# VATERITE AND $\mu$-CALCIUM CARBONATE.

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Two crystalline forms or habits of anhydrous calcium carbonate, differing essentially from the well known modifications, calcite and aragonite, have been described[1] and have formed the subject of considerable controversy. These are *vaterite* and *$\mu$-calcium carbonate*.

In 1916 Johnston, Merwin and Williamson[2] gave very definite evidence in favor of the existence of $\mu$-$CaCO_3$ and at the same time came to the conclusion that vaterite is nothing more than spherulites of fibrous calcite. According, however, to sundry considerations emphasized by Spangenberg[3] and by the X-ray analyses of Rinne[4] and of Heide[5] it seems that vaterite is really a crystalline species distinct from calcite and aragonite. Both Spangenberg and Heide, moreover, cast grave doubts on the existence of $\mu$-$CaCO_3$.

*Vaterite.*[6] The precise nature of the substance designated "vaterite" or "Vater's Third Modification" seems to have been known with very little certainty. The original vaterite, obtained, together with a large amount of calcite, by slow diffusion of calcium chloride (containing barium chloride) into potassium carbonate, was described as consisting of spherical fibrous aggregates of density 2.54 which were converted to rhombs of calcite by heating or by boiling with water. These properties seem to have been taken as sufficient to characterize it as a new form of calcium carbonate, but it should be remarked that none of them is reliable. First, more than one type of spherulitic $CaCO_3$ is known; second, as the product

[1] For summary of the work published on this subject see Doelter, Handbuch der Mineralchemie (Leipzig, 1912), vol. 1, p. 113; Boeke und Eitel, Physikalisch-Chemische Petrographie, Berlin 1923, p. 442 ff.; H. Vater, papers in Zeit. Kryst. 1893-1901; O. Bütschli, Abh. Göttinger Akad. N. F.: **4**, 3 (1908); J. Johnston, H. E. Merwin, and E. D. Williamson, this Jour. **41**, 473 (1916); K. Spangenberg, Zeit. Kryst. **56**, 432 (1921); F. Rinne, Zeit. Kryst. **60**, 55 (1924); F. Heide, Centralblatt für Min. etc. **1924**, 641.

[2] Hereinafter referred to as J.-M.-W.

[3] Op. cit. p. 433.

[4] Op. cit. p. 66.

[5] Op. cit. p. 651.

[6] The name "vaterite" was first used an an abbreviation for "Vater's Third Modification of calcium carbonate" by Meigen in 1911. Despite the fact that the form has not been found in nature and that the preparations so called have been ill-defined, the name has persisted in literature.

did not consist of definite crystals but of fibrous aggregates capable of sorbing water and other materials, the significance of the density is doubtful; and, third, it seems that there was always $\mu$-$CaCO_3$ in the preparation and this may have been the source of the calcite found after the substance was heated. Moreover, the possibility of recrystallization from the spherulitic to the rhombic form of calcite is not to be ignored. In addition Vater examined the spherules optically and stated[7] that in radial splinters the smallest refractive index lay along the fibers, or, in other words, that the aggregates were optically negative.

The work of Bütschli in 1908 introduced a change in the properties of the substance known as "Vater's Third Modification." This investigator prepared very pure samples of spherules of $CaCO_3$ in two ways:

1. By allowing a solution of potassium carbonate to diffuse very slowly into a solution of calcium chloride. This product, which consisted of spherules almost free from calcite rhombohedra, we will call "vaterite A."

2. By allowing the jelly prepared by mixing concentrated solutions of potassium carbonate and calcium chloride to crystallize in the presence of excess of potassium carbonate. We will call this "vaterite B."

Vaterite B resembled Vater's modification superficially but differed from it in that the aggregates of which it was composed were optically positive, and differed also in density and behavior with Meigen's reaction. On the other hand, vaterite A consisted of spherulites which were optically negative, which were more strongly double refracting than vaterite B and, in short, whose properties were in complete agreement with those of Vater's original preparation. Bütschli describes the two products in considerable detail and ends with the statement, "Although the spherulites 1 and 2, both in their behavior to the cobalt test and in their specific gravity, exhibit important differences, I am at present of the opinion that they must belong to the same modification of $CaCO_3$."

The reason for such a view is not given. Here, in our opinion, lies the source of any misunderstanding which has arisen as to the identity of vaterite. The product obtained by the crystallization of colloidal $CaCO_3$ (vaterite B) was not "Vater's modification" in the original application of the term, but apparently some later investigators have given the name

[7] See Bütschli, op. cit.

"vaterite" to this preparation and have denied it to the optically negative spherulites (vaterite A) which J.-M.-W. concluded were essentially calcite. It should be remarked that in all the investigations of Spangenberg, Rinne, and Heide, etc., vaterite B was the substance used.

