

The structure of monohydrocalcite and the phase composition of the beachrock deposits of Lake Butler and Lake Fellmongery, South Australia

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ABSTRACT

Samples of beachrock from Lakes Butler and Fellmongery, near Robe, South Australia, were examined by neutron and X-ray powder diffraction. Considerable variation in phase composition was observed, although all samples possessed monohydrocalcite, calcite, aragonite, and magnesian-calcite. The Rietveld refinement of the structure of monohydrocalcite showed significant changes in the orientation of water molecules and a major change in the orientation of a carbonate group with respect to the currently accepted structure. The current refinement shows that the hydrogen-bonding structure consists of three distinct networks, with each of the three carbonate groups being bonded to a single water molecule via one linear and one bifurcated hydrogen bond.

Keywords: Monohydrocalcite, carbonate minerals, magnesian-calcite, powder diffraction

INTRODUCTION

Monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$), formerly also known by the discredited name hydrocalcite, has been reported as a breakdown product of ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) (Krauss and Schriever 1930; Ito et al. 1999), from marine sources (Dahl and Buchardt 2006), as a product in air conditioner systems (Marschner 1969), as moonmilk inside caves (Onac 2000), and in lacustrine deposits (Sapozhnikov and Tsvetkov 1959; Stoffers and Fischbeck 1974, 1975; Krumbein 1975; Taylor 1975).

Monohydrocalcite was discovered to be a principal component of beachrock in two lakes, Lake Fellmongery and Lake Butler, along the Limestone Coast of South Australia, near the town of Robe (Taylor 1975). Here the beachrock appears to be produced from wind-blown spume from the lakes, in which a variety of blue-green algae are found. Other lacustrine deposits of monohydrocalcite have been documented at Lake Issyk-Kul, Kyrgyzstan (Sapozhnikov and Tsvetkov 1959), Lake Kivu, Congo, and Solar Lake, Sinai (Stoffers and Fischbeck 1974, 1975; Krumbein 1975).

Studies have been performed on the influence of Ba^{2+} and Mg^{2+} on the precipitation of aragonite, calcite, and monohydrocalcite, as well as the partitioning of these ions between solution and crystalline phases (Kitano et al. 1979). Thermochemical investigations have shown that monohydrocalcite, like ikaite, is always metastable with respect to mixtures of water and anhydrous calcium carbonate, and, similar to the formation of ikaite, the presence of inhibitors such as Mg^{2+} and polyphosphates appears to encourage its production over that of anhydrous calcium carbonate (Hull and Turnbull 1973). Monohydrocalcite has been reported as decomposing to aragonite in air (Brooks et al. 1950). Most reports have suggested that it may slowly decompose to calcite in the presence of water (Taylor 1975).

Explanations for the origin of monohydrocalcite in caves have

included an evaporation-aerosol mechanism (Fischbeck and Müller 1971) and a biochemical genesis (Broughton 1972). In these environments, monohydrocalcite has been reported in association with hydromagnesite [$\text{Mg}_4(\text{OH})_2(\text{CO}_3)_3 \cdot \text{H}_2\text{O}$], dolomite, nesquehonite ($\text{MgCO}_3 \cdot \text{H}_2\text{O}$), calcite, and aragonite. Monohydrocalcite has also been reported in several bizarre biological locations, including the gall bladder of a guinea pig (Skinner et al. 1977), the otoliths of a tiger shark (Carlstrom 1963), being produced from the decomposition of Ca-oxalate during the final stages of decomposition of the saguaro cactus (Garvie 2003, 2006), and as spherulites in domesticated animal dung (Shahack-Gross et al. 2003). These, and the presence of blue-green and green algal films on the deposits at Lakes Butler and Fellmongery (Taylor 1975), suggest that a biochemical route is a strong possibility for production of monohydrocalcite.

