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FORAMINIFERA

PART IV. ADDITIONAL RECORDS FROM THE WEDDELL SEA SECTOR FROM MATERIAL OBTAINED BY THE S.Y. 'SCOTIA'

by

Arthur Earland, F.R.M.S.

WITH A REPORT ON SOME CRYSTALLINE COMPONENTS OF THE WEDDELL SEA DEPOSITS

by

F. A. Bannister, M.A.

with CHEMICAL ANALYSES *by*

M. H. Hey, M.A., B.Sc.

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REPORT ON SOME CRYSTALLINE COMPONENTS OF THE WEDDELL SEA DEPOSITS

By F. A. BANNISTER, M.A.
With chemical analyses by M. H. HEY, M.A., B.Sc.
Assistant Keepers in the Mineral Department of the British Museum (Natural History)

(Plates II, II *A*)

During his study of the Foraminifera present in oceanic bottom samples brought back by the Scotia Expedition (1902–4) from the Weddell Sea, Mr A. Earland picked out a number of minute crystals and crystalline nodules which he separated by external characters into three groups. A brief description of these crystalline components and an account of their examination by optical and X-ray methods seemed desirable chiefly because the substances identified have not hitherto been recorded from ocean bottom deposits.

HYDRATED CALCIUM OXALATE, $CaC_2O_4.2H_2O$

The first group consists of minute "envelope" crystals recorded from a number of stations in the very deep water of the central Weddell Sea, from depths of 2425–2739 fathoms (4434–5008 m.) (Plate II, fig. 1). These crystals are transparent, colourless, tetragonal bipyramids varying in size from 0·2 × 0·1 to 0·3 × 0·15 mm. When immersed in a liquid and viewed under the microscope they present sharp, square outlines with well-marked diagonals showing the intersection of the four uppermost pyramid faces. Intergrowths of two or more individuals are not uncommon but the grouping appears to be accidental and not in conformance with any twin-law. The "envelope" crystals are sparsely distributed in the deep-sea deposits. A gram of unpicked material from St. 286 yielded about fifty crystals weighing only half a milligram, the mineral residue consisting principally of fragments and rounded pebbles of clear, colourless quartz. Fragments of green hornblende, pink almandine, orange hessonite, brown biotite and glauconite were also detected.

When examined with convergent polarized light each "envelope" crystal gives a positive uniaxial figure consisting of a black cross surrounded by two interference rings; approximate birefringence = 0·02. If monochlorobenzene be used as the immersion liquid the crystal outline completely vanishes; hence the refractive index $\omega = 1{\cdot}523 \pm 0{\cdot}005$. The specific gravity could not be determined by balancing in a mixture of bromoform and benzene owing to their minute size and lack of colour. Several, however, were mounted on thin glass fibres and each in turn accurately centred in a parallel beam of light restricted in diameter by an iris diaphragm and pin-hole collimator. By such means it was possible to measure the angle between pyramid faces. The average value for the angle between a pyramid face *r* and the basal plane *c* (001) is $cr = 30° 35'$.

At this stage the tetragonal symmetry of a crystal was confirmed by a Laue photograph taken with the X-ray beam passing along the *c* axis [001]. Rotation photographs were also taken with a square edge vertical (Plate II, fig. 3), with a diagonal vertical and also about the *c* axis [001] (Plate II, fig. 4). The smallest tetragonal unit cell which can be assigned to the crystals on the basis of these photographs has the dimensions *a* 12·40, *c* 7·37 ± 0·02 Å. The indices of the pyramid faces are therefore {101}. The calculated axial ratio is $c:a = 0{\cdot}594:1$ corresponding to a calculated *cr* angle = 30° 42½′, in close agreement with the goniometric value, 30° 35′. Rotation and oscillation photographs about the [100] axis were then indexed and the unit cell found to possess the symmetry of the space-group $C_{4h}^5 = I\,4/m$.

