Conchite, a new Form of Calcium Carbonate.[1]

By Agnes Kelly.

(Communicated by Prof. H. A. Miers.)

[Read June 19th, 1900.]

IN the course of an investigation on calcareous secretions in the animal kingdom, and more particularly on molluscan shells, I found that the latter did not consist of aragonite, as G. Rose[2] and Sorby[3] had supposed, but of a negative, uniaxial mineral, which is distinguished by most of its properties from calcite, and for which I propose the name conchite (κόγχη, shell). I further found that conchite occurred naturally in many localities—always as a crystal aggregate. Its properties were investigated on such, as well as on the conchite in shells.

Chemical Composition.—Several shells consisting of conchite were analysed, both qualitatively and quantitatively. In Cardium edule, besides $CaCO_3$ and possible traces of NaCl, I found no inorganic constituent. The following percentages of CO_2 and CaO were determined:—

$$\begin{aligned} CO_2 &= 42{\cdot}45 \text{ per cent.} \\ CaO &= 54{\cdot}63 \quad ,, \\ \hline &\quad 97{\cdot}08 \text{ per cent.} \end{aligned}$$

The remaining 2·92 per cent. was organic matter, which could not be determined directly. In Cyrena (sp ?) only CaO was determined, the calculated $CaCO_3$ was 97·2 per cent.

No quantitative analyses were made of naturally occurring conchite, but the various incrustations consisted mainly of $CaCO_3$; those formed under observation in kettles and water baths contained also traces of iron.

---

[1] A communication on conchite was laid before the Bavarian Academy on 5th May, 1900, and afterwards published in the *Sitzungsberichte der math.-phys. Classe* of that Academy.

[2] G. Rose, *Vorkommen des Aragonits und Kalkspaths in der organischen Natur*; *Abh. k. Akad. d. Wiss in Berlin*, 1858.

[3] Sorby, Presidential Address, *Quarterly Journal of the Geological Society*, 1879.

Solubility.—Conchite dissolves readily in acids, but it has not yet been shown by direct experiment whether it is more soluble than calcite or not. That it is certainly very much less stable than calcite under the action of atmospheric agencies is seen by comparing the behaviour of conchite and calcite-shells found as fossils. Sorby showed that in all older formations those shells only which he considered to be calcite were preserved as such, the others were either disintegrated or present as casts alone. I have been able to confirm most of Sorby's statements as to the presence of calcite; his aragonite shells are generally conchite, for no aragonite whatsoever is to be found in the animal kingdom. Cornish and Kendall[1] published a long list of the fossils found as shells or as casts in the Coralline Crag, stating that the shells were calcite, the casts aragonite. In this case also I have been able, for many of the genera mentioned, to demonstrate the calcite character of the one series, and the conchite character of the other series, by direct observation. In only one case, that of Serpula, does a fossil occur well preserved, which I have proved to consist of conchite.

The instability of conchite is further shown by Klement's[2] experiments on the artificial preparation of dolomite. Finely-powdered $CaCO_3$, together with crystalline magnesium sulphate and a saturated solution of NaCl, was heated in a closed retort to a constant temperature for a definite number of hours. The solution was then filtered and washed, and the percentage of $MgCO_3$ determined. Calcite heated for 10 hours to 100° gave traces only of $MgCO_3$; aragonite heated for 48 hours to 91° gave 34·6 per cent.; for 68 hours to 90°, 38 per cent. $MgCO_3$. Corals from a group in which I have been able to find conchite secretions only, gave:—Madrepora prolifera heated for 48 hours to 90° 38·5 per cent., Madrepora humilis 41·4 per cent. and Stylopora (sp?) 41·9 per cent. $MgCO_3$. Klement concluded that these corals consisted of aragonite, since conchite was unknown to him, but the increase in the amount of $MgCO_3$ formed in the experiment with the corals over that in the experiments with aragonite, indicate, quite apart from direct observation, that there is a still more unstable form of $CaCO_3$, this being conchite. Since all the important reef-building corals have skeletons of conchite, its instability and the possibility of its transformation into dolomite are of importance for the theory of the origin of dolomite.

---

[1] *Geological Magazine*, 1888, p. 66. "On the Mineralogical Constitution of Calcareous Organisms."

[2] Ueber die Bildung des Dolomit. *Tscherm. Min. Petr. Mitt.* 1895, XIV, 526.

