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A REFINEMENT OF THE CRYSTAL STRUCTURE OF $Na_2CO_3 \cdot H_2O$

by

B. Dickens,* F. A. Mauer,+ and W. E. Brown#

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

\+ Solid State Physicist, Crystallography Section, National Bureau of Standards, Washington, D. C. 20234

\# Research Associate from the American Dental Association in the Dental Research Section, National Bureau of Standards, Washington, D. C. 20234

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Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

ABSTRACT

The crystal structure of synthetic $Na_2CO_3 \cdot H_2O$ has been refined using 1231 unique x-ray diffraction data collected by the peak height method on a diffractometer. $R = 0.034$. The unit cell is $\underline{a} = 6.474(2)$, $\underline{b} = 10.724(3)$ and $\underline{c} = 5.259(2)$ Å with $Z = 4$ and space group $P2_1ab$. The calculated density is the same as the observed density, 2.26 $g \cdot cm^{-3}$. The structure contains sheets of CO_3^{2-} ions bonded to Na^+ ions and water molecules roughly halfway between the sheets. Each CO_3^{2-} bonds edgewise to both Na^+ ions. The Na^+ ions have irregular but similar coordinations of seven neighbors. Each water molecule is bonded to both Na^+ ions and forms hydrogen bonds to both neighboring CO_3^{2-} layers.

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*Director, Research Associate Program of the American Dental Association at the National Bureau of Standards.

1. INTRODUCTION

The crystal structure of $Na_2CO_3 \cdot H_2O$ was determined except for the hydrogen positions, by Harper [1] in 1936 using qualitative estimates of the x-ray intensities. In our program of studies on coordination in hydrated carbonates [2] and phosphates [3], we have refined Harper's structure for $Na_2CO_3 \cdot H_2O$ using new x-ray data. $Na_2CO_3 \cdot H_2O$ is the mineral thermonatrite and often occurs with $Na_2CO_3 \cdot 10H_2O$ (natron) and $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (trona) [4,5,6].

2. DETERMINATION OF THE STRUCTURE

Formula: $Na_2CO_3 \cdot H_2O$. Unit cell: Orthorhombic with $\underline{a}$ = 6.474(2) Å, $\underline{b}$ = 10.724(3) Å, $\underline{c}$ = 5.259(2) Å at 24°C as calculated from three pairs of 2θ values of axial reflections from a single crystal and observed on a diffractometer. The standard deviations of the cell parameters are in parentheses and are estimates based on experience with the technique. Cell volume: 365.1 $Å^3$. Wavelength used: 0.710688 Å (Mo $K\alpha$). Filter: 0.025 mm Nb. Space Group: $P2_1ab$. Cell contents in formula Wts: 4. Equivalent positions: x,y,z;1/2+x,-y,-z;1/2+x,1/2-y,z;x,1/2+y,-z. Reciprocal lattice extinctions: $h0\ell$, $h \neq 2n$; $hk0$, $k \neq 2n$. Observed density: 2.255 $g \cdot cm^{-3}$ [7]. Calculated density: 2.256 $g \cdot cm^{-3}$. Habit: Fragment from plate. Size of crystal: ~0.35 mm max. ~0.05 mm min.

Origin: Evaporation of aqueous solution at 60°C. *Linear absorption coefficient*: 4.37 cm^{-1}. *Absorption corrections:* None applied. Maximum error in any intensity from absorption is ~10%. *Number of reflections*: 2189 were collected from 2 octants and merged into a unique set of 1231 of which 1132 are "observed" reflections and 99 are less than 2σ above background and are "unobserved". *Maximum sinθ/λ for data*: 0.904 Å^{-1}. *Method used to estimate data*: peak height measurement [8] with a single crystal diffractometer [9] and some peak heights standardized against θ/2θ scans. *Scattering factors*: Na, C, O, for neutral atoms given in reference [10]; H from reference [11]. *Least-squares refinements*: Full-matrix, with $\Sigma(w||F_o|-|F_c||)^2$ minimized. Refinements include unobserved reflections for which the intensities are calculated more than 2σ above background. *Least-squares weights*: $1/\sigma^2$ normalized so that maximum weight is 1. *Definitions*: counts in peak = I = $P-(T/2T_B)(B_L + B_H)$, $\sigma(I) = (P+(B_L + B_H)(T/(2T_B))^2)^{\frac{1}{2}}$, $F = ((AF)(LP)(I))^{\frac{1}{2}}$, $\sigma(F) = (\sigma(I)/2)(LP/I)^{\frac{1}{2}}$ where P = counts at the peak position, B_L and B_H = background counts at lower and higher 2θ respectively, T = time spent counting peak, T_B = time spent counting background, AF = attenuator factor, LP = Lorentz polarization correction. $R_w = (\Sigma(w||F_o|-|F_c||)^2/\Sigma(w|F_o|)^2)^{\frac{1}{2}}$ $R = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$. *Final R_w*: 0.029. *Final R*: 0.032.

Average shift/error for last cycle: 0.015. Thermal parameters: anisotropic with form $\exp(-1/4(\underline{a}^{*2}\underline{B}_{11}\underline{h}^2 + \underline{b}^{*2}\underline{B}_{22}\underline{k}^2 + \underline{c}^{*2}\underline{B}_{33}\ell^2 + 2\underline{a}^*\underline{b}^*\underline{B}_{12}\underline{hk} + 2\underline{a}^*\underline{c}^*\underline{B}_{13}\underline{h\ell} + 2\underline{b}^*\underline{c}^*\underline{B}_{23}\underline{k\ell})$.

The structure was refined isotropically from Harper's parameters using the X-ray 67 system [12] of computer programs to $R_w = 0.065$; the $\underline{x}$ parameter of Na(1) was fixed at $\underline{x} = 0$. The structure was refined anisotropically to $R_w = 0.044$ and the hydrogens were found unambiguously as the two highest peaks in the difference synthesis in which the coefficients were weighed by the least-squares weights. The two next highest peaks were less than 3/4 as high as the peaks assigned to hydrogens and were (a) halfway between C and O(3) in the CO_3 group and (b) 0.7 Å from O(1) of the CO_3 group. The hydrogens were included with variable positional parameters and fixed thermal parameters (B_H = 1 Å^2) in the final refinement to R_w = 0.029. The largest correlation coefficients are ~0.25 between the scale factor and the $\underline{B}_{11}$ thermal parameters of the two Na ions and ~0.15 between these $\underline{B}_{11}$ thermal parameters. Most correlation coefficients are less than 0.05.

