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Progress Report

on

THE CRYSTAL STRUCTURE OF THE ARAGONITE PHASE OF $CaCO_3$

by

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The Crystal Structure of the Aragonite Phase of $CaCO_3$

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Abstract

Aragonite ($CaCO_3$) crystallizes in the unit cell $\underline{a}$ = 4.9598(5) Å, $\underline{b}$ = 7.9641(9) Å, and $\underline{c}$ = 5.7379(6) Å at 25°C with four formula weights in space-group Pmcn. The structure has been refined to $\underline{R_w}$ = 0.024, $\underline{R}$ = 0.040 using 765 X-ray reflections from a single crystal. The Ca ion is coordinated to nine oxygens with Ca...O distances in the range 2.414(1) Å to 2.653(1) Å. The two unique C-O distances in the CO_3 group are 1.288(2) Å (on the mirror plane) and 1.283(1) Å. The two unique O-C-O angles are 119.62(4)° (across the mirror plane) and 120.13(8)°.

1. INTRODUCTION

Aragonite ($CaCO_3$) is found in nature as a mineral and is an important biomineral because of its presence in coral, clam shells, gallstones and otoliths. It is isomorphous with the carbonates of large divalent cations such as Ba, Sr and Pb.

Aragonite is less stable than the calcite phase of $CaCO_3$ at room temperature, but is denser than calcite. This suggests that aragonite is more stable than calcite at low temperatures and/or high pressures. More details are available in reference 1. Because of the importance of aragonite, and because of the possibility of performing calculations on the lattice energies of selected carbonates along the lines suggested by Busing[2], we have collected new X-ray data from a single crystal of aragonite and have refined the structure from the positions given in 1924 by Bragg [3].

2. STRUCTURE DETERMINATION

<u>FORMULA</u> (ideal): $CaCO_3$ (aragonite phase); <u>UNIT CELL</u>: orthorhombic with $\underline{a}$ = 4.9598(5) Å, $\underline{b}$ = 7.9641(9) Å, $\underline{c}$ = 5.7379(6) Å at 25°C (calculated by least squares from 12 2θ values observed on a diffractometer); volume: 226.65 Å^3; radiation, Mo($K_{\alpha 1}$), λ = 0.70926 Å; monochromator; highly