The optical and crystallographic data so far obtained show that the crystals cannot be identified with any known tetragonal mineral. Fortunately, determinative data for all organic and inorganic substances known to possess tetragonal symmetry have recently been compiled by Hey,[1] and independently by J. D. H. Donnay and J. Mélon (1934). These data follow the determinative method suggested by T. V. Barker (1930). Allowing a possible error of ± 1° in the measured *cr* value, fifteen compounds are found to have *cr* values ranging from 29½ to 31½°. Several of these are soluble in water and therefore are excluded; of the remainder only the salt commonly known as calcium oxalate trihydrate, $CaC_2O_4.3H_2O$, possesses the same appearance and optical properties as the crystals under consideration. The *cr* value tabulated by Donnay and Mélon for $CaC_2O_4.3H_2O$ is 30° 7′. The presence of calcium in the deep-sea crystals was readily confirmed by dissolving one in a drop of dilute sulphuric acid and obtaining gypsum needles. A test for the oxalic acid radicle would, however, have consumed most of the crystals so far separated from the Weddell Sea deposits; certainly a complete chemical analysis was out of the question.[2]

A less direct method of confirming the above identification was therefore sought. The methods described by A. Souchay and E. Lenssen (1856) for synthesizing $CaC_2O_4.3H_2O$ did not promise a product sufficiently pure for chemical work. "Envelope" crystals are also present in the cells of certain plants (A. W. P. Zimmerman, 1892), and in the gall and urine of many mammals and fish. No reference, however, has yet been found to crystals of plant or animal origin measuring more than 0·17 mm. across, so that a separation of the requisite amount for exact chemical analysis would probably be impossible. It was suggested by Mr Hey that larger crystals of the compound might constitute the coating of certain renal calculi. This suggestion proved valuable. At the invitation of the Curator of the Royal College of Surgeons I was permitted to examine all their specimens of renal calculi taken from human bladders. Two calcium oxalate calculi were found coated with platy crystals, and these were kindly loaned to the Mineral Department for investigation.

The calculi differ somewhat in appearance; one, catalogue number C. 90, is spherical in shape, diameter 25 mm., and has a white powdery surface encrusted with white translucent platy crystals with clear edges. The second calculus (an unregistered duplicate) is roughly ellipsoidal in shape, measures 25 × 15 mm., and is encrusted with pale brown crystals of the same type. The matrix like that of C. 90 is white but more compact. Golding Bird (1842) has described similar renal calculi from the Guy's Hospital

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[1] Unpublished.

[2] The crystals weigh approximately 1×10^{-5} gm. each.

Museum collection. He identified the calcium oxalate crystals with the much smaller "envelope" crystals found in human urine. "Sometimes these crystals are opaque and the octahedron is remarkably flattened: the calculus then looks as if studded with pearl-spar." His careful study shows that the calcium oxalate may be intergrown with uric acid, sodium urate, ammonium urate, magnesium ammonium phosphate, calcium phosphate or calcium carbonate. Golding Bird does not give, however, the dimensions of the renal crystals of calcium oxalate. The crystals of both the calculi I have examined are roughly square in outline, measuring 2–3 mm. across, but the pyramidal faces are curved and the thickness of the crystals varies considerably owing to subparallel growth and possibly twinning. Only small transparent wedge-shaped fragments suitable for optical and X-ray work could be detached from the edges. These give a positive uniaxial picture and yield approximate refractive indices ω 1·523, ϵ 1·544 (Becke method). The broken fragments exhibit no well-marked cleavage directions; their hardness is about 4, Mohs' scale. Light reflections from the pyramid faces show that their curvature is due to the presence of a large number of vicinal faces between (101) and (001). A few crystal fragments give values *cr* varying from 30° 1′ to 30° 56′, but natural faces are too imperfect for refractive index measurements by the prism method and the fragments are too small to be ground and polished. Gypsum needles crystallized from a solution of a crystal fragment in sulphuric acid, and the residual liquid also decolorized a drop of potassium permanganate solution. These preliminary measurements and chemical tests therefore suggested the identity of the deep-sea crystals and the crystals from the renal calculi.

