Vaterite from Ballycraigy, Larne, Northern Ireland.

(With Plate XII)

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Summary. Vaterite, the third unstable polymorph of $CaCO_3$, is recognized by optical and X-ray powder techniques as a major constituent in a carbonated calcium silicate hydrogel complex formed from larnite at Ballycraigy, Larne, Northern Ireland. Re-indexed X-ray powder data obtained on synthetic vaterite are provided indicating a hexagonal unit cell with dimensions $a = 7{\cdot}135$ Å. and $c = 8{\cdot}524$ Å., $Z = 6CaCO_3$. The re-indexing is endorsed by the results of electron diffraction study of synthetic vaterite. Vaterite is shown to correspond to the hypothetical $CaCO_3$ member of the bastnäsite–synchisite mineral series on the basis of extrapolated cell dimensions and optical properties. A structural scheme for vaterite is proposed in which Ca layers replace the CeF layers in bastnäsite, and near-vertical CO_3 groups are present. The stability relations of natural vaterite are discussed and comment made on the recent observation of vaterite, in a like environment, in carbonated cements and mortars.

THE first accurate description of a third polymorph of $CaCO_3$ was given by Johnston, Merwin, and Williamson in 1916. It occurred, in certain preparations, as hexagonal plates or lenses yielding a positive uniaxial figure with refractive indices $\epsilon = 1{\cdot}650$, $\omega = 1{\cdot}550$, and sp. gr. 2·54. They suggested that the determined density might be low owing to the fibrous nature of the material. An analysis of the purified material was presented (p. 485), and they designated the phase μ-$CaCO_3$.

Some little confusion arose subsequently in that other workers, namely Rinne (1924) and Heide (1924), on observing spherulitic aggregates of $CaCO_3$ identified them, correctly or incorrectly, with similar preparations described by Vater (1893 and subsequent papers). These had already been called vaterite by Meigen (1911). X-ray powder analyses by Rinne (1924) and Heide (1924) showed that the spherulitic aggregates constituted a species of $CaCO_3$ distinct from calcite or aragonite. The connexion between this spherulitic material and μ-$CaCO_3$, as originally defined, was demonstrated by Gibson, Wyckoff, and Merwin in 1925. They showed, by X-ray powder methods, that the two preparations were identical and distinguished also between spherulitic aggregates of calcite and of μ-$CaCO_3$ as prepared by a method due to Bütschli (1908). Spherulites of μ-$CaCO_3$ they designated vaterite B, admitting equivalence with the material studied by Rinne and Heide; spherulites of calcite they called vaterite A and suggested that Vater's original preparations comprised principally this material.

Currently all three terms, vaterite, vaterite B, and μ-$CaCO_3$ are used in the literature to describe the third polymorph of $CaCO_3$. Since X-ray powder data allow of its ready identification regardless of habit the third polymorph of $CaCO_3$ will be described throughout the present paper simply as vaterite (see also Hey, 1955, p. 76).

Natural occurrence of vaterite. Further examination of hydrogel pseudomorphs after larnite (McConnell, 1954, 1955; Long and McConnell, 1959) showed, in one instance, the presence of a very finely fibrous or platy mineral with high birefringence. In thin section this phase showed some evidence of preferred orientation, in terms of observed birefringence, within the limits of small areas representing pseudomorphed single crystals of larnite. The length of fibres or plates was optically negative and suitable areas, showing uniformly low polarization colours, gave a uniaxial positive interference figure and indicated the possibility of a plate-like habit for the mineral.

The highly birefringent material was observed only in very minor amount in one thin section and from this a small fragment was removed for optical, microchemical, and X-ray examination. The refractive index of the material was determined as 1·491 and part of the fragment, when placed in dilute HCl, dissolved with vigorous effervescence leaving a silica-gel pseudomorph. An X-ray photograph taken on a single crystal camera using oscillation technique showed no evidence of preferred orientation effects and its character suggested that the size of the individual crystals present was very small indeed since a normal powder photograph was obtained from the small fragment used (volume 0·001 mm.^{3}). The absence of appreciable line broadening on the photograph defined a lower size limit of 0·1μ approximately. The powder photograph yielded the *d* spacings listed in table I, and comparison with available data indicated that the material is vaterite (A.S.T.M. 1–1033, 4–0844).