*μ-Calcium Carbonate*, although indefinitely described first by Vater, who noticed lens-shaped aggregates and hexagonal plates among some of his preparations, was not recognized as a separate form until J.-M.-W. prepared and examined it in 1916.[8] They described it as occurring in hexagonal plates or flat star-shaped crystals (sometimes lenses) which were optically positive, of density around 2.54, and had refractive indices $\epsilon = 1.650$ and $\omega = 1.550$. It is, on the whole, a very well defined substance.

It is the object of this paper to confirm, mainly from the results of X-ray analyses, the conclusion of J.-M.-W. that $\mu$-$CaCO_3$ is a modification of calcium carbonate separate and distinct from calcite and aragonite, and to show that vaterite B is a fibrous spherulitic variety of $\mu$-$CaCO_3$, in fact that it bears the same relation to $\mu$-$CaCO_3$ as spherulitic calcite (vaterite A) does to calc spar.

## PREPARATION, OPTICAL AND CHEMICAL EXAMINATION OF VATERITE AND $\mu$-$CACO_3$.

1. *Vaterite A.* A sample of spherulites of calcium carbonate was prepared by the method of J.-M.-W.[9] The product was washed thoroughly with hot water and dried with alcohol and ether. Microscopic examination showed that there were no rhombs of calcite present, the preparation consisting entirely of spherical aggregates of fibrous structure and varying in size between 10 and 20$\mu$. Several radial splinters were examined and the highest refractive index obtained was 1.650. The spherules were optically negative. In short the product resembled that of J.-M.-W. in all respects.

2. *Vaterite B.* This was prepared by allowing a colloidal precipitate of calcium carbonate to crystallize at 5°C. in the presence of a large excess of potassium carbonate according to the method of Heide.[10] The preparation was washed and dried with alcohol and ether. As far as could be seen the pro-

[8] Op. cit. p. 484.
[9] Op. cit. p. 486.
[10] Op. cit. p. 645.

duct was not contaminated with aragonite or calcite, but consisted entirely of spherulites about 10 to 15$\mu$ in diameter which were quite different from those obtained in experiments (1) above. They were optically positive, the highest refractive index being along the fibers. The refractive indices were $\epsilon = 1.640\text{-}1.645$ and $\omega = 1.550$. These figures were so strikingly like those given for $\mu$-$CaCO_3$ by J.-M.-W. that it seemed justifiable to assume that the two might really be habits of the same form. On being boiled with water, the preparation yielded aragonite, and on being boiled with sodium chloride solution it gave calcite. A violet coloration was developed with cobalt nitrate (Meigen's reaction).

3. *$\mu$-$CaCO_3$.* Two different methods were used for preparing this substance and, as the products differed superficially, an account of each will be given.

(a) 0.1M solutions of calcium chloride and potassium carbonate were dropped slowly (at the rate of 40 cc. in 2 hours) into 600 cc. water heated to 60° and gently stirred. Care was taken to prevent adventitious crystals of calcite or aragonite having access to the liquid in the reaction vessel, as the method depends on the solution being supersaturated with respect to these forms so that the more soluble $\mu$-$CaCO_3$ may crystallize out.

In the first two experiments the product consisted of needles of aragonite mixed with 15-20 per cent of well-formed hexagonal plates of $\mu$-$CaCO_3$. In subsequent experiments, however, the yield was not so large, there never being more than 10 per cent of $\mu$-$CaCO_3$ in the final mixture. The hexagonal plates of $\mu$-$CaCO_3$ were separated from the bulk of the aragonite by flotation in a liquid of density 2.65.

Microscopic examination showed that apart from the aragonite, the preparation consisted of hexagonal six-rayed crystals of great variety, resembling snow flakes. They gave perfectly uniaxial positive interference figures and the refractive index, $\omega$, was 1.550 (the same as given in the previous paper). The crystals all had central nuclei, the refractive index of which was slightly higher than the value given.

(b) As a method for the preparation of $\mu CaCO_3$ that just described leaves much to be desired. It is uncertain; $\mu$-$CaCO_3$ may be formed or it may not, and at best the product is largely contaminated with aragonite, the complete removal of which is impossible.

It has already been stated that, as $\mu$-$CaCO_3$ is so much more

soluble than aragonite or calcite, it is necessary that the solution be supersaturated with respect to these varieties before crystallization of the μ-form takes place. It is also certain that at the temperature of the experiment a considerable amount of μ-$CaCO_3$ is transformed to aragonite. Experience has shown that the least stable phase is generally the first to appear during the primary stages in the crystallization of a very sparingly soluble substance. It was, therefore, thought possible that the presence of large excess of carbonate (or calcium) ions during the precipitation of calcium carbonate, would, by driving back the solubility, render more probable the appearance of the μ-form. Moreover, by making the μ-$CaCO_3$ less soluble, the presence of carbonate should increase its stability.