The atomic parameters are given in table 1. The observed and calculated structure factors are given in table 2. The hydrogen positions obtained from the weighted difference synthesis and from the refinements differ by ~0.17 Å. "Calculated" hydrogen positions were derived by applying the geometry of free water (O-H = 0.958 Å, ∠H-O-H = 104.5°) with the constraint that the O-H...O angles be as near to linear as possible. These hydrogen positions differ from the other positions by about 0.3 Å. The three sets of hydrogen positions are compared in table 3. The distances and angles which involve hydrogen were obtained using the "calculated" hydrogen positions.

3. DESCRIPTION OF THE STRUCTURE

The structure (fig. 1) contains CO_3 anions whose planes are almost perpendicular to *a* and which form sheets at $x \simeq 0.25$ and $x \simeq 0.75$. Because the C atoms lie close to the planes of the *a* glides, they form columns along *a* at $y = 0.25$, $z \simeq 0.60$. Two adjacent CO_3 groups in a column are held together by both being ionically bonded to four Na ions and hydrogen bonded by one water molecule. The four Na ions and the water molecule form a pentagon roughly halfway between the CO_3 sheets. Adjacent CO_3 groups in a given sheet are linked by the Na ions that lie above and below the sheet.

3.1. The Carbonate Anion and Environment

The dimensions in the CO_3 anion are given in table 4 and the environment is detailed in table 4 and figure 2. The CO_3 group is nearly trigonal. As can be seen in figures 1 and 2, O(2) is the only oxygen which is not hydrogen bonded, being instead ionically bonded to four Na ions. The absence of hydrogen bonding to O(2) may account for the observation that the C-O(2) bond is apparently the shortest of the three. O(1) is coordinated to three Na ions and is the acceptor in the hydrogen bond O(1)...H(1)-O(4) from the water molecule. O(3) is bonded strongly to two Na ions and more weakly (2.822 Å) to a third Na(2). O(3) is the acceptor in the hydrogen bond O(3)...H(2)-O(4) from the water molecule.

Since the planes of the CO_3 groups are all essentially perpendicular to a, this is expected to be the direction of lowest refractive index, as was found by Harper [1]. Later workers [13,14] apparently did not permute the refractive indexes when they permuted the unit cell axes to fit crystallographic convention.

3.2. The Sodium Environments

The two crystallographically distinct Na ions in the structure are in general positions. Their environments are shown in figure 3 and are given in table 5.

Na(1) is bonded ionically to five oxygens from CO_3 groups, and strongly to one water oxygen. Four of the CO_3 oxygens, O(1), O(2′), O(3), O(3′), figure 3, define an approximate square about Na(1), and water oxygen O(4) forms the apex of a square pyramid. The fifth carbonate oxygen, O(2), is in the same CO_3 group as O(1); the CO_3 group is therefore coordinated edgewise to Na(1). The position of O(2) is such that the coordination about Na(1) cannot be considered octahedral. The next oxygen in the direction of the octahedral apex is the water oxygen O(4′), which is relatively far (3.669 Å) from Na(1).

The coordination of Na(2) is similar to that of Na(1). Na(2) is slightly displaced from the center of an approximate square of carbonate oxygens, O(1′), O(2″), O(1″), O(2‴). The displacement is towards the strongly bonded water molecule O(4), which is the apex of a square based pyramid (base down in figure 3). The coordination of Na(2) is completed by O(4″) (2.936 Å) which is the remaining apex of an approximate octahedron, and by O(3′) which is in the same CO_3 group as O(2″). Thus the CO_3 group is coordinated edgewise to Na(2) also, this time using O(2) and O(3) instead of O(1) and O(2), which are used to coordinate to Na(1). This edgewise coordination is shown in figure 2. The coordination to Na(2) comprises five carbonate oxygens and two water molecules instead of four carbonate oxygens and two water molecules as suggested by Harper [1] and noted by Wells [15].

3.3. The Water Environment

The water environment is given in table 6 and shown in figure 3. The water molecule is bonded to Na(1) and Na(2) with distances of 2.434 and 2.384 Å respectively, and forms hydrogen bonds to oxygens O(1) and O(3) of neighboring CO_3 groups. Na(1), Na(2), O(1), and O(3) are arranged approximately tetrahedrally about the water oxygen. The distortion of this tetrahedron is considerable as can be seen from the angles listed in table 6. The closest H...Na distance is H(1)...Na(2) = 2.42 Å, which is in the normal range.

The calculated hydrogen positions in table 3 were obtained using the geometry of free water and imposing the condition that the O-H...O angles both be as linear as possible. Because H(2)...O(3) is shorter (1.74 Å) than H(1)...O(1) (1.96 Å) it is possible that the hydrogen bond O(4)-H(2)...O(3) is strictly linear. Assuming the same water geometry, the hydrogens would then be ≃ 0.14 Å away from the positions given in table 3 at 0.145, -0.046, 0.182 for H(1) and -0.065, -0.095, 0.102 for H(2). The O(4)-H(1)...O(1) angle would then be 156°, and the H(1)...O(1) and H(2)...O(3) distances would be 2.01 Å and 1.73 Å, respectively. The closest H...Na distance would be H(1)...Na(2) = 2.39 Å.