oriented graphite crystal; space-group: Pmcn; contents 4($CaCO_3$); reciprocal lattice extinctions, hk0: $h + k = 2n + 1$, h0ℓ: $\ell = 2n + 1$; observed density, 2.947(2) $g\cdot cm^{-3}$ [4]; calculated density, 2.944 $g\cdot cm^{-3}$; CRYSTAL: material available heavily twinned; small wedge largest single crystal fragment found; this wedge was attached to thin borate glass fiber with clear household cement; fiber attached to insert in goniometer head with epoxy cement; origin of crystal, mineral sample #75538 from National Museum of Natural History, Smithsonian Institution, Washington, D. C. Supplied by J. S. White, Jr.; linear absorption corrections made by 8 x 8 x 8 Gaussion quadrature using subroutines written by C. W. Burnham [5] and adapted by B. Dickens; maximum and minimum corrections for absorption = 0.963 and 0.880 (transmission factors). INTENSITY DATA: number of reflections, 2356 collected from 2 octants and merged into a unique set of 765, of which 619 are "observed" and 146 are "unobserved"; unobserved reflections are those less than 2σ above background; maximum $\sin\theta/\lambda$ for data 0.907 $Å^{-1}$; method used to estimate data: $\theta/2\theta$ scan, scintillation counter; diffractometer: Picker 4-circle single-crystal diffractometer automated by PDP 8/I computer through FACS-1 interface and adapted to include least significant digit of counts; COMPUTATION: setting programs, those of reference [6] as adapted by Picker Nuclear Corporation; scan range: $1.4° + 114.6 \frac{\Delta\lambda}{\lambda}$, $\Delta\lambda = 0.692$, $\lambda = 0.70926$ Å; scan parameters: backgrounds counted at higher and lower 2θ for 100 sec. each; $\theta/2\theta$ scan at 0.25°/min for 2θ from one background position to the other; attenuators: 0.025 mm thick layers of Nb, 1 layer for first attenuator, 2 for second, 3 for third; scan range correction: table look-up method to obtain values recommended in reference [7]; paper tape processing program written by B. Dickens for Univac 1108 computer, contains adaptions of similar program by F. A. Mauer (NBS), standard reflection plotting routine and extince reflection editing routine from programs by J. M. Stewart, University of Maryland; this program uses an intense standard reflection at low angle to correct for change in intensity of the primary X-ray beam. 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. Data merging program for equivalent reflections, written by B. Dickens for Univac 1108 computer; in this program each set of equivalent reflections is treated as follows: Reflections which were all unobserved were averaged and given the largest individual standard deviation in the set. Unobserved reflections in the presence of at least one observed reflection were discarded. Observed reflections which, subsequent to this step, occurred only once in the list were copied unchanged but their standard deviations were increased by a factor of three. Observed reflections with magnitudes which agreed within the counting statistics and reflections with magnitudes whose ratios fell within the range 0.95 to 1.06 were averaged and given as standard deviation the maximum of the standard deviation from counting statistics and the standard deviation from the range estimate [8,9]. Under these circumstances, reflections whose magnitudes did not pass the criteria were discarded. If no reflections passed the criteria, the highest magnitude was taken and the associated standard deviation multiplied by five. The justification for these arbitrary increases of standard deviations is that without some corroboration, every reflection is suspect because of the possibilities of multiple reflection, including the "tail" of nearby intense reflections in its measurement, change in intensity of X-ray beam, misalignment of crystal, etc. Scattering factors: those for

the neutral atoms in reference 10; least-squares refinements; full-matrix, with $\Sigma(w||F_o|-|F_c||)^2$ minimized; refinements include unobserved reflections which calculate higher than 2 σ above background; least-squares weights: $1/\sigma^2$; $\underline{R}_w = (\Sigma(w||F_o|-|F_c||))^2/\Sigma(w|F_o|)^2)^{\frac{1}{2}}$, $\underline{R} = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; thermal parameters have the form $\exp(-1/4(\underline{a}^{*2}\underline{B}_{11}\ \underline{h}^2 + \underline{B}_{22}\ \underline{k}^2 + \underline{c}^{*2}\ \underline{B}_{33}\ \underline{\ell}^2 + 2\underline{a}^*\underline{b}^*\underline{B}_{12}\underline{hk} + 2\underline{a}^*\underline{c}^*\underline{B}_{13}\ \underline{h\ell} + 2\underline{b}^*\underline{c}^*\underline{B}_{23}\underline{k\ell})$.
Least squares and electron density synthesis calculations carried out with X-ray 67 system [11] of computing programs.
FINAL REFINEMENT: $\underline{R}_w = 0.024$; $\underline{R} = 0.040$, average shift/error for last cycle = 0.0017; standard deviation of an observation of unit weight = $(\Sigma(w(F_o-F_c))^2/(765-28))^{\frac{1}{2}} = 0.775$.

The highest peak in an electron density difference synthesis calculated after the final anisotropic refinement to $\underline{R}_w = 0.024$ corresponded to about 1/3 of an electron and was about 0.95 Å from C towards O(1). The largest correlation coefficients are 0.34-0.44 between the scale factor and the $\underline{B}_{11}$, $\underline{B}_{22}$ and $\underline{B}_{33}$ temperature factors of Ca.

The atomic parameters are given in table 1. The observed and calculated structure factors are given in table 2.

3. DESCRIPTION OF THE STRUCTURE

The structure of aragonite, the main points of which are well known, is shown in figure 1. The Ca ions lie in pseudo-hexagonal layers parallel to (001) and the layer sequence is

ABAB. The Ca layers are separated by CO_3 groups which lie in two layers parallel to (001), and form columns parallel to [001].

