NATIONAL BUREAU OF STANDARDS REPORT

9985

Progress Report

on

THE CRYSTAL STRUCTURE OF $CaCO_3 \cdot 6H_2O$ at $-120^\circ C$



U.S. DEPARTMENT OF COMMERCE

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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

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Brian Dickens and Walter E. Brown*

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

ABSTRACT

The crystal structure of $CaCO_3 \cdot 6H_2O$ has been determined from 1420 x-ray diffraction data collected photographically by the oscillation technique from a single crystal held at about -120°C. The unit cell is $\underline{a}$ = 8.87 ± .02 Å, $\underline{b}$ = 8.23 ± .01 Å, $\underline{c}$ = 11.02 ± .02 Å, β = 110.2 ± .2° and the space group is C2/c or Cc with z = 4. Refinement is satisfactory in C2/c. $R_w = \sqrt{(\Sigma(w||F_o|-|F_c||)^2/(\Sigma w|F_o|)^2)} = 0.12$. $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.10$. The calculated density at about -120°C is 1.80 g/ml, the observed density at about 0°C is 1.82 g/ml. The structure contains discrete $CaCO_3$ ion pairs, each surrounded by an envelope of 18 water molecules. Thus Ca is preferentially coordinated to CO_3.

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

$CaCO_3 \cdot 6H_2O$ was found to be more stable than $CaCO_3 \cdot H_2O$ in water near 0°C. The formation of $CaCO_3 \cdot 6H_2O$ from an equivalent amount of calcite ($CaCO_3$) and water is accompanied by a 20% decrease in volume. This may be important in explaining the scarcity of calcareous material in life in the ocean depths.

INTRODUCTION

In calcium carbonate mineralization, nearly all of the attention has been given to the anhydrous $CaCO_3$ forms (calcite, aragonite and vaterite), which are known to occur both simultaneously and individually in the shells of molluscs[1] and in other biological minerals,[2] including gallstones.[3] The two known hydrated calcium carbonates, $CaCO_3 \cdot 6H_2O$ [4,5] and $CaCO_3 \cdot H_2O$ [4,6] have been neglected in this respect, possibly because of their metastability with respect to the anhydrous salts. This neglect may not be warranted because in aqueous environments (a) very small particles of hydrated salts frequently may have greater stability than similar particles of anhydrous salts because of their probably lower surface energies, (b) hydrated crystals tend to grow more easily than anhydrous crystals, (c) polyphosphate[4] and magnesium[6] ions repress the growth of anhydrous calcium carbonates more than that of the hydrated salts, and (d) low temperatures and high pressures, such as those in the oceanic deeps, should favor the formation of the hydrated compounds.

The report of the structure of $CaCO_3 \cdot 6H_2O$ given here is part of a larger study of hydrated salts which have potential importance in biological mineralization. The structures of $CaNa_2(CO_3)_2 \cdot 5H_2O$ (gaylussite)[7] and $CaNa_2(CO_3)_2 \cdot 2H_2O$ (pirssonite)[7,8] have been reported. One of the major objectives of our studies is to learn more about the interaction between water molecules and the calcium and carbonate ions in hydrated salts.

Early work on $CaCO_3 \cdot 6H_2O$ and $CaCO_3 \cdot H_2O$, including some chemical properties and preparative details using crystal growth poisons, is summarized by Brooks, Clark and Thurston.[4] Powder x-ray diffraction data have been reported.[4]

EXPERIMENTAL METHODS

Crystals of $CaCO_3 \cdot 6H_2O$ up to 2 mm in diameter were grown from calcium carbonate gels left for several months at 3-5°C in a solution containing 400 ppm sodium polyphosphate. The calcium carbonate gels were prepared following a procedure similar to that given by Brooks, Clark and Thurston.[4] Thus, 2.4 g $CaCl_2$ dissolved in 100 ml water were added to 150 ml water containing 4.6 g Na_2CO_3 and 0.5 g sodium polyphosphate. After about six days the gel, which formed initially, had disappeared and spherulites had formed. These were identified

as $CaCO_3 \cdot H_2O$ from an x-ray powder pattern. On standing for several months, the spherulites dissolved and crystals of $CaCO_3 \cdot 6H_2O$ were formed.