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Table 1 - Atomic Parameters of $Na_2CO_3 \cdot H_2O$

Atom	x	y	z	B^*_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na(1)	.0000	.1938(1)	.1398(1)	1.40(3)	1.54(3)	1.36(3)	.17(3)	.17(3)	.08(2)
Na(2)	.0651(2)	.0020(1)	-.3786(2)	1.44(3)	1.19(3)	1.76(3)	.31(2)	.25(3)	.09(3)
C	-.2151(3)	.2556(2)	.6025(3)	.45(6)	1.11(6)	1.17(5)	-.06(5)	-.05(5)	-.03(5)
O(1)	-.2010(3)	.1381(1)	.5457(3)	1.56(6)	0.72(5)	2.72(7)	.08(5)	-.15(6)	-.47(4)
O(2)	-.2027(3)	.3369(1)	.4267(2)	1.73(6)	1.27(5)	1.24(5)	-.05(5)	-.04(5)	.47(4)
O(3)	-.2398(3)	.2876(1)	-.1639(2)	1.42(6)	2.14(6)	0.90(4)	-.28(5)	.25(4)	-.32(4)
O(4)	.0325(3)	-.0296(1)	.0683(3)	1.64(7)	1.43(6)	1.92(6)	-.21(5)	-.25(5)	.39(4)

Figures in parentheses are standard errors in last significant figure quoted, and were computed in the final cycle of full-matrix least-squares refinement.

* Thermal parameters are in $Å^2$

Table 2

Observed and Calculated Structure Factors for $Na_2CO_3 \cdot H_2O$[a]