3.1. The Ca ion environments

The Ca ion lies on the mirror plane at $\underline{x} = 1/4$. Its environment is shown in figure 2 and summarized in table 3. The coordination contains three CO_3 edges, $O(1,2)$, $O(1^{I},2^{I})$ and $O(2^{IV},2^{V})$ and three apexes, $O(1^{II},2^{II},2^{III})$. The apparent thermal motion of Ca is almost isotropic, (table 1, Fig. 2).

3.2. The CO_3 group

The dimensions of the CO_3 group are given in table 4. All C-O distances in the CO_3 group are essentially equal with an average of 1.286 Å. This agrees well with the C-O distance of 1.283(2) reported [12] for calcite. There appears to be some significant deviation from trigonality in the angles; the reported angle of 119.62° for $O(2)-C-O(2^{I})$ is consistent with the $O(2,2^{I})$ edge of the CO_3 group being coordinated slightly more strongly to Ca as judged from the Ca...O distances. If the apparent thermal motions of the atoms in the CO_3 group are attributed to thermal motion rather than to slight positional disorder, there seems to be oscillation within the CO_3 layer, i.e., more or less perpendicular to the edge coordination to Ca. Similarly, O(1) may be undergoing some additional wagging out of the CO_3 layer.

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Table 1 Atomic Parameters in Aragonite ($CaCO_3$)

Atoms	x	y	z	B_{11}*	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	.25000	.58507(5)	.25974(6)	.664(9)	.599(9)	.601(9)	.0000	.0000	-.01(1)
C	.25000	.2386(2)	.4148(3)	.75(5)	.85(5)	.46(5)	.0000	.0000	.07(5)
O(1)	.25000	.0770(2)	.4043(2)	1.50(5)	.54(4)	1.04(4)	.0000	.0000	.03(4)
O(2)	.4737(2)	.3196(1)	.4131(2)	.71(3)	1.03(3)	1.02(3)	-.32(3)	-.02(3)	-.09(3)

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 $\mathring{A}^2$

0,K,0
2 60 -61
4 290 -289
6 363 -357
8 264 -268
10 140 142
12 285 284
14 42 20

0,K,1
1 20 21
2 472 -469
3 355 -344
4 654 -655
5 230 228
6 47 46
7 60 72
8 320 324
9 73 -75
10 153 151
11 79 80
12 40 33
13 80 -77
14 161 -159

0,K,2
0 206 -210
1 577 558
2 409 -401
3 68 -69
4 238 234
5 16• -3
6 344 346
7 91 95
8 62 57
9 55 -61
10 133 -124
11 57 -59
12 140 -134
13 58 48
14 76 -69

0,K,3
1 51 -50
2 491 489
3 17• 23
4 17• -1
5 30 30
6 13• 16
7 21• 21
8 112 -113
9 21• 0
10 230 -222
11 53 -31
12 120 121
13 27• -11

0,K,4
0 102 103
1 340 334
2 253 251
3 51 50
4 160 -160
5 67 45
6 262 -258
7 21• 14
8 22• -28
9 103 -109
10 113 110
11 80 -66
12 100 98
13 69 69

0,K,5
1 96 96
2 226 -223
3 134 134
4 283 -286
5 200 -199
6 25• 31
7 126 -126
8 212 208
9 61 63
10 113 108
11 26• -10
12 20• 11

