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

By

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Abstract

Examination of the micro-crystals in the prismatic layer of *Atrina japonica* REEVE by means of the X-rays convinced the writer that the micro-crystals in this layer are in the form of calcite, and that the crystals are arranged fibrously, the principal axes of the crystals being parallel to the direction perpendicular to the surface of the shell. This is in accordance with the results of observations made by different means by the previous authors.

The problems of whether the micro-crystals of calcium carbonate in molluscan shells are in the form of the calcite or in that of the aragonite and of what their arrangement is, have already been studied by G. Rose and others[1] physically, microscopically and chemically, but as such means are always not without defect, it appeared to me more or less hopeful to attack the same problems by means of x-rays.

Although the shells are not the same in chemical composition or physical structure in different species of animals, they are mainly composed of pure calcium carbonate, an organic base known as conchiolin, allied to chitin, and a small amount of a phosphate of calcium.

The shell of *Atrina japonica* REEVE or *Tairagi* as it is commonly called in Japanese, consists of three layers: a very thin periostracal or the uppermost layer, a prismatic or middle layer and, a nacreous or the lowest layer. The present investigation is concerned mainly with the prismatic layer. The prismatic layer shows a columnar structure

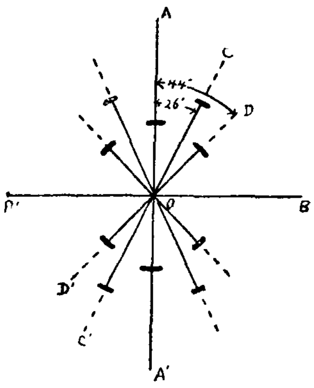
1 G. Rose, G. Bournon, De La Beche, Necker: Winterstein :- Handbuch der vergleichenden Physiologie, Bd. III, Teil 1, Heft 1.

and the axes of the columns are nearly parallel to the direction perpendicular to the surface of the shell. The carbonate of calcium in this layer is already known to be in the form of calcite and this has been confirmed by the writer too by means of Hull's powdered crystal method.

Then, in order to examine the arrangement of the micro-crystals of calcite in the prismatic layer the writer took the Laue-photographic method. The x-rays used for the device were from a molybdenum-target in a Coolidge-tube. A pair of narrow circular slits or apertures were used to get a narrow beam of x-rays, and a photographic plate was set perpendicularly to this beam of x-rays. A specimen of the prismatic layer, about 0.7 mm. in thickness, was put just behind the second slit which was against the photographic plate. The distance between the specimen and the photographic plate was 4.1 cm. throughout the experiments.

The photograph reproduced in Fig. 1, Plate I, is one obtained with the prismatic layer of the *Atrina japonica* Reeve, the axis of the columns having been set perpendicularly to the incident x-ray beam in this case. We see that the pattern in this picture consists of many intense spots about a central spot impressed by the direct beam of the x-rays and some radiating bands starting from the central spot and passing outward through the intense spots.

Fig. I



The accompanying figure shows such a pattern diagrammatically. The line A O A′ has been drawn parallel to the axis of the column of the layer and C O C′, D O D′ represent the successive bands arranged symmetrically about the vertical and horizontal lines A O A′, B O B′. There is no doubt that the radiating bands are due to the reflection of X-rays from various atomic planes of the micro-crystals which are arranged fibrously. Fig. 2, Plate I, shows the next case, in which the axis of the column of the layer was set parallel to the x-ray beam, and the appearance of concentric rings in this case, instead of the radiating bands as in the former case, indicates that the axis of the fibrous arrangement of micro-crystals coincides nearly at least with the axis of the column of the layer. I experimented in this way with the various portions of the prismatic layer of the shell, and no difference was ever detected so far as the present experiment is concerned.

Since the spots on the radiating bands owe their origin to the reflection of the K-radiations of molybdenum from the various atomic planes of the crystals, we can find the indices of these atomic planes from the distances between these spots and the central one. Let us denote the distance between a spot and the central one by r, the distance between the photographic plate and the specimen by a and the glancing angle of the beam of x-rays to an atomic plane which is to be determined, by θ. Then the value of θ will be calculated by the following equation:

$$\tan 2\theta = \frac{r}{a}.$$

Finding the value of θ in this manner and by taking 7.1 A. U. as the mean wave-length of the K-lines of molybdenum, the spacing between the consecutive atomic planes will be obtained by Bragg's equation:

$$n\lambda = 2d \sin\theta$$

where n is an integer, and is taken to be unity in the present case. The spacings d corresponding to various radiating bands thus determined are tabulated in Table I, and are compared with those observed by W. L. Bragg[1]. As the two results are in good accordance with each other we can safely assign the indices given by Bragg to the corresponding bands.

