

Weddellite in modern sediments, Florida

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Summary. Euhedra of weddellite have been recognized in modern, unconsolidated sediments collected from depths of water not exceeding one fathom, along the south-east coast of Florida. For weddellite, the following data have been determined: crystals simple with r {011} accompanied by a {010} in some cases; goniometric axial ratio is $a:c = 1:0.593$ (meas.), $1:0.5938$ (calc.); $a_0 = 12.360$ Å, $c_0 = 7.340$ Å; space group $I4/m$, $I4$ or $I\bar{4}$; $\alpha = 1.529$, $\gamma = 1.544$, $\delta = 0.015$, uniaxial, positive; $d_{22^\circ\text{C}} = 1.941$. Heat treatment of weddellite led to development of whewellite, calcite, and calcium oxide in turn as higher temperatures were employed; fully indexed X-ray diffraction powder data are given for weddellite, in addition to d -spacings and intensities for whewellite.

It is suggested that weddellite developed in the calcareous Florida sediments under conditions of storage over a two-year period, and almost certainly was not a constituent of those sediments at the time of collection. This raises the question whether weddellite was present in the Weddell Sea material at the actual time they were recovered by members of the Scotia Expedition.

WEDDELLITE, $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, a common constituent of kidney and bladder calculi (Fron del and Prien, 1942; Prien and Fron del, 1947, Lucas *et al.*, 1950, and Philipsborn, 1953), has been reported only once, until now, in modern sediments, and the type locality is in the central Weddell Sea at depths of 2425–2739 fathoms (Bannister and Hey, 1936).

This paper describes a second occurrence of weddellite in modern sediments, and it is believed that this circumstance, as in the case of the original instance, may be secondary; in other words, weddellite was not present in the sediments when collected, but, instead, may have formed after collection while the sediments were stored pending laboratory analysis.

Sediment samples, collected along the south-western coast of Florida during the summer of 1959, were removed from water depths up to one

fathom. Sediment cores were collected manually by pushing a plastic tube, with piston, into unconsolidated sediments that range up to 4 feet in thickness, withdrawing the tube and rod simultaneously, extruding the sediment, and, at selected localities, measuring the pH of surface and interstitial sea water. Cores were arbitrarily divided into 15-centimetre segments unless changes of texture, colour, or grain size necessitated more closely spaced divisions. Samples were then placed into polyethylene bags, sprayed with ethyl alcohol to inhibit bacterial activity, twist-sealed with paper covered wire, and stored in waxed cartons.

In the Ten Thousand Islands area,¹ Florida, two sediment cores of great interest were collected at locality R-3. The pH of core A was determined at the moment it was collected (table I), then alcohol was added to the samples before storage, whereas core B was packaged without addition of alcohol, and pH determinations were not made.

TABLE I. Comparison of pH of sea water and of interstitial water of underlying sediment for sample R-3A, collected during 1959

Depth in inches beneath sediment-water interface	pH	Sediment description
Sea water	7.3	
1	6.8	Organic-rich shelly quartz sand
6	6.7	Organic-rich shelly quartz sand
12	6.9	Organic-rich shelly quartz mud
18	6.8	Peat
24	6.9	Peat

Samples were manually mixed in the sample bags and then portions were removed for grain size, chemical, and mineralogical analysis approximately two years after having been collected. Samples were washed on a brass screen with openings of 0.062 mm (no. 250 of the Tyler standard screen scale series) before determining grain size distribution by the pipette method. Particles retained on the screen were dried in an oven at approximately 100° C for 24-hour periods and then examined with the aid of a binocular microscope. In this fraction two porcellaneous euhedral minerals immediately became apparent, namely, bassanite and whewellite, both of which form as a result of water loss from the original compounds, gypsum and weddellite respectively.

Examination of unheated sediment samples showed that principal constituents include: quartz, aragonite, low-magnesium calcite, dolomite, organic matter, botryoidal masses of pyrite adhering to sticks and plant fibres, euhedral gypsum, and minor amounts of weddellite

¹ Approximately 40 miles SSE of Naples, Florida, on the Gulf of Mexico.

(approximately 60–80 crystals of weddellite per gram of dry sediment) and heavy minerals.

Physical properties

Weddellite crystals, generally colourless, may be yellow to brown owing to organic stains. Inclusions of vegetative matter are usually present and these may rank largely in the volume of individual crystals. Optical properties have been determined as follows: $\alpha = 1.529$, $\gamma = 1.544$, both ± 0.002 ; $\gamma - \alpha = 0.015$; uniaxial and positive.

