On the Structure of Vaterite, CaCO₃*

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X-ray and optical data have been obtained on vaterite single crystals grown by ionic diffusion in aqueous solution. These data indicated that vaterite has hexagonal symmetry with a prominent pseudo-cell where $a' = 4 \cdot 13$, $c' = 8 \cdot 49$ Å, $Z' = 2$. Five weak superstructure reflections have also been observed. These show the true cell to be turned 30° to the pseudo-cell so that

$$a = a'\sqrt{3} = 7 \cdot 16, \ c = 2c' = 16 \cdot 98 \text{ Å}, \ Z = 12.$$

The average positions of the calcium atoms and carbonate groups in the structure have been determined by analysis of the X-ray intensities corresponding to the pseudo-cell.

Introduction

In the course of experiments carried out in this laboratory in connection with the *in vitro* mineralization of organic polymers, small, rather imperfect single crystals of vaterite were synthesized. Though far less common mineralogically than the calcite and aragonite forms of calcium carbonate, vaterite is of particular interest where the mechanism of crystal nucleation is under investigation. Vaterite may be the first phase formed in certain invertebrate exoskeletons under specific conditions (Wilbur & Watabe, 1961). Vaterite is also known to occur in the repair of mineralized tissue of certain gastropods (Mayer & Weineck, 1932) and has been observed as a constituent of gallstones (Phemister et al., 1939; Meier & Moenke, 1961).

Recently, a number of papers have appeared which have touched directly or indirectly upon the structure of vaterite. There is general agreement that optical data indicate vaterite to be the end member of the rare earth-calcium-fluoro-carbonate series bastnaesite-roentgenite-synchisite... vaterite (Donnay & Donnay, 1953, 1961; Semenov, 1959; McConnell, 1960). Specific interpretations of X-ray diffraction data obtained from vaterite, however, have been less conclusive. Olshausen (1925) indexed the X-ray powder pattern of vaterite on the assumption of a hexagonal cell with $a = 4 \cdot 11$ and $c = 8 \cdot 51$ kX. While this accounted for most of the observed spacings, doubt remained as to the proper indexing of some of the very weak lines. Meyer (1959) proposed an orthorhombic cell for vaterite, listing tentative atomic coordinates, but the evidence for this structure was not given, and so cannot be evaluated. McConnell

(1960), on the basis of some electron-diffraction photographs of finely crystalline material, has suggested that the true cell is $a = a'\sqrt{3}$, $c = c'$. The cells proposed by Meyer & McConnell appear to account for more of the observed spacings than does Olshausen's cell.

Experimental

Single crystals of vaterite, in the form of hexagonal plates, or lenses, approximately 0·1 mm across, were grown by connecting two test tubes containing 0·1 M solutions of CaCl₂ and K₂CO₃ with a distilled water bridge into which the ions diffused. The arrangement was permitted to stand undisturbed in a constant-temperature bath for three or four days, at the end of which time the inner walls of the bridge had become partially coated with a crystalline precipitate of calcite, aragonite, and vaterite, in varying proportions. The relative amounts of the three modifications of calcium carbonate, as well as the crystal sizes and habits, were dependent upon the temperature at which the experiment was performed. Temperatures in the region of 45° to 60° C were found to yield the most useful vaterite crystals for single-crystal study. The crystals are imperfect, and under high magnification can be seen to be aggregates of uniformly oriented hexagonal plates. Lucas (1948) has described a method of synthesis which appears to result in similar crystals. The microscopic plates give good uniaxial positive interference figures with $n_\omega = 1 \cdot 55$ and $n_\varepsilon = 1 \cdot 65$, in agreement with Johnston et al. (1916).

X-ray precession photographs and measurements made with a Picker diffractometer equipped with a General Electric single-crystal orienter indicate a hexagonal symmetry with a (pseudo) cell $a' = 4 \cdot 13 \pm 0 \cdot 01$, $c' = 8 \cdot 49 \pm 0 \cdot 02$ Å. Specific gravity measurements show this cell to contain 2 CaCO₃, where $G_o = 2 \cdot 6$ g.cm⁻³ and $G_c = 2 \cdot 68$ g.cm⁻³.

