An Examination of the Micro-Crystals of Calcium Carbonate in Molluscan Shells by means of X-Rays, Part II.

By

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ABSTRACT

By means of X-rays it is confirmed that the micro-crystals of calcium carbonate in the nacreous layer of *Atrina japonica* REEVE are in the form of an aragonite instead of a calcite, and it is also found that they are arranged fibrously, the orthorhombic *c*-axes of its crystals being arranged parallel to the direction perpendicular to the surface of the nacreous layer.

After the determination of the crystal-form and the arrangement of the micro-crystals of calcium carbonate in the *prismatic layer* of the *Atrina japonica* REEVE, the result of which has already been reported in Part I,[1] the writer continued the same examination of the micro-crystals with the *nacreous layer* of the same shell, by using the same X-ray tube and the apparatus as in the former experiment. That the micro-crystal of calcium carbonate in the nacreous layer of the shell of *Atrina japonica* REEVE is in the form of an aragonite is already known, having been suggested by the observations by various means of many previous investigators.

This fact was stillmore confirmed in the present experiment by taking a powder-photograph with X-rays.

The photograph reproduced in Fig. 1, Plate I, was obtained with the nacreous layer of the *Atrina japonica* REEVE, by setting the surface of the nacreous layer perpendicular to the incident X-ray beam, and by

1 These Memoirs, A, 11, (1928).

placing the photographic plate at right angles to the direct X-ray beam at a distance 4.7 cm. behind the specimen. In the accompanying figure, Fig. 1, the diffraction-pattern in Fig. 1, Plate I is shown diagrammatically. In this figure the line AOA′ represents the direction on the surface of the photographic plate, which is parallel to the surface-normal of the nacreous layer, and the lines COC′, DOD′ etc. represent the positions of the radiating bands. In this figure we see the radiating bands arranged symmetrically about the horizontal and the vertical lines BOB′, AOA′. Fig. 2, Plate I was taken with the incident beam of the X-rays proceeding perpendicularly to the surface of the layer; and it consists of concentric rings without any radiating band as seen in Fig. 1, Plate I. These facts indicate that the micro-crystal in the nacreous layer is arranged fibrously and that the axis of the fibre is nearly in a direction perpendicular to the surface of the nacreous layer.

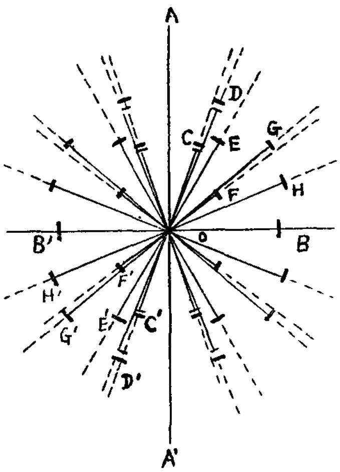


Fig. 1,

An arragonite-crystal belongs to the orthorhombic system, and its lattice-structure was investigated by W. L. Bragg[1] and other investigators[2]. According to Bragg, the dimensions of its elementary cell containing four molecules of calcium carbonate is:

$a=4.94$A.U.; $b=7.94$A.U.; $c=5.72$A.U.

In order to know the crystallographic axis of the fibrous arrangement of the micro-crystals, we must determine the indices of the atomic planes by which the radiating bands in Fig. 1, Plate I, are caused. This was done by measuring the distance r between the centre of the central spot and the position of an intense spot on any radiating band. As such intense spot on a radiating band is nothing but the spectrum of the K-radiation of the Mo-target of the X-ray tube, the value of the spacing d between two consecutive atomic planes, and, consequently, the indices of that atomic plane, which is responsible for the radiating band under consideration, will be obtained from the wave-length of the K-radiation of molybdenum.

1 Proc. Roy. Soc. CV, 16, (1924).
2 Huggins: Phys. Rev. (2)19, 354, (1922), S. I. Tomkeieff: Min. Mag. XX, 408, (1925).

Table I.

spots	r in cm.	θ (obs.) in degrees	spacing (obs.) in A. U.	Bragg's data		d (calc.) in A. U.	indices of reflecting planes
				d in A. U.	indices of planes		
F	1.00	6°. 06′	3.38	—	—	3.38	111
B	1.40	8°. 18′	2.45	2.47	100	2.47	100
C	1.27	7°. 30′	2.70	—	—	2.69	012
E	1.40	8°. 18′	2.45	2.47	102	2.47	102
G	1.85	10°. 45′	1.89	1.86	101	1.87	101
H	1.70	9°. 55′	2.06	—	—	2.04	211
D	1.97	11°. 23′	1.79	—	—	1.78	103

The values of the spacings d, thus obtained, between two consecutive atomic planes for various radiating bands, are given in the fourth column in Table I.

