The Arrangement of Micro-Crystals in the Banded "Supposed Aragonite (Arareishi)".

By

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Abstract

By means of x-rays it was ascertained that the banded "supposed aragonite" is an aggregate of micro-crystals of calcite, and that most of them are so arranged that their principal axes are perpendicular to the surfaces of the layers in the mineral.

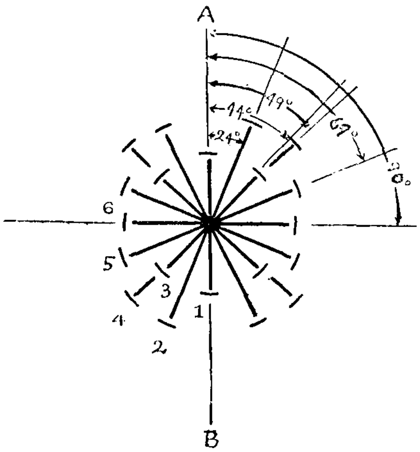
Nature sometimes produces banded minerals. It is naturally supposed that, in these minerals, the micro-crystals are arranged in some regular manner. If so, the determination of their manner of arrangement in various banded minerals seems to be of much interest, as it seems to have some connection with the problem of the atomic forces. This has already been studied microscopically in the case of some minerals, but even this method is not always without defect, and it is not applicable to all cases. Thus the writer employed the x-rays, and examined the arrangement of the micro-crystals, first, in the "supposed aragonite (arareishi)," the banded mineral whose constituent was proved to be calcite and not aragonite, as will be described below.

The specimen used by the writer was the "arareishi" as it is usually called by mineralogists, and which is produced at Oshikamura, Shinano, Japan. As shown in Fig. 1, Plate I, it is a banded block of light brown colour; and the writer confirmed, by the powder photograph method, that it is composed actually of calcite and not of aragonite. The "arareishi" obtained at Tahiramura, Shinano, which had been usually believed by mineralogists to be composed of aragonite, has already been proved by means of x-rays to be calcite by Y. Ozawa[1], and he called that mineral "supposed aragonite." The writer will assign this name also to the "arareishi" produced at Oshikamura, Shinano.

At first, a specimen in the form of a thin plate of about 0.5 mm. in thickness was cut out along the layers of the supposed aragonite; and a narrow beam of x-rays, radiated from a Coolidge tube with a molybdenum target, was made to strike the specimen in the direction perpendicular to the surfaces of the layers of the specimen. The photographic plate was placed perpendicularly to the incident beam of x-rays at a distance of 3.5 cms. behind the specimen. The photograph thus taken is shown in Fig. 2, Plate I. The presence of concentric rings only in the photograph informs us that the orientation of the micro-crystals is symmetrical about the normal to the surfaces of the layers.

Next, the writer prepared another specimen by stripping it off perpendicular to the layers from the same block of arareishi as before. An x-ray beam was made to strike the specimen in a direction perpendicular to the normal of the surfaces of the layers, and the diffraction pattern was obtained on a photographic plate placed perpendicularly to the incident x-ray beam at a distance of 4.2 cms. behind the specimen. The diffraction pattern thus obtained is reproduced in Fig. 3, Plate I. As is seen in the figure, we can detect 20 prominent bands radiating outward from the central spot. The intense spots situated at the ends of these bands were confirmed to correspond to the K_α radiation reflected from various atomic planes of calcite.

Fig. 1



In Fig. 1. the distribution of the bands and spots in Fig. 3, Plate I are represented diagramatically. In this figure, the direction A B is drawn parallel to that of the normal to the surfaces of the layers in the specimen. As can be seen from this figure, or from Fig. 3, Plate I, the distribution of the bands and the spots is symmetrical about the line A B. This is in accordance with

1 Y. Ozawa : Science Reports, Tohoku, **14**, 33(1925)

the fact that the orientation of the micro-crystals is symmetrical about the direction of the normal to the surfaces of the layers; and consequently we may infer that the supposed aragonite has a fibrous structure whose axis is in the direction perpendicular to the surfaces of the layers of the specimen.