Crystallisation from aqueous solution.—The conditions under which conchite crystallises out of water have not been determined with any exactitude. It was noticed, however, that in an a paratus used for obtaining distilled water, the spiral which was immersed in the ordinary hard tap water of Munich was thickly coated with $CaCO_3$ at the top, where it was hot, less thickly in the middle turns, where it was hardly warm to the touch, and was quite bare at the bottom, where the temperature was that of the water. The incrustations from the top and middle of the spiral consisted entirely of conchite, only the very lowest deposits contained some calcite as well.

On leaving solutions of calcium bicarbonate to evaporate at ordinary temperatures, calcite only was obtained, but at temperatures from 30° to 100° C. conchite in increasing proportions was also deposited. G. Rose, in his experiments on the artificial formation of aragonite, considered that the prisms formed under those conditions were aragonite. A careful examination of their properties, and especially the measurement of the index of refraction for the ordinary ray, shows them to be conchite. The prisms obtained on mixing boiling solutions of $CaCl_2$ and Na_2CO_3 or $NaHCO_3$ can similarly be shown to be conchite. I was able to examine only one deposit formed at a temperature markedly above 100° C., viz. an incrustation formed in a boiler under 7·5 atmospheres at 168° C., and it consisted entirely of aragonite, as proved by the biaxial interference figure.

We know little of the conditions of crystallisation of the calcareous secretions in the animal kingdom, but the following two points are noticeable :—

(1) The conditions under which calcite or conchite crystallises out seem to differ very slightly, for we get the outer layer of Pinna and Mytilus formed of calcite, the inner of conchite. Also in animals which secrete various calcareous structures we may get both varieties represented in the same animal, for example, Helix shell and Spiculum Amoris consist of conchite, its epiphragm and egg-shell of calcite; and Teredo has valves consisting of conchite and a tube of calcite.

(2) We cannot trace the influence of temperature as in deposition from bicarbonate solutions. In the secretions of cold-blooded animals, *i.e.* at ordinary air or water temperatures, we get on the whole more conchite than calcite. The only shells formed at comparatively high temperatures are bird's egg shells (about 37°C), and they are without exception calcite.

Though, like Vater,[1] I have so far been unable to obtain anything but calcite deposits from inorganic solutions at ordinary temperatures, the existence of conchite molluscan shells points to the possibility, under suitable conditions, of the deposition of conchite also at such temperatures.

Behaviour on heating.—Conchite resembles aragonite and ktypeite in being converted into calcite by heating, but differs from aragonite in undergoing the change at a considerably lower temperature.

This can be most readily demonstrated by parallel experiments; for example, in mercury vapour (360° C.) or in melting lead (325°) conchite is converted into calcite, but aragonite undergoes no change. Aragonite crystals break up between 373° and 380°, but only after heating to 405° was I able to see a uniaxial interference figure, and thus demonstrate the change.

Conchite begins to undergo the alteration between 300° and 310°, as can be proved by the occurrence of the twinned planes and cleavage characteristic of calcite. During the change the position of the principal axis is unaltered.

In aragonite and conchite we have two unstable forms of $CaCO_3$, as proved by the change which they undergo on heating, and in the case of aragonite by the greater solubility, as determined by Dr. H. W. Foote.[2] We have had indications that the solubility of conchite is also great, but exact measurements have yet to be made. The fact that up to 100° we get conchite as well as calcite crystallising out of solution, and at 168° aragonite only, is another instance of Ostwald's general statement in his *Grundriss der allgemeinen Chemie*, that on a change of condition and passage into a more stable one, not the variety of the substance which is most stable under the new conditions will tend to be formed, but that which is the least stable.

Specific Gravity.—Since only crystal aggregates were at my disposal there was always a tendency for the specific gravity to come out too low on account of porousness. The highest value obtained by a direct measurement was = 2·865 for an incrustation from a kettle. Crystal aggregates from Karlsbad and other incrustations from kettles and water baths were between 2·830 and 2·845. For Cyrena, from determinations of the specific gravity, the percentage of $CaCO_3$, and the specific gravity of organic matter, the value 2·874 was calculated.

---

[1] Ueber den Einfluss der Lösungsgenossen auf die Krystallisation des Calcium carbonats, *Theil II*, *Zeitsch. f. Kryst.* 1894, XXII, 209; *Theil IV*, 1895, XXIV, 378.

[2] *Zeitsch. f. Phys. Chemie*, 15th June, 1900. "Uber die physikalich-chemischen Beziehungen zwischen Aragonit und Calcit."

The hardness is considerably greater than that of calcite.

No *cleavage* was observed.