Taylor (1975) reviewed the literature covering the synthesis of monohydrocalcite, and noted that it is often produced during attempts to crystallize dolomite. Recently, it also has been suggested that a low-temperature route of dolomite production may be via decomposition of hydrous precursor phases of Mg-rich Ca-carbonates (de Leeuw and Parker 2001; Kelleher and Redfern 2002). Candidates therefore include ikaite and possibly monohydrocalcite. The diffraction pattern of monohydrocalcite has been used to identify it as an intermediate phase in a complex transition from portlandite, $\text{Ca}(\text{OH})_2$, to CaCO_3 inside ordinary Portland cements during hydration (Stepkowska et al. 2007). Recently, the structure of monohydrocalcite has been used in EXAFS fits for comparison to amorphous calcium carbonates in studies pertaining to biomineralization (Levi-Kalisman et al. 2000; Neumann and Epple 2007). For these reasons a re-examination of the crystal structure seemed in order.

EXPERIMENTAL METHODS

Attempts were made to prepare fully deuterated monohydrocalcite from artificial seawater, created from reactor-grade D_2O , as we had successfully created fully deuterated ikaite from deuterated solutions in the past. However, while

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some mineralization occurred, it did not generate sufficient volume for neutron diffraction.

Therefore natural samples were taken from locations in which high proportions of monohydrocalcite were known to occur. Rock samples were obtained, courtesy of the South Australian Museum (Table 1). These consisted of one sample from Lake Fellmongery (LF) and four samples from Lake Butler (LB, LB1, LB2, LB3). Small pieces were broken off and visible shell fragments were discarded. The remaining components were ground to a fine powder in a mortar and pestle.

There are disadvantages to using natural samples for a neutron diffraction study: the first being the inevitable impurity phases, and the second being the incoherent scattering from the hydrogen in the structure. Nevertheless, for small proportions of hydrogen to non-hydrogen atoms the level of incoherent scattering is often manageable. The negative scattering length of ^1H for hydrogen in waters of crystallization can yield strong orientational information, as the hydrogen atoms are inevitably surrounded by atoms with positive scattering lengths (Swainson et al. 2003).

The samples were loaded into a cylindrical vanadium can 5 mm in diameter, and room temperature neutron powder diffraction was performed on the C2 neutron powder diffractometer, located in the NRU reactor at the Chalk River Laboratories of Atomic Energy of Canada Limited. This consists of an 800-wire BF_3 detector that floats on high-pressure air pads across an epoxy dance floor. Two sets of data were collected for each sample: one at a short wavelength (ca. 1.33 Å) over the range $10\text{--}90^\circ 2\theta$ and one at "pyrolytic graphite wavelength" (ca. 2.37 Å), for which a pyrolytic graphite filter (fabricated from Panasonic supergraphite) was placed in the incident beam. Both patterns were collected at $92.7^\circ 2\theta_{\text{in}}$. During refinements, the two zero parameters, and the value of the longer wavelength, which is less accurately determined, were allowed to float. The four phases were refined across the two data sets. The purpose of the longer wavelength data are to help reduce the effects of peak overlap in the 1.33 Å data set, so that any model must be able to reproduce the pattern out to high 2θ in the short wavelength data set (high- Q), where overlap is stronger, as well as at low- Q , which has much reduced peak overlap in the 2.37 Å data set. The neutron powder data were Rietveld refined with the GSAS package (Larson and Von Dreele 1994), making use of EXPGUI (Toby 2001).

X-ray powder diffraction data from a subsample of LB1 were later taken on a Rigaku Ultima III system, using a silica glass deep pack powder sample holder in Bragg-Brentano geometry. The incident radiation was $\text{CuK}\alpha_1$, collimated with a 1° slit. Data were taken from 5 to $140^\circ 2\theta$. Initially the X-ray data were refined separately. Subsequently the two neutron and one X-ray data sets were co-refined. During this triple refinement, the two neutron wavelengths and zero parameters were allowed to float with respect to the $\text{CuK}\alpha_1$ refinement. A CIF file is on deposit.¹

CRYSTALLOGRAPHY OF MONOHYDROCALCITE

In their review of calcium carbonate hydrates and their structures, Brooks et al. (1950) had suggested a hexagonal cell with $a = 6.15$ Å and $c = 7.61$ Å on the basis of powder diffraction data. Lippmann (1959) and Kohatsu and McCauley (1973) both commented on the existence of a primitive trigonal cell with $a \sim 6.1$ Å and $c \sim 7.6$ Å as well as a primitive trigonal supercell with $a \sim 10.6$ Å and $c \sim 7.55$ Å. Kohatsu and McCauley (1973) noted that their solution in the subcell required disorder.