X-ray rotation photographs of some crystal fragments from both the renal calculi were then taken about the supposed [100] axis, i.e. about an edge of a square plate. All the spots of each photograph correspond exactly in position and intensity with those of a similar photograph of a deep-sea crystal. These photographs constitute the most reliable test of the identity of the two compounds since they do not depend upon the perfection of crystal form but only upon the atomic arrangement within a crystal. A chemical analysis of carefully selected fragments from the renal calculi should therefore reveal the chemical composition of the deep-sea crystals.

The specific gravities of crystal fragments from both calculi were separately determined by balancing in mixtures of bromoform and benzene. Values varying from 1·98 to 2·00 were obtained, but no systematic difference could be detected between the specific gravities of the white and pale-brown crystals. The first chemical analysis on white crystals, sp. gr. 1·99, from C. 90, gave CaO 37·3 per cent (by ignition), C_2O_3 46·1 per cent (by titration with potassium permanganate solution), H_2O 16·7 per cent (loss of weight at 270° C.), total 100·1 per cent, which corresponds to a chemical formula $CaC_2O_4 . 1\frac{1}{2}H_2O$ and was the first indication that the usually accepted trihydrate formula might be incorrect. The formula relating the specific gravity d, atomic contents nM and unit-cell dimensions of a tetragonal compound is $nM \times 1{\cdot}648/a^2c = d$. Since X-ray rotation photographs of the deep-sea crystals and renal calculi crystals are identical the values a 12·40, c 7·37 Å. may be inserted in the above formula. The value of M corresponding to $CaC_2O_4 . 1\frac{1}{2}H_2O$ is 155, the observed specific gravity is 1·99, so that

$n = 1{\cdot}99 \times 12{\cdot}4^2 \times 7{\cdot}37/155 \times 1{\cdot}648 = 8{\cdot}82$. Hence it appears that the tetragonal unit cell contains approximately $9CaC_2O_4 . 1\frac{1}{2}H_2O$. The crystal-structure of oxalic acid and many oxalates have now been worked by W. H. Zachariasen (1934) and S. B. Hendricks (1935). In all of them the C_2O_4 group has constant shape and dimensions. Both the unit-cell dimensions and the space-group of the renal calculi crystals would lead us to expect an even, not an odd number of C_2O_4 groups per unit cell. It is difficult in the face of the X-ray evidence to imagine how more than eight C_2O_4 groups can be accommodated. Therefore either the observed specific gravity or the chemical composition or both are inconsistent with the X-ray data.

In the meantime it had been found that the powdery material forming the matrix of the renal calculi crystals effervesces when dissolved in dilute acids and gives a reaction for phosphate. This is also true of the crystals themselves, probably due to fine-grained inclusions of the matrix. Moreover, a small residue of organic tissue remains after solution of a calculus crystal or matrix in acid. The first analysis on the white crystals must therefore be rejected, since it is clear that the presence of organic matter would disturb the permanganate titration and give too high a value for the oxalate content. The phosphate content of the crystals is also appreciable and possibly due to admixture of the calcium oxalate salt with dahllite, $3Ca_3(PO_4)_2 . CaCO_3$. The latter constituent is extremely fine-grained and attempts to separate sufficient from the crystals for optical tests or from the matrix for chemical analysis proved unsuccessful.

Two further chemical analyses were now made on pale-brown crystals, sp. gr. 1·99, from the unnumbered calculus. It is impossible to determine the water content directly since the crystals when dried at 270° C. still contain about 6 per cent H_2O and if the temperature is raised above 270° C. the oxalate begins to decompose. Nor can the oxalate be determined by titration with potassium permanganate owing to interference by included organic tissue. Accordingly the powdered crystals (10·06 mg. for analysis 1, 14·115 mg. for analysis 2) were weighed into a small crucible, dried at 270° C., heated at 580° C. to decompose the oxalate, reweighed and then ignited at 950° C. The residue was weighed and the phosphate content determined as ammonium phosphomolybdate. The ignitions at 580 and 950° C. correspond to the following reactions:

(*a*) Hydrated calcium oxalate + dahllite $\xrightarrow{580^\circ \text{C.}}$ $CaCO_3 + Ca_3(PO_4)_2 + CO + HO_2$.