0,K,0		
2	253	237
4	421	452
6	556	561
8	135	113
10	119	119
12	48	43
14	53	50
16	53	52
18	47	60
1,K,0		
2	156	151
4	523	519
6	254	236
8	153	166
10	86	88
12	45	47
14	139	116
16	58	73
18	18	15
2,K,0		
0	39	37
2	843	932
4	362	529
6	283	286
8	128	126
10	311	318
12	30	31
14	34	35
16	44	49
18	35	51
3,K,0		
2	176	171
4	428	415
6	252	251
8	127	127
10	144	145
12	53	59
14	38	43
16	55	59
18	19	19
4,K,0		
2	345	339
4	236	223
6	245	274
8	233	228
10	52	32
12	37	39
14	52	54
16	33	25
18	32	46
5,K,0		
2	131	96
4	171	167
6	29	30
8	115	113
10	24	23
12	37	39
14	113	119
16	60	61
6,K,0		
0	86	76
2	333	296
4	199	192
6	73	68
8	130	129
10	126	125
12	50	57
14	47	48
16	13*	7
7,K,0		
2	87	87
4	143	142
6	127	127
8	52	55
10	86	88
12	25	19
14	12*	2
8,K,0		
0	153	158
2	148	148
4	40	42
6	51	61
8	136	135
10	80	79
12	73	72
14	35	54
9,K,0		
2	28	28
4	37	38
6	33	51
8	53	53
10	16	19
12	56	31
10,K,0		
0	53	88
2	88	90
4	66	58
6	12*	9
8	43	47
10	39	43
11,K,0		
2	36	39
4	29	32
6	43	40
0,K,1		
0	259	274
1	77	74
2	22	19
3	5*	3
4	211	192
5	284	268
6	200	147
7	159	157
8	360	345
9	146	189
10	115	125
11	9*	8
12	168	191
13	9*	9
14	85	88
15	32	36
16	57	55
17	13	9
18	25	31
19	13*	1
1,K,1		
0	5*	0
1	44	39
2	66	66
3	307	314
4	350	353
5	206	204
6	83	86
7	269	275
8	144	147
9	165	166
10	147	151
11	33	31
12	60	63
13	120	122
14	83	85
15	29	26
16	67	69
17	44	44
18	17	7
19	37	36
2,K,1		
0	604	605
1	444	449
2	299	309
3	326	329
4	275	270
5	28	27
6	105	101
7	80	80
8	94	91
9	125	124
10	205	208
11	61	64
12	51	53
13	53	61
14	66	82
15	34	29
16	52	35
17	48	42
18	92	66
19	39	35
3,K,1		
0	5*	0
1	157	186
2	126	123
3	292	291
4	182	177
5	123	127
6	67	61
7	223	224
8	74	97
9	71	70
10	93	96
11	91	94
12	17	14
13	88	88
14	90	93
15	33	38
16	75	78
17	45	43
18	12*	6
4,K,1		
0	368	374
1	61	62
2	28	27
3	25	23
4	125	121
5	128	126
6	183	182
7	105	105
8	194	191
9	111	110
10	116	114
11	28	28
12	130	127
13	16	11
14	61	63
15	16	20
16	55	53
17	33	32
18	15	14
5,K,1		
0	7*	0
1	127	126
2	43	49
3	29	28
4	153	151
5	219	221
6	102	102
7	57	65
8	76	74
9	104	111
10	77	89
11	62	57
12	48	48
13	49	50
14	28	32
15	45	41
17	25	23
6,K,1		
0	189	195
1	166	171
2	94	93
3	113	111
4	125	124
5	28	37
6	74	74
7	93	90
8	29	25
9	70	56
10	144	142
11	47	46
12	27	27
13	19	20
14	37	37
15	12*	6
16	36	41
7,K,1		
0	7*	0
1	106	111
2	56	53
3	46	44
4	41	40
5	110	109
6	49	56
7	62	65
8	23	23
9	12	11
10	23	21
11	67	70
12	32	30
13	17	10
14	51	53
15	39	42
8,K,1		
0	174	182
1	47	49
2	82	84
3	28	31
4	48	46
5	42	47
6	90	89
7	31	31
8	47	41
9	29	29
10	58	56
11	12*	17
12	43	44
13	12*	6
14	35	34
9,K,1		
0	12*	0
1	40	43
2	25	25
3	61	63
4	63	66
5	76	77
6	39	40
7	24	27
8	25	26
9	60	62
10	29	29
11	27	26
12	14	15
10,K,1		
0	67	74
1	44	49
2	33	36
3	35	36
4	52	55
5	24	26
6	16	15
7	47	49
8	45	48
9	42	43
11,K,1		
0	12*	0
1	36	36
2	15	13
3	13*	10
4	17	17
5	32	34
6	39	39
0,K,2		
0	353	337
1	117	139
2	143	141
3	152	166
4	129	123
5	58	56
6	132	132
7	73	72
8	111	115
9	53	54
10	135	141
11	11	17
12	23	24
13	9*	10
14	10*	1
15	74	71
16	19	17
17	106	106
18	26	26
1,K,2		
0	13	0
1	856	831
2	113	113
3	427	440
4	27	20
5	495	504
6	121	121
7	113	113
8	47	49
9	124	123
10	77	82
11	149	149
12	47	48
13	22	16
14	41	43
15	67	66
16	47	50
17	39	56
18	12*	5
2,K,2		
0	133	134
1	319	331
2	174	177
3	222	227
4	226	233
5	157	165
6	72	72
7	204	205
8	36	39
9	257	268
10	74	74
11	74	72
12	37	37
13	41	36
14	30	31
15	26	25
16	21	22
17	35	35
18	13*	15
3,K,2		
0	6	0
1	389	402
2	88	90
3	119	122
4	57	55
5	377	348
6	41	41
7	164	165
8	59	60
9	130	129
10	63	66
11	99	96
12	25	24
13	78	81
14	41	43
15	58	56
16	46	49
17	12*	1
18	12*	0
4,K,2		
0	210	209
1	115	117
2	91	90
3	91	67
4	55	55
5	58	55
6	86	64
7	170	117
8	72	71
9	82	85
10	92	95
11	25	18
12	19	19
13	16	16
14	14	15
15	69	66
16	13	15
17	71	72
5,K,2		
0	7*	0
1	171	170
2	34	34
3	336	440
4	18	19
5	135	154
6	92	92
7	143	141
8	13	14
9	70	89
10	42	45
11	50	82
12	38	58
13	71	72
14	25	27
15	12*	14
16	26	30
17	45	46
6,K,2		
0	61	61
1	139	143
2	74	76
3	85	86
4	81	41
5	80	81
6	24	22
7	65	65
8	27	29
9	137	136
10	45	44
11	49	48
12	23	24
13	55	56
14	24	26
15	27	25
16	17	17
7,K,2		
0	8*	0
1	91	95
2	24	25
3	105	109
4	37	37
5	59	67
6	10*	7
7	127	127
8	35	36
9	58	56
10	35	35
11	11*	10
12	11*	3
13	64	66
14	20	21
15	20	16
8,K,2		
0	97	102
1	32	33
2	53	54
3	61	62
4	13	12
5	35	37
6	36	35
7	98	94
8	24	24
9	51	52
10	33	34
11	42	41
12	12*	10
13	17	17
9,K,2		
0	10*	0
1	19	16
2	10*	5
3	106	107
4	16	16
5	29	31
6	67	65
7	57	57
8	11*	3
9	49	55
10	15	13
11	21	19
10,K,2		
0	50	31
1	66	72
2	30	53
3	37	41
4	22	22
5	40	44
6	12*	10
7	12*	7
8	17	15
9	38	41
11,K,2		
0	12*	0
1	24	25
2	12*	4
3	51	54
4	15	16
5	13*	11
0,K,3		
0	279	278
1	55	55
2	458	469
3	86	86
4	168	170
5	208	214
6	15	13
7	118	121
8	209	235
9	205	205
10	33	27
11	26	30
12	122	120
13	10*	0
14	27	30
15	11*	5
16	21	23
17	53	55
18	61	62
1,K,3		
0	6*	0
1	88	87
2	148	153
3	236	242
4	182	188
5	41	48
6	168	175
7	141	185
8	77	80
9	123	125
10	22	20
11	59	58
12	47	47
13	104	133
14	50	51
15	45	43
16	16	16
17	54	53
18	22	22
2,K,3		
0	211	215
1	120	122
2	179	186
3	144	148
4	70	71
5	10	9
6	120	120
7	157	162
8	153	153
9	35	33
10	34	38
11	17	13
12	20	19
13	55	60
14	90	91
15	50	46
16	36	36
17	67	66
18	30	26
3,K,3		
0	8*	0
1	194	198
2	96	95
3	172	175
4	144	148
5	104	105
6	173	178
7	164	146
8	63	65
9	82	83
10	31	32
11	67	68
12	66	66
13	71	71
14	28	29
15	54	55
16	12*	6
17	65	62
4,K,3		
0	237	237
1	54	54
2	220	220
3	26	22
4	149	155
5	127	151
6	84	86
7	77	77
8	103	99
9	137	136
10	106	109
11	35	36
12	75	72
13	15	12
14	56	57
15	12*	8
16	33	53
17	54	52
5,K,3		
0	7*	0
1	45	45
2	102	106
3	111	111
4	88	89
5	114	119
6	78	79
7	74	75
8	31	31
9	89	92
10	25	26
11	61	57
12	50	51
13	57	37
14	29	32
15	35	32
16	28	31
6,K,3		
0	133	130
1	64	66
2	47	47
3	66	70
4	27	27
5	27	27
6	101	106
7	116	115
8	25	25
9	40	39
10	39	39
11	23	20
12	29	29
13	27	31
14	57	37
15	24	23
7,K,3		
0	9*	0
1	106	111