At this stage it was realized that the material studied was composite, comprising vaterite in extremely intimate association with a hydrogel phase in the pseudomorphs studied. This conclusion accords with the low refractive index of the composite material (1·491 as compared with

Table I. X-ray powder data for natural vaterite from Ballycraigy. Cu-$K\alpha$ radiation.

d, Å.	*I*.	*d*, Å.	*I*.
4·25	vw	1·853	w
3·57	s	1·820	m
3·28	s	1·647	w
2·728	s	1·309	vvw
2·062	ms	1·286	vw

refractive indices for vaterite, $\omega = 1{\cdot}550$, $\epsilon = 1{\cdot}650$), the presence of a silica gel residue on treatment with dilute HCl, and the absence of any indication of a second phase in the X-ray powder analysis (the hydrogels studied previously yielded X-ray diffraction maxima only on lengthy exposure).

Synthesis of vaterite. Vaterite was subsequently synthesized in quantity to obtain more accurate and complete X-ray powder data for comparison. Initially the method recommended by Gibson and others (1925) was used but was only partly successful; vaterite in the form of hexagonal plates and lenses was observed but not in sufficient amount and purity, the main components being aragonite with minor amounts of calcite. Vaterite was prepared in bulk, and free from both calcite and aragonite, as follows: A 0·1 M solution of calcium chloride was added, very slowly and with careful stirring, to a solution of 50 g. of K_2CO_3 in 700 ml. of water, containing 300 p.p.m. of Calgon,[1] maintained at 60° C. Vaterite began to crystallize only when the solution was appreciably supersaturated with respect to calcite and aragonite, and crystallized in the form of minute spherulitic crystal aggregates of the order of 10 μ in diameter.

These spherulites were optically positive. Synthetic aragonite from the earlier experiments and synthetic vaterite with spherulitic habit are illustrated in plate XII.

X-ray powder data. An X-ray diffractometer trace of synthetic vaterite showed appreciable line broadening effects, which were equated with small crystal size. Data obtained from a standard X-ray powder photograph are listed in table II.

A hexagonal unit cell with dimensions $a = 7{\cdot}135$ Å., $c = 8{\cdot}524$ Å., and $Z = 6CaCO_3$, calculated density 2·65, was indicated. Intensity maxima with $h-k = 3n$ were very much stronger than those with $h-k \neq 3\,n$ indicating a pseudocell with $a' = a/\surd 3$ and $c' = c$. The

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[1] Commercial sodium hexametaphosphate.

pseudocell, with $Z = 2CaCO_3$, corresponds to the unit cell defined by Olshausen (in Heide, 1924, and Olshausen 1924).[1]

Table II. Indexed X-ray powder data for synthetic vaterite. Camera diameter 9·0 cm., radiation Cu-$K\alpha$. Intensities from visual comparison.

I.	*d*, Å.	$\sin^2\theta$ obs.	*hkil.*	$\sin^2\theta$ calc.	*I.*	*d*, Å.	$\sin^2\theta$ obs.	*hkil.*	$\sin^2\theta$ calc.
m	4·26	0·0327	0002	0·0327	vw	1·185	0·4230	$50\bar{5}2$	0·4218
s	3·58	0·0463	$11\bar{2}0$	0·0467	w	1·166	0·4370	$24\bar{6}0$	0·4358
s	3·30	0·0545	$11\bar{2}1$	0·0549	w	1·141	0·4565	$14\bar{5}4$	0·4577
s	2·73	0·0796	$11\bar{2}2$	0·0794	w	1·112	0·4808	$22\bar{4}6$	0·4812
wb	2·33	0·1098	$12\bar{3}0$	0·1090	w	1·064	0·5254	0008	0·5235
	2·30	0·1124			w	1·034	0·5557	$15\bar{6}3$	0·5561
w	2·23	0·1200	$11\bar{2}3$	0·1203	w	1·019	0·5727	$11\bar{2}8$	0·5702
w	2·127	0·1314	0004	0·1309	w	0·979	0·6205	$14\bar{5}6$	0·6213
s	2·059	0·1401	$30\bar{3}0$	0·1401	w	0·964	0·6395	$25\bar{7}2$	0·6397
w	1·856	0·1725	$30\bar{3}2$	0·1728	w	0·946	0·6648	$30\bar{3}8$	0·6636
s	1·825	0·1784	$11\bar{2}4$	0·1776	w	0·913	0·7132	$33\bar{6}6$	0·7147
wb	1·648	0·2189	$22\bar{4}2$	0·2195	w	0·877	0·7726	$40\bar{4}8$	0·7725
vw	1·544	0·2492	$40\bar{4}0$	0·2490	w	0·872	0·7823	$34\bar{7}5$	0·7804
vw	1·480	0·2715	$30\bar{3}4$	0·2710	w	0·862	0·7989	$70\bar{7}2$	0·7953
vw	1·416	0·2965	$23\bar{5}0$	0·2957	w	0·836	0·8494	$14\bar{5}8$	0·8504
vw	1·369	0·3171	$22\bar{4}4$	0·3176	w	0·826	0·8701	$34\bar{7}6$	0·8703
w	1·316	0·3429	$11\bar{2}6$	0·3412	w	0·814	0·8961	$17\bar{8}1$	0·8953
vw	1·288	0·3585	$14\bar{5}2$	0·3596					