Loss of weight due to evolution of $CO + H_2O$.

(*b*) $CaCO_3 + Ca_3(PO_4)_2 \xrightarrow{950^\circ \text{C.}} CaO + Ca_3(PO_4)_2 + CO_2$.

Loss of weight due to evolution of CO_2.

Table I gives the results of the two analyses, together with the recalculated figures allowing for deduction of dahllite. Table II shows that the two recalculated analyses correspond approximately to $CaC_2O_4 . 2H_2O$. The observed specific gravity 1·99 should also be corrected for a content of 4 per cent dahllite, see Table I. Assuming a specific gravity 3·1 for the latter constituent, the corrected value for the renal calculi crystals is 1·94. The specific gravity calculated from the X-ray data and assuming that the tetragonal unit cell contains $8CaC_2O_4 . 2H_2O$ is 1·91. The chemical and X-ray data are therefore in fair agreement considering the indirect methods used for analysis. There is no doubt that the usually accepted trihydrate formula for the tetragonal calcium oxalate is incorrect, and there is at least a strong probability that the formula should be $CaC_2O_4.2H_2O$.

Table I. *Chemical analyses of renal calcium oxalate crystals, sp. gr.* 1·99

Observed percentages				Equivalent to				Recalculated to 100 % after deduction of dahllite		
CaO	P_2O_5	Loss at 580° C.	Loss at 950° C.	Dahllite	CaO	CO_2	$CO+H_2O$	CaO	CO_2	$CO+H_2O$
37·46	1·78	37·34	23·42	4·32	35·10	23·24	37·34	36·61	24·24	39·15
36·81	1·75	36·22	25·22	4·24	34·50	25·04	36·22	36·03	26·14	37·83

Table II

	Analysis 1	Analysis 2	Mean	Theoretical percentage for CaC_2O_4		
				H_2O	$2H_2O$	$3H_2O$
CaO	36·61	36·03	36·32	38·39	34·18	30·80
CO_2	24·24	26·14	25·19	24·15	26·81	31·50
CO	—	—	—	15·38	17·06	19·17
H_2O	—	—	—	29·67	21·95	12·33
$CO+H_2O$	39·15	37·83	38·49	45·05	39·01	31·50

It is interesting to note that this conclusion is in agreement with the results of the earliest workers (T. Graham, 1838). No completely satisfactory analysis of the salt, however, has yet been published. A. Frey (1925), who claims to have produced artificial crystals $\frac{1}{2}$ mm. across, records a figure for the water content only and deduces the formula $CaC_2O_4.3H_2O$. It is not, however, obvious with what measure of success he separated the tetragonal salt from associated products of crystallization. His optical data are also at variance with mine; he gives ω 1·552, ϵ 1·583, presumably measured on the artificial salt and it is significant that these values are close to those that would be observed for a crystal of whewellite, $CaC_2O_4.H_2O$, lying on the face x (011), viz. γ' 1·551, α' 1·592. In view of this disagreement in refractive index measurements some of his identifications of the tetragonal crystals in plants must be accepted with reserve.

