The Crystal Structure of Calcium Carbonate Hexahydrate at ~ −120°

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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 ~ −120°. The unit cell parameters are $a = 8.87$ (2) Å, $b = 8.23$ (1) Å, $c = 11.02$ (2) Å, and $\beta = 110.2$ (2)°, and the space group is C2/c with $Z = 4$. The calculated density at ~ −120° is 1.80 g cm⁻³, and the observed density at ~0° is 1.82 g cm⁻³. The final R factor is 0.10. The structure contains discrete $CaCO_3$ ion pairs, each surrounded by an envelope of 18 water molecules. Thus, Ca^{2+} is coordinated to only one CO_3^{2-}. Six of the surrounding H_2O molecules are bonded to Ca^{2+}, eight are hydrogen bonded to oxygens of the CO_3^{2-} group, and four are bonded to adjacent ion pairs and to other water molecules in the envelope. $CaCO_3 \cdot 6H_2O$ was found to be more stable than $CaCO_3 \cdot H_2O$ in water near 0°. 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 studies of 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 mollusks[2a] and in other biological minerals,[2b] 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, possibly because they are known to be less stable than the calcite and aragonite phases of $CaCO_3$ and are probably less stable than the vaterite phase.

We are studying hydrated salts which have potential importance in biological mineralization. One of our major objectives is to learn more about the interaction between water molecules and the calcium and carbonate ions in hydrated salts. The crystal 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. Here we report the determination of the crystal structure of $CaCO_3 \cdot 6H_2O$.

Early work on $CaCO_3 \cdot 6H_2O$ and $CaCO_3 \cdot H_2O$, including the description of some chemical properties and preparative details using crystal growth poisons, was summarized by Brooks, Clark, and Thurston.[4] Previous X-ray work on $CaCO_3 \cdot 6H_2O$ has been limited to the report[4] of powder diffraction data.

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° in a solution containing 400 ppm of 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 of $CaCl_2$ dissolved in 100 ml of water was added to 150 ml of water containing 4.6 g of Na_2CO_3 and 0.5 g of sodium polyphosphate. After about 6 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. After the preparation had stood for several months, the spherulites had dissolved and crystals of $CaCO_3 \cdot 6H_2O$ had formed.

Two habits of the $CaCO_3 \cdot 6H_2O$ crystals were common. The first habit was 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 b; the trace of the (110)–($\bar{1}$10) angle, 93.4°, yields an axial ratio $a/b = 1.05$. The second habit was short, highly birefringent {010} plates with the slow direction, N_γ, extinguishing at 17° from c in acute β, and gave $\beta = 109.4°$ and $c/a = 1.28$. Although difficulties in working with unstable crystals prevented precise optical and morphological measurements, our values are in reasonable agreement with those reported in ref 5, and the axial ratios and angles agree with those derived from the X-ray data.

Single crystals of $CaCO_3 \cdot 6H_2O$ were sealed in borate glass capillaries at about 0° and transferred to a precession camera for preliminary studies. A stream of air at about 2° was blown over the crystal. A crystal with a maximum diameter ~0.3 mm and a minimum diameter ~0.2 mm ($\mu_{Mo} = 8.8$ 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 to ~ −120° in a stream of cold gaseous nitrogen. The unit cell dimensions at ~ −120° were determined from Weissenberg and oscillation photographs to be $a = 8.87$ (1) Å, $b = 8.23$ (1) Å, $c = 11.02$ (1) Å, and $\beta = 110.2°$, assuming λ_{Mo} 0.71069 Å, with space group C2/c or Cc (reciprocal lattice extinctions $h + k = 2n + 1$ for hkl, $l = 2n + 1$ for $h0l$). [The uncertainties (given in parentheses) in the cell dimensions are estimates (in units of Å × 10⁻²) of the standard errors of the average values. The value given for β is an average of the two measurements 110.23 and 110.12°.] A superimposed aluminum powder pattern ($a = 4.0493$ Å) taken at room temperature was used as a standard. With four formula weights per unit cell, the calculated density at ~ −120° is 1.80 g cm⁻³, and the density observed[10] at about 0° is 1.82 g cm⁻³. Data from one hemisphere of the reciprocal lattice were collected in 18 oscillations about the c axis with an inclination angle of 30°. The molybdenum radiation was filtered through 0.001 in. of Nb; eight photographic films, interleaved with 0.001-in. brass sheets, were used. The

(1) Director, Research Associate Program of the American Dental Association at the National Bureau of Standards.

(2) (a) K. M. Wilbur in "Physiology of Mollusca," Vol. 1, K. M. Wilbur and C. M. Yonge, Ed., Academic Press, New York, N. Y., 1964, Chapter 8, and references therein; (b) T. Pobeguin, *Ann. Sci. Nat., Botan. Biol. Vegetale*, **15**, 29 (1954).

(3) D. J. Sutor and S. E. Wooley, *Science*, **159**, 1113 (1968), and references therein.

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

(5) J. Johnston, H. E. Merwin, and E. D. Williamson, *Am. J. Sci.*, **41**, 473 (1916).