0,K,6
0 484 -506
1 80 -83
2 22• -13
3 106 -113
4 111 111
5 51 -47
6 214 210
7 34 35
8 136 144
9 80 83
10 80 -92
11 48 40

0,K,7
1 89 -92
2 186 174
3 64 69
4 257 251
5 24• 16
6 25• -14
7 43 37
8 195 -193
9 29• 37
10 87 -90

0,K,8
0 134 135
1 74 -82
2 123 123
3 102 108
4 106 -104
5 25• 20
6 160 -157
7 64 -64
8 51 -51
9 30• -26

0,K,9
1 70 64
2 147 -150
3 27• -16
4 48 -44
5 57 -52
6 27• 0
7 46 -38

0,K,10
0 48 -36
1 109 -110
2 88 -85
3 58 -52

1,K,0
1 54 -61
3 464 477
5 49 45
7 131 -129
9 216 -212
11 22• -5
13 93 72

1,K,1
1 423 421
2 160 153
3 51 -49
4 175 168
5 300 -300
6 20• 33
7 192 -187
8 88 -92
9 21• 13
10 34 -20
11 185 187
12 49 -44
13 91 89
14 47 39

1,K,2
0 471 454
1 407 -404
2 16• -7
3 476 -471
4 16• -10
5 214 -217
6 153 -156
7 181 185
8 44 -42
9 241 242
10 24• -4
11 108 104
12 86 84
13 113 -109
14 30• 17

1,K,3
1 510 -505
2 101 -95
3 27 -25
4 83 -82
5 363 365
6 18• -3
7 315 319
8 48 53
9 47 -43
10 42 40
11 150 -157
12 25• 3
13 184 -178

1,K,4
0 96 85
1 290 287
2 84 -82
3 363 365
4 61 65
5 193 189
6 20• -6
7 157 -160
8 23• 17
9 222 -226
10 42 -44
11 104 -107
12 25• 7
13 101 97

1,K,5
1 257 249
2 32 25
3 20• -14
4 20• 0
5 218 -218
6 22• -31
7 158 -162
8 23• 4
9 23• 6
10 45 -34
11 153 152
12 47 45

1,K,6
0 60 60
1 21• -23
2 36 34
3 237 -239
4 43 -39
5 39 -31
6 54 -56
7 86 74
8 23• -15
9 152 152
10 38 33
11 27• 5

1,K,7
1 146 -142
2 68 -97
3 33 15
4 94 -96
5 139 140
6 23• -9
7 88 90
8 97 95
9 25• -7
10 46 42

1,K,8
0 181 -187
1 117 110
2 47 -20
3 143 146
4 36 27
5 80 81
6 135 133
7 85 -89
8 28• 37
9 111 -111

1,K,9
1 145 145
2 95 93
3 29• 0
4 96 89
5 126 -129
6 43 3
7 131 -132

1,K,10
0 47 42
1 95 -98
2 63 66
3 118 -119

2,K,0
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2 477 -466
4 151 146
6 615 635
8 21• 4
10 71 -71
12 205 -201
14 119 -117

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1 264 254
2 653 659
3 253 -247
4 270 272
5 117 119
6 51 50
7 90 -85
8 256 -253
9 49 -55
10 227 -230
11 47 54
12 28• 28
13 28• 14
14 146 144

2,K,2
0 515 513
1 123 120
2 141 142
3 61 -58
4 234 -237
5 189 -194
6 188 -184
7 158 157
8 158 -157
9 65 -69
10 146 148
11 46 42
12 180 155
13 39 36

2,K,3
1 33 29
2 46 -50
3 18• 10
4 391 -393
5 38 -44
6 126 129
7 21• -24
8 177 180
9 22• 12
10 64 62
11 26• 21
12 38 -8
13 29• 12

2,K,4
0 338 -336
1 18• 8
2 94 -86
3 116 -117
4 176 182
5 187 -188
6 116 117
7 163 162
8 132 129
9 24• 3
10 127 -129
11 54 56
12 135 -130

2,K,5
1 201 -202
2 290 292
3 123 122
4 165 164
5 22• 10
6 23• 17
7 132 129
8 182 -180
9 46 37
10 150 -150
11 89 -96
12 48 27