Two distinct views of the $CaCO_3 \cdot 6H_2O$ crystals were common. (a) Plates with low birefringence and parallel extinction. These, when modified by (110)-type faces, exhibited 2/m symmetry with symmetrical extinction and with the fast direction, N_β, parallel to $\underline{b}$; the trace of the (110) $(\bar{1}10)$, 93.4°, yields an axial ratio $\underline{a}/\underline{b}$ = 1.05. (b) Short, highly birefringent {010} rods or plates with the slow direction, N_γ, extinguishing at 17° from $\underline{c}$ in acute $\underline{\beta}$; these give $\underline{\beta}$ = 109.4° and $\underline{c}/\underline{a}$ = 1.28. Difficulties in working with unstable crystals prevented precise optical and morphological measurements, but these values are in reasonable agreement with those derived from x-ray data and they serve to orient the optical properties with respect to the unit cell.

Single crystals of $CaCO_3 \cdot 6H_2O$ were sealed in borate glass capillaries at about 0°C and transferred to a precession during which a stream of air at about 2°C was blwon over the crystal camera for preliminary studies./ A crystal with maximum diameter about 0.3 mm (μ_{Mo} = 8.8 cm^{-1}) was mounted on a Weissenberg camera modified[9] to allow the routine collection of inclined oscillation data at low temperatures and was cooled down to -120°C in a stream of cold gaseous nitrogen. The unit cell* at -120°C was determined from Weissenberg and oscillation photographs to be $\underline{a}$ = 8.87 ± .02 Å, $\underline{b}$ = 8.23 ± .01 Å, $\underline{c}$ = 11.02 ± .02 Å, β = 110.2 ± .2° (assuming λ_{Mo} = 0.71069 Å) with space group C2/c or Cc (reciprocal lattice extinctions $h + k = 2n + 1$ for $hk\ell$, $\ell = 2n + 1$ for $ho\ell$). A superimposed aluminum powder pattern ($\underline{a}$ = 4.0493 Å) taken at room temperature was used as a standard. With four formula weightsper unit cell, the calculated density at about -120°C is 1.80 g/ml;

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*The uncertainties in the cell dimensions are estimates derived from the measurements. In the authors' opinion these may be treated as standard deviations.

the density observed at about 0°C is 1.82 g/ml.[10] Data from one hemisphere of the reciprocal lattice were collected in 18 oscillations about the c axis with an inclination angle of 30°. Molybdenum radiation filtered through 0.001 inch Nb and eight films interleaved with 0.001 inch brass sheets were used. The oscillation photographs were indexed using a program written in FORTRAN V from a flow sheet of a similar program written in MAD by Schilling and Nordman.[11] Oscillation photographs, rather than Weissenberg photographs, were taken to decrease the time of data collection, to enable us to place all the data on a common scale from one crystal setting, and to collect data with higher ℓ than would be possible from c axis equi-inclination photographs alone.

About 5,000 reflections were estimated by visual comparison with an intensity scale prepared from timed exposures of a single reflection of the crystal. They were corrected for the Lorentz-polarization and Cox-Shaw[12] effects and a common scale was calculated from the scale factors

$$K_{ij} = \left(\sum_{\ell=1}^{18} K_{i\ell}K_{\ell j}\right)/N$$

between the i and j photographs where N is the number of $K_{ie}K_{ej}$ pairs which gave non-zero products. Rejection tests were used to discard individual inter-reflection ratios which differed from the average by more than three times the mean deviations.

After two cycles of rejections, the scale factors relating all other films to the first film remained relatively . All the reflections were then merged into a unique set. No corrections for absorption were made and the steady formation of a thin layer of ice on the capillary was ignored because it did not appear to affect the relative intensities. If absorption is attributed entirely to the crystal, an estimated maximum absorption error of about 7% was thus introduced into the observed diffracted intensities.