These considerations were justified by experiment and it has been found possible to obtain fairly well crystallized μ-$CaCO_3$, containing as little as a tenth to a half of one per cent of aragonite. The method was to drop slowly (20 cc. in 2 hours) a 0.1M solution of calcium chloride into a solution of potassium carbonate which was gently stirred and maintained at a temperature of 60°. The volume of the potassium carbonate solution was from 600 to 700 cc. in all the experiments but the concentration of the salt was varied as follows:

1. With a solution of 100 grams $K_2CO_3$ in 700 cc. water an unrecognizable product was obtained. It did not contain any distinct μ-form at all.

2. With 50 grams in the same volume of solution a very pure preparation of μ-$CaCO_3$ resulted but instead of occurring as hexagonal plates it was mostly in the form of lenses.

3. With 20 grams of $K_2CO_3$ in 700 cc. water a preparation containing about 50 per cent aragonite and 50 per cent μ-$CaCO_3$ was obtained. Seven experiments were made at this concentration and the result was always the same, provided that the temperature was kept at 60° and that the dropping of the $CaCl_2$ into the solution, to begin with, was not less than 1 cc. per 5 min.

4. In one experiment where 10 grams of $K_2CO_3$ in 700 cc. of water was used a very good preparation was obtained. It was well crystallized and contained only a trace of aragonite. Unfortunately subsequent experiments with this concentration did not yield such good results.

It was noticed that as each drop of $CaCl_2$ solution entered

the liquid in the reaction vessel, a white colloidal precipitate of calcium carbonate was formed momentarily but rapidly dissolved. After three or four cc. of the calcium chloride solution had been added, a white, crystalline powder separated from the solution. The precipitation was generally stopped after 2 or $2\frac{1}{2}$ hours.

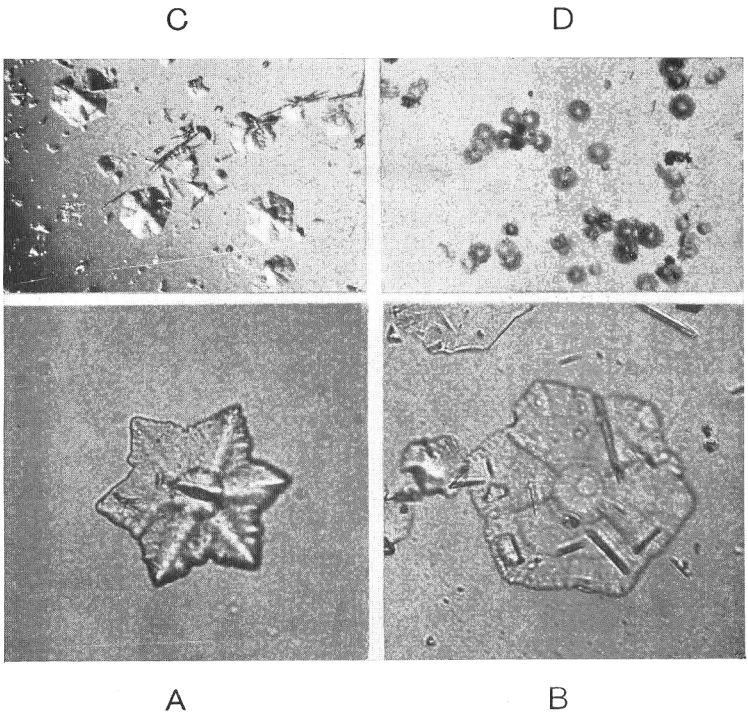


Fig. 1.—Microphotographs of certain types of crystals mentioned in this paper. A and B show single crystals of $\mu$-$CaCO_3$ magnified 600 diameters. C, taken with oblique illumination illustrates the thickening of the crystals of $\mu$-$CaCO_3$ around the center. Needles of aragonite are also visible. Magnification 300 diameters. D shows a sample of vaterite B taken with the same magnification.

Preparation (2), method (b), when examined under the microscope, was found to contain little or no aragonite and around one half of one per cent of calcite in addition to the $\mu$-form. The crystals were lens-shaped bodies which were 0.03-0.06 mm. in diameter and less than 0.01 mm. thick. They thinned out to ragged edges or were rounded hexagonal in

outline and gave either good uniaxial or slightly biaxial, positive interference figures. The refractive indices were, $\omega = 1.545\text{-}1.548$, $\epsilon = 1.645\text{-}1.650$, the lower values representing the first stages of growth. The crystals giving biaxial interference figures exhibited other evidences of being composite.

Preparations (3) and (4) did not differ from that just described except that there was more aragonite present and that the crystals were well formed hexagonal plates, identical with those of J.-M.-W. and obtained by method (a) described above. Fig. 1 shows microphotographs of crystals of $\mu$-$CaCO_3$ illustrating the various habits.