2	43	45
3	29	27
4	76	80
5	74	75
6	73	74
7	76	76
8	36	38
9	25	23
10	16	15
11	46	52
12	38	40
13	16	14
14	16	15
8,K,3		
0	104	110
1	50	53
2	30	26
3	22	24
4	77	80
5	57	60
6	40	42
7	29	29
8	27	25
9	51	52
10	73	76
11	19	21
12	15	12
9,K,3		
0	11*	0
1	25	27
2	32	35
3	72	72
4	33	36
5	53	55
6	24	25
7	14	14
8	12*	5
9	45	67
10	29	30
10,K,3		
0	35	36
1	20	23
2	20	20
3	50	34
4	22	22
5	23	26
6	37	40
7	36	60
8	23	26
11,K,3		
0	12*	0
1	43	42
2	22	23
0,K,4		
0	633	493
1	18	16
2	54	56
3	31	79
4	253	287
5	14	17
6	153	147
7	158	174
8	23	20
9	13	14
10	142	148
11	13*	5
12	57	64
13	74	77
14	11*	5
15	11*	1
16	57	65
17	30	56
1,K,4		
1	121	120
2	111	116
3	137	143
4	150	152
5	59	74
6	137	109
7	156	165
8	33	32
9	81	86
10	30	40
11	33	31
12	60	63
13	33	26
14	45	47
15	27	28
16	16	17
17	13*	15
2,K,4		
0	235	231
1	153	152
2	177	182
3	47	53
4	87	83
5	137	111
6	214	227
7	24	25
8	74	75
9	54	53
10	136	136
11	81	94
12	21	23
13	35	40
14	59	69
15	11*	3
16	29	37
17	53	51
3,K,4		
1	77	73
2	128	135
3	153	165
4	154	153
5	25	27
6	83	86
7	113	114
8	24	33
9	57	71
10	29	26
11	12	19
12	24	31
13	14	15
14	28	28
15	31	31
16	12*	11
4,K,4		
0	233	246
1	17	19
2	163	168
3	57	60
4	175	178
5	13	14
6	44	62
7	125	123
8	135	133
9	13	11
10	56	70
11	12	9
12	74	73
13	53	56
14	23	23
15	12*	13
16	45	41
5,K,4		
1	87	89
2	24	24
3	33	29
4	61	57
5	65	71
6	52	53
7	78	100
8	43	43
9	40	51
10	41	43
11	28	30
12	62	66
13	24	22
14	51	52
15	13*	13
6,K,4		
0	14	17
1	33	34
2	131	132
3	44	44
4	57	58
5	52	56
6	72	74
7	38	39
8	86	98
9	62	61
10	45	44
11	42	43
12	34	34
13	16	16
14	59	60
7,K,4		
1	37	57
2	57	56
3	102	104
4	83	84
5	11	10
6	51	52
7	41	43
8	25	29
9	29	31
10	16	17
11	12*	10
12	10	9
13	17	16
8,K,4		
0	43	44
1	18	19
2	92	96
3	32	36
4	52	54
5	11*	9
6	36	58
7	53	58
8	44	67
9	12*	12
10	20	17
11	15	12
9,K,4		
1	45	48
2	17	17
3	25	24
4	22	20
5	38	41
6	15	12
7	33	33
8	26	25
9	19	19
10,K,4		
0	47	57
1	30	31
2	46	46
3	23	22
4	38	43
5	28	32
0,K,5		
0	147	144
1	57	46
2	11	12
3	35	36
4	101	102
5	14	15
6	27	28
7	64	61
8	95	69
9	7*	4
10	17*	6
11	57	56
12	87	82
13	17	18
14	12	11
15	29	32
16	41	35
1,K,5		
1	171	127
2	48	73
3	249	249
4	97	101
5	91	82
6	37	39
7	101	99
8	27	25
9	45	45
10	37	35
11	29	34
12	11	15
13	47	50
14	33	34
15	29	27
16	14	13
2,K,5		
0	121	116
1	187	187
2	155	168
3	96	96
4	35	55
5	37	36
6	54	55
7	118	119
8	50	33
9	71	70
10	67	61
11	54	52
12	11*	4
13	21	22
14	73	67
15	12*	1
16	13*	14
3,K,5		
1	71	71
2	32	37
3	170	170
4	52	36
5	83	49
6	11	12
7	111	111
8	42	43
9	17	17
10	20	15
11	75	76
12	25	29
13	47	49
14	38	39
15	25	24
4,K,5		
0	325	326
1	38	37
2	51	51
3	40	43
4	72	73
5	16	14
5	16	14
5	15	14
7	61	61
7	61	61
7	61	61
9	34	34
10	27	26
11	43	44
12	72	68
13	26	27
14	12*	1
15	19	20
5,K,5		
1	167	169
2	48	51
3	122	121
4	59	62
5	112	115
6	41	41
7	15	17
8	10*	6
9	35	37
10	24	27
11	14	12
12	14	15
13	12*	13
14	19	16
6,K,5		
0	95	97
1	94	100
2	65	65
3	45	47
4	55	54
5	37	32
6	45	48
7	55	54
8	18	14
9	34	33
10	63	59
11	47	48
12	18	13
13	28	26
7,K,5		
1	35	37
2	11	14
3	34	54
4	11	9
5	56	54
6	11*	4
7	53	51
8	28	30
9	31	55
10	12*	6
11	51	58
8,K,5		
0	59	60
1	19	19
2	57	59
3	28	30
4	33	32
5	16	17
6	41	42
7	31	35
8	26	23
9	34	36
9,K,5		
1	40	41
2	17	14
3	51	30
4	22	20
5	49	53
6	22	22
7	22	22
0,K,6		
0	27	25
1	95	92
2	76	76
3	54	55
4	9*	4
5	39	37
6	21	25
7	63	52
8	73	70
9	20	21
10	86	82
11	11*	14
12	68	67
13	47	42
14	46	44
15	26	20
1,K,6		
1	93	90
2	35	53
3	13	17
4	29	31
5	124	119
6	74	71
7	43	42
8	50	63
9	51	31
10	46	49
11	79	79
12	34	32
13	33	33
14	36	36
2,K,6		
0	33	28
1	53	57
2	84	78
3	24	24
4	31	53
5	23	20
6	13*	9
7	71	44
8	12	11
9	16	33
10	41	37
11	63	51
12	33	51
13	32	28
14	82	31
3,K,6		
1	62	61
2	14	12
3	138	139
4	22	22
5	62	80
6	53	53
7	31	32
8	57	50
9	54	51
10	35	37
11	35	55
12	32	26
13	29	23
14	44	41
4,K,6		
0	78	77
1	71	68
2	44	64
3	39	37
4	17	13
5	42	40
6	24	24
7	33	34
8	59	56
9	30	30
10	67	62
11	16	12
12	81	51
13	57	54
5,K,6		
1	44	44
2	57	57
3	53	49
4	44	44
5	41	41
6	57	55
7	77	79
8	28	32
9	34	55
10	33	54
11	40	42
12	18	16
6,K,6		
0	25	26
1	34	33
2	56	54
3	37	33
4	24	23
5	15	13
6	13*	6
7	31	32
8	12*	3
9	34	56
10	32	32
11	80	50
7,K,6		
1	11*	8
2	18	13
3	79	79
4	39	39
5	11*	9
6	23	25
7	29	10
8	29	29
9	30	31
8,K,6		
0	77	76
1	28	26
2	40	41
3	14	15
4	20	21
5	30	28
6	19	17
7	18	15
9,K,6		
1	30	31
2	24	27
0,K,7		
0	90	88
1	27	29
2	160	136
3	17	11
4	49	47
5	45	37
6	11*	11
7	50	43
8	69	64
9	41	35
10	11*	1
11	38	34
12	13*	9
13	63	39
1,K,7		
1	43	42
2	56	35
3	57	56
4	55	55
5	39	37
6	67	65
7	56	57
8	11*	7
9	25	21
10	14	12
11	25	24
12	39	39
13	30	27
2,K,7		
0	83	88
1	30*	16
2	31	44
3	20	14
4	33	23
5	47	39
6	44	42
7	33	24
8	47	50
9	27	24
10	39	37
11	38	33
12	25	24
3,K,7		
1	44	44
2	66	67
3	24	24
4	75	74
5	64	63
6	69	65
7	24	25
8	21	21
9	32	31
10	19	15
11	34	34
12	33	29
4,K,7		
0	81	78
1	21	21
2	107	101
3	30	27
4	49	44
5	37	32
6	22	27
7	40	34
8	39	34
9	53	28
10	41	40
11	32	30
5,K,7		
1	32	34
2	20	17
3	62	41
4	11*	4
5	11*	9
6	43	42
7	43	43
8	12*	10
9	15*	12
10	30	25
6,K,7		
0	82	80
1	14	9
2	11*	3
3	24	21
4	16	12
5	39	56
6	46	45
7	28	23
8	19	17
7,K,7		
1	20	27
2	56	37
3	23	24
4	49	48
5	56	37
6	38	37
0,K,8		
0	19	9
1	11*	7
2	11*	6
3	45	40
4	57	53
5	63	57
6	11*	9
7	65	56
8	23	16
9	23	15
10	48	47
1,K,8		
1	11*	9
2	38	33
3	43	37
4	38	38
5	27	26
6	45	41
7	37	36
8	18	17
9	37	38
10	24	22
2,K,8		
0	76	71
1	72	65
2	54	32
3	56	67
4	15	11
5	55	51
6	72	67
7	15	14
8	26	24
9	13*	12
3,K,8		
1	11*	2
2	25	23
3	47	38
4	12*	11
5	27	23
6	39	37
7	39	36
8	15	18
9	31	37
4,K,8		
0	11*	7
1	14	14
2	34	35
3	38	35
4	48	44
5	48	45
6	14	13
7	47	41
8	32	28
5,K,8		
1	18	13
2	27	27
3	25	24
4	34	37
5	33	32
6	25	20
6,K,8		
0	13*	11
1	54	51
2	67	60
3	62	60
0,K,9		
0	79	81
1	22	14
2	13	11
3	21	17
4	84	76
5	28	24
6	10	13
1,K,9		
1	20	16
2	13*	9
3	58	59
4	24	22
5	25	21
6	24	27
2,K,9		
0	21	19
1	44	47
2	68	62
3	13*	6
4	27	24
5	25	23
3,K,9		
1	20	12
	15	11
	35	01