The generally accepted structure of monohydrocalcite is that of Effenberger (1981). She solved the structure of monohydrocalcite from single-crystal diffraction. The structure was initially solved in $P3_121$ with cell parameters $a = 6.0931$ Å and $c = 7.5446$ Å, which as previous workers had discovered, requires orientationally disordered carbonate groups. Much of the Effenberger structure was solved by Patterson methods, while the water oxygen and one carbonate oxygen were found by Fourier

TABLE 1. The wt% phase abundance derived from the four-phase Rietveld refinement of the neutron data

Mineral	LB	LB1	LB2	LB3	LF
Monohydrocalcite	22.7(3)%	78.0(1)%	29.3(3)%	62.6(3)%	33.1(3)%
Aragonite	2.3(2)%	3.4(3)%	3.7(2)%	5.0(3)%	17.8(3)%
Calcite	50.5(3)%	4.6(3)%	37.3(4)%	7.8(3)%	9.7(2)%
High-Mg calcite	24.5(6)%	14.0(4)%	29.7(3)%	24.5(5)%	39.3(4)%

Notes: Samples labeled LB are from Lake Butler. LF is from Lake Fellmongery. LB1–LB3 and LF are unregistered samples from the South Australian Museum, while LB is from sample G19222 of the museum collection.

difference synthesis. The hydrogen atoms were found by crystal chemical and geometric arguments. A superstructure in $P3_1$ with $a = 10.5536$ Å and $c = 7.5446$ Å, was then determined on the basis of weak superlattice reflections, in which the carbonate groups were orientationally ordered. The positions were mapped from the $P3_121$ substructure, and the ordered orientations of the carbonate groups were refined using rigid bodies (RBs).

Similar to the structure of ikaite (Swainson and Hammond 2001, 2003; Lennie et al. 2004; Lennie 2005), monohydrocalcite consists of eightfold coordinated Ca^{2+} ions, in which some of the oxygen coordination is direct to carbonate groups and some to water molecules. Ikaite consists of an ion pair structure in which the eightfold Ca-coordination consists of two bonds to different O atoms on one carbonate group, and six independent bonds to water molecules. In monohydrocalcite the eightfold Ca coordination consists of bonding to four neighboring carbonate groups and two water molecules. Two of the carbonate groups are involved in two bonds from Ca to two separate O atoms, and two others are involved in one bond from Ca.

RESULTS

The only phases of significance in the samples were monohydrocalcite, aragonite, calcite, and a fourth phase with highly broadened peaks. The mineralogy of the beachrock is similar to that of the Lake Kivu deposits, which includes calcite, aragonite, monohydrocalcite, and excess-Ca dolomite ($\text{Ca}_{0.63\text{--}0.60}\text{Mg}_{0.37\text{--}0.40}$) (Stoffers and Fischbeck 1974). It appears from the refined lattice parameters that the fourth phase in these South Australian deposits is not dolomite, but magnesian calcite, as noted by Taylor (1975). By comparison of the refined cell parameters of this phase to known data of magnesian calcite, it appears the composition is probably in the range of ca. 10–15 mol% MgCO_3 content (Goldsmith et al. 1961; Bischoff et al. 1983). Broadened peaks of magnesian calcite have been reported in calcite from algae including *Lithothamnium sp.*, and may be a result of very fine crystallite sizes, or inhomogeneities in composition (Bischoff et al. 1983). Although there appears to be no study of the algae in Lakes Butler and Fellmongery, "Lithothamnion-like algal growths" form the limestones in another lake in the Robe region (Mawson 1929; Taylor 1975).