2,K,6
0 230 230
1 50 48
2 155 157
3 105 109
4 72 -69
5 75 63
6 343 -346
7 55 -55
8 24• -1
9 62 -71
10 57 47
11 30• -30

2,K,7
1 34 28
2 252 -253
3 72 68
4 129 -133
5 116 -118
6 27• -28
7 27• -22
8 186 152
9 28• 23
10 149 147

2,K,8
0 180 -180
1 53 -52
2 88 -83
3 63 -70
4 97 103
5 53 52
6 113 117
7 46 -46
8 85 84

2,K,9
1 50 -50
2 56 52
3 37 -8
4 156 153
5 72 65
6 59 -51

2,K,10
0 106 105
1 44 37
2 51 39

3,K,0
1 191 -190
3 318 -323
5 19• 33
7 34 22
9 225 229
11 39 24
13 101 -102

3,K,1
1 256 -259
2 208 -201
3 51 -46
4 18• 4
5 290 288
6 65 -58
7 172 169
8 44 43
9 45 -39
10 54 63
11 144 -146
12 27• 13
13 101 -88

3,K,2
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1 206 204
2 74 -73
3 360 360
4 19• -25
5 200 204
6 189 198
7 194 -198
8 23• -21
9 198 -198
10 23• 9
11 90 -87
12 47 -47
13 105 83

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2 72 76
3 102 -99
4 59 57
5 221 -224
6 21• 3
7 268 -266
8 45 -42
9 24• -8
10 47 -38
11 179 184
12 28• -2

3,K,4
0 38 33
1 168 -169
2 20• 18
3 305 -303
4 74 -77
5 191 -191
6 59 56
7 179 179
8 60 -59
9 189 186
10 46 46
11 87 86
12 28• 15

3,K,5
1 195 -197
2 40 33
3 21• -19
4 71 -72
5 220 213
6 49 47
7 154 146
8 26• 23
9 24• -20
10 25• -4
11 120 -123

3,K,6
0 64 -64
1 88 85
2 23• -27
3 203 204
4 41 39
5 24• -7
6 47 45
7 28• -18
8 27• 18
9 164 -162
10 48 -28

3,K,7
1 107 114
2 119 120
3 24• 19
4 43 48
5 150 -150
6 26• 22
7 79 -87
8 68 -70
9 29• 26

3,K,8
0 129 122
1 82 -85
2 51 43
3 136 -136
4 29 -12
5 94 -82
6 151 -153
7 96 94

3,K,9
1 183 -187
2 89 -90
3 84 35
4 78 -78
5 89 92

4,K,0
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2 39 39
4 152 -145
6 268 -275
8 196 -171
10 116 116
12 225 217

4,K,1
1 19• 4
2 266 -268
3 106 -111
4 335 -340
5 86 93
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7 37 37
8 236 237
9 50 -43
10 128 129
11 51 56
12 30• 23

4,K,2
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1 187 189
2 203 -202
3 48 -52
4 161 159
5 21• 16
6 234 236
7 46 43
8 61 58
9 45 -34
10 100 -101
11 28• -36
12 120 -117

4,K,3
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2 260 272
3 21• 10
4 77 71
5 26• 26
6 22• 2
7 37 20
8 112 -111
9 25• 0
10 164 -170
11 27• -28
12 92 92

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1 175 176
2 169 163
3 35 30
4 123 -128
5 47 88
6 192 -192
7 31 -7
8 48 -35
9 61 -80
10 66 89
11 49 -46

4,K,5
1 63 74
2 175 -177
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4 203 -207
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6 25• 21
7 92 -91
8 169 165
9 29• 40
10 110 94

4,K,6
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2 36 -21
3 96 -86
4 92 79
5 47 -38
6 190 182
7 27• 30
8 106 105
9 67 67

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4 191 191
5 27• 23
6 24• -11
7 30• 34
8 152 -152

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2 100 97
3 90 91
4 94 -67
5 29• 10
6 124 -126

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7 138 -144
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11 28• 0

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4 113 119
5 164 -161
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7 131 -134
8 81 -76
9 42 -10
10 42 25
11 141 160

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1 206 -210
2 49 -54
3 234 -232
4 21• -11
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6 43 -38
7 104 101
8 66 -56
9 183 186
10 26• 1
11 91 80

