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REFINEMENT OF THE CRYSTAL STRUCTURE OF ARAGONITE

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ABSTRACT

The lattice constants and positional parameters of aragonite have been redetermined from single-crystal X-ray diffraction data. Space group *Pmcn*; *a* 4.9616(2), *b* 7.9705(6), *c* 5.7394(4) Å. $R=0.022$ for the observed reflexions. A small pyramidal deformation of the CO_3 group is confirmed.

We submitted to this journal a paper on the refinement of the crystal structure of aragonite, but the Editor informed us that a paper on the same argument by J. P. R. de Villiers (1971) was already accepted. Since the same unexpected and interesting results were reported in both papers, a brief account of the work carried out independently in this laboratory is of some interest.

A very pure sample of aragonite (Vertaizon-Alvernia) has been used for this research; a chemical analysis by atomic absorption method yielded a weight percent of Ca that is about 99.9 percent of the theoretical value. A small sphere with radius of 0.16 mm was used for collecting the X-ray diffraction data. The crystal was rotated about the diagonal axis [101] and integrated Weissenberg photographs were taken by using Cu Kα radiation and multiple-film packs. Lorentz-polarization, absorption ($\mu R=3.31$) and $\alpha_1-\alpha_2$ spot-doubling corrections were applied to the photometrically measured intensities. The 422 recorded intensities were reduced to 277 independent values, about 96 percent of those possible with Cu Kα radiation; 73 spots were too weak to be accurately measured and were therefore considered as unobserved. The space group *Pmcn* given by Bragg (1924) was confirmed. A structure-factor calculation carried out using Bragg's atomic coordinates gave a index R of 0.26 ($R=\sum|\Delta F|/\sum|F_0|$).

After some cycles by the method of least-squares with anisotropic thermal parameters, solved also for the secondary extinction coefficient, the R index was reduced to 0.055 for the observed reflexions. The refinement could be considered satisfactory, but the analysis of the CO_3 group showed, contrary to all expectations, an imperfect planarity with the carbon atom lying at -0.017 Å from the plane passing through the three oxygens. This deviation is not very large but is considerably greater than its standard deviation. On the other hand all attempts to put the carbon atom and the oxygens on the same plane were rejected by the least-squares calculation. It was thought possible that the pyramidal deformation could have resulted from the quality of the experimental data. Therefore we collected a new set of experimental data using the same crystal on the Wooster automatic diffractometer.

The crystal cell dimensions were redetermined by the least-squares method applied to high order reflexions with $2\theta > 100°$. The unit cell parameters so obtained are: a 4.9616(2), b 7.9705(6), c 5.7394(4) Å. The intensities of 947 reflexions between $2\theta = 19°$ and $2\theta = 155°$ corresponding to 271 independent values (about 94 percent of Cu $K\alpha$ limiting sphere) were measured automatically with the diffractometer. Nickel-filtered Cu $K\alpha$ radiation was used with a scintillator counter. The ω scan technique was employed with a scan angle of 3° and a scan speed of $1° \text{ min}^{-1}$. Measurements of a reference reflexion were repeated after every group of 30 reflexions; no systematic drift was in evidence. Lorentz-polarization and absorption corrections were applied; 58 reflexions, for which the net intensity was less than 1 percent of the highest intensity measured, were recorded as unobserved.

A structure-factor calculation made by using the atomic parameters deduced from the photographic refinement gave $R = 0.033$ for the 213 observed reflexions. After one cycle of least-squares with anisotropic thermal parameters and solving for the secondary extinction coefficient, the refinement stopped at $R = 0.022$ and $R_{\text{tot}} = 0.033$.

After this refinement the pyramidal deformation of the CO_3 group was even larger than that from the photographic refinement. At this stage it was decided to carry out one cycle by using the weighting scheme:

$$\sqrt{w} = 1/\sigma = 1 \Big/ \sqrt{I + (B_1 + B_2)\frac{B>}{B<}}$$

where I is the measured intensity, B_1 and B_2 are the backgrounds recorded at each side of the scan range; the $B>/B<$ term is an empirical factor, ≥ 1, introduced to take into account the decrease in reliability of a measure when the background asymmetry increases. After this cycle the final R index was 0.036. Observed and calculated structure-factors are listed in Table 1.[1] Positional parameters with their standard deviations are listed in Table 2; the analysis of the anisotropic thermal parameters is shown in Table 3.

At the end of the refinement with the weighting scheme, the pyramidal

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[1] To obtain a copy of Table 1, listing observed and calculated structure-factors of aragonite, order NAPS Document 01380 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, N.Y. 10022; remitting in advance $2.00 for microfiche or $5.00 for photocopies, payable to CCMIC-NAPS.

TABLE 2. FRACTIONAL ATOMIC COORDINATES WITH THEIR STANDARD DEVIATIONS IN PARENTHESES.