Although there is considerable variation in composition from one Lake Butler sample to another, the most impure sample was from Lake Fellmongery. Some of this variation in composition, particularly in the proportion of aragonite and calcite, may represent differences in the effectiveness of separating shell fragments when preparing the ~ 1 cc sample for neutron diffraction.

The sample with the highest proportion of monohydrocalcite was LB1 so it was this data set on which the efforts at structure

¹ Deposit item AM-08-029, CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 2A. Crystallographic data from monohydrocalcite in $P3_1$ from the simultaneous refinement of neutron and X-ray data

Name	x	y	z	U_{iso}
C1	0.1003(25)	0.1835(25)	0.969(4)	0.0097(23)
O1	0.202(4)	0.245(4)	1.086(5)	0.0123(13)
O2	0.068(4)	0.0573(25)	0.905(5)	0.0123(13)
O3	0.031(4)	0.2485(35)	0.915(5)	0.0123(13)
C2	0.7463(25)	0.5162(29)	0.0491(34)	0.0097(23)
O4	0.8848(24)	0.589(4)	0.083(7)	0.0123(13)
O5	0.6639(32)	0.3924(31)	0.127(5)	0.0123(13)
O6	0.690(4)	0.567(4)	-0.063(7)	0.0123(13)
C3	0.4177(20)	0.8485(25)	1.0608(34)	0.0097(23)
O7	0.5586(21)	0.917(4)	1.076(5)	0.0123(13)
O8	0.3386(27)	0.7306(26)	1.151(4)	0.0123(13)
O9	0.3560(29)	0.8980(35)	0.956(5)	0.0123(13)
Ca1	0.1811(26)	0.0958(20)	0.33333	0.0113(7)
Ca2	0.8506(29)	0.4257(20)	0.3402(22)	0.0113(7)
Ca3	0.5174(27)	0.7551(21)	0.3571(13)	0.0113(7)
Ow1	0.401(6)	0.195(5)	0.841(5)	0.0092(22)
H1	0.350(9)	0.225(11)	0.922(13)	0.032(6)
H2	0.327(7)	0.130(11)	0.760(11)	0.032(6)
Ow2	0.069(7)	0.542(5)	0.849(6)	0.0103(22)
H3	0.004(10)	0.464(9)	0.771(11)	0.032(6)
H4	0.009(8)	0.578(8)	0.899(10)	0.032(6)
Ow3	0.730(5)	0.858(5)	0.837(5)	0.0103(22)
H5	0.663(8)	0.793(12)	0.750(11)	0.032(6)
H6	0.672(8)	0.885(12)	0.909(13)	0.032(6)

Note: $a = 10.5547(3)$ Å, $b = 10.5547(3)$ Å, $c = 7.5644(3)$ Å, $V = 729.788$ Å³.

TABLE 2B. Refinement statistics and radiation used in the joint refinements of monohydrocalcite

Radiation	(Å)	N_{obs}	wR_p	R_p
Neutron	1.3309(2)	1009	2.29%	1.81%
Neutron	2.3743(3)	641	2.79%	2.05%
X-ray	1.54060	3115	12.53%	7.69%

Note: N_{obs} is the number of data points, wR_p , the weighted profile R -factor, and R_p the profile R -factor.

refinement of this phase were concentrated. The $P3_1$ superstructure reported by Effenberger (1981) was chosen as a starting model. The space group has no special points of symmetry so that the whole structure can slide along the z -axis. The z -coordinate of Ca1 was fixed at 1/3 to prevent this, following the choice of Effenberger (1981).

The initial Effenberger $P3_1$ structure proved to be unstable during refinement. Therefore we tried an approach that we have successfully used in the past for determining the orientation of molecular ions in freshly indexed, orientationally ordered phases that have descended from an orientationally disordered, high-symmetry parent. In such cases, only the centers-of-mass of the molecules can be mapped using group-subgroup relations, and the orientations must be determined. This can be successful even in cases where the center-of-mass has changed significantly from the mapped position (e.g., Swainson et al. 2002). Constraints are necessary in this multiphase refinement, as there are 71 parameters for the atomic coordinates alone for monohydrocalcite. Both carbonate groups and water molecules were defined as RBs, as they were in the single-crystal refinement of monohydrocalcite of Effenberger (1981). The carbonate group was defined as a regular planar trigonal form with bond length 1.29 Å, and the water molecule was defined with an O-H bond length of 0.97 Å