The next problem is to find out the crystallographic axis which is arranged in the direction parallel to the axis of the fiber. For this purpose the writer used the values of θ and β obtained from the position of the spots and the angular distribution of the bands[1]. Here θ is the glancing angle of the K_α radiation of molybdenum to an atomic plane of calcite, and β the angle between the normal to an atomic plane and the crystallographic axis of the fiber which is to be determined. The observed values of θ and β are tabulated in Table I. The indices

Table I

No. of the bands and the spots	Indices of the planes	Spacing d in A.U.	Distance from the centre to the spot(mm)	$\theta_{calc.}$	$\theta_{obs.}$	$\beta_{calc.}$	$\beta_{obs.}$
1	(111)	2.86	10	7°11′	7°	0°	0°
2	(110)	1.91	16.5	10°43′	11°	26°32′	26°
3	(100)	3.03	10	6°44′	7°	44°40′	44°
4	($\bar{1}$22)	2.02*	16.5	10° 7′	11°	44°37′	49°
5	(12$\bar{2}$)	2.30*	14	8°53′	8°	74°19′	69°
6	($\bar{1}$10)	2.49	12.5	8°12′	8°	90°	90°

of the atomic plane which is responsible for a radiating band is obtained from the value of θ, and are given in the second column of Table I. From the values of β and the indices for every radiating band, and by using the globe and the spherical scale devised by U. Yoshida[2], the crystallographic axis of the fiber was found to be the principal axis 111 of the calcite crystal: i.e. the principal axes of the microcrystals of calcite in the supposed aragonite were found to be arranged parallel to the axis of the fibre which is perpendicular to the surfaces of the layers. This arrangement of the micro-crystals of calcite is the same as that observed by Mr. J. Tsutsumi[3] in the prismatic layer of a shell.

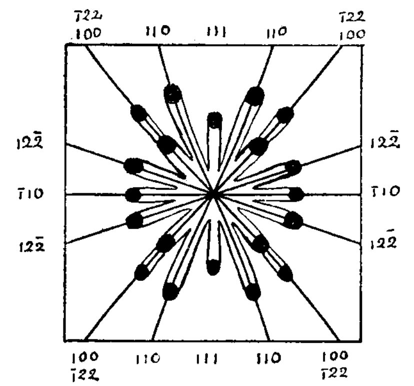
1 S. Nishikawa : Sū. Butu. Kw. K., Tokyo, **7**, 131 (1913-1914)
2 U. Yoshida : Jap. Jour. of Phys, **4**, 133 (1927)
3 J. Tsutsumi : These Memoirs, A. **11**, (1928).

The calculated and the observed values of θ and β are compared in Table I, and the discrepancies between them seems to be within the limit of experimental errors. As to the planar spacings d, the values observed by W. L. Bragg[1] are given in the table for 4 different atomic planes, and for the two others they were calculated by using Bragg' data: $d_{100}=3.03$ A. U. and they are marked by asterisks in Table I.

If the principal axes of all the microcrystals are exactly parallel to the axis of the fibre, the spots 1, which seems to be caused by the plane (111), are not able to present themselves. Consequently it must be considered that, though the majority of the micro-crystals in the supposed aragonite are arranged in the fibrous structure before mentioned, there are some whose orientations deviate a little from the ideal one. The fact that the bands are not sharp but diffused, is well in accordance with this consideration. In order that the reflection of the K_α line of molybdenum may occur from the atomic plane (111), the glancing angle must be $7^\circ\ 11'$. Therefore the deviation of the principal axes of some of the micro-crystals from the ideal orientation must be at least $7^\circ\ 11'$. But at the same time, the absence of the concentric rings which usually appear besides the radial bands, in the case of Aluminium wire[2] or others, implies that scarcely any micro-crystals with much more deviation than the critical angle above mentioned, are present.