Many references to the presence of calcium oxalate in the waste products of plants and animals also record the size of the "envelope" crystals. C. Schmidt (1846) studied their formation in yeast covered by beer for many days. He also detected them in the gall of rabbit, dog and pike. The crystals usually measured 0·01 × 0·005 mm. and were never greater than 0·03 mm. across. Frey has observed crystals definitely of the tetragonal form in *Begonia* species of size 0·023 × 0·013 mm. They are also a usual constituent of human urine especially during the summer months. A sample of urine of patients suffering from oxaluria kindly sent to me by Mr L. W. Proger, Pathological Curator of the Royal College of Surgeons, shows many "envelope" crystals 0·02–0·025 mm. across, refractive index $\omega = 1·52$. Golding Bird (1843) made a microscopic and chemical study of "envelope" crystals in human urine and was the first worker to record their low birefringence and approximate refractive index. It is also clear that he recognized and was puzzled by the difference in optical properties of the "envelope" crystals and of the dumbbell-shaped spherulitic aggregates of whewellite sometimes found in urine. Apparently he did not suspect the existence of two hydrates of calcium oxalate. The largest envelope crystals detected in human urine by Golding Bird (1843) measured 0·056 mm. across, but he found still larger light amber crystals, 0·17 mm. across in horse urine (1845). These he preserved dry since they were "invisible in canada balsam".

Although the deep-sea crystals are about ten times larger than those observed in plant cells and ten times smaller than those from renal calculi, they are only a little larger than urine crystals. The possibility that the deep-sea crystals have been deposited from the urine of some marine organism is unlikely for three reasons. (i) Crystals deposited from urine might well be expected in all oceanic bottom deposits, whereas Mr Earland's extensive study of ocean bottom deposits from all over the world so far shows that the "envelope" crystals are not only a minor constituent but are restricted to very deep water in the Weddell Sea. (ii) Louis Heitzmann (1934) has observed that urine and renal crystals of calcium oxalate turn black at first on slow ignition owing to included organic tissue. The deep-sea crystals, however, change to calcium carbonate and at a higher temperature to lime without change of colour. (iii) The deep-sea crystals possess sharp edges and faces free from scratches so that there seems little doubt that they were formed *in situ*. It is obviously important to continue the search for calcium oxalate crystals in other ocean bottom deposits. The more urgent problem of the constitution of the blue and red sea-bottom muds may have led mineralogists to overlook this rare constituent. It is essential to make a careful study of oceanic deposits before removing the calcium carbonate by digestion with dilute hydrochloric acid, since this treatment would also remove calcium oxalate.

Although the monoclinic hydrate, $CaC_2O_4 . H_2O$, the more commonly observed salt in plants (raphides) (Vesque, 1874) occurs as the mineral whewellite in coal measures from various localities, the tetragonal salt has not hitherto been observed as a mineral. H. Braconnat (1825) has indeed recorded a growth of lichen on limestone containing nearly half by weight of calcium oxalate and J. Liebig (1853) named a similar incrustation, thierschite. Neither author, however, gives figures for the water content and I have not been able to secure a specimen of the original material for identification. A section of a lichen spore reveals irregularly shaped crystals which, however, prove to be whewellite not the tetragonal salt. Thierschite should then be regarded as an uncertain species since the name was given to the material on the basis of an incomplete chemical analysis. It would also be unwise to give a mineral name to the tetragonal crystals of hydrated calcium oxalate from the Weddell Sea deposits until the dihydrate formula is placed beyond question.

The origin of calcium oxalate in the ocean bottom mud of the central Weddell Sea is entirely conjectural. The writer finds it impossible to suggest how any sedimentary constituent of the earth's crust can be restricted to one small region, more particularly when that constituent is widely distributed in small quantities in numerous living organisms. It is easier, however, to offer reasons for the formation of the tetragonal salt rather than whewellite in very deep water, given a suitable concentration of calcium oxalate. Frey has found that the "envelope" crystals are most stable in alkaline solutions containing a high calcium content, and that their stability is also favoured by immersion in viscous media. H. Wattenburg (1933) has observed the variation of specific alkalinity with depth of water in the south Atlantic ocean. It is interesting that his records for many stations show a marked increase in alkalinity between 4000 and 5000 m., corresponding with a slight "undersaturation" of calcium carbonate. Hence the formation of tetragonal calcium oxalate crystals at depths of 4434 to 5008 metres in the Weddell Sea may be favoured by a similar increase in specific alkalinity of the ocean bottom water and by the viscosity of the enclosing muds.