(6) F. Lippmann, *Naturwissenschaften*, **46**, 553 (1959).

(7) B. Dickens and W. E. Brown, *Inorg. Chem.*, **8**, 2093 (1969).

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

(9) B. Dickens, Report 66-9, U. S. Naval Ordnance Station, Indian Head, Md. 20640 (1966).

(10) J. Hume and B. Topley, *J. Chem. Soc.*, 2932 (1926).

oscillation photographs were indexed using a program written in FORTRAN V from a flow chart 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 indices than would be possible from c-axis equiinclination photographs alone.

About 4200 reflections [(sin θ)/$\lambda \leq 1.05$)] of observable intensity were estimated by visual comparison with an intensity scale prepared from timed exposures of a single reflection of the crystal. Only those reflections of observable intensity which could be indexed unambiguously were used in subsequent calculations. The observed reflections were corrected for the Lorentz–polarization and Cox–Shaw[12] effects, and a common scale was calculated from the scale factors

$$K_{ij} = (\sum_{l=1}^{18} K_{il}K_{lj})/N$$

between the i and j photographs where N is the number of $K_{il}K_{lj}$ pairs which give nonzero products. Rejection tests were used to discard individual interreflection 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 constant. All the reflections were then merged into the unique set of 1669 data. 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, we estimate from the crystal shape that a maximum absorption error of about 6% 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] ($\langle|E^2|\rangle$ 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 ref 14, except for those of hydrogen, which were taken from ref 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_{hkl}/I_1 for reflections less intense than I_1, 1.0 for reflections between I_1 and I_2, and I_2/I_{hkl} 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_{hkl} is the intensity after scaling in the multiple-film pack but uncorrected for Lorentz–polarization and Cox–Shaw effects.

The position of the Ca ion was found from the sharpened, origin-removed Patterson function, calculated from the $(E^2 - 1)$ coefficients, and the rest of the

(11) J. Schilling and C. E. Nordman, private communication.

(12) E. G. Cox and W. F. B. Shaw, *Proc. Roy. Soc.* (London), **A127**, 71 (1930).

(13) 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.

(14) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(15) R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

structure was found in subsequent F_o Fourier syntheses. The structure was refined isotropically to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.14$ using the 1669 observed reflections.

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 141 reflections within 1 cm of the center line of the films because misalignment greatly affects their Lorentz and polarization corrections; (b) the 45 reflections with (sin θ)/$\lambda < 0.35$ because of high background on the films at low angles; and (c) the 63 $hk0$ reflections because of streaking by white radiation. The number of observed reflections was thus reduced to 1420. Rejection of class b means that the positions of the hydrogen atoms cannot be determined unequivocally from the X-ray data.

The structure was further refined isotropically to $R = 0.10$ with the Ca temperature factor 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 I, and the atomic parameters are given in Table II. 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 higher than a hydrogen atom was expected to be or was in a plausible position for a hydrogen atom or any other unassigned atom. Nine of these peaks were associated with previously assigned atoms, perhaps as uncorrected anisotropic thermal motion. The other, the eighth in height, was attributed to variability in the background of the difference synthesis. As expected, the hydrogen atoms could not be found because the reflections at low sin θ had been discarded. Probable hydrogen positions, Table III, were calculated using the hydrogen-bonding scheme derived from stereochemical considerations and described in the section on water environments.

Besides the correlation coefficient of 0.89 between the scale factor and the Ca isotropic temperature factor, the largest correlation coefficients are ~0.45 between the x and z parameters of atoms in general positions, 0.22–0.35 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^{2+} and CO$_3^{2-}$ ions lie on twofold 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. No ion is bonded to more than one other ion. 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

Table I

Observed and Calculated Structure Factors[a] for $CaCO_3 \cdot 6H_2O$
(Columns are l, $10F_o$, $10F_c$)