[a] The columns are k, $10F_o$, $10F_c$. "Unobserved" reflections are marked by *. F_o and F_c are on an absolute seale.

Table 3 - The Hydrogen Positions in $Na_2CO_3 \cdot H_2O$

Atom	Weighted difference synthesis			Least squares refinements			Calculated*		
	x	y	z	x	y	z	x	y	z
H(1)	.12	-.07	.14	.11	-.06	.15	.134	-.056	.190
H(2)	-.08	-.08	.14	-.10	-.08	.12	-.077	-.089	.084

*Assuming the geometry of free water with O-H = 0.958 Å and ∠H-O-H = 104.5°, and making the O-H...O hydrogen bonds as linear as possible.

Table 4 - The CO_3 Group

Atoms	Distances, Å, or angle, deg.
C,O(1)	1.299(3)
C,O(2)	1.274(2)
C,O(3)	1.285(2)
O(1),O(2)	2.223(2)
O(1),O(3)	2.229(2)
O(2),O(3)	2.230(2)
O(1),C,O(2)	119.6(2)
O(1),C,O(3)	119.2(2)
O(2),C,O(3)	121.2(2)
O(1),Na(1)	2.570(2)
O(1),Na(2)	2.293(2)
O(1),Na(2′)	2.307(2)
O(1),O(4)	2.907(2)
O(1),H(1)	1.96
O(2),Na(1)	2.521(2)
O(2),Na(1′)	2.468(2)
O(2),Na(2′)	2.508(2)
O(2),Na(2)	2.491(2)
O(3),Na(1)	2.444(2)
O(3),Na(1′)	2.330(2)
O(3),Na(2)	2.822(2)
O(3),O(4)	2.684(2)
O(3),H(2)	1.74

In all tables of interatomic distances and angles, the quantities in parentheses are standard errors in the last significant figure and were computed from the standard errors in the atomic positional parameter and in the cell parameters. The primes refer to atoms in figure 2.

Table 5 - The Sodium Environments

Atoms	Distance, Å
Na(1),O(1)	2.570(2) Å
Na(1),O(2)	2.521(2)
Na(1),O(3)	2.444(2)
Na(1),O(4)	2.434(2)
Na(1),O(2′)	2.468(2)
Na(1),O(3′)	2.330(2)
Na(1),O(4′)	3.669(2)
Na(2),O(4)	2.384(2) Å
Na(2),O(1′)	2.293(2)
Na(2),O(1″)	2.307(2)
Na(2),O(2″)	2.508(2)
Na(2),O(2‴)	2.491(2)
Na(2),O(4″)	2.936(2)
Na(2),O(3′)	2.822(2)

The primes refer to the atoms in figure 3.

