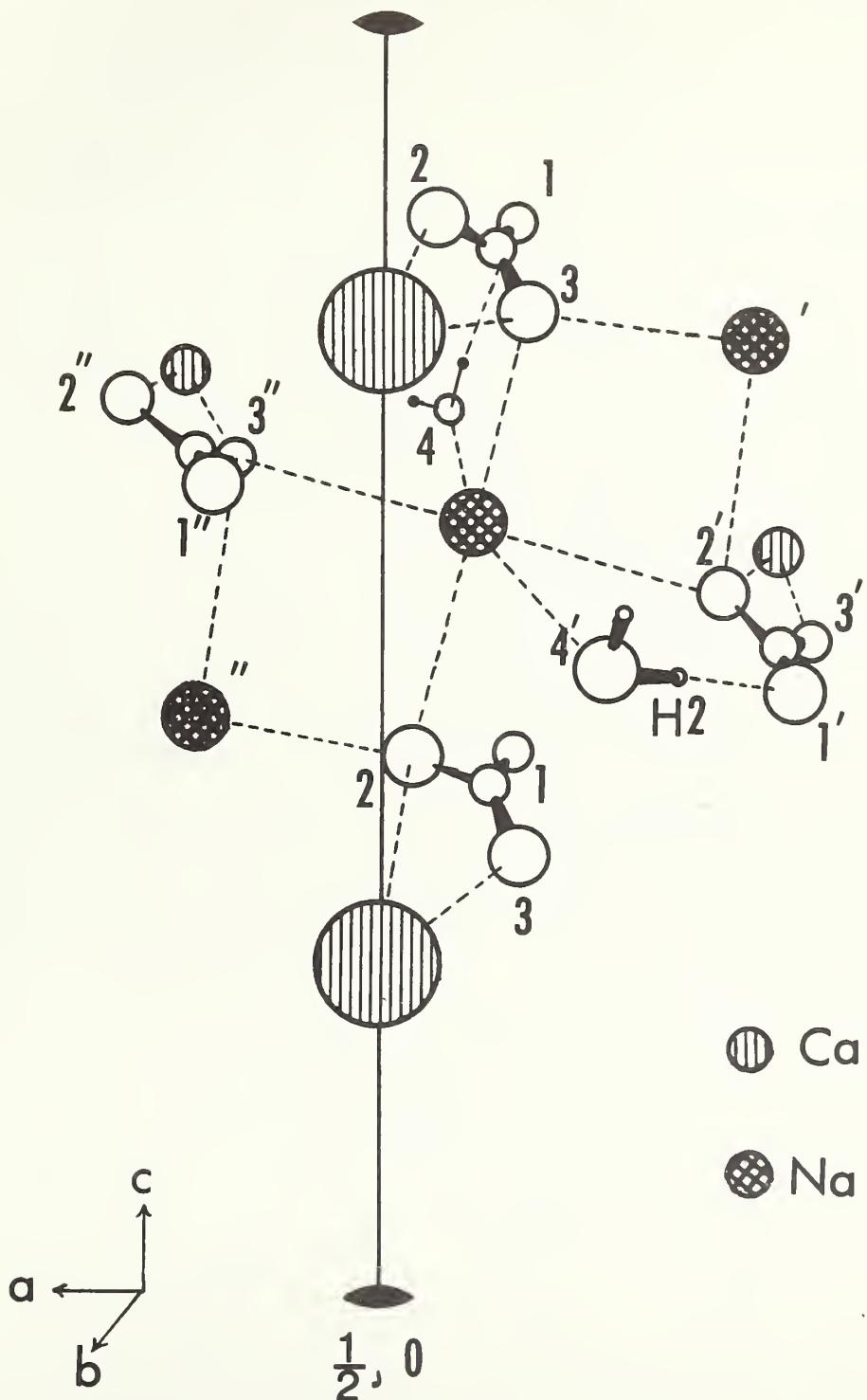


Fig. 7. The sodium ion environment in pirssonite.