l	10Fo	10Fc
2,0,L		
-14	156	-230
-12	351*	386
10	395	-428
12	413	430
14	398	-425
4,0,L		
2	813*	-1185
4	695	805
6	293	-225
8	338	282
10	451	-430
12	435	467
6,0,L		
-14	288	-321
-12	327	356
-8	720*	914
-6	455	-433
2	574*	-861
4	525	512
6	365	295
10	539	-510
8,0,L		
-14	241	-253
-12	447	496
-10	476	-521
-8	503	501
-6	384	-405
-4	334	334
-2	448*	-561
4	518	559
10,0,L		
-14	262	-316
-12	268	265
-10	249	-226
-6	515*	-822
-4	254	273
12,0,L		
-12	255	270
-10	479*	-614
-8	353	375
-6	234	-240
-4	304	424
-2	273	-305
14,0,L		
-14	339	-356
-12	134	140
-10	259	-263
-8	454	448
-6	337	-317
-4	251	299
-2	315	-351
16,0,L		
-14	262	-313
-12	163	201
-8	279	341
-6	451	-476
-4	252	271
18,0,L		
-12	185	180
-8	315	285
1,1,L		
11	147	-126
13	180	-161
14	231	-234
15	194	170
3,1,L		
6	199	193
7	250	260
10	350	-346
15	269	263
5,1,L		
-10	411	-423
-9	332	289
2	134	-168
3	315	347
4	427	459
5	233	-144
6	211	-179
9	265	-234
12	338	257
7,1,L		
-10	117	-96
-9	113	91
-8	493	529
-7	266	-200
-6	351	-367
-5	83	-61
-3	265	-271
-1	413*	549
1	97	75
2	357	-352
9	139	-133
9,1,L		
-15	125	-117
-13	350	354
-10	271	-276
-8	219	194
-6	191	-181
-5	365	404
-4	110	94
-3	157	-142
2	369	-332
4	238	188
5	191	-170
11,1,L		
-15	139	-121
-11	228	-194
-10	256	-225
-9	157	127
-8	242	214
-5	151	152
-3	115	-129
-2	162	-137
-1	128	130
13,1,L		
-15	152	-129
-14	173	-165
-13	180	148
-11	217	-205
-9	155	145
-8	223	214
-6	327	-340
-4	148	136
-3	291	-286
-2	119	37
-1	151	161
15,1,L		
-15	164	-170
-13	192	187
-8	207	202
-4	115	96
-2	154	-176
17,1,L		
-14	181	-188
-13	146	148
-7	118	-168
-6	181	-219
0,2,L		
7	570*	771
9	128	-99
12	283	-304
13	282	-363
14	115	107
2,2,L		
8	478	-422
9	369	-415
11	284	337
13	151	-179
14	262	258
15	158	152
4,2,L		
4	311	-349
5	435	-546
6	102	-96
7	549	733
8	132	-193
9	309	-385
10	308	295
13	115	-104
15	336	322
6,2,L		
-8	324	-378
-7	347	-437
-5	631*	897
-3	548*	-743
-2	490*	647
-1	158	160
1	123	-112
2	168	-140
3	402	434
4	344	-331
5	470	-474
9	319	273
11	236	225
12	198	-152
13	178	-151
8,2,L		
-15	291	-321
-14	234	259
-13	212	231
-12	203	-195
-11	207	-237
-10	109	-90
-9	322	323
-8	200	-201
-7	342	-351
-5	307	299
-3	262	-413
-1	397*	507
1	327	-277
2	194	145
3	200	174
5	346	-284
6	199	157
7	401*	311
8	191	-134
9	343	-279
10,2,L		
-15	245	-234
-13	383	416
-11	359	-364
-10	253	217
-9	153	149
-8	143	-142
-7	132	-142
-6	149	127
-5	285	303
-4	259	-245
-3	362	-413
-2	142	126
-1	349*	463
12,2,L		
-15	276	-274
-14	142	120
-13	369	365
-11	321	-322
-10	163	143
-7	85	-76
-6	134	108
-5	345	389
-4	170	-160
-3	372	-451
-2	94	80
14,2,L		
-15	245	-278
-14	105	109
-13	183	186
-10	161	141
-9	315	376
-8	140	-104
-7	250	-249
-4	177	-156
-3	175	-193
-2	178	170
-1	308	371
16,2,L		
-14	145	130
-13	265	321
-11	322	-348
-9	169	162
-8	204	-174
-5	145	148
-3	247	-282
-2	137	159
-1	232	295
18,2,L		
-15	156	-177
-12	136	-166
-11	181	-205
-9	147	166
-5	164	155
-4	121	-95
-3	125	-173
1,3,L		
-15	166	-141
-14	262	278
-13	81	-30
8	282	-258
9	94	-72
10	309	338
12	304	-353
14	228	254
15	160	161
3,3,L		
4	246	-218
5	411	-431
7	282	264
8	299	-296
10	306	341
12	237	-272
14	251	218
15	161	131
5,3,L		
-6	216	195
-5	418	428
1	150	-125
2	312	355
3	73	78
4	316	-333
5	177	-162
6	235	240
7	184	181
8	205	-241
11	182	142
12	203	-190
14	284	256
7,3,L		
-15	170	-155
-14	220	232
-13	114	93
-12	206	-229
-11	194	-173
-10	262	239
-9	93	53
-8	347	-387
-6	346	380
-5	216	155
-4	205	-191
-3	312	-309