Table 6 - The Water Environment

atom	distance Å or angle, deg.
O(4),Na(1)	2.434(2) Å
O(4),Na(2)	2.384(2)
O(4),Na(2′)	2.936(2)
O(4),O(1)	2.907(2)
O(4),O(3)	2.684(2)
H(1),O(1)	1.96
H(2),O(3)	1.74
Na(1),O(4),Na(2)	91.15(6)°
O(1),O(4),Na(1)	109.70(7)
O(1),O(4),Na(2)	133.83(9)
O(3),O(4),Na(1)	129.28(9)
O(3),O(4),Na(2)	110.29(7)
O(1),O(4),O(3)	88.12(6)
O(4),H(1),O(1)	168.
O(4),H(2),O(3)	167.

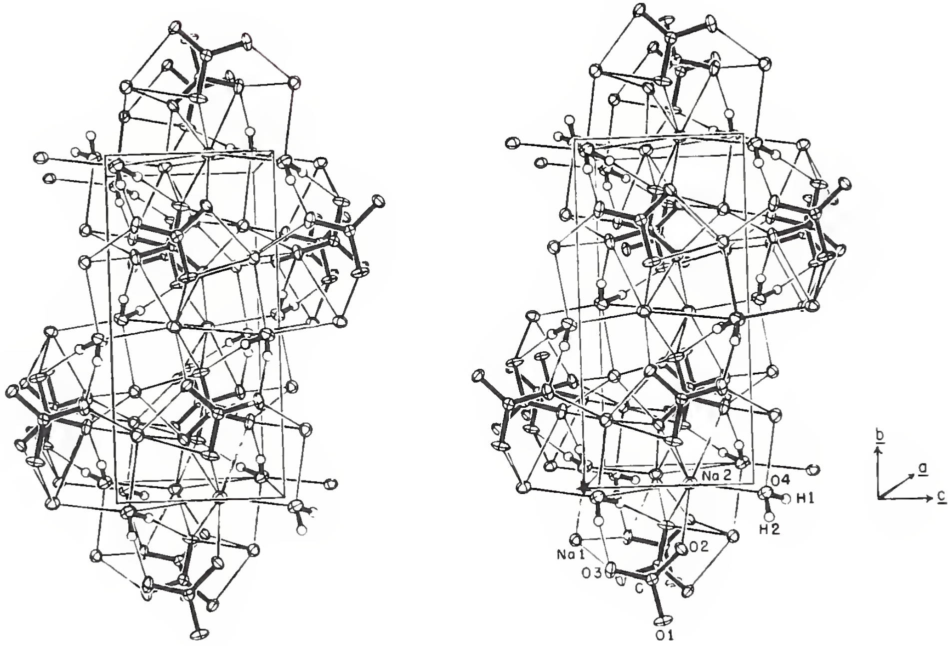
The prime refers to an atom in figure 3.