The oxalate forms very simple, doubly terminated, more or less equidimensional, envelope-shaped crystals with $r\{011\}$ as the only form in most instances, but a few crystals with $a\{010\}$, inconspicuously developed, were seen. The form $c\{001\}$ appears to be absent. Crystals rarely exceed 0.2 mm in maximum diameter, and perfectly developed crystals 0.04 mm are common. Twinning was not detected, but growth penetration was frequently noted.

Stage goniometer measurements of the interfacial angle $011 \wedge 010$ led to an average value of $59^\circ 20'$. This value corresponds to a calculated $a:r$ angle of $59^\circ 18'$. The goniometric axial ratio $a:c = 1:0.593$, compared to a calculated ratio of $1:0.5938$. Standard angles have been calculated from unit cell dimensions and are as follows:

	$a:c = 1:0.5938,$		$p_0:r_0 = 0.5938:1$	
	ϕ	ρ	A	\bar{M}
$a\ 010$	$0^\circ 00'$	$90^\circ 00'$	$90^\circ 00'$	$45^\circ 00'$
$r\ 011$	$0^\circ 00'$	$30^\circ 42'$	$90^\circ 00'$	$68^\circ 51'$

Single crystal studies show that the mineral is tetragonal; unit cell dimensions are $a_0 = 12.360 \text{ \AA}$, ± 0.005 , $c_0 = 7.340 \pm 0.005$, compared to those reported by Bannister and Hey (1936, p. 61), viz. $a_0 = 12.40 \text{ \AA}$, $c_0 = 7.37 \pm 0.02$. On the basis of the single crystal data the powder pattern has been fully indexed, and d -spacings have been calculated for all reflections recognized on Weissenberg films. These data are set out in table II. Bannister and Hey (1936, p. 61), without any supporting evidence, stated that the space group is $C_{4h}^5 = I 4/m$. However, an inspection of c -axis Weissenberg films clearly shows an absence of planes of symmetry parallel to c^* . Accordingly, the Laue group is $4/m$, and as there are no systematic extinctions other than those for body-centring, or an I lattice, the possible space groups are $I 4/m$, $I 4$, and $I \bar{4}$. A close study of the crystals failed to show any growth features that might help

to distinguish the crystal class, and attempts to produce etch figures were not rewarding. Therefore, at this time, the ambiguity so far as space group is concerned cannot be resolved.

Determinations of density of inclusion-free crystals by suspension in bromoform-ethyl alcohol mixtures consistently gave a value of 1.941 ± 0.002 at 22°C , a figure that is comparable to the calculated value of 1.944 obtained by assuming that the molecular weight of weddellite is 164.13 and composition conforms to the formula $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The calculated value recorded here is considerably higher than that reported by Bannister and Hey (1936, p. 63) for crystals from renal calculi because their cell dimensions are somewhat greater than these reported here; furthermore, they used a value of 1.648 for the weight of the unit atom. Palache *et al.* (1951, p. 1102) quoted Bannister and Hey's density and cell dimension data, but incorrectly reported the cell dimensions as kX units when the latter authors used Ångstrom units.

Heat treatment of weddellite

When weddellite is heated in air for 10 minutes at 200°C the pale brown, stained crystals acquire a white porcelain-like appearance, and at the same time, such crystals, as well as unstained examples, lose their transparency. If a crystal so treated is mounted with the c -axis of weddellite as rotation axis, it yields a single crystal pattern distinct from that of weddellite, except that the identity distance parallel to the rotation axis is approximately the same as that found for weddellite, that is, 7.34 \AA . The word approximately is used advisedly because the reflections in the pattern yielded by the heat-treated crystal are not precisely defined, as in the apparently well-ordered, unheated weddellite, but are, instead, diffuse and much elongated along the Debye-Scherrer arcs. A crystal of weddellite that was heated in air at 230°C for 60 minutes yielded a pattern similar to that obtained for a crystal heated at a somewhat lower temperature for a shorter period of time. The powder pattern obtained for this product may be compared to those recorded by LeComte, Pobequin, and Wyart (1945, p. 25) for calcium-oxalate monohydrate, and Prien and Frondel (1947, pp. 961-962) for whewellite (table III). The d -spacings reported in this paper are more comparable to those recorded by LeComte *et al.*, and the main points of distinction are possibly to be attributed to a better state of resolution in the present writers' films. Notable intensity differences exist, however, between more or less comparable reflections in the data reported here and those recorded by Prien and Frondel. The heat-treated material, presumably