Choice of the larger unit cell justifies arguments by Bunn (1945, p. 285), who pointed out that the CO_3 groups in vaterite must be vertical to account for the observed optical sign, but this being the case, vaterite could not at the same time be hexagonal (or trigonal) with $Z = 2CaCO_3$.

Electron diffraction data. Synthetic vaterite from the bulk sample was used for electron optic and diffraction studies using a Siemens Elmiskop 1 operating at 100 kV ± 3 %. The smallest crystal fragments studied (0·2 μ) were composite and yielded only preferred orientation diffraction patterns one of which is illustrated in fig. 1. This diffraction pattern

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[1] Olshausen's later data (1924, p. 485) on conversion from kX agree closely with the present results: $\sqrt{3}\,a' = 7{\cdot}133$ Å., $c = 8{\cdot}540$ Å. They appear to be more accurate than his earlier values as quoted by Heide (1924, p. 650), which are currently quoted in the literature and which on conversion give: $\sqrt{3}\,a' = 7{\cdot}150$ Å., $c = 8{\cdot}573$ Å. (cf. Wyckoff, 1931). A note to the effect that the true unit cell for vaterite has $a = \sqrt{3}a'$ appears, in the form of a personal communication from Wickman (1952), in Graf and Lamar, 1955. There is no evidence to suggest that this conclusion was reached by re-indexing X-ray powder data.

was indexed but no attempt was made to derive accurate *d* spacings and cell parameters from it.[1]

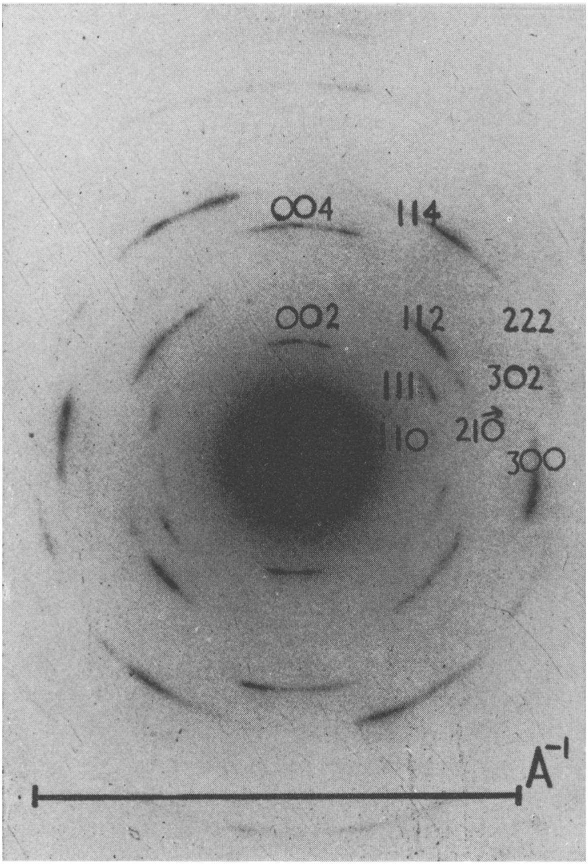

Fig. 1. Preferred orientation electron diffraction photograph of synthetic vaterite.