## X-RAY DIFFRACTION MEASUREMENTS.

Powder photographs, obtained in the usual way, have been made from various forms of $CaCO_3$. In agreement with previous measurements[11, 12] they show clearly the existence of a third modification of $CaCO_3$ with a pattern distinct from that of calcite on the one hand and aragonite on the other. The spacings of the observed lines of this $\mu$-$CaCO_3$ were calculated from comparison photographs of films of mixed $\mu$-$CaCO_3$

TABLE I. Powder Photographic Data on $\mu$-$CaCO_3$.

| Spacing (in A°) | Estimated Intensity |
|---|---|
| 3.59A° | s |
| 3.29 | s |
| $2.71_9$ | s— |
| $2.31_3$ | ff |
| $2.05_8$ | s+ |
| 1.85* | f |
| 1.82* | f |
| 1.64* | m |
| $1.53_7$ | f |
| $1.46_7$ | ff |
| $1.36_4$ | ff |
| $1.28_3$ | m |
| 1.14* | ff |
| $1.10_5$ | ff |

Note: In this table s, m, f, and ff stand for strong, medium, faint, and very faint, respectively. The lines marked with an asterisk are less accurately measured than the others.

[11] F. Rinne, op. cit.
[12] F. Heide, op. cit.

and NaCl. On account of its platy character there is danger of a preferential orientation of the small crystals in a powder specimen of $\mu$-$CaCO_3$. In order to avoid this as much as possible the sample received a preliminary grinding with a small quantity of powdered glass. The average results from four comparison photographs are recorded in Table I.

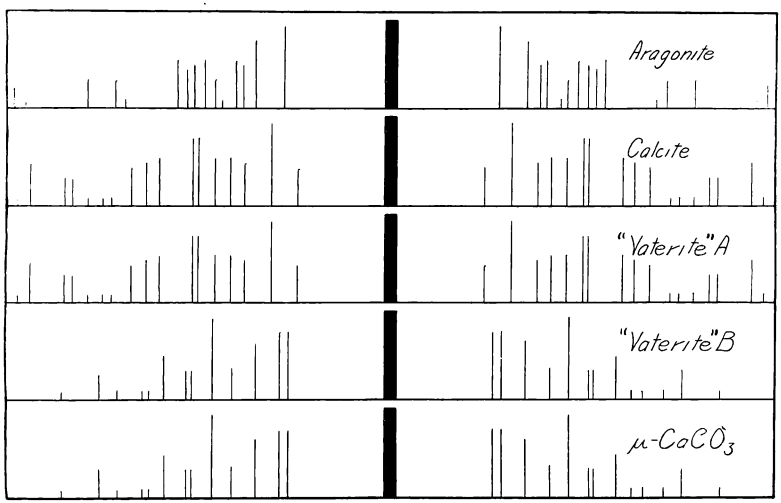


Fig. 2.—A tracing of the strongest lines in the powder photographs of the various preparations of calcium carbonate referred to in this paper. For each of these five diagrams the abscissas are proportional to distance on the film and the heights of the lines measure their estimated relative intensities.

They appear to agree with the qualitative data figured by Rinne[13] for vaterite; the measurements of Heide[14] are not

TABLE II.

| Preparation | Powder pattern |
|---|---|
| Vaterite A | Calcite |
| Vaterite B | $\mu$-$CaCO_3$ (see Table I) |
| $\mu$-$CaCO_3$ (Hexagonal plates) | $\mu$-$CaCO_3$ |
| $\mu$-$CaCO_3$ (Lenses) | $\mu$-$CaCO_3$ |

[13] F. Rinne, op. cit.
[14] F. Heide, op. cit.

stated in a manner sufficiently quantitative to permit of comparison.

The results of X-ray examination of the various preparations described in this paper are given in Table II and are shown diagrammatically for the purpose of direct comparison in Fig. 2.

## SUMMARY

A critical examination of the literature on "Vaterite" has shown that this name has been applied to two entirely different spherulitic habits of calcium carbonate. The first of these, which was investigated by Vater and later by Johnston, Merwin and Williamson, has now been shown, by X-ray powder photographs, definitely to be calcite, thereby confirming the conclusion of the last-named authors. The second, which was studied by Bütschli, Spangenberg, Rinne and Heide has proved to be essentially μ-calcium carbonate.

A reliable method for the preparation of distinct crystals of μ-calcium carbonate in fairly large yields has been obtained. The principal lines in the X-ray powder photographs of this modification are given. Reviewing all the work in this field, therefore, we are able to state that anhydrous calcium carbonate may exist at ordinary temperature and pressure in three distinct crystalline forms, calcite, aragonite and μ-calcium carbonate.

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