TABLE II. X-ray powder diffraction data for weddellite, Florida. X-ray film no. 1402. Cu- K_{α} (Ni filter), $K_{\alpha} = 1.5418 \text{ \AA}$. Camera diameter = 114.59 mm, cut-off at $c. 18.5 \text{ \AA}$. Spacings corrected for film shrinkage. Intensities determined visually. $a_0 = 12.36 \text{ \AA}$, $c_0 = 7.34$; $a_0:c_0 = 1:0.5938$. $I_4/m, I_4$, or I_4

hkl	d calc.	d meas.	I	hkl	d calc.	d meas.	I
110	8.75	8.75	2	552, 712	1.5785	1.580	1 D
011	6.32	—		613	1.564	1.564	1 D
200	6.18	6.17	9 VB	642	1.5535		
121	4.42	4.40	6 B	334	1.553		
220	4.37			424	1.529	1.530	< 1 D
310	3.90			3.90	3	741, 811	1.501
002	3.67	3.67	$2\frac{1}{2}$	820	1.499	1.499	$1\frac{1}{2}$
031	3.59	3.59	< 1	732	1.485	1.488	$\frac{1}{2}$
112	3.39	3.37	$1\frac{1}{2}$ VB	015	1.458		
202	3.15	3.15	1	750	1.4375	1.439	< 1
321	3.100	3.09	4	703	1.4325		
400	3.090			802	1.425		
222	2.812			2.815	1	831	1.420
411	2.765	2.7735	10 VB	215	1.419		
420	2.7635			822, 534	1.388	1.389	$3\frac{1}{2}$ D
312	2.6765	2.675	< 1	840	1.382		
510	2.4245	2.420	4	604	1.3705	1.371	< 1
013	2.400	2.399	4	910	1.365		
402	2.363	$\left\{ \begin{array}{l} 2.360 \\ 2.339 \end{array} \right\}$	$\left\{ \begin{array}{l} \frac{1}{2} \\ 1 \end{array} \right\}$	235	1.3495		
113	2.356			752	1.338	1.339	< 1
431	2.343			653	1.329		
051	2.342			921, 671	1.319	1.320	2
332	2.281			2.270	$\frac{1}{2}$	415	1.3185
123	2.237	2.235	7	842	1.293		
422	2.208	2.207	2	554	1.266	1.268	< 1
521	2.191			833	1.245		
530	2.119	2.118	5	941	1.237	1.237	< 1
512	2.022	2.019	3	006	1.223	1.224	< 1
323	1.991	1.993	1	734	1.2155	1.215	< 1
611	1.958	1.956	$6\frac{1}{2}$	10.2.0	1.212		
620	1.9545			950	1.201	$\left\{ \begin{array}{l} 1.200 \\ 1.199 \end{array} \right\}$	$\frac{1}{2}$
413	1.8955			1.8955	7		206
442	1.878			615	1.190	1.190	$2\frac{1}{2}$
451	1.867			226	1.1785		
004, 532	1.835	1.835	6	10.0.2	1.1715	1.172	< 1
602	1.797			824	1.161		
631	1.787	1.7875	1	10.2.2	1.151	1.151	3 D
204	1.7595	1.760	< 1	635	1.1485		
710, 550	1.7485	1.742	3 B	754	1.1315	1.130	$\frac{1}{2}$ D
433	1.7395			961	1.129		
622	1.7255			336	1.128		
640	1.7145			11.1.0	1.119		
224	1.6915	1.692	$1\frac{1}{2}$	725	1.110	1.111	< 1 D
523	1.6735			11.2.1	1.093	1.093	1
134	1.660			516	1.092		
721	1.654	1.654	< 1	11.3.0	1.084		
730	1.623	1.623	1	655	1.0765	1.075	1

TABLE II (cont.)