-2	185	187
-1	269	259
1	149	-127
2	367	402
3	197	-164
6	210	180
7	434	409
9	333	-273
10	316	253
11	199	-136
12	411	-357
9,3,L		
-14	127	115
-13	247	247
-12	190	-191
-10	330	329
-7	121	83
-5	327	327
-3	382	-443
-2	221	220
-1	104	-78
1	151	122
2	299	279
3	320	250
4	162	-144
5	195	-160
6	334	257
8	303	-241
11,3,L		
-15	240	-203
-14	189	178
-13	283	246
-9	278	221
-8	181	-154
-7	200	-165
-6	362	312
-5	145	-120
-4	349	-351
-3	127	-112
-2	131	133
-1	282	356
2	305	312
13,3,L		
-14	185	159
-13	341	306
-11	225	-194
-10	272	247
-8	352	-326
-6	242	238
-5	144	126
-4	207	-218
-3	118	-92
-2	165	174
-1	174	139
15,3,L		
-14	166	191
-13	135	107
-12	153	-134
-11	207	-202
-10	187	176
-8	280	-292
-6	247	234
-5	158	134
-4	133	-138
-3	179	-174
-2	157	180
17,3,L		
-15	116	-114
-14	155	173
-12	195	-202
-10	125	143
-9	177	157
-5	208	220
-2	120	178
0,4,L		
6	160	-110
7	89	-74
8	421	-457
9	98	67
10	503*	653
11	279	-295
12	234	-263
13	202	186
14	105	101
2,4,L		
-15	114	120
-14	283	307
-13	80	-64
-12	328	-398
-11	193	173
4	450	-531
5	84	49
6	410	432
7	402	-405
8	200	-192
9	169	155
10	249	290
12	329	-327
13	194	189
14	211	250
15	205	-221
4,4,L		
-15	107	92
-14	249	258
-13	153	-153
-12	290	-307
-11	225	202
-10	238	223
-9	120	-101
-8	421	-513
-7	106	89
-6	475*	647
1	270	305
2	526*	725
3	491	-605
6	212	185
7	126	102
9	241	244
10	269	278
11	224	-226
12	420	-494
14	261	260
6,4,L		
-15	136	128
-12	265	-298
-11	119	114
-10	497	580
-9	437	-436
-7	198	166
-6	253	249
-5	212	207
-4	134	-84
-3	277	270
-2	235	225
-1	338*	-466
2	392*	593
3	82	-74
4	131	-101
5	267	278
9	157	145
10	269	254
11	179	-141
12	263	-243
13	178	146
14	271	238
8,4,L		
-15	128	105
-14	127	157
-13	262	-271
-12	287	-286
-10	399	431
-8	244	-261
-7	322	328
-6	240	221
-5	231	-229
-4	406	-410
-1	151	-142
1	282	274
4	383	-393
6	260	212
7	129	-124
8	213	-189
14	312	293
10,4,L		
-14	219	220
-11	277	234
-10	241	232
-9	169	-126
-6	357	359
-4	172	-163
-3	167	149
-2	132	135
2	383	385
3	205	-163
4	486	-460
5	214	167
12,4,L		
-15	157	157
-12	162	-146
-10	299	256
-9	230	-184
-8	470	-426
-7	217	171
-6	297	281
-2	178	197
-1	87	-101
14,4,L		
-14	153	164
-13	111	-106
-12	262	-257
-11	126	128
-10	171	160
-8	165	-143
-6	323	330
-5	134	-137
-4	258	-300
-3	182	195
-2	119	118
16,4,L		
-15	130	145
-14	120	142
-10	159	148
-8	249	-245
-7	186	189
-6	260	302
-4	190	-226
-1	121	-155
18,4,L		
-8	195	-223
-6	122	144
1,5,L		
-15	258	263
-13	251	-259
-12	126	108
-11	120	104
-10	75	41
-9	235	-186
-8	113	-114
-7	318	301
-6	221	-203
-5	329	-332
-4	237	195
3	331	-319
4	236	-203
5	238	197
6	322	-330
7	258	-232
8	295	283
9	373	409
10	158	145
11	194	-165
12	193	-165
15	242	-241
3,5,L		
-15	187	211
-13	259	-246
-11	196	179
-10	117	80
-9	173	-150
-8	261	-233
-7	241	209
-6	233	-187
-5	308	-305
-4	501*	637
-3	462*	553
3	242	-209
5	555	557
6	199	-174
7	202	-233
8	63	62
10	121	115
11	262	-239
13	256	265
14	117	-114
5,5,L		
-14	120	-109
-13	253	-244
-12	215	-189
-11	76	53
-9	130	-110
-8	164	164
-7	465	494
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13	237	222
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-6	136	-132
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5	155	-151
6	161	130
8	221	-181
4,16,L		
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3	245	222
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1,17,L		
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3,17,L		
-2	202	202