STRUCTURE DETERMINATION

The subsequent calculations were performed using the crystallographic computing system (X-ray 63) assembled under the editorship of J. M. Stewart at the University of Maryland. Statistics on the quasi-normalized structure factors,[13] ($<|E^2|>$ made equal to 1) indicate that the space group is probably centrosymmetric, i.e. C2/c. The structure refined to a satisfactory residual in this space group and refinement in Cc was therefore not attempted. The atomic scattering factors used were taken from reference 14, except for those of hydrogen, which were taken from reference 15. The quantity $\Sigma(w||F_o|-|F_c||)^2$ was minimized in the full matrix least squares refinements. The intensities were given weights of $I_{hk\ell}/I_1$ for reflections less intense than I_1, 1.0 for reflections

between I_1 and I_2, and $I_2/I_{hk\ell}$ for reflections more intense than I_2. I_1 and I_2 were chosen as the lower and upper ends of the easily readable range of the intensity scale used in the visual estimation, and $I_{hk\ell}$ is the intensity after scaling in the multiple film pack, but uncorrected for Lorentz-polarization and Cox-Shaw effects.

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 $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.14$.

Because of the many high-angle reflections to which Ca makes the primary contribution, a high correlation was found between the scale factor and the Ca isotropic temperature factor. The Ca temperature factor was therefore fixed at $B_{Ca} = 0.1$ Å^2. Several classes of reflections were considered unreliable and were not used in subsequent calculations. These were (a) the reflections with $\sin\theta/\lambda < 0.35$ because of high background on the films at low angles; (b) the reflections within 1 cm of the center line of the films because misalignment greatly affects their Lorentz-polarization

corrections; (c) the hk0 reflections because of streaking by white radiation, and (d) reflections with $\sin\theta/\lambda > 1.05$ because of difficulties with indexing. The number of observed reflections was thus reduced to 1420. Rejection of class (a) means that the positions of the hydrogen cannot be determined unequivocally from the x-ray data.

The structure was refined isotropically to R = 0.10 with the Ca temperature factor and the hydrogen parameters kept constant. This agreement is considered to be the limit of the experimental data. Two cycles of anisotropic refinement did not decrease R_w significantly. The observed and calculated structure factors are given in Table 1, and the atomic parameters are given in Table 2. A difference electron density synthesis in which the coefficients were weighted by the least squares weights was calculated. None of the ten highest peaks in this difference synthesis was in a plausible position for a hydrogen atom or any other unassigned atom. As expected, the hydrogen atoms could not be found because the reflections at low $\sin\theta$ had been discarded. Probable hydrogen positions, Table 3, were calculated from stereo-chemical considerations, as described in the section on water environments.

Table 1

Observed and Calculated Structure Factors[a] for $CaCO_3 \cdot 6H_2O$.

Columns are ℓ, $10F_o$, $10F_c$

(a) F_o and F_c are on an absolutely scale. Reflections marked * are considered to contain extinction and/or film scaling errors.

Table 2

Atomic Parameters in $CaCO_3 \cdot 6H_2O$

Atom	x	y	z	B(Å²)
Ca*	.5000	.6472(1)	.2500	.10
C	.5000	.3067(6)	.2500	.37(5)
O(1)	.5000	.1408(6)	.2500	.77(5)
O(2)	.5263(4)	.3849(3)	.1582(3)	.49(3)
O(3)	.6163(4)	.7229(4)	.0916(4)	.70(4)
O(4)	.7883(4)	.5576(4)	.3825(3)	.59(4)
O(5)	.6703(4)	.8842(3)	.3593(3)	.53(3)

The quantities in parenthesis are standard errors in the last significant figures, as computed in the full matrix least squares refinements.

*temperature factor of Ca held fixed at 0.1 Å²

Average shift/error for last cycle, neglecting scale factor, =0.09.

Maximum shift/error for last cycle, neglecting scale factor, =0.29.

Average shift/error for last cycle, including scale factor, =0.29.

Table 2

The Proposed Hydrogen Positions

Atom	x	y	z
H(1)	.568	.696	.002
H(2)	.644	.835	.092
H(3)	.872	.598	.354
H(4)	.822	.588	.472
H(5)	.774	.891	.350
H(6)	.616	.981	.319

Besides the correlation coefficient of 0.89 between the scale factor and the Ca isotropic temperature factor, the largest correlation factors are 0.45 between the x and z parameters of atoms in general positions, 0.22 to 0.35 between the scale factor and the temperature factors of atoms other than Ca, and 0.15 between the temperature factors themselves. Most correlation coefficients are less than 0.02.