Optical Properties.—Conchite is uniaxial and negative like calcite. It is true that, more particularly in true nacreous layers, which invariably consist of conchite, a biaxial interference figure with a small optical angle is sometimes seen, although in general we have accurately uniaxial interference figures. Since nacreous layers consist of numbers of thin parallel lamellæ two possibilities are open—(1) that the mineral forming the nacreous layer is biaxial, and as in the case of uniaxial mica the uniaxial character is due to superposed lamellæ of equal thickness with all the principal axes parallel, but the secondary axes of successive lamellæ at right angles to one another; (2) that the mineral is uniaxial, and that the biaxial character is due to want of exact parallelism of the optical axes of the lamellæ. The reasons for thinking the second alternative the more probable are—

(1) The comparative rareness of the biaxial interference figure, and the want of constancy of the optical angle. In quite a small section of the shell of Cyclas cornea, for example, the angle varied considerably, and on examining a number of shells some were found to give accurately uniaxial interference figures.

(2) In sections through prismatic structures, such as the outer layer of Pandorina inæquivalvis, or the inner of Lithodomus dactylus or Chama macrophylla, and most inorganic incrustations, where there is no possibility of there being superposed lamellæ, the interference figure is always uniaxial.

The *indices of refraction* were determined for sodium light.

(*a*) By the *method of total reflection.* Since only crystal aggregates with the axes of the crystals more or less parallel, and no single crystals, were at my disposal, it was impossible to obtain very exact readings. Many observations were made by means of a prism (Wollaston method). The means for polished slabs of the following shells were:—Strombus gigas, $\epsilon = 1{\cdot}527$, $\omega = 1{\cdot}661$; Cyrena, $\epsilon = 1{\cdot}527$, $\omega = 1{\cdot}662$; Trigonia Lamarkii, $\epsilon = 1{\cdot}524$; Pinna squamosa (nacreous), $\epsilon = 1{\cdot}524$; Turbo sp.?; $\epsilon = 1{\cdot}527$.

Mr. W. J. Pope was kind enough to determine for me the values of ϵ for two shells by means of the Abbé Pulfrich Total-refractometer, and found for Strombus gigas $\epsilon = 1{\cdot}523$ and for Cyrena $\epsilon = 1{\cdot}526$.

Dr. Melczer also made some very careful readings for me by means of a similar instrument. A highly polished slab of Strombus gigas was found to behave as a biaxial mineral with a small optical angle, the indices being $\alpha = 1{\cdot}523$, $\beta = 1{\cdot}659$, $\gamma = 1{\cdot}662$.

(*b*) *Microscopic Method.*—Prismatic crystals were examined under the microscope with one nicol. When parallel to the one arm of the cross wires, ϵ would have its minimum value; when parallel to the other arm, ω would be obtained. Two Thoulet's solutions were prepared, the first of such a concentration that its refractive index for sodium light was the same as ϵ, so that in sodium light, on focussing up or down, the crystal did not appear either lighter or darker than the solution; the second was similarly adjusted to equal ω. The refractive indices of the solutions were measured either directly on an Abbé's refractometer, or the specific gravity was measured and the refractive index calculated from Goldschmidt's tables. Both methods were found to agree to a unit in the third decimal place, so the latter as the simpler was usually resorted to.

The mean values obtained were $\epsilon = 1{\cdot}524$ and $\omega = 1{\cdot}661$.

Probably we may take these values as being correct to ± 1 in the 3rd decimal place, since they agree with the best values obtained by the method of total reflection.

The *birefringence* of conchite is accordingly considerably lower than that of calcite, about 0·137. This was also proved directly by observing sections of conchite and calcite of the same thickness in polarised light; for in sections parallel to the optic axis conchite shows colours of a lower order than calcite, and in sections perpendicular to the optic axis conchite shows fewer rings in its interference figure.

The *forms* in which conchite crystals may occur are as follows:—

(1) Prisms and acicular crystals. As such it is deposited from aqueous solutions on evaporation. The various naturally-occurring crystal aggregates all consist of prisms, and some shells, *e.g.* Pandorina inæquivalvis, consist in part of conchite prisms.

(2) Plates parallel to the base. This is the form in which the conchite of nacreous layers occurs.

(3) Rhombohedron-like crystals, with the long axis of the rhombohedron inclined at about 45° to the optical axis. They occur in Strombus and most other gastropods.