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8 54 39
9 73 -67
10 27• 25
11 77 -83

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4 43 37
5 101 102
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10 29• -28

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2 35 6
3 108 107
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3 56 -51
4 157 161
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7 47 -45
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10 139 -136

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3 23• 7
4 126 -123
5 75 -62
6 141 -139
7 66 60
8 89 -92
9 47 -43
10 104 101

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4 201 -191
5 38 -28
6 67 64
7 26• -17
8 105 107
9 27• 5

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4 109 107
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6 103 105
7 86 79
8 83 79
9 26• 6

6,K,5
1 89 -93
2 168 168
3 49 82
4 116 119
5 52 20
6 28• 6
7 89 84
8 129 -127

6,K,6
0 186 174
1 29• 32
2 91 79
3 60 67
4 71 -53
5 29• 37
6 201 -203

6,K,7
1 49 30
2 152 -151
3 46 25
4 104 -98

7,K,0
1 124 -122
3 177 -172
5 27• 20
7 29• -11
9 171 167

7,K,1
1 124 -126
2 103 -92
3 41 -37
4 43 41
5 171 175
6 55 -41
7 97 105
8 41 11

7,K,2
0 25• -10
1 82 82
2 44 -39
3 184 179
4 26• -23
5 116 116
6 130 122
7 128 -127
8 47 -42

7,K,3
1 228 211
2 43 37
3 86 -82
4 36 26
5 97 -94
6 28• 1
7 157 -151
8 89 -23

7,K,4
0 50 52
1 81 -73
2 25• 1
3 175 -165
4 54 -51
5 113 -116
6 49 45
7 132 122

7,K,5
1 115 -112
2 31• 28
3 29• -21
4 82 -77
5 136 139

7,K,6
0 48 -46
1 73 70
2 30• -16
3 126 124

8,K,0
0 247 235
2 47 42
4 50 -54
6 181 -172

8,K,1
1 26• -5
2 147 -143
3 27• -10
4 142 -142
5 28• 13
6 28• 10

8,K,2
0 127 -122
1 50 42
2 85 -89
3 29• -33
4 92 90
5 40 25

8,K,3
1 40 -19
2 120 115
3 28• 2
4 90 87
5 28• 17

8,K,4
0 100 96
1 63 59
2 80 78
3 30• 15

Table 3

The Ca environment in aragonite ($CaCO_3$)

Atoms	Distance, Å
Ca, O(1^{II})	2.414(1)
Ca, O(2^{II}, 2^{III})	2.445(1)
Ca, O(2, 2^{I})	2.520(1)
Ca, O(2^{IV}, 2^{V})	2.544(1)
Ca, O(1, 1^{I})	2.653(1)

In all tables of interatomic distances and angles, the figures in parentheses are standard deviations in the last digit and were calculated from the standard deviations in the atomic positional parameters and the unit cell parameters.

Table 4

The CO_3 group and its environment in aragonite ($CaCO_3$)

Atoms	Distance, Å, or angle, deg.
C, O(1)	1.288(2) Å
C, O(2)	1.283(1)
O(1), O(2)	2.229(1)
O(2), O(2^{I})	2.219(1)
O(1), C, O(2)	120.13(8)°
O(2), C, O(2^{I})	119.62(4)
O(1), Ca^{V}	2.414(1) Å
O(1), (Ca^{II}, Ca^{III})	2.653(1)
O(2), Ca	2.445(1)
O(2), Ca^{II}	2.520(1)
O(2), Ca^{IV}	2.544(1)

Figure legends

1. A stereoscopic illustration of the crystal structure of aragonite ($CaCO_3$). A unique set of atoms is labelled. The origin of the crystallographic coordinate system is marked by *.