Uncorrected *d* spacings and the indices of the diffraction maxima are set out in table III. On the preferred orientation electron diffraction photograph it was possible to demonstrate the presence, in the correct

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[1] The *d* spacings given are correct to ±3 %, a limit set by the on-off high-voltage fluctuation on the electron microscope. It was inconvenient to use an internal standard in the present diffraction experiments. (In order to match the data given in table III with the X-ray diffraction data the former require to be scaled linearly by a factor of approximately 1·013.)

position, of weak intensity maxima $21\bar{3}0$ and $40\bar{4}0$, for which $h-k \neq 3n$, indicative of the larger unit cell chosen on the basis of X-ray powder indexing.

TABLE III. Electron diffraction data for synthetic vaterite.

d, Å.	*I*.	*hkil*.	*d*, Å.	*I*.	*hkil*.
4·18	s	0002	1·83	w	$30\bar{3}2$
3·58	m	$11\bar{2}0$	1·80	s	$11\bar{2}4$
3·27	m	$11\bar{2}1$	1·62	w	$22\bar{4}2$
2·69	s	$11\bar{2}2$	1·53	vvw	$40\bar{4}0$*
2·28	vvw	$12\bar{3}0$*	1·28	w	$14\bar{5}2$
2·10	s	0004	1·05	w	0008
2·03	s	$30\bar{3}0$			

* $h-k \neq 3n$.

The relationship of vaterite to the mineral series bastnäsite–synchisite. In 1953 Donnay and Donnay presented an account of the bastnäsite–synchisite mineral series, demonstrating definite stoichiometric ratios of $CeFCO_3$ and $CaCO_3$ for the minerals parisite, röntgenite, and synchisite in terms of measured cell parameters, structure, and optical properties. The relevant data are summarized in fig. 2 of this paper.

In the course of the present work it became obvious that vaterite must be equated with the $CaCO_3$ end-member of the bastnäsite–synchisite series. Fig. 2, which illustrates the linear gradation in cell parameters and optical properties in this series, has been drawn to demonstrate this relationship. The full lines are due to Donnay and Donnay, the dotted extrapolations are due to the present author.

Donnay and Donnay (op. cit.) discussed the structural aspects of the bastnäsite–synchisite series in terms of the structure of bastnäsite, space group $P\bar{6}2c$, indicating that the CeF layers of the bastnäsite structure are replaced regularly, and in definite sequence and proportion, by Ca layers in the compounds parisite, röntgenite, and synchisite. It is natural to extend their structural argument to vaterite, which since it is optically positive must, *a priori*, have vertical CO_3 groups. To a first approximation the structure of vaterite may be derived by replacing all the CeF layers of bastnäsite with Ca layers. The space group $P\bar{6}2c$ is no longer admissible, however, since a strong $11\bar{2}1$ intensity maximum has been recorded both from X-ray and from electron diffraction experiments (for $P\bar{6}2c$, $hh\overline{2h}l$ should appear with l even only). Further, the unit cell of vaterite shows considerable collapse in the c direction ($c = 8·524$ Å.) relative to that of bastnäsite ($c = 9·787$ Å.), ruling out the possibility of a vertical stacking sequence of CO_3 groups identical with that of bastnäsite.