[a] F_o and F_c are on an absolute scale. Reflections marked with asterisks may contain extinction, film-scaling, and/or absorption errors.

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 planes parallel to (100) point in opposite directions; those lying in 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
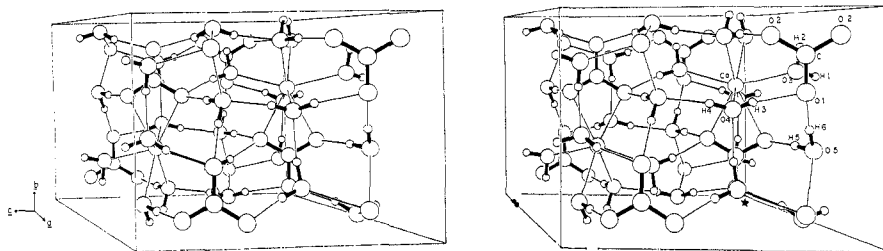
Figure 1.—A stereoscopic illustration of the $CaCO_3 \cdot 6H_2O$ structure.   The contents of the unit cell are shown.   The origin of the unit cell is marked by the asterisk.

TABLE II

ATOMIC PARAMETERS IN $CaCO_3 \cdot 6H_2O^a$

Atom	x	y	z	B, Å²
Ca[b]	0.5000	0.6472 (1)	0.2500	0.10
C	0.5000	0.3067 (6)	0.2500	0.37 (5)
O(1)	0.5000	0.1508 (6)	0.2500	0.77 (5)
O(2)	0.5263 (4)	0.3849 (3)	0.1582 (3)	0.49 (3)
O(3)	0.6163 (4)	0.7229 (4)	0.0916 (4)	0.70 (4)
O(4)	0.7883 (4)	0.5576 (4)	0.3825 (3)	0.59 (4)
O(5)	0.6703 (4)	0.8842 (3)	0.3593 (3)	0.53 (3)

^{a} The quantities in parentheses are standard errors in the last significant figures, as computed in the full-matrix least-squares refinements.   Average shift per error for last cycle, neglecting scale factor, 0.09.   Maximum shift per error for last cycle, neglecting scale factor, 0.29.   Average shift per error for last cycle, including scale factor, 0.29. ^{b} Temperature factor of Ca held fixed at 0.1 Å².

TABLE III

THE PROPOSED HYDROGEN POSITIONS^a

Atom	x	y	z
H(1)	0.568	0.696	0.002
H(2)	0.644	0.835	0.092
H(3)	0.872	0.598	0.354
H(4)	0.822	0.588	0.472
H(5)	0.774	0.891	0.350
H(6)	0.616	0.981	0.319

^{a} Calculated using an idealized water geometry and the hydrogen-bonding scheme described in the water-environments section.

and at the same time permits water molecules coordinated to calcium ions 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 IV.

TABLE IV

THE CALCIUM ENVIRONMENT

Atoms	Dist, Å	Atoms	Dist, Å
Ca–O(2)	2.429 (3)^a	Ca–O(4)	2.576 (3)
Ca–O(3)	2.397 (4)	Ca–O(5)	2.506 (3)

^{a} 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.

In the ion pair, O(2) and O(2') of the CO_3 group are coordinated to Ca (2.429 Å).   The shortest $Ca \cdots O$ 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 8. All the Ca-to-O distances are in the normal range.
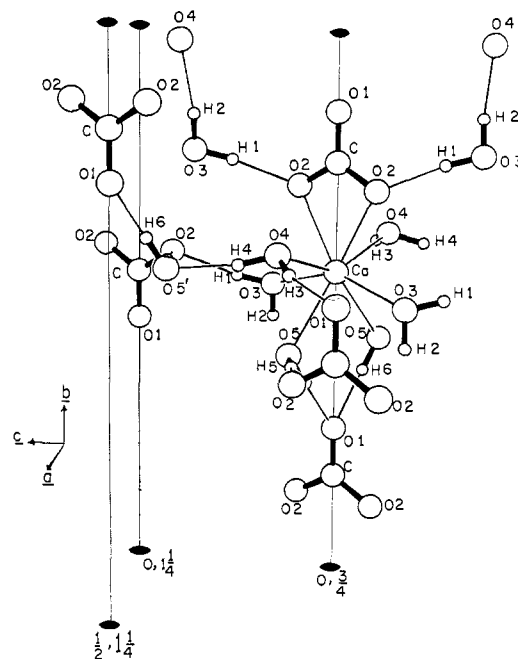
The Carbonate Environment.—The CO_3 is required

Figure 2.—The calcium environment, ion-pair geometry, and a proposed hydrogen-bonding scheme in $CaCO_3 \cdot 6H_2O$. Distances and angles are given in the environment tables.
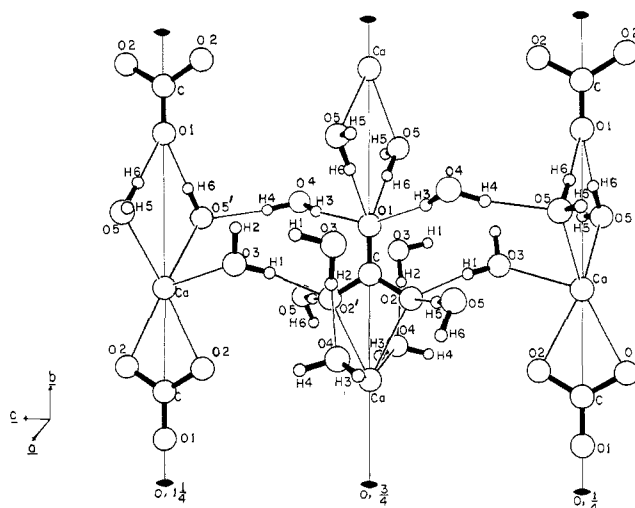