GYPSUM, $CaSO_4.2H_2O$

The second group of crystals received from Mr Earland consists of two samples from different stations: St. 428, 66° 57′ S, 11° 13′ W, 2715 fathoms (= 4965 m.), and St. 391, 66° 14′ S, 31° 18′ W, 2630 fathoms (= 4809 m.). These are lenticular crystals up to 2·0 × 1·0 × 0·5 mm. in size which are readily shown by optical properties, specific gravity and chemical tests to be gypsum (Plate II, fig. 2). The crystal forms present are (111) and (110), only the latter being transparent. The faces (111) are corroded and the crystals resemble much larger crystals of similar form observed by Baret (1888) and others from saline deposits. Crystals identical in form but smaller in size have also been separated from ocean bottom samples brought back by the Discovery Expedition from the Weddell Sea in 1925. These latter crystals, which were found by Mr E. Heron-Allen, F.R.S., come from St. WS 553, 63° 33¾′ S, 60° 33½′ W, 5029 m. Gypsum has not hitherto been recorded from ocean bottom deposits and it is to be noted that this constituent, like calcium oxalate, would be removed at least partially by initial treatment of the sediments with acid. Since gypsum is one of the first minerals to be deposited when samples of sea water are evaporated (J. Usiglio, 1849) its formation in deep-sea deposits is of great interest. J. H. van't Hoff (1912) has studied the conditions of formation of gypsum in the Stassfurt salt deposits. There beds of gypsum, $CaSO_4.2H_2O$, and anhydrite, $CaSO_4$, form the lowest layers. The temperature of transition of gypsum to anhydrite under ordinary conditions is 63·5° C. The pressure due to 5000 metres of sea-water is about 500 atmospheres and the consequent lowering of the transition temperature about 25° C. Since the temperature of sea-water at such depths is approximately $-2°$ C. the formation of calcium sulphate as crystals of gypsum rather than anhydrite is not surprising. The perplexing fact is that so common a mineral should not be found in other contemporary ocean-bottom samples; that indeed its distribution is governed by conditions, as far as we know, peculiar to the Weddell Sea. A knowledge of these conditions would probably throw light upon other problems of the Weddell Sea and would form a useful addition to oceanography (see I. Igelsrud, 1932).

EARLANDITE, $Ca_3(C_6H_5O_7)_2.4H_2O$

The third group of crystalline constituents differs completely from the calcium oxalate and gypsum crystals. They were separated from fine and coarse samples from St. 417, 71° 22′ S, 16° 34′ W, 1410 fathoms = 2580 m. consisting chiefly of quartz grains, foraminifera, etc. The fine samples also contain a moderate number of pale yellow to white nodules $\frac{1}{2}$–1$\frac{1}{2}$ mm. in diameter, with a warty surface, whilst the coarse samples yielded some larger nodules up to 2 mm. in diameter and a few fragments up to 3 mm. across, obviously portions of the crusts of still larger but hollow nodules (Plate II *A*, fig. 1). Of particular interest were a nodule attached by siliceous cement to the wall of a specimen of the foraminifer *Rhabdammina linearis*, Brady (Plate II *A*, fig. 2) and another nodule which had been incorporated with other mineral grains in the tube of a marine worm. The discovery of these two specimens by Mr Earland places entirely beyond doubt the fact that this third crystalline component is also of deep-sea origin and has not resulted from accidental contamination of the sea-bottom samples. Both large and small nodules are polycrystalline and very fine-grained $< 10^{-4}$ mm. They vary in specific gravity from 1·80 to 1·95 and the aggregate refractive index of crushed nodules is 1·56. X-ray powder photographs of a nodule of sp. gr. 1·80 and another of sp. gr. 1·95 are identical (Plate II *A*, fig. 3) but quite different from powder photographs of the tetragonal and monoclinic hydrates of calcium oxalate. Nevertheless the nodules give a definite reaction for calcium, dissolve in dilute acid and decolorize potassium permanganate solution. They must therefore be composed of a calcium salt of an organic acid other than oxalic acid. Efforts were then made to establish the identity of the nodules by comparison with other insoluble calcium salts of organic acids known to exist in plant cells. Both calcium tartrate and calcium malate have been recorded as plant constituents (A. Zimmerman, 1892) but powder photographs of both artificially prepared salts are found to be quite different in pattern from the powder photograph of the nodules from St. 417. Since citric acid is present in many fruit juices Mr Hey suggested that calcium citrate, a very insoluble salt, should also be compared. Powder photographs of the artificially prepared salt and the deep-sea nodules are identical (Plate II *A*, fig. 3). Moreover, the specific gravity of the artificial salt is 1·951, i.e. identical with the highest observed specific gravity of the nodules and the aggregate refractive index is the same for both, viz. 1·56. The artificial salt shows a marked tendency to spherulitic formation, but the individual crystal plates are sufficiently large to yield single crystal X-ray photographs. Since crystallographic and optical data for calcium citrate are not recorded in the literature we hope to publish measurements on single crystals at a later date.