F, B, C, etc., in the first column of the same table correspond respectively to the spots F, B, C. etc., in Fig. 1. In comparison Bragg's data for the values of d for three different atomic planes are given in the fifth column. The values of d for many atomic planes were also calculated by the writer from the Bragg data given before, and are placed down in the seventh column of the table. From the agreement between the calculated and the observed values of d, as shown in the Table, the indices given in the last column are assigned for various radiating bands respectively.

Table II.

radiating bands	indices of the atomic planes	α (obs.)
COC′	012	19°
DOD′	103	21°
EOE′	102	30°
FOF′	111	53°
GOG′	101	50°
HOH′	211	68°
BOB′	100	90°

In Table II, the indices of the atomic planes which caused the radiating bands and the angle α which the line AOA′ in Fig. 1 makes with the line connecting the centre of the central spot and the intense spot on a radiating band are tabulated. From these values of α for various atomic planes, the angles β which the normals to various atomic planes make with the direction of the axis of the fibre can be calculated readily, by taking the angle between the axis of the fibre and the incident X-ray beam as 90°, so as to fit in our case. The values of β thus calculated for various radiating band and the indices of the corresponding atomic planes are tabulated in Table III.

Table III.

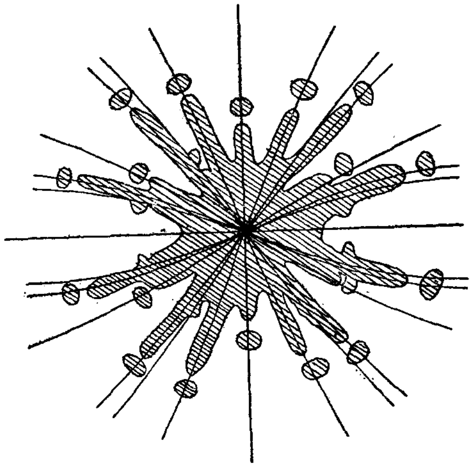
indices of atomic planes	001 axis or c-axis	β
111	53°. 45′	52°. 55′
100	90°. 00′	90°. 00′
012	19°. 45′	18°. 00′
101	49°. 10′	48°. 30′
102	30°. 00′	29°. 30′
103	20°. 55′	20°. 10′
211	69°. 08′	67°. 57′

These of β must be respectively the same with an angle between the normals to various atomic planes tabulated in Table III and the crystallographic axis arranged in the direction of the axis of the fibre. Taking this fact into consideration, the crystallographic axis, which is the axis of the fibre, was reached with the aid of the globe and the spherical scale devised by Prof. U. Yoshida; and it was found that the angular relation shown in Table III could only be accounted for by taking the c-axis of the orthorhombic crystal of aragonite as the axis of the fibre. The angles between the c-axis and the normals to various atomic planes are given in the second column of Table III. The agreement between the values of these angles and those of β is remarkable.

In Fig. 2, the curve drawn in full lines and the spots on these curves show respectively the radiating bands and the positions of the spectrum of the K-radiation of Mo on these bands, which are expected to appear on the photographic plate from ths above consideration; and the shaded parts represent the portions actually observed on the photograph as shown in Fig. 1, Plate I. The agreement between the calculation and the observation is found again to be satisfactory.

Thus we are enabled to conclude that unmistakably the calcium carbonate in the nacreous layer of *Atrina japonica* REEVE is an aggregate of the micro-crystals of aragonite, which are arranged in a fibrous manner; and that the orthorhombic c-axis of the micro-crystals of aragonite are arranged in a direction perpendicular to the nacreous layer of

Fig. 2.



the shell, which is at the same time the direction of the axis of fibre.

The writer is now planning to examine the molluscan shells belonging to various genera and species and a general conclusion is hoped to be attained in the near future.

In conclusion, the writer's sincere thanks are due to Professors U. Yoshida and T. Kawamura for their kind guidance and encouragement throughout this research.

Plate I

Fig. 1

The direction parallel to the surface-normal of the nacreous layer.

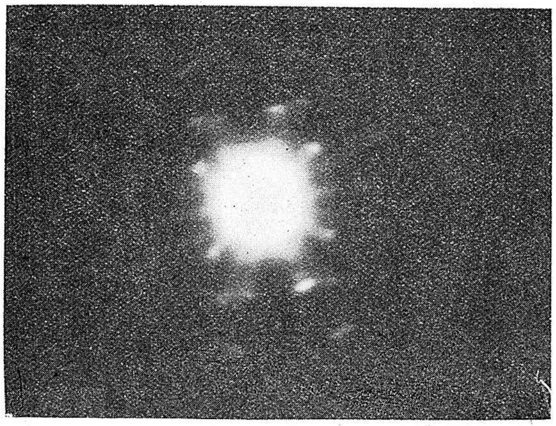


Fig. 2