Table I

Bands	α	d in A. U. (obs.)	d (Bragg)	Indices.
A O A′	0°	2.84	2.86	(111)
C O C′	26°20′	1.92	1.91	(110)
D O D′	44°10′	3.03	3.03	(100)

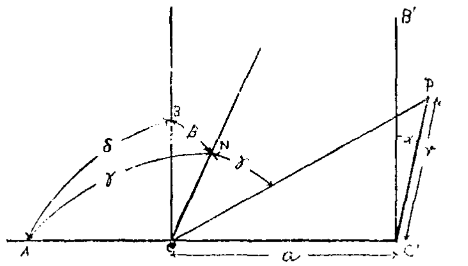
Thus the indices of the reflecting atomic planes responsible for every radiating band are known, while the crystallographic axis of the calcite, which is in the direction parallel to the axis of the fibre, will

1 Roy. Soc. Proc. London. Vol. **105**, (1924)

be known from the angular distribution of these radiating bands. The angles α between the lines connecting the central spot and the intense spots on every radiating band and the direction A O A′ on the photographic plate, which is parallel to the axis of the fibre, are also given in the second column of Table I.

A C C′ in Fig. 2 represents the beam of the incident x-rays which makes an angle δ with the direction of the axis of the fibre C B, and C N the normal to a reflecting atomic plane which makes the angles β and γ with C B and C A respectively. So the angle γ is the angle of incidence to the atomic plane under consideration, and is the complement of the glancing angle θ. The x-ray beam reflected from the atomic plane falls at P on the photographic plate B′ C′ P standing normally to the incident beam at C′, the line B′ C′ on the photographic plate being here drawn parallel to the line B C. Now, in the spherical triangle A B N we have the following relation:

Fig. 2



$$\cos\beta = \cos\gamma\ \cos\delta + \sin\gamma\ \sin\delta\ \cos\alpha,$$

where α is the angle between the plane B C A and the plane N C A. If A C is perpendicular to C B as in the case of Fig. 1, Plate I, the above relation can be reduced to $\cos\beta = \sin\gamma \cos\alpha$. Since γ is known for a given wave-length of x-rays and for a definite reflecting atomic plane, the values of β, the angle between the axis of the fibre and the normal of a reflecting atomic plane, can be readily obtained from the observed values of α respectively. The values of β thus determined are tabulated in Table II. It has already been stated

Table II.

Bands	Indices	β (obs.)	β (calc.)
COC′	(111)	26°40′	26°22′
DOD′	(100)	44°20′	44°40′

that the band ACA′ in Fig. 1 lies, nearly at least, parallel to the axis of the fibre; moreover it was shown in Table I that this band is caused by the reflection of x-rays from the atomic plane 111. From these facts it seems natural to take the principal axis 111 of the calcite as the axis of the fibre, and the values of β calc. in the fourth column of Table II are calculated under this consideration. Such fair agreement between the observation and the calculation seems to show reversely that the principal axis of the calcite is the axis of the fibrous arrangement. This was also tested by using a spherical scale and a globe devised by U. Yoshida[1], and it was observed that the distribution of the radiating bands under consideration could not be accounted for in any way other than this. Here it must be noted that, if the principal axes of all the micro-crystals were arranged exactly in the same direction, the band corresponding to the plane 111 could not appear on the photograph; but as a weak impression of the band is detectable in the picture, we must consider that the parallelism of the principal axes of the micro-crystals is not very exact; and that, though the majority of the micro-crystals are arranged nearly in the ideal orientation, some of them deviate a little from that direction.

Thus the results of my experiment with x-rays are the same as those obtained by different means by the previous authors[2]: and it seems to me entirely established that the micro-crystals in the prismatic layer of the shell *Atrina japonica* REEVE are calcite and that the principal axes of these micro-crystals of calcite lie almost parallel to the direction of the column in this layer.

Lastly it must be noted that the micro-crystals of this shell are rather coarse, since the x-ray photographic picture appears as an assemblage of many distinct Laue-spots. It is this circumstance that hindered a little the accurate determination of the positions of the bands, though the conclusion is not to be disturbed. My examination of the arrangement of the micro-crystals of aragonite in the nacreous layer of the shell of the same animal is now going on and the results will be published in the near future.

In conclusion, I desire to express my sincere thanks to Professors U. Yoshida and T. Kawamura for their kind supervision throughout this research.

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1 U.Yoshida; Jap. J. Phys., **4**, 133(1927)

2 G. Rose, V. Ebner, Leydolt, Valentin: Winterstein:- Handbuch der vergleichenden Phsyiologie, Bd. III, Teil 1, Heft 1.

Plate I

Fig. 1

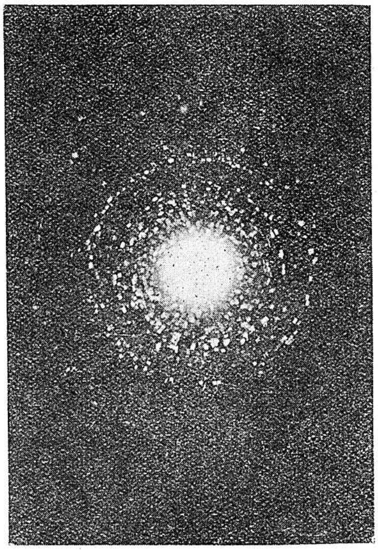

Fig. 2