By the courtesy of Dr E. Hope the Dyson Perrins laboratory, Oxford, undertook the microchemical analysis of the deep-sea nodules and obtained the results given in Table III.

Mr Hey also made residue determinations on two separate samples of nodules and on artificially prepared calcium citrate. The chemical work confirms the X-ray determination and shows that the nodules have a composition close to the theoretical composition of hydrated calcium citrate, $Ca_3(C_6H_5O_7)_2.4H_2O$. The departures are probably due to adsorbed water and small variable amounts of impurities. A spectrographic examination of the residue left after ignition of the second sample (4·075 mg.) studied by Mr Hey shows in addition to calcium, traces of strontium, barium, magnesium, manganese and iron; also minute traces of copper (Plate II *A*, fig. 4). No impurity (except perhaps magnesium) amounts to more than 0·01 per cent, e.g. the phosphorus (probably present as phosphate) cannot be detected with certainty by ordinary chemical methods. The nature of the small amounts of impurities in the calcium citrate nodules is additional evidence that the nodules were formed at the sea-bottom (J. V. Samoilov, 1917). Their distribution is even more restricted than calcium oxalate and gypsum, and their origin is equally conjectural. So far as is known this is the first reported occurrence of calcium citrate in nature. We therefore propose to name the new mineral *earlandite* in recognition of Mr Arthur Earland's long-continued contributions to the study of ocean deposits.

Table III. *Chemical analyses of earlandite,* $Ca_3(C_6H_5O_7)_2.4H_2O$, *from St.* 417, *Weddell Sea, and of artificial calcium citrate*

			M. H. Hey		
	Dyson Perrins earlandite	Theoretical	Earlandite		Artificial calcium citrate
C (%)	24·01	25·24	—	—	—
H (%)	3·48	3·18	—	—	—
CaO (%)	28·63	29·48	31·6	29·01	29·70
Material used: mg.	3·601	—	1·816	4·075	526·2

SUMMARY

Three crystalline components from the ocean bottom of the Weddell Sea have been identified as crystals of calcium oxalate dihydrate, $CaC_2O_4.2H_2O$, crystals of gypsum, $CaSO_4.2H_2O$, and polycrystalline nodules of calcium citrate, $Ca_3(C_6H_5O_7)_2.4H_2O$, for which the name earlandite is proposed. X-ray photographs of the deep-sea crystals of calcium oxalate show that the unit tetragonal cell has dimensions *a* 12·40, *c* 7·37 Å. and possesses the symmetry of the space-group $C_{4h}^5 = I\,4/m$. Crystals from renal calculi yielding identical X-ray photographs are found to have the probable composition $CaC_2O_4.2H_2O$. Both the deep-sea and renal calculi crystals are identical with, but larger than "envelope" crystals found in the waste products of many plants and animals. The trihydrate formula usually given to the "envelope" crystals is incorrect.

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