Figure 3.—The carbonate environment and a proposed hydrogen-bonding scheme in $CaCO_3 \cdot 6H_2O$.   Distances and angles are given in the environment tables.

by symmetry to be planar, and its dimensions are in the normal range (Table V).   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 V.   Besides being coordi-

TABLE V

THE CARBONATE ANION

Atoms	Dist, Å	Atoms	Angle, deg
C–O(1)	1.283 (7)	O(1)–C–O(2)	120.0 (2)
C–O(2)	1.287 (5)	O(2)–C–O(2′)	119.9 (4)
O(1)–O(2)	2.226 (5)		
O(2)–O(2′)	2.228 (6)		

O(1) Environment		O(2) Environment	
Atoms	Dist, Å	Atoms	Dist, Å
O(1)–O(5)	2.700 (5)	O(2)–Ca	2.429 (3)
O(1)–H(6)	1.75	O(2)–O(3)	2.749 (5)
O(1)–O(4)	2.854 (4)	O(2)–H(1)	1.80
O(1)–H(3)	1.92	O(2)–O(5)	2.764 (6)
		O(2)–H(5)	1.81

nated to Ca by O(2) and O(2′), the CO₃ 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 four hydrogen bonds from four water molecules while O(2) accepts only two hydrogen bonds. This appears reasonable since O(2) is coordinated to Ca, but O(1) is not.

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 1–3 and in Table VI. The water molecules

TABLE VI

THE WATER ENVIRONMENTS

O(3) Environment

Atoms	Dist, Å	Atoms	Angle, deg
O(3)–Ca	2.397 (4)	O(2)–O(3)–O(4)	115.3 (2)
O(3)–O(2)	2.749 (5)ᵃ	O(3)–H(1)–O(2)	172
O(3)–O(4)	2.867 (4)ᵃ	O(3)–H(2)–O(4)	172
H(1)–O(2)	1.80		
H(2)–O(4)	1.92		

O(4) Environment

Atoms	Dist, Å	Atoms	Angle, deg
O(4)–Ca	2.576 (3)	O(1)–O(4)–O(5)	126.8 (1)
O(4)–O(1)	2.854 (4)ᵃ	O(1)–O(4)–O(3)	94.9 (2)
O(4)–O(5′)	2.781 (5)ᵃ	O(1)–O(4)–O(5′)	89.2 (2)
O(4)–O(3)	2.867 (4)ᵃ	O(5)–O(4)–O(3)	97.7 (1)
O(4)–H(2)	1.92	O(5)–O(4)–O(5′)	119.7 (1)
O(4)–O(5)	2.864 (4)	O(3)–O(4)–O(5′)	175.6 (2)
H(3)–O(1)	1.92	O(4)–H(3)–O(1)	163
H(4)–O(5′)	1.85	O(4)–H(4)–O(5′)	163

O(5) Environment

Atoms	Dist, Å	Atoms	Angle, deg
O(5)–O(1)	2.700 (5)ᵃ		
O(5)–O(2)	2.764 (6)ᵃ	O(1)–O(5)–O(2)	112.0 (1)
O(5)–O(4)	2.781 (5)ᵃ	O(1)–O(5)–O(4)	99.9 (1)
O(5)–O(4)	2.864 (4)	O(2)–O(5)–O(4)	106.4 (1)
O(5)–H(4)	1.85	O(5)–H(5)–O(2)	174
H(5)–O(2)	1.81	O(5)–H(6)–O(1)	174
H(6)–O(1)	1.75		

ᵃ Suggested hydrogen bonds, assuming O–H = 0.958 Å and H–O–H = 104.5°.

are all coordinated to Ca and also provide extensive hydrogen bonding to CO₃ ions and other water molecules. The following hydrogen-bonding scheme is proposed. Water oxygen O(3) has only 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 because the H–O–H angle in water should be near 104.5°. 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.

Water oxygen O(5) has three near neighbor oxygens suitable for hydrogen bonding, O(1) at 2.700 Å, O(2) at 2.764 Å, 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 similar to the calculation for the hydrogen positions in CaNa₂(CO₃)₂·5H₂O[7] and CaNa₂(CO₃)₂·2H₂O.[7] The water molecules, with the geometry of free water (H–O–H = 104.5°, O–H = 0.958 Å), were oriented so that their hydrogen bonds were as linear as possible. The resulting hydrogen positions are given in Table III. The short H···O distances and the near linearities of the O–H···O angles lend credence to this scheme. Each hydrogen is involved in one hydrogen bond; there are no bifurcated hydrogen bonds. No hydrogens are unbonded. The O···O distances (2.700–2.867 Å) in this hydrogen-bonding scheme all lie in the normal range. The only O···O distance less than 3 Å not involved in the above hydrogen-bonding scheme is O(4)···O(5), 2.864 Å, which is an edge of the Ca coordination.