TABLE 3. PLATON analysis of potential hydrogen bonds and schemes

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A(°)	A...H...A*(°)	Sum (°)
Network 1						
O(w1)-H1...O1	0.96	2.09	3.0359	168		
O(w1)-H1...O2	0.96	2.60	3.0975	112	56	336.00
O(w1)-H2...O3	0.96	2.02	2.9455	161		
Network 2						
O(w2)-H3...O5	0.96	2.52	3.1629	124		
O(w2)-H3...O6	0.96	1.97	2.9288	177	58	359.00
O(w2)-H4...O4	0.96	1.96	2.8560	154		
Network 3						
O(w3)-H5...O8	0.96	2.53	3.1060	119		
O(w3)-H5...O9	0.96	1.73	2.6820	167	60	346.00
O(w3)-H6...O7	0.96	1.88	2.8342	171		

Notes: Criteria for hydrogen bond: $d(D...A) < R(D) + R(A) + 0.50$ Å, $d(H...A) < R(H) + R(A) - 0.12$ Å, $D-H...A > 100.0^\circ$, where D = Donor, A = Acceptor, d = distance, r = radius, Sum defines the sum of 3 angles about the H atom in a bifurcated bond: one A-H...A* and two D-H...A angles.

The most likely D-H...X angle for a 2-Center (linear) hydrogen bond is 160° .

For a 3-Center (bifurcated) hydrogen bond, ideally the Sum of 3 angles about H = 360° (Jeffrey et al. 1985; Jeffrey and Saenger 1991; Spek 2003).

TABLE 4. Selected bond lengths of the Ca-O polyhedra, and refined O-H and C-O interatomic distances of the rigid bodies

Bond	Å	Bond	Å	Bond	Å
all C-O	1.293(4)	all O-H	0.964(11)		
Ca1-O1	2.38(4)	Ca2-O4	2.50(3)	Ca3-O1	2.39(4)
Ca1-O2	2.32(3)	Ca2-O5	2.43(3)	Ca3-O3	2.48(4)
Ca1-O2	2.61(4)	Ca2-O5	2.42(4)	Ca3-O7	2.63(3)
Ca1-O3	2.45(3)	Ca2-O6	2.43(4)	Ca3-O8	2.36(3)
Ca1-O4	2.37(4)	Ca2-O7	2.43(4)	Ca3-O8	2.47(3)
Ca1-O6	2.57(4)	Ca2-O9	2.53(4)	Ca3-O9	2.40(4)
Ca1-Ow3	2.51(4)	Ca2-Ow1	2.46(5)	Ca3-Ow2	2.54(5)
Ca1-Ow3	2.53(4)	Ca2-Ow1	2.53(5)	Ca3-Ow2	2.44(6)

with an H-O-H bond angle of 104.5° . The bond lengths of the RBs were refined during later stages.

Copies of each RB were placed on the sites defined by the Effenberger (1981) $P3_1$ model in a random orientation. Then the orientation was refined for each molecular group. Refining with this approach resulted in convergence for all data sets (Tables 2a and 2b). Small but significant differences were found between the positions of hydrogen atoms H3-H6 from this refinement and those of the Effenberger (1981) structure. An analysis of the hydrogen bonding, subject to the criteria in PLATON (Jeffrey et al. 1985; Jeffrey and Saenger 1991; Spek 2003), shows that there are three independent networks, each consisting of one water molecule and one carbonate group, such that one hydrogen atom on each water molecule is involved in a linear hydrogen bond and the other is involved in a bifurcated hydrogen bond to the carbonate group (Table 3); e.g., the H atoms from Ow1 bond to O atoms on the C1 carbonate group, those from Ow2 to the C2 carbonate group, and those from Ow3 to the C3 carbonate group. Equivalent calculations on the Effenberger (1981) $P3_1$ structure do not show such a regular hydrogen bonding system. Other selected bond distances are given in Table 4.