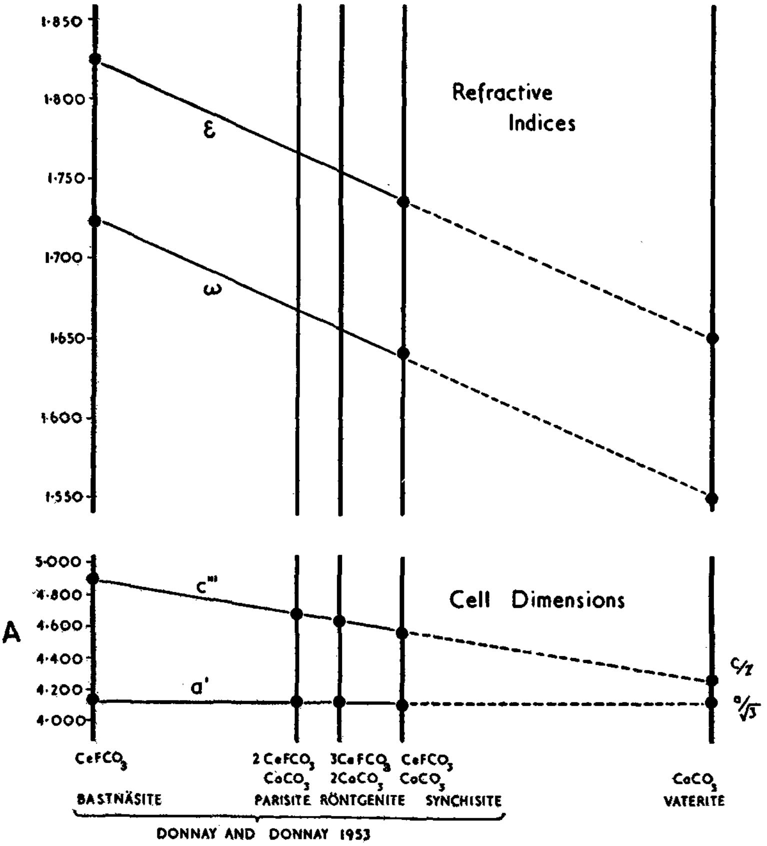

FIG. 2. Cell dimensions and refractive indices in the mineral series bastnäsite–vaterite. Data on the series bastnäsite–synchisite from Donnay and Donnay, 1953.

In this connexion Donnay and Donnay (op. cit., p. 950) considered that the CO_3 groups in a structural unit between adjacent CeF and Ca layers in parisite, röntgenite, and synchisite require to be tilted out of the vertical plane since the distance between such layers is only 4·56 Å. as compared with 4·89 Å. in the bastnäsite structure. This collapse of 0·33 Å. is close to half the corresponding collapse between adjacent Ca layers in the vaterite structure, which equals 0·63 Å. It is impracticable to consider, in the latter case, that the collapse is due solely to tilting of the normal to the CO_3 group out of the horizontal plane since this degree of tilt ($\approx$ 29°) can readily be shown to produce material reduction in the optical birefringence. Comparison of the observed birefringence of vaterite (0·100–0·102, Gibson *et al.*, 1925, pp. 327 and 331) and bastnäsite (0·101, average of eight values quoted by Donnay and Donnay, op. cit., p. 960, table 7) suggests rather that the CO_3 groups remain vertical in vaterite but require to be offset in vertical sequence. This is possible because the sites occupied by F ions in the bastnäsite structure are unoccupied in vaterite.

Further work on the structure of vaterite must await more complete diffraction data, which may possibly be obtained by electron-diffraction technique on better crystallized material.

Stability relationships of vaterite. Vaterite is unstable in the presence of water at room temperature and pressure, dissolving readily with concomitant precipitation of calcite; on heating, in the dry, at 400° C. it transforms to calcite in a few minutes (Johnson *et al.*, 1916; Lucas, 1947).

The occurrence of vaterite in the natural environment accordingly requires explanation since it must be considered to have some considerable measure of stability in this instance.

Two primary factors that may control the formation and preservation of a metastable phase may be considered here. The initial precipitation of a metastable phase may be induced by conditions of supersaturation in solution; this in practice constitutes the basis of the methods by which vaterite has been synthesized. The other important factor is the influence of structures already present in the case of a reaction that proceeds essentially within a solid medium; in this case a considerable measure of stability may be derived for the metastable reaction product owing to co-operative effects. In such cases it is clearly no longer possible to consider the stability relationships of the metastable phase independently of its environment, in particular if it is finely crystalline and intimately associated with an additional phase.

It is primarily on the basis of the second of the above factors that one may usefully seek to explain the development of vaterite in a hydrogel complex at Ballycraigy. There can be little doubt that its initial development was due to the carbonation of a high-lime hydrogel (Long and McConnell, 1959) and that in this case the presence of imperfectly crystalline $Ca(OH_2)$ would favour the development of the layer type vaterite structure. Comparison of the cell-dimensions of vaterite and portlandite also favours this conclusion. The ready breakdown of vaterite to calcite was observed in thin section.

An analogue to the natural carbonation process, in which vaterite is developed, has recently been described by Cole and Kroone (1959). These authors point out that vaterite occurs at an early stage in the carbonation of cements and mortars, and they suggest a sequence of hydration-carbonation reactions for cement minerals that constitutes a close parallel to the natural hydration-carbonation reaction sequence as observed for larnite and bredigite at Ballycraigy. They cite the following steps: anhydrous cement minerals ⟶ siliceous residue + calcium hydroxide ⟶ ill-crystallized vaterite, calcite, and aragonite ⟶ well-crystallized calcite. The corresponding steps in the natural hydration-carbonation process are: β-Ca_2SiO_4, by solid-state hydration at high pH under CO_2-deficient conditions ⟶ a high-lime hydrogel, $1{\cdot}5\ CaO.SiO_2.H_2O$ (Long and McConnell, 1959), then by carbonation ⟶ a vaterite–hydrogel complex, which breaks down ⟶ calcite + a siliceous residue.