Following the precession-camera and diffractometer

observations, a rotation photograph of long exposure was taken of the crystal about [11·0]. This picture reveals faint layer lines corresponding to a larger cell rotated 30° about the c-axis from the former cell and having $a = a'\sqrt{3}$. Subsequent precession pictures clearly show the additional reflections to be on lines corresponding to $c = 2c'$, rather than $c = c'$ as reported by previous workers. Five symmetrically independent superstructure reflections have been observed. These are the 20·3, 21·1, 20·5, 21·3 and 40·1. The 21·1 and 20·5 reflections account for the low, somewhat broad peak at about $2\theta = 39°$ which is observed on diffractometer traces of vaterite, and which cannot be indexed on the basis of the small cell.

All diffraction spots were found to be disc- or umbrella-shaped owing to the laminated structure of the vaterite lenses. The superstructure reflections were judged to be no different in character from those of the pseudo-cell. In addition to the distortion of the diffraction spots, vaterite reflections were also noted on the diffractometer to be somewhat broad in 2θ; intensities of the pseudo-cell reflections were recorded on the diffractometer by scanning each peak in 2θ. The intensities fell off rapidly at moderate angles, and no diffraction maxima were observed beyond $2\theta = 100°$. Intensity measurements could be only approximated for reflections at the higher angles.

Analysis of the pseudo-cell

Since almost all the diffracted energy can be accounted for by those reflections which are indexable on the pseudo-cell, an analysis of the contents of this cell should reveal the principal features of the structure of vaterite.

When indexed on the pseudo-cell, no $hh·l$ reflections are observed with $l \neq 2n$. Further, reflections where $l = 2n$ are found to be generally much stronger than the others, indicating calcium atoms at $(0, 0, z)$ and $(0, 0, z+\frac{1}{2})$. As Meyer suggested, these observations make it appear likely that vaterite has a structure related to that of nickel arsenide.

Since vaterite is uniaxial positive, the planes of the carbonate groups must be parallel, or nearly so, to the c-axis. Bunn (1948) has pointed out the apparent inconsistency with the fact that $Z = 2$. Insofar as the pseudo-cell is concerned, then, the author assumed that the carbonate group was randomly distributed among three or more orientations to satisfy the observed symmetry. The observation that the calcium atoms form a trigonal prism with a height nearly equal to the edge of the base suggested the positions of the carbonate groups in the unit cell. When the carbon atom was placed in the center of the prism and the vertical carbonate group oriented so that each oxygen atom was equidistant from the two nearest calcium atoms (Fig. 1), the resultant calcium–oxygen interatomic distances were found to have the expected values. A trial structure was
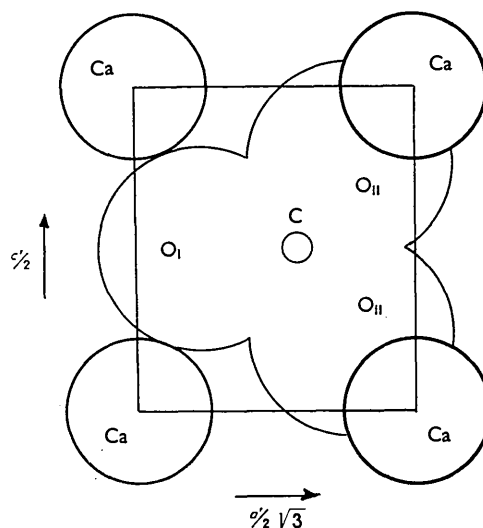

Fig. 1. Vertical projection of vaterite showing orientation of carbonate group relative to calcium atoms.