<i>hkl</i>	<i>d</i> , calc.	<i>d</i> meas.	<i>I</i>	<i>hkl</i>	<i>d</i> calc.	<i>d</i> meas.	<i>I</i>
745	1.060	1.061	2	736	0.9775	0.978	$\frac{1}{2}$ D
536	1.0595			12.4.0	0.977		
4.11.1	1.046			11.4.3	0.970	0.969	< 1
626	1.037	1.036	1	437	0.965		
12.0.0, 127	1.030			945	0.954	0.955	< 1
10.0.4	1.025	1.026	$\frac{1}{2}$ D	826	0.948	0.948	< 1
11.5.0	1.023			756	0.932	0.932	1
12.1.1	1.0165	1.017	$\frac{1}{2}$ D	457	0.922		
12.2.0	1.016			228	0.898		
10.2.4	1.011			11.2.5	0.883	0.884	< 1 VD
11.2.3	1.0075	1.006	< 1	10.0.6	0.8695		
556	1.0025			11.4.5	0.857		
646	0.995			538	0.842		
12.0.2	0.992	0.992	$\frac{1}{2}$ D	12.3.5	0.826		
417	0.990						

VB: very broad line; VD: very diffuse line; BB: broad band; D: diffuse line.

the monohydrate, appears to be in a state of some disorder because (1) the reflections usually tend to be diffuse, and (2) the arcs recorded on the films appear to be due, in most instances, to the most intense reflections yielded by well-crystallized whewellite (cf. Pecora and Kerr, 1954; Gude, Young, Kennedy, and Riley, 1960).

The weddellite crystal that had been heated initially at 200° C for 10 minutes was later heated to 400° C for 60 minutes in air, and the single crystal so treated yielded an almost perfect powder pattern, but with traces of reflections due to the remnants of a single crystal superimposed thereon; the latter reflections are almost certainly due to the anhydrous form of calcium oxalate. Upon measurement, the powder lines were found to have *d*-spacings that are identical with those recorded by Swanson and Fuyat (1953) for calcite. The last-mentioned crystal was then heated to 590° C for 60 minutes, and the crystal so treated was found to yield a powder pattern of CaO with faint lines due to calcite. A second crystal of previously unheated weddellite, when placed in the furnace at 600° C and maintained at that temperature for 30 minutes in air, yielded a perfect powder pattern of CaO with a cell edge of $4.81 \text{ \AA} \pm 0.01 \text{ \AA}$. A similar condition was brought about when weddellite was maintained at 530° C for 2 hours in air. These data point up the dangers involved in attempting to determine the compositions of the different phases formed during heat treatment by measurement of loss of weight at different temperatures where reactions are reversible and take place

TABLE III. X-ray diffraction patterns of calcium oxalate monohydrate (= whewellite) developed from weddellite. Film no. 1438. Cu-K_α (Ni filter), $K_\alpha = 1.5418 \text{ \AA}$. Camera diameter = 114.59 mm, cut-off at c. 18.5 \AA . Spacings corrected for film shrinkage. Intensities determined visually

1		2		3	
$d, \text{\AA}$	<i>I</i>	$d, \text{\AA}$	<i>I</i>	$d, \text{\AA}$	<i>I</i>
5.89	i	{ 5.97	8 VB	—	—
3.65	i	{ 5.84	3	—	—
—	—	3.65	10	3.69	8
—	—	—	—	3.36	1
2.95	i	{ 2.97	4 D	3.00	9
—	—	{ 2.91	1	2.92	1
—	—	2.84	1	2.85	5
—	—	2.51	< 1 ?	2.51	7
2.49	f	2.483	2 VD	2.44	1
—	—	2.414	< 1	—	—
2.33	fairly i	2.351	6 B	2.36	10
2.25	vf	2.254	< 1	2.27	6
—	—	2.211	< 1	2.21	3
—	—	—	—	2.14	1
2.06	m	2.072	1½ D	2.08	7
—	—	1.989	1	1.99	4
1.94	m	1.950	1 D	1.94	5
—	—	—	—	1.90	4
—	—	1.859	< 1	—	—
—	—	1.842	< 1	—	—
1.81	f	1.815	< 1	—	—
1.733	vf	1.738	< 1 D	—	—
—	—	1.692	< 1 D	—	—
1.184	f	1.184	< 1 D	—	—
1.153	vf	1.134	< 1 D	—	—
1.099	vf	—	—	—	—
0.9597	vf	—	—	—	—

i = intense, f = faint, D = diffuse, VD = very diffuse, VB = very broad, m = moderate, vf = very faint, B = broad.