2. The Ca environment in aragonite ($CaCO_3$). The labels refer to atoms in table 3.

3. The CO_3 group environment in aragonite ($CaCO_3$). The labels refer to atoms in table 4.

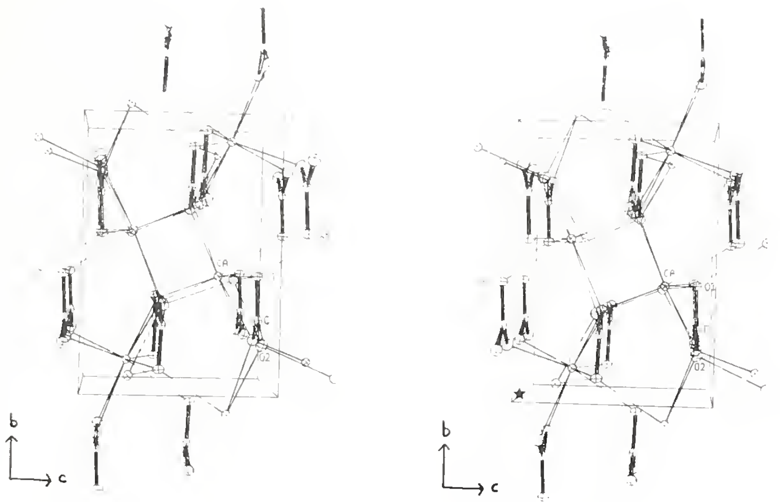

fig 1

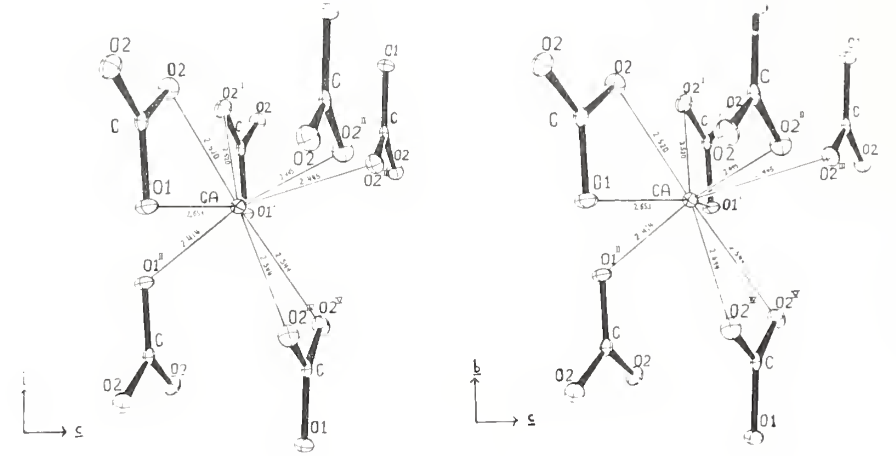

fig 2

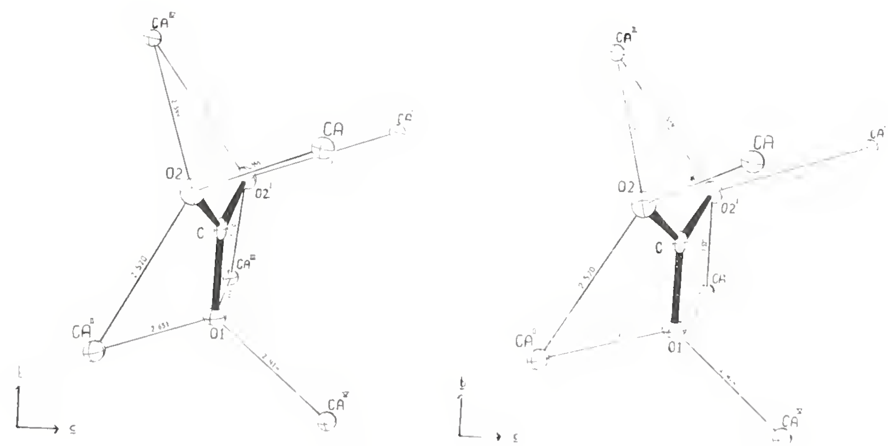

fig 3