prepared based on the symmetry elements of space group $P6_3/mmc$. The two calcium atoms were placed in the a positions. The two carbon atoms were distributed in h positions with $x = 0·33$ so that $\frac{1}{3}$ of a carbon occupied each of the six positions. Similarly, two oxygen atoms, O_I, were distributed in h positions with $x = 0·15$, and four oxygens, O_{II}, in the k positions with $x = 0·42$ and $z = 0·10$. This structure has each calcium atom irregularly coordinated by six oxygen atoms. An R factor of 0·44 was computed for the structure. Three cycles of least-squares refinement using the Busing–Levy ORXLS program written for the IBM 704 computer reduced the R factor to 0·16 for all the reflections listed in Table 1. This value of R is thought to approach the limits of accuracy of

Table 1. *Observed and calculated structure factors for vaterite (indexed on the pseudo-cell where $a' = 4·13$, $c' = 8·49$ Å)*

Cu $K\alpha$ radiation

hk·l	F_o	F_c	hk·l	F_o	F_c
002	14	14	106	8	7
100	20	20	212	8	8
101	19	−17	205	0	−1
102	20	19	213	0	1
103	4	−5	300	8	7
004	15	14	301	0	−2
110	29	29	116	6	4
112	13	14	107	1	3
104	20	21	302	6	5
200	8	8	214	5	5
201	4	3	206	5	5
202	12	14	303	0	1
105	0	1	008	10	7
203	5	4	215	0	−1
114	6	6	304	4	3
006	2	4	220	6	5
204	7	8	108	4	2
210	5	−5	222	0	2
211	3	−3	310	3	3

Table 2. *Atomic parameters*

	x	y	z
Ca (a)	0	0	0
C (h)	0·29	0·58	¼
O_I (h)	0·12	0·24	¼
O_{II} (k)	0·38	0·76	0·12

the data. The rather large isotropic temperature factor of $B = 6·8$ determined in the computations is due to the rapidity of decline of intensities with 2θ, presumably associated with disorder in the structure. Table 2 lists the final parameters of the oxygen atoms. The standard error for these values is estimated to be $\pm 0·07$ Å for O_I and $\pm 0·05$ Å for O_{II}. As was to be expected, the limitations of the data did not permit the accurate location of the carbon atoms. The least-squares refinement retained the value of $x = 0·33$ for these atoms. Moving the carbon to the center of the triangle of oxygen atoms where $x = 0·29$, the position listed for carbon in Table 2, does not increase the R factor in the second decimal place. The computed distance between O_I and its two nearest calcium neighbors is 2·29 Å. The distance between O_{II} and its two nearest calcium neighbors is 2·48 Å. The sum of the Pauling crystal radii for calcium and oxygen is 2·39 Å.

Discussion

Analysis of the X-ray data obtained from vaterite single crystals has established the unit cell and the average positions of the calcium atoms and the carbonate groups in the structure. The small number of weak superstructure reflections indicate the existence of some degree of long-range ordering. These reflections are found to be no more intense in the vaterite single crystals grown by ionic diffusion than in rapidly crystallized vaterite powders precipitated, for example, by a method described by Wray & Daniels (1957).

Mention should be made here of the relation between the temperature at which calcium carbonate is precipitated and the coordination number of calcium in the polymorph which predominates at that temperature. In the diffusion experiments, at temperatures of about 25 °C or lower, calcite, with a six-fold coordination of calcium by oxygen atoms, is found to be the predominant form present. At temperatures above about 60 °C, aragonite, with its nine-fold coordination is the preferred form. It may be noted

of vaterite that while calcium is coordinated by six oxygen atoms at distances of about 2·4 Å, there are two more oxygen atoms sufficiently close (2·9 Å) to each calcium atom to be considered bonded to them. The coordination of calcium in vaterite, then, can be regarded as eight. Presumably, thermal vibrations at temperatures of about 25–60 °C increase the effective radii of the calcium atoms and thus stabilize the structure with this coordination number. At higher temperatures, thermal vibrations similarly account for the stability of aragonite and its nine-fold coordination of calcium. It is possible that the significance of the superstructure reflections in vaterite lies in small adjustments of the calcium atoms and carbonate groups, which would increase the regularity of the eight-fold coordination of the calcium atoms.

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