1. Monohydrate A, LeComte, Pobequin, and Wyart, 1945, p. 25.
2. Weddellite, heated in air for 60 minutes at 230° C, Florida Bay, U.S.A.; this study.
3. Whewellite from urinary calculus, Prien and Frondel, 1947, table 3, pp. 961–962.

in air (*vide* Bannister and Hey, 1936; Duval, 1953; Peters and Wiedemann, 1959).

LeComte, Pobequin, and Wyart (1945) have described two hydrates of calcium oxalate and they appear to give these hydrates the status of distinct species; furthermore, they maintain that they are both trihydrates.

Their hydrate B was crystallized from cold acid solutions, whereas hydrate C is stated to be the form found in nature. They are of the opinion that the C form is the more stable compound of the two, and that it is morphologically distinct from the B form. The principal refractive indices for the latter are given as $\alpha = 1.55$, $\gamma = 1.58$, whereas hydrate C has 'indices appaaraissent voisins de ceux de l'hydrate B' (LeComte *et al.*, 1945).

First of all, the refractive indices recorded by LeComte *et al.* differ very widely from those reported by Bannister and Hey (1936), Palache *et al.*, and the present writers for weddellite. If these were the only data by which to make comparisons, one would venture to suggest that neither of the hydrates B and C are calcium oxalate dihydrate or weddellite. The *d*-spacings recorded by LeComte *et al.* for hydrates B and C are, however, comparable to those reported in this paper, except that upon close inspection it will be observed that in most instances, only the more intense reflections appear to have been recognized by LeComte *et al.*; furthermore, many lines that are rather closely spaced do not seem to have been precisely resolved by them. It should be noted that the *d*-spacings recorded for the two hydrates are virtually identical, except for the curious absence of the 3.84 Å line in the C form.

From a morphological point of view, a study of plate 2 (LeComte *et al.*, 1945) would appear to suggest that *r* {011} is the only form present in C crystals, whereas the B hydrate exhibits well-developed *a* {010} forms in addition to the pyramids. In our sample we have found crystals that are strictly comparable to those typical of the two hydrates, but in other respects these are identical and we have no basis whatever for giving each a separate status.

Results of attempts to induce precipitation of weddellite artificially. Notable differences in the forms developed on weddellite crystals were noted in the samples collected in 1959. Core R-3A, preserved in ethyl alcohol, had much more weddellite than core R-3B, which was packaged without preservatives. In addition, weddellite crystals in core A exhibited almost exclusively the form *r* {011}, whereas those formed in the sample without alcohol, core B, showed *a* {010} to be well developed in addition to the pyramid. Because weddellite was not identified in a sample collected in 1962 (core 62-260), it was assumed that a handling procedure was possibly responsible for precipitation of weddellite in the samples collected in 1959. To test this possibility, core 62-260 was split into eight 15-cm segments, and each segment into five portions. One portion from each segment was carefully examined at the time of

separation, and the remaining four portions, 32 samples, were treated as follows:

1. To one portion of each segment dilute HCl was added on account of the possibility that some acid, used to clean the pH electrodes in the field, had accidentally been incorporated into the sediment before it was packed.
2. In the second portion of each segment pH electrodes were inserted into the bagged sediment samples.
3. To the third portion of each segment, ethyl alcohol was added to determine whether this constituent may have influenced the development of crystal form in weddellite.
4. The fourth portion of each segment was left undisturbed in the original containers as reference material.

Results of these attempts to stimulate precipitation of weddellite were disappointingly negative; no weddellite was noted, although gypsum did precipitate in all samples after seven months. The presence of gypsum suggests that the association of gypsum and pyrite noted in the 1959 samples (R-3) is a result of gypsum precipitation after sediment collection. The lack of visible weddellite precipitation is disturbing, although possibly we may find weddellite in these sediments *after* they have remained packaged for more than two years as did the samples collected in 1959.

Conclusions. From this study it is tentatively suggested that the occurrence of weddellite in the Weddell Sea sediments may not be primary; that is to say, weddellite may not have been present in the original samples when they were collected by members of the Scotia Expedition, but, instead, precipitation took place during an interval between the time of actual collection and the unspecified date at which Earland observed and removed the unusual crystals from the sediments during his study of the foraminifera.

This study also emphasizes the importance of separating sediment samples from their interstitial water as soon after collection as it is convenient to do so, because of the possibility of precipitation of minerals from the interstitial water due to evaporation, activity of bacteria, or some other cause.

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