Recognition of vaterite as the end member of the bastnäsite–synchisite mineral series suggests that more careful study will show that vaterite occurs, possibly in syntectic intergrowth with synchisite, in carbonatite paragenetic environments. Some evidence of this is already provided in that paramorphs of calcite after vaterite have been described recently by Ilyinsky (1958).

To the best of the author's knowledge vaterite has not previously been recorded as a natural mineral. It is known to occur in the repair tissue of certain young gastropods (Mayer and Weineck, 1932), in urinary calculi (Prien and Frondel, 1947), and, as already noted, as a carbonation product in hydrated cements and mortars (Cole and Kroone, 1959).

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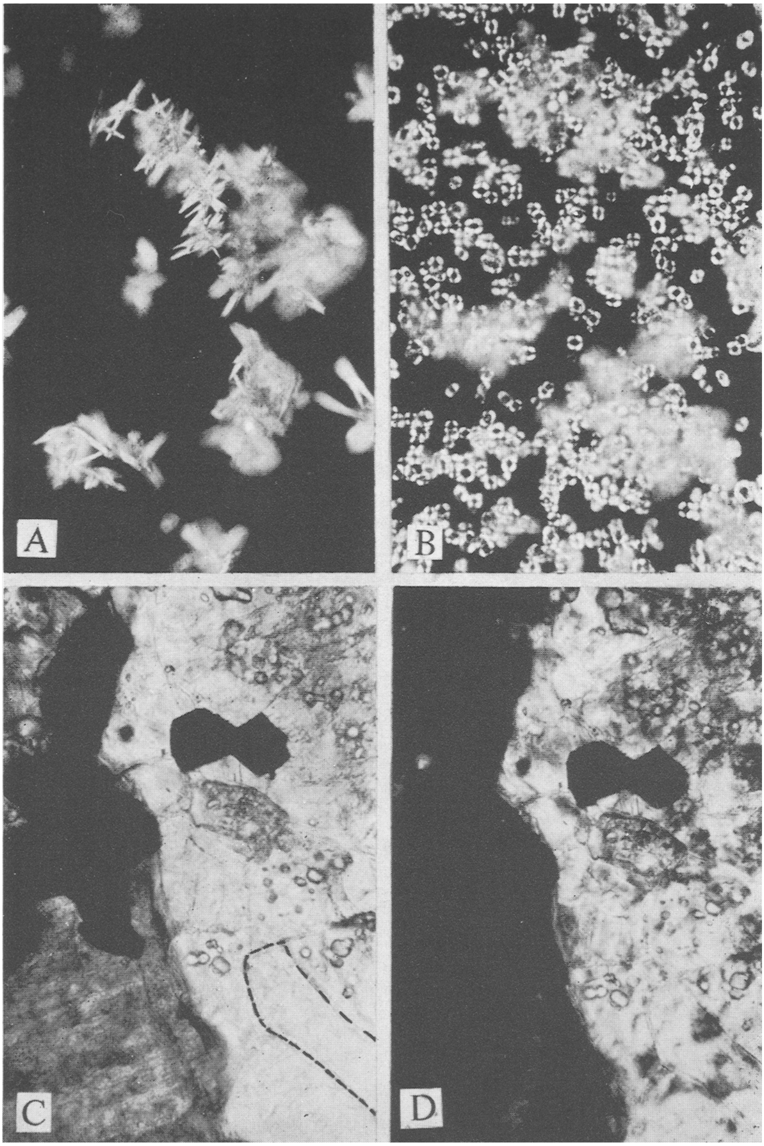
EXPLANATION OF PLATE XII.

FIG. A. Synthetic aragonite; crossed nicols, × 220.
FIG. B. Synthetic vaterite; crossed nicols, × 220.
FIG. C. Vaterite in hydrogel pseudomorphs after larnite. The limits of one pseudomorphed grain have been indicated; ordinary light, × 220.
FIG. D. As in C but with crossed nicols, × 220.



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