Occurrence of Conchite. Animal Kingdom.—A series of about 150 specimens, chosen from all the lime-secreting groups of the animal kingdom, was examined. That no aragonite is present is proved by the constant occurrence of uniaxial interference figures, by the value of ω not exceeding 1·661 (for aragonite $\beta_D = 1{\cdot}6816$, $\gamma_D = 1{\cdot}6859$), and by the change to calcite at about 300°. The following tests were applied to distinguish between calcite and conchite.

(1) Specific gravity—calcite, 2·715; conchite, 2·87.
(2) Presence or absence of the twinning planes characteristic of calcite.
(3) Minimum value of ϵ—for calcite $\epsilon_D = 1·486$; conchite $\epsilon_D = 1·524$.
(4) Presence or absence of a change on heating.

As thus determined, the occurrence of conchite or calcite in the animal kingdom is as follows:—

Foraminifera, calcite.

Calcareous sponges, calcite.

Hydrocorallinæ, conchite.

Alcyonaria, calcite, except Heliopora, which is conchite.

Madreporaria, conchite.

Echinodermata, calcite.

Polyzoa, calcite.

Brachiopoda, calcite.

Mollusca. Lamellibranchiata.—Anomia, Ostrea, Pecten and the outermost layers of Pinna and Mytilus, calcite; all the rest conchite.

Gastropoda.—All conchite except Patella and Ianthine.

Opercula of Turbo and Nerita, conchite.

Cephalopoda and Scaphopoda, conchite.

Chætopoda.—Tube of Serpula, conchite.

Crustacea, calcite.

Egg shells of Bulimus, Helix, Alligator, and all birds, calcite; of Tortoise, conchite.

Otoliths of Gadus and Frog, conchite; of Sturgeon, calcite.

The same tests were applied to distinguish conchite in *inorganic nature*. It was found to occur in the following localities:—

Karlsbad, as the spheres in a pisolitic deposit. The spheres are considerably larger than those found to consist of ktypeite. Also as various varieties of Sprudelstein.

Schemnitz in Hungary, blue and brown incrustations.

Alt-sohl in Hungary, a brown incrustation.

Ringenwechsel near Schwatz in Tyrol, a blue incrustation.

Yellowstone Park, Sinter.

Various specimens of Flos Ferri were all found to be conchite, and the fur in kettles was generally conchite, sometimes with an admixture of calcite.

Amorphous Calcium Carbonate.

F. Linck showed that when $CaCO_3$ is precipitated it often appears first in the form of little spheres, which do not depolarise, and only later become crystalline. If a calcium salt and a carbonate be allowed to diffuse into one another across a very viscid gum solution, such globules, together with crystals, may be obtained as a permanent preparation. As will be seen from their behaviour on heating, these globules constitute the most unstable of all the forms of $CaCO_3$, so that their appearance forms another case in illustration of Ostwald's generalisation, and one would indeed expect them to be precipitated first of all whenever the conditions were favourable. Whether they can crystallise afterwards as conchite, aragonite, or ktypeite or only as calcite is not known; the other unstable forms of $CaCO_3$ can all be converted by heat into calcite, but, so far as is known, never into each other. If the conversion of the globules into calcite is alone possible, their appearance would always condition the formation of calcite, and conchite, for example, could only be deposited when no globules had appeared.

I found in the course of these investigations that the calcium carbonate in the two posterior æsophageal glands of the earth-worm consists of just such globules in the amorphous condition. Moistened with water they very quickly become crystalline, but if they are dried at 100° and the last traces of water removed by treatment with absolute alcohol, they remain permanently amorphous.

Lowering the temperature has no action upon the globules; no change was called forth by leaving for several hours at the temperature of boiling water, but raising the temperature to only 160° to 170°C is enough to cause them to become crystalline.

An exact determination of the specific gravity was not possible, but by means of determinations of the specific gravity of the dried glands, of the organic substance, and of the percentage of $CaCO_3$, the specific gravity can be calculated to have the value 2·1. Similar determinations on the carapaces of Astacus and Julus gave values of 2·2, but these are still more inexact, for as well as about 50 per cent. $CaCO_3$, there is about 6 per cent. $Ca_3(PO_4)_2$ present.

The index of refraction was measured by the microscopic method, and found to be 1·538. Even under the highest magnification, and with the most sensitive methods, no action on polarised light could be observed.

Amorphous calcium carbonate occurs frequently in the animal kingdom, for example, as globules in the mucus of Helix, and not as globules in the carapaces of Astacus, Squilla, Julus and in the egg shell of the grass snake. On maceration with water or on heating it becomes crystalline, which explains why it is not found to occur as a mineral.