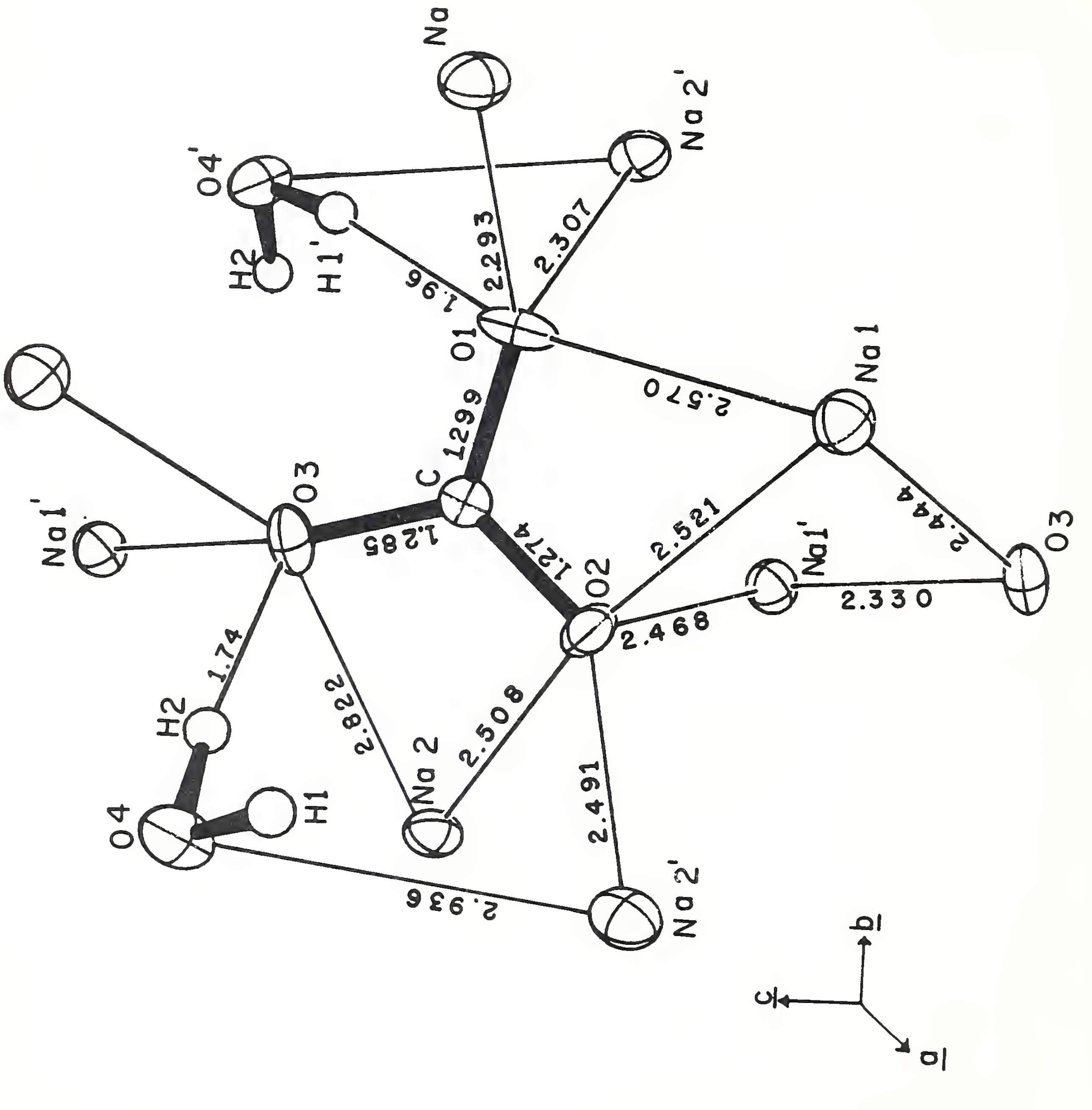
Figure Legends

Figure 1. A stereoscopic illustration of $Na_2CO_3 \cdot H_2O$ viewed along $\underline{a}$. The origin of the unit cell is marked by the asterisk.

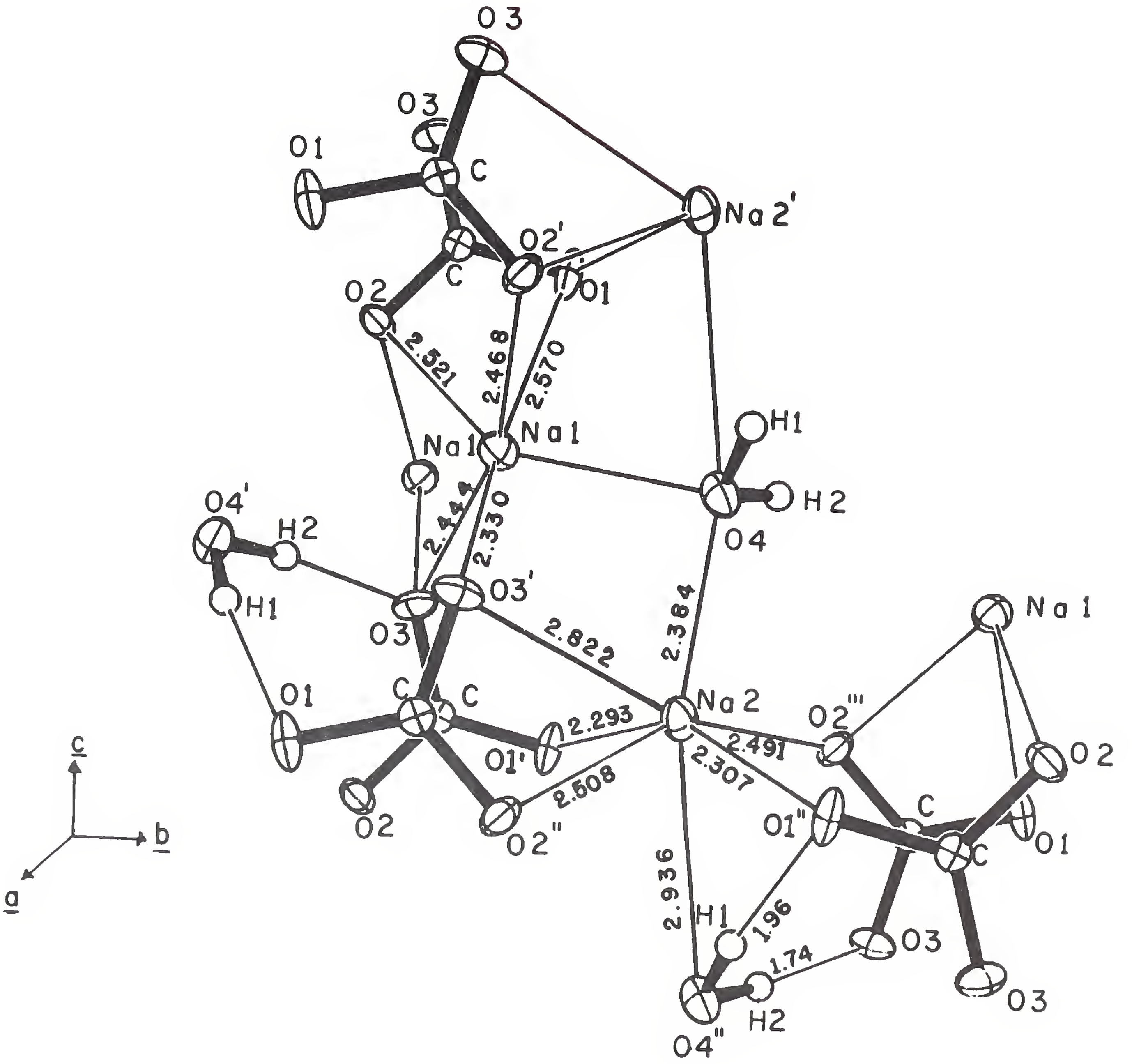
Figure 2. The carbonate group environment in $Na_2CO_3 \cdot H_2O$. The primes refer to atoms in table 4.

Figure 3. The water and sodium environments in $Na_2CO_3 \cdot H_2O$. The primes refer to atoms in tables 5 and 6.


O4
H1
H2
Na 2
O2
Na 1
O3
C
O1
b
a
c



Na 2
Na 2'
O4'
H2
H1'
1.96
2.293
2.307
O1
Na 1
2.570
Na 1
1299
C
O3
Na 1'
1.285
1.274
O2
2.521
2.444
O3
Na1'
2.330
2.468
1.74
H2
2.822
2.508
Na 2
2.491
O4
H1
2.936
Na 2'
c
b
a


O3
O3
O1
C
Na2'
C
O2'
O1
O2
2.521
2.468
2.570
Na1
Na1
H1
H2
O4
O4'
H2
2.444
2.330
H1
O3
O3'
2.822
2.384
Na1
O1
C
C
Na2
2.293
O2'''
2.491
O2
2.307
O1'
2.508
O2
O2''
O1''
C
C
O1
2.936
H1
1.96
1.74
O3
O3
H2
O4''
c
b
a