Being coloured light brown as stated before, the supposed aragonite seems to involve some impurities. But, as the spots and the bands in Fig. 3, Plate I are all explainable by the reflection of x-rays from calcite crystals only, the impurities, if any exist, seems to be of very small amount.

Fig. 2



The curves plotted in Fig. 2 represent the calculated ones obtained by taking the principal axis of the calcite crystal as the axis of the fibre, and by considering that the axis of the fibre and the photographic plate are both perpendicular to the incident x-rays. The positions of the bands and the spots on the photograph are shown in the figure. The agreement between the observation and the calculation

1 W. L. Bragg: Roy. Soc. Proc., **105**, (1924)
2 T. Fujiwara: Mem. Coll. Sci. Kyoto, A. **8**, (1925)

may be easily seen in this figure. The reason why the bands and the spots due to the atomic plane (111) appeared on the photograph, has already been stated; and the theoretical curve corresponding to this atomic plane is omitted in the figure.

In conclusion, the writers' hearty thanks are due to Prof. U. Yoshida for his kind guidance in this research, and the writer also expresses his sincere thanks to Mr. J. Tsutsumi for his various suggestions.

Plate I.

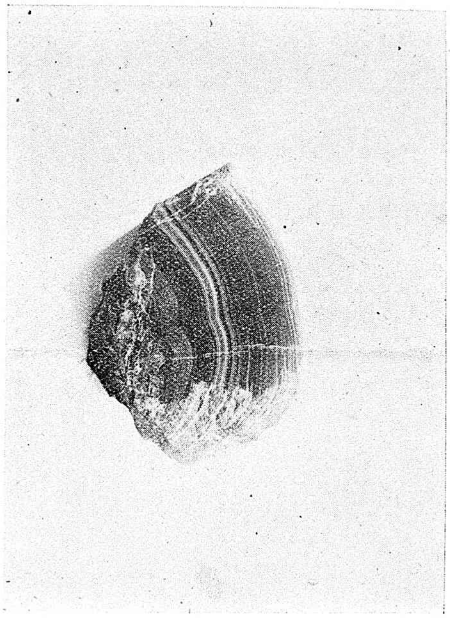


Fig. 1

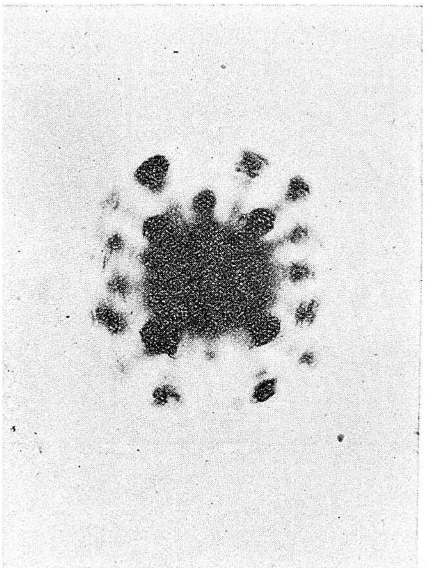


Fig. 3

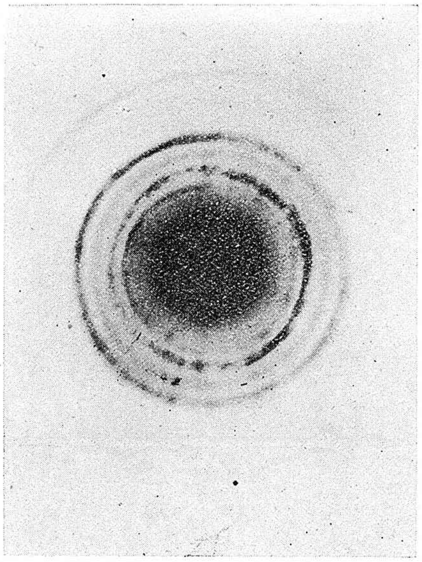


Fig. 2