Surprisingly, however, large differences in atomic positions were found in oxygen atoms belonging to carbonate groups: O5, O6, O8, and O9. In particular, O5 is shifted along z by over 1.5 Å, so that the orientation of the C2 carbonate group is radically different from that of the Effenberger (1981) structure (Fig. 2). The same mutual orientation of carbonate groups is found in the neutron refinements of data from all samples. To eliminate the possibility of a local minimum, the refinements were restarted

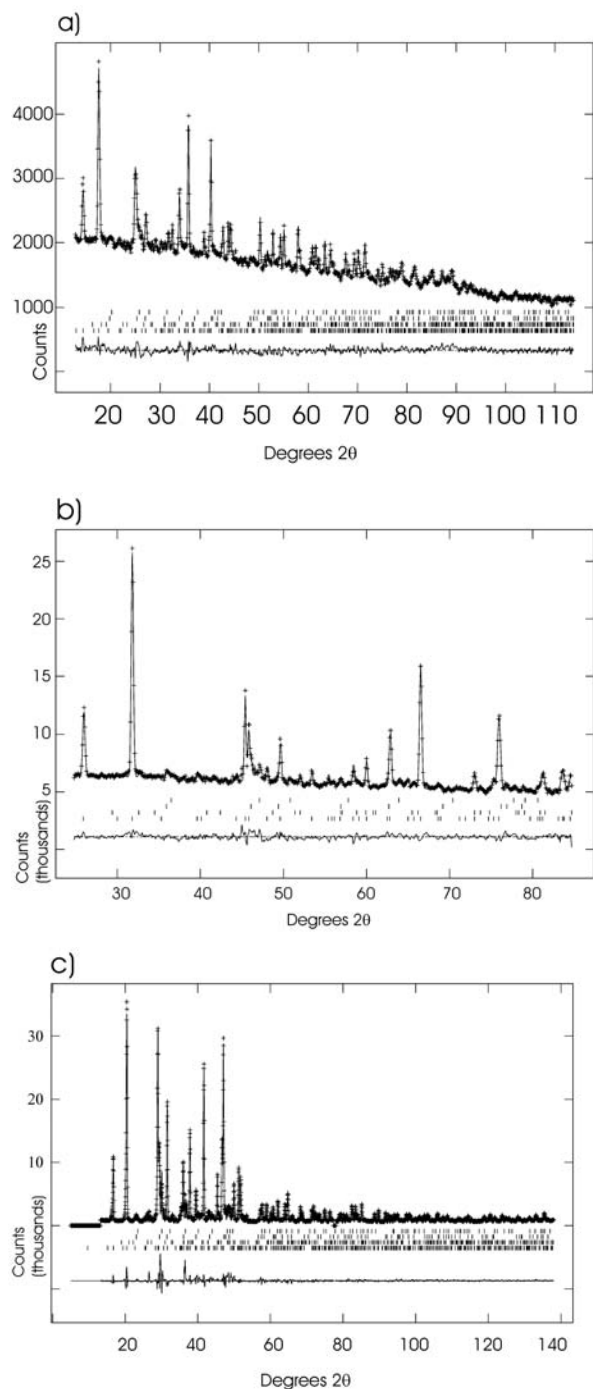


FIGURE 1. Final fits to the LB1 sample to data from short (a) and long (b) neutron wavelengths, and $\text{CuK}\alpha_1$ X-ray (c) wavelengths. The tick marks represent reflections from monohydrocalcite, aragonite, calcite, and magnesian calcite (from bottom to top).

from many random orientations within each sample and each refinement converged to yield the same mutual orientation of carbonate groups. A further test was undertaken to see if the orientation of the carbonate groups was a local solution from the neutron data by refining an X-ray data set from sample LB1