Description of the Structure

The Ca and CO_3 ions lie on the two-fold axes and the water molecules are all in general positions. The two ions form an ion pair in which the Ca is bonded to an edge of the CO_3 group. Each ion pair is isolated from the other pairs by an envelope of 18 water molecules. Six of these 18 waters are bonded to the Ca and eight are hydrogen bonded to oxygens of the CO_3 groups. Four are not bonded to this $CaCO_3$ ion pair, but are bonded to adjacent ion pairs and to other water molecules in the envelope. No water molecule is bonded to both ions in a given ion pair.

When viewed along b, the diads on which the ion pairs lie form a pseudohexagonal array of Ca-CO_3 columns. Adjacent columns lying in plane parallel to (100) point in opposite directions; those lying in a planes parallel to (001) point in the same direction but are staggered by b/2. This arrangement appears to maximize the attractions between nearest-neighbor ion pairs and at the same time permits water molecules coordinated to calciums in one column to hydrogen bond to CO_3 groups in adjacent columns.

The calcium environment.--The environment of Ca is shown in Figures 1 and 2 and is given in Table 4. In the ion pair, O(2) and O(2') of the CO_3 group are coordinated to Ca (2.429 Å). The shortest Ca...O distance (2.397 Å) is to water oxygens O(3, 3') and is slightly shorter than the distance (2.429 Å) to the carbonate oxygens O(2, 2'). The coordination of Ca is completed by the pairs of water oxygens O(4, 4') and O(5, 5') thus giving Ca a coordination number of eight. The eight oxygens form a distorted tristetrahedron. All the Ca-to-O distances are in the normal range.

Table 4

The Calcium Environment

Atoms	distance, Å
Ca,O(2)	2.429(3)*
O(3)	2.397(4)
O(4)	2.576(3)
O(5)	2.506(3)

*In all tables of distances and angles the figures in parentheses are standard errors in the last significant figures and are calculated from the standard errors in the atomic parameters and the cell dimensions.

The carbonate environment.--The CO_3 is required by symmetry to be planar, and its dimensions are in the normal range (Table 5). Coordination of the CO_3 to Ca does not distort the trigonal symmetry of the CO_3 significantly. The environment is summarized in Figures 1 and 3 and Table 5. Besides being coordinated to Ca by O(2) and O(2'), the CO_3 anion is hydrogen bonded by all the water molecules if the assumed hydrogen positions are approximately correct. Carbonate oxygen O(1) is hydrogen bonded by H(6) to the O(5) water and by H(3) to the O(4) water; O(2) is hydrogen bonded by H(1) to the O(3) water and by H(5) to the O(5) water. The carbonate groups are all parallel to a plane containing b and inclined to c by -12°. This is in reasonable accord with the observation that the highest index of refraction seen down b is 17° from c in acute β. Carbonate oxygen O(1) accepts 4 hydrogen bonds from four water molecules while O(2) accepts only 2 hydrogen bonds. This appears reasonable since O(2) is coordinated to Ca, but O(1) is not.

Table 5

The Carbonate Anion

Atoms	distance, Å
C,O(1)	1.283(7)
C,O(2)	1.287(5)
O(1),O(2)	2.226(5)
O(2),O(2')	2.228(6)
Coordinated atoms	**Angle, deg.**
O(1),C,O(2)	120.0(2)
O(2),C,O(2')	119.9(4)

O(1) environment

Atoms	distance, Å
O(1),O(5)	2.700(5)
O(1),H(6)	1.75
O(1),O(4)	2.854(4)
O(1),H(3)	1.92

O(2) environment

Atoms	distance, Å
O(2),Ca	2.429(3)
O(2),O(3)	2.749(5)
O(2),H(1)	1.80
O(2),O(5)	2.764(6)
O(2),H(5)	1.81

The water environments and proposed hydrogen bonding scheme.--The environments of the water molecules O(3), O(4) and O(5) are summarized in Figures 1, 2 and 3 and in Table 6. The water molecules are all coordinated to Ca and also provide extensive hydrogen bonding. The following hydrogen bonding scheme is proposed. Water oxygen O(3) has two oxygen near neighbors, O(2) (2.749 Å) and O(4) (2.867 Å); all other oxygens are more than 3 Å away. The O(2)...O(3)...O(4) angle of 115.3° suggests that approximately linear hydrogen bonds are formed from O(3) to these two oxygens. Thus, H(1) may form a hydrogen bond from O(3) to O(2); similarly, H(2) may hydrogen bond O(3) to O(4).