Atom	x	y	z
Ca	0.25	0.4151 (1)	0.2403 (1)
C	0.25	0.7627 (5)	0.0850 (7)
O(1)	0.25	0.9231 (4)	0.0952 (6)
O(2)	0.4729 (4)	0.6801 (3)	0.0870 (4)

deformation of the CO_3 group was nearly double that deduced from the photographic refinement. The equation of the plane passing through the oxygens 0(13), 0(22) and 0(27) is: $0.02430\, y + 0.99971\, z = 3.5268$, where y and z are the atomic coordinates in Å units referred to the crystallographic axes and 3.5268 is the distance of the plane from the origin in Angstrom units. The deviation of the C(1) atom from this plane is -0.027 (4) Å. Even if this deviation is not very large, it seems to have some physical significance because it appears in both refinements, and the carbon atom is always out of the plane on the same side. The deviation of the carbon from the plane of the oxygen atoms could be imputed to three of the six Ca atoms which are around to each C atom at distances respectively of 2.911, 3.413, 2.939, 3.242, 2.939 and 3.413 Å. The three Ca atoms with the shortest Ca-C separations could repel the carbon and

TABLE 3. ANALYSIS OF THE ANISOTROPIC THERMAL PARAMETERS[a]

Atom	r.m.s.	α	β	γ
Ca	0.089 (3)	90	99	170
	0.091 (3)	0	90	90
	0.096 (3)	90	170	80
C	0.089 (9)	90	66	156
	0.103 (7)	0	90	90
	0.110 (8)	90	156	113
O(1)	0.106 (7)	90	154	64
	0.132 (6)	90	64	25
	0.136 (5)	180	90	90
O(2)	0.098 (5)	159	71	80
	0.130 (4)	76	77	18
	0.137 (4)	105	157	74

[a] Root mean square thermal vibrations along the ellipsoid axes (Å) and angles (°) between the crystallographic axes and principal axes of the vibration ellipsoids.

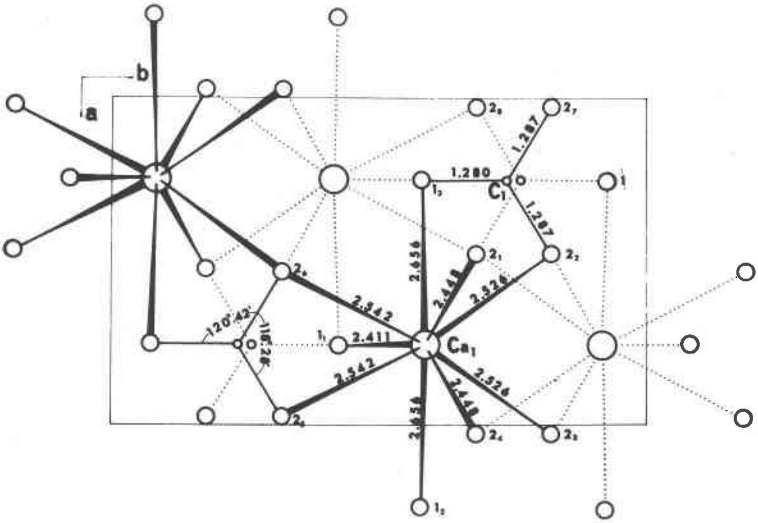

FIG. 1. The crystal structure of aragonite viewed along [001]. The standard deviations of the Ca-O distances vary from ±0.001 to ±0.003 Å.

force it out the plane, because at those distances some repulsive interaction between these atoms is not unlikely.

The present work confirms the nine-fold coordination around the Ca atom (see Fig. 1). The Ca polyhedron, as it appears in Figure 2, is distorted with all the distances Ca-O a little longer than those found in dolomite (Steinfink and Sans, 1959) and in calcite.

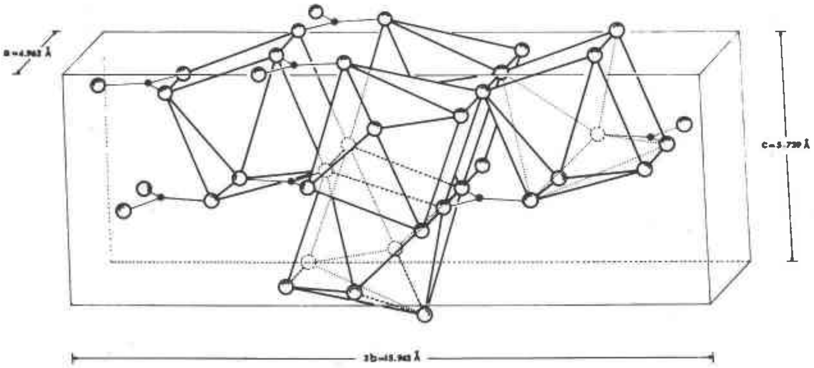

FIG. 2. Clinographic projection of some CaO_9 polyhedra connected one another by common edges and by carbon atoms. The six dashed lines of the polyhedron at the bottom indicate the edges shared by other polyhedra.

In the Figure 2 the network of the Ca polyhedra is also shown; every polyhedron is surrounded by six CO_3 groups. Each of three CO_3 groups gives two oxygens to form the three shortest edges of a CaO_9 polyhedron [2.212(4), 2.231(3), 2.231(3) Å]; the remaining three oxygens of the polyhedron belong to the three other CO_3 groups. Each CaO_9 polyhedron has six edges shared with other polyhedra.

The lengths of the edges of the polyhedron range from 2.212(4) to 3.603(4) Å. The C-O distances [1.280(5) and 1.287(3) Å] are in good agreement with those found in the literature.

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