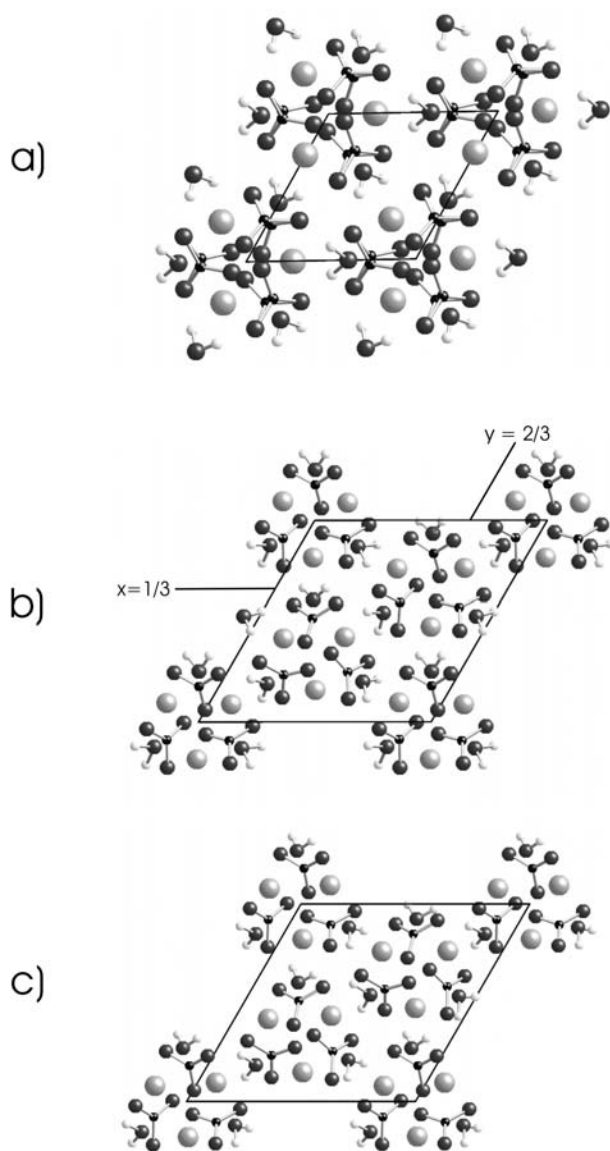


FIGURE 2. The structure of monohydrocalcite viewed down 001. (a) The $P3_121$ subcell structure of Effenberger (1981) showing the disordered carbonate groups, (b) the superstructure $P3_1$ model of Effenberger, and (c) the structure refined in $P3_1$ from sample LB1. The principal difference between structures b and c can be seen in the orientations of the carbonate groups about the screw axis at $(1/3, 2/3, z)$.

taken on the Rigaku Ultima III. This refinement also resulted in the same orientations of the carbonate groups. The fits to the three data sets are shown in Figure 1. The difference between the Effenberger structure and that refined here is evident in Figure 2 near the vicinity of the screw axis lying at $1/3, 2/3, z$. The two structures were compared in Structure Tidy in PLATON (Parthé and Gelato 1984; Gelato and Parthé 1987; Spek 2003; Hu and Parthé 2004), and it is evident that the two structures are distinct. With respect to the Effenberger (1981) $P3_121$ subcell, these differences represent two distinct ways of ordering the orientations of the carbonate groups about the screw axes in a

$P3_1$ lattice. Since there have been few detailed studies of monohydrocalcite, it is possible that both ways of ordering carbonate groups exist in nature. However, it is most likely that that the difference lies in the choices made by Effenberger (1981) in mapping from the $P3_121$ cell, in which the initial structure was solved, to the $P3_1$ cell.

It is hoped that the new structural data provided here will be of use for those using full profile methods of phase analysis of hydrous calcium carbonate phases, and since the data involve the oxygen coordination about Ca they should also prove useful for EXAFS studies of biomineralization. The data, including the improved hydrogen bonding description, should also be useful in the interpretation of vibrational spectroscopy; e.g., the eventual mode assignment of infrared and Raman spectra. Furthermore, computer simulations of the bulk phase, and the interaction of monohydrocalcite surfaces with aqueous solutions, important in understanding crystallization, should benefit from this improvement in description of the structure.

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