Water-oxygen O(4) has four near oxygen neighbors. One of these, O(3), is already the donor in a hydrogen bond to O(4). Further, a hydrogen bond from O(4) to O(5) (2.864 Å) would put the hydrogen near Ca (2.2 Å). Therefore, the probable scheme is that O(4) is the donor of H(3) to O(1) and of H(4) to O(5'); the O...O distances for these bonds are 2.854 and 2.781 Å, respectively. Since the O(5)-O(4)-O(1) angle is 126.8°, deviations from linearity in the hydrogen bonds will be small.

Table 6

The Water Environments

O(3) environment

Atoms	distance, Å
O(3),Ca	2.397(4)
O(3),O(2)	2.749(5)
O(3),O(4)	2.867(4)*
H(1),O(2)	1.80
H(2),O(4)	1.92
Coordinated atoms	**angle, deg.**
O(2),O(3),O(4)	115.3(2)
O(3),H(1),O(2)	172°
O(3),H(2),O(4)	172°

O(4) environment

Atoms	distance, Å
O(4),Ca	2.576(3)
O(4),O(1)	2.854(4)*
O(4),O(5)	2.781(5)*
O(4),O(3)	2.867(4)*
O(4),H(2)	1.92
O(4),O(5)	2.864(4)
H(3),O(1)	1.92
H(4),O(5')	1.85
Coordinated atoms	**angle, deg.**
O(1),O(4),O(5)	126.8(1)
O(1),O(4),O(3)	94.9(2)
O(1),O(4),O(5')	89.2(2)
O(5),O(4),O(3)	97.7(1)
O(5),O(4),O(5')	119.7(1)
O(3),O(4),O(5')	175.6(2)
O(4),O(4),H(3),O(1)	163°
O(4),O(4),H(4),O(5')	163°

Table 6
(continued)

O(5) environment

Atoms	distance, Å
O(5),O(1)	2.700(5)*
O(5),O(2)	2.764(6)*
O(5),O(4)	2.781(5)*
O(5),H(4)	1.85
H(5),O(2)	1.81
H(6),O(1)	1.75

Coordinated atoms	angle, deg.
H(5),O(5),H(6)	116.
O(1),O(5),O(2)	112.0(1)
O(1),O(5),O(4)	99.9(1)
O(2),O(5),O(4)	106.4(1)
O(5),O(5),H(5)	174°
O(5),O(5),H(6)	174°

*Suggested hydrogen bonds

Water-oxygen O(5) has three near neighbor oxygens suitable for hydrogen bonding, O(1) at 2.700, O(2) at 2.764 and O(4) at 2.781 Å. One of these, O(4), has been assigned as a donor in a hydrogen with O(5). Therefore, O(5) may be considered to be the donor in hydrogen bonds to O(2) using H(5) and to O(1) using H(6). The O(1)-O(5)-O(2) angle, 112.0°, suggests that these hydrogen bonds will be almost linear.

Assuming that this hydrogen bonding scheme is correct, we calculated possible positions for the hydrogen atoms in a way identical to the calculation for the hydrogen position in $CaNa_2(CO_3)_2 \cdot 5H_2O$ and $CaNa_2(CO_3)_2 \cdot 2H_2O$.[7] The water molecules, with the geometry of free water (H-O-H angle = 104.5°, O-H distance = .96 Å), were oriented so that their hydrogen bonds were as linear as possible. The resulting hydrogen positions are given in Table 3. The short H...O distance and the near-linearities of the O-H...O angles lend credence to this scheme.

DISCUSSION

The outstanding feature in the structure is the presence of isolated ($CaCO_3°$) ion pairs, each surrounded by water molecules. This is the first instance, to our knowledge, of the existence of this ion pair in a crystal structure, and provides insight into its structure and its relationship with the water environment. The ($CaCO_3°$) ion pair may have a significant concentration in solutions saturated with respect to calcium carbonates.[16] Its lack of ionic charge suggests that it may play an important role in diffusion through membranes in the same way that has been suggested for the ($CaSO_4°$) ion pairs.[17] The