The outstanding feature in the structure is the presence of (CaCO₃⁰) 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 hydrated (CaCO₃⁰) 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
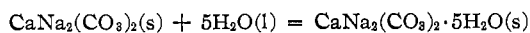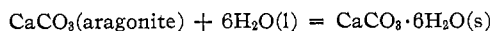
(16) I. Greenwald, *J. Biol. Chem.*, **141**, 789 (1941).

in the same way that has been suggested for the (Ca-SO₄⁰) ion pair.[17]

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 calcium ions are bonded to the edges of CO_3^{2-} 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.

Discussion

The observation that $CaCO_3 \cdot H_2O$ spherulites dissolve with concomitant formation of $CaCO_3 \cdot 6H_2O$ as noted in the description of the preparation of $CaCO_3 \cdot 6H_2O$ crystals is proof that, in dilute solutions (*i.e.*, when activity of water $\simeq 1$) and near 0°, $CaCO_3 \cdot 6H_2O$ is less soluble and hence more stable than $CaCO_3 \cdot H_2O$.

On the basis of unit cell and density data, the reactions

$$CaCO_3(\text{calcite}) + 6H_2O(l) = CaCO_3 \cdot 6H_2O(s)$$

$$CaCO_3(\text{aragonite}) + 6H_2O(l) = CaCO_3 \cdot 6H_2O(s)$$

$$CaNa_2(CO_3)_2(s) + 5H_2O(l) = CaNa_2(CO_3)_2 \cdot 5H_2O(s)$$

would be accompanied by 20, 18, and 13% decreases in volume, respectively, at atmospheric pressure. These volume changes suggest that, at high hydrostatic pressures, such as those that occur in the abyssal layer of the oceans or in hydrostatic vessels, the formation of $CaCO_3 \cdot 6H_2O$ in particular and hydrated salts in general will be favored. This is possibly related to the observations that most deep-sea animals have little or no calcareous materials in their skeletons[18] and that there is very little calcium carbonate in 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. It has been suggested[20] from electron microscopic examinations that almost all the calcium carbonate in deep-sea sediments is of organic origin (and therefore anhydrous) and has not been changed after deposition. Since $CaCO_3 \cdot 6H_2O$ decomposes rapidly to the anhydrous forms at normal temperatures and pressures, precautions should be taken during sample recovery to test the possibility that there may be hydrated forms of calcium carbonate as well as the anhydrous forms at these depths.

The previous neglect of the hydrated calcium carbonates in studies of calcium carbonate mineralization may not be warranted because of the following factors.

(a) It has been conjectured[21] that very small particles of hydrated salts have lower interfacial energies in aqueous environments than correspondingly small particles of the anhydrous salts. Since the interfacial energy is a large factor in the total energy of very small particles, the initial formation of crystallization nuclei consisting of hydrated salts may be favored in aqueous systems. These nuclei may subsequently develop into less hydrated forms.

(b) Hydrated salts sometimes crystallize in preference to their anhydrous counterparts. For example, $CaHPO_4 \cdot 2H_2O$ and $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ are frequently formed under conditions where $CaHPO_4$ or $Ca_{10}(PO_4)_6(OH)_2$ is the stable salt thermodynamically.

(c) Polyphosphate[4] and magnesium[6] ions, both of which are found *in vivo*, repress the growth of anhydrous calcium carbonates more than that of the hydrated forms.

(d) Low temperatures and high pressures, such as those in the oceanic deeps, should favor the formation of the hydrated forms under certain mineralization conditions.

(e) Most nucleation processes are thought to be heterogeneous and presumably occur on collagen and other proteins in biological mineralization. Because of their hydrophilic nature these proteins would perhaps stabilize nuclei of hydrated salts more than those of anhydrous salts.

Thus, hydrated salts may play an important part in biological mineralization, in particular, and in crystallization from aqueous environments, in general. Far too little consideration has been given to the possibility that the salt that is found after crystal growth may have been preceded by nuclei of a more hydrated species. Such a hydrated precursor could, through epitaxic or topotaxic effects, control the habits and even identity of the crystal that is finally formed. Any study of crystal growth in aqueous systems which does not include a search for hydrated precursors, possibly using high-pressure techniques, may therefore overlook essential information.

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Sciences Division of the School of Aerospace Medicine, USAF; the National Institute of Dental Research; and the Veterans Administration. The structure and some of the considerations in this paper were presented at the 46th General Meeting of the International Associ-

ation for Dental Research, San Francisco, Calif., March 21, 1968, and at the Symposium on the Structural Properties of Hydroxyapatite and Related Compounds held at the National Bureau of Standards, Sept 12–14, 1968.