The ion pair found in $CaCO_3 \cdot 6H_2O$ may be contrasted to the $Ca(CO_3)_2$ triplets found in $CaNa_2(CO_3)_2 \cdot 5H_2O$ [7] and $CaNa_2(CO_3)_2 \cdot 2H_2O$.[7,8] In all three salts, the calciums are bonded to the edges of CO_3 groups. In $CaCO_3 \cdot 6H_2O$, the ion pairs are completely isolated by water envelopes; in $CaNa_2(CO_3)_2 \cdot 5H_2O$, the triplets are isolated from one another by sodium ions and water molecules; in $CaNa_2(CO_3)_2 \cdot 2H_2O$, which contains the least water, there is bonding between the calcium of one triplet and the apex oxygens of the carbonates of adjacent triplets. We have discussed the structures of $CaNa_2(CO_3)_2 \cdot 5H_2O$ and $CaNa_2(CO_3)_2 \cdot 2H_2O$ in more detail in reference 7.

The hydrated calcium carbonates may be compared with the anhydrous forms as follows.

The eventual conversion in aqueous environments of the hydrated calcium carbonates to anhydrous modifications is proof that the hydrated salts are the most soluble forms. The observation that $CaCO_3 \cdot H_2O$ spherulites dissolve with concommittant formation of $CaCO_3 \cdot 6H_2O$, as noted in the description of the preparation of $CaCO_3 \cdot 6H_2O$ crystals, is similar proof that, in dilute solutions (i.e., when activity of water 1) and near 0°C, $CaCO_3 \cdot 6H_2O$ is less soluble and hence more stable than $CaCO_3 \cdot H_2O$.

At atmospheric pressure, the reactions

$$CaCO_3 \text{ (calcite)} + 6H_2O \text{ (liq.)} = CaCO_3 \cdot 6H_2O \text{ (solid)}$$

$$CaCO_3 \text{ (aragonite)} + 6H_2O \text{ (liq.)} = CaCO_3 \cdot 6H_2O \text{ (solid)}$$

$$CaNa_2(CO_3)_2 \text{ (solid)} + 5H_2O \text{ (liq.)} = CaNa_2(CO_3)_2 \cdot 5H_2O \text{ (solid)}$$

would be accompanied by 20, 18 and 13 percent decreases in volume respectively. This suggests that at high hydrostatic pressures (such as those that occur in the abyssal layer of the oceans or in hydrostatic vessels) $CaCO_3 \cdot 6H_2O$ in particular, and hydrated salts in general, may act as nucleating particles in crystallization for the reasons mentioned earlier and under these conditions they may be the most stable forms. This is possibly related to the observations that most deep sea animals have little or no calcareous materials in their skeletons;[18]

and that calcium carbonate is essentially absent from sediments collected at depths greater than 5000 m.[19] Any enhancement of the stability of the hydrated forms might prevent the formation of normal skeletal material. Although it has been suggested[20] from electron microscopic examinations that almost all the calcium carbonate in deep sea sediments is of organic origin and has not been changed after deposition, the possibility must be considered that at great depths the calcium carbonates in such sediments may have been converted in part into hydrated forms which decompose rapidly to the anhydrous forms at normal temperatures and pressures during sample recovery.