Kinetics and Mechanism of Electron Exchange between Chromium(II) and Some Chromium(III)–Oxalate Complexes[1]

By D. H. HUCHITAL

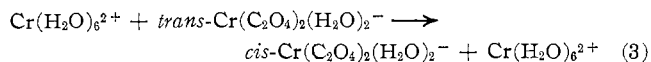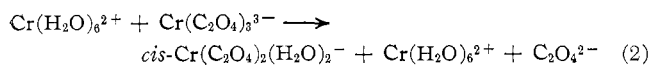*Received September 8, 1969*

Chromium(II) catalyzes the aquation of one oxalate group from $Cr(C_2O_4)_3{}^{3-}$ and the *trans–cis* isomerization of $Cr(C_2O_4)_2(H_2O)_2{}^-$. Both reactions obey the rate law $-d[Cr(III)]/dt = k[Cr(II)][Cr(III)]$ for the chromium(II)-catalyzed path. The values of k in M^{-1} sec^{-1} (enthalpies of activation follow in parentheses) at 25° and 1.2 M ionic strength are 0.129 (8.2) and 0.108 (11.9) for $Cr(C_2O_4)_3{}^{3-}$ and *trans*-$Cr(C_2O_4)_2(H_2O)_2{}^-$, respectively. The results are discussed in terms of a chromium-(II)–chromium(III) electron exchange utilizing two oxalate ligands as bridging groups. Evidence for such a mechanism is adduced from isotope tracer studies on the above reactions and the electron exchange between chromium(II) and *cis*-$Cr(C_2O_4)_2(H_2O)_2{}^-$.

The electron-exchange reaction between the aquo ions of chromium(II) and chromium(III) in acidic perchlorate solutions is very slow.[2] Addition of various anions, either free in solution[3] or coordinated to the chromium(III), results in an increase in the rate of the electron-exchange process.[4] Spinner and Harris[5] have studied the rate of electron exchange between chromium(II) and $Cr(C_2O_4)(H_2O)_4{}^+$ using isotopically labeled chromium, the net reaction being

$$Cr(H_2O)_6{}^{2+} + {}^*Cr(C_2O_4)(H_2O)_4{}^+ \longrightarrow$$
$$Cr(C_2O_4)(H_2O)_4{}^+ + {}^*Cr(H_2O)_6{}^{2+} \quad (1)$$
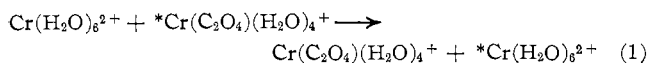
We report here the results of a study of the electron exchange between aquochromium(II) and the complexes $Cr(C_2O_4)_3{}^{3-}$ and *trans*- and *cis*-$Cr(C_2O_4)_2(H_2O)_2{}^-$. The feature of a net chemical reaction for the first two reactions

$$Cr(H_2O)_6{}^{2+} + Cr(C_2O_4)_3{}^{3-} \longrightarrow$$
$$cis\text{-}Cr(C_2O_4)_2(H_2O)_2{}^- + Cr(H_2O)_6{}^{2+} + C_2O_4{}^{2-} \quad (2)$$

$$Cr(H_2O)_6{}^{2+} + trans\text{-}Cr(C_2O_4)_2(H_2O)_2{}^- \longrightarrow$$
$$cis\text{-}Cr(C_2O_4)_2(H_2O)_2{}^- + Cr(H_2O)_6{}^{2+} \quad (3)$$

allows for the compilation of rate data without resort to isotopic labeling.

Experiments using isotopically labeled complexes are reported in an effort to adduce a mechanism for the above reactions. The results indicate that an electron-exchange process is taking place between chromium(II) and the various chromium(III) complexes with the transfer of two oxalate groups.

Experimental Section

Materials.—Sodium tris(oxalato)chromate(III) was prepared following the procedure given in ref 6. *Anal.* Calcd for Na$_3$-[Cr(C$_2$O$_4$)$_3$]·5H$_2$O: Cr, 10.9; C, 15.17; H, 2.12. Found: Cr, 10.9; C, 14.94; H, 2.14.

Sodium *trans*-bis(oxalato)diaquochromate(III) was prepared by the method of Werner.[7] The purity of the complex was ascertained by analysis for chromium, carbon, and hydrogen and by comparing the absorption spectrum of the *cis* isomerization product with the spectrum reported in the literature.[8] *Anal.* Calcd for Na[Cr(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·2H$_2$O: Cr, 16.1; C, 14.87; H, 2.50. Found: Cr, 16.3; C, 15.07; H, 2.47.

Solutions of chromium(II) perchlorate were prepared by zinc amalgam reduction of chromium(III) perchlorate. The concentration of chromium(II) was assumed to be equal to that of the chromium(III) solution from which it was made. The concentration of chromium(III) was determined by conversion to $CrO_4{}^{2-}$ with alkaline peroxide and measuring the optical density at 373 mμ (ϵ_{373} 4815).[9] In a few cases this procedure was checked by oxidation of the chromium(II) solution with excess iron(III) followed by titration of the released iron(II) with standard dichromate.[10]

Kinetics Measurements.—The reaction vessels were 2-cm quartz absorption cells with narrow openings. For the tris-(oxalato)chromate(III) reactions, all reagents except chromous ion were added to the cell which was then fitted with a serum cap. The cell and contents were aerated with argon for 15 min using a 23 gauge hypodermic syringe needle for an inlet and a 25 gauge needle for an outlet. Chromous ion was added to initiate the reaction. Spectrophotometric measurements indicated no aquation occurred prior to the addition of chromous ion.

(1) Presented in part before the Division of Inorganic Chemistry, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

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