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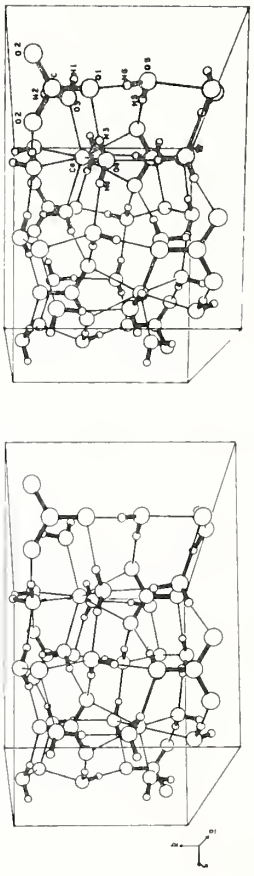
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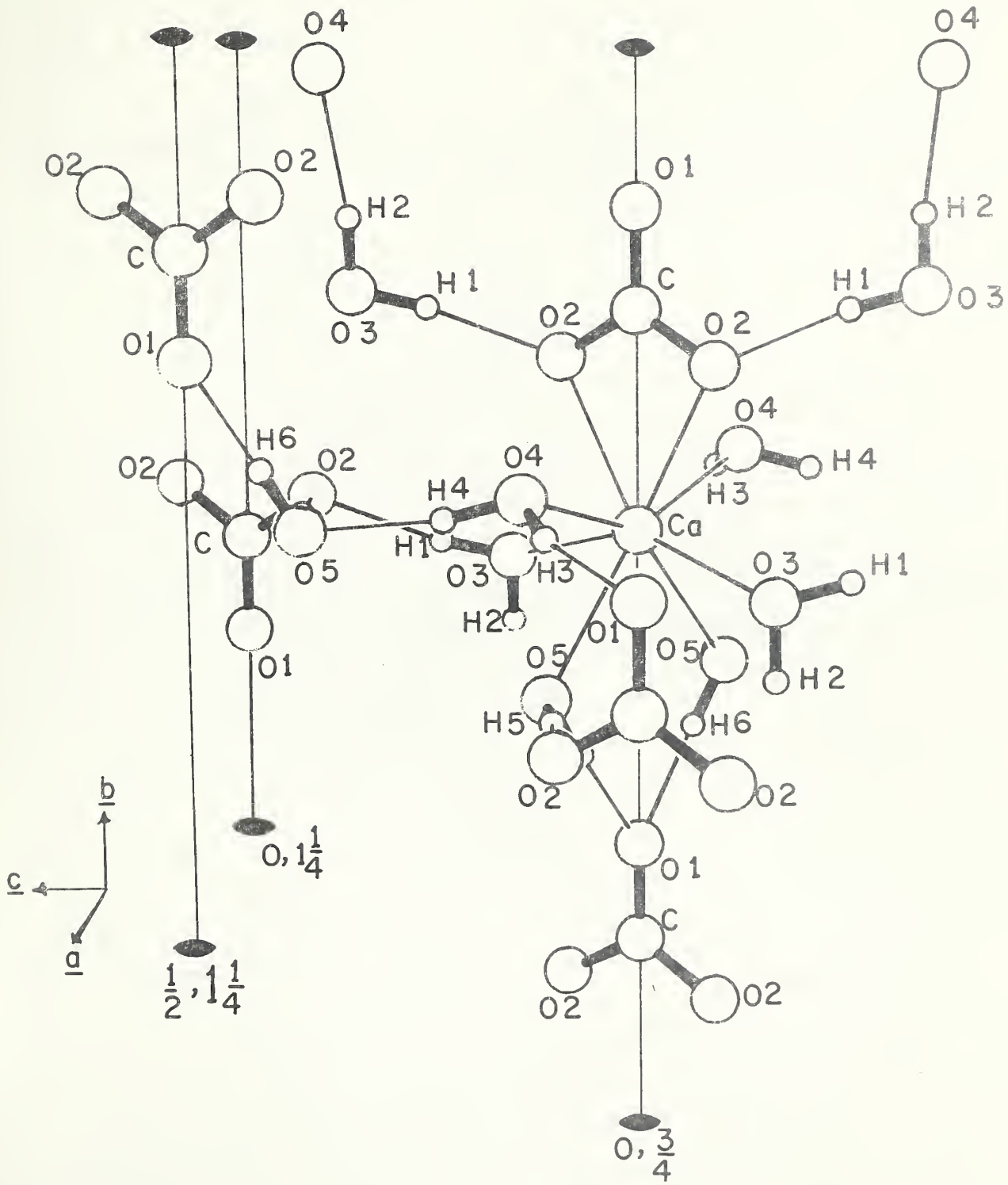
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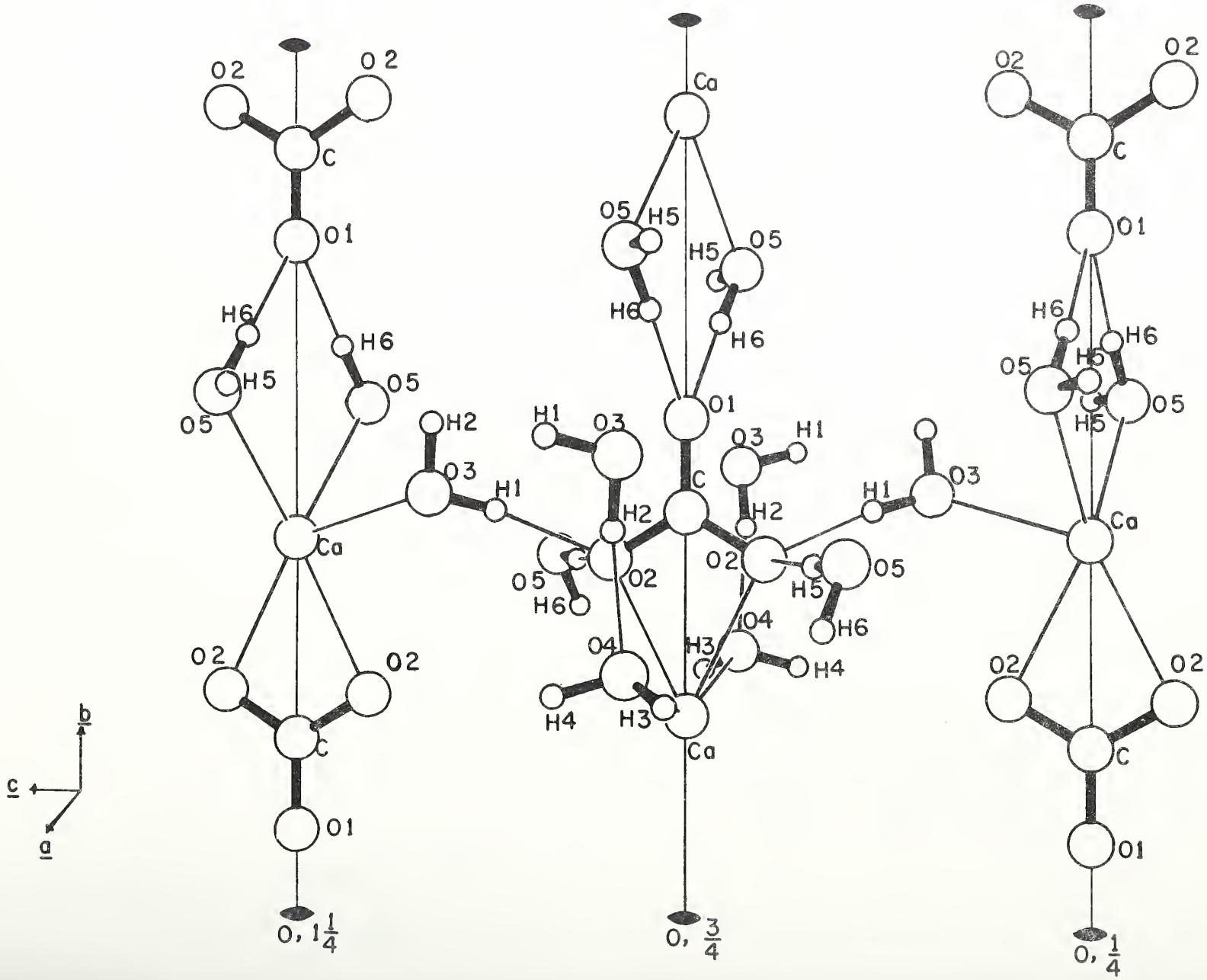
Figure 1. A stereoscopic pair of the $CaCO_3 \cdot 6H_2O$ structure. The contents of the unit cell is shown.

Figure 2. The calcium environment ion pair geometry and a proposed hydrogen bonding scheme in $CaCO_3 \cdot 6H_2O$.

Figure 3. The carbonate environment and a proposed hydrogen bonding scheme in $CaCO_3 \cdot 6H_2O$.




O4
O2
O2
H2
C
H1
O3
O1
O2
O1
C
O2
O4
H2
H1
O3
H6
O2
O2
O4
H4
H4
H3
C
Ca
H1
O5
O3
H3
O3
H1
H2
O1
O5
O5
H2
H5
H6
O2
O2
O1
C
O2
O2
0, 1 1/4
1/2, 1 1/4
0, 3/4
b
c
a


O2
O2
C
O1
H6
H6
H5
O5
O5
H2
O3
H1
Ca
O2
O2
C
O1
0, 1 1/4
Ca
O5
H5
H5
O5
H6
H6
O1
H1
O3
O3
H1
C
H2
H2
O2
O5
H6
O5
H5
H6
O4
H3
O4
H4
H4
H3
Ca
0, 3/4
O2
O2
C
O1
H6
H6
O5
H5
O5
H5
Ca
O2
O2
C
O1
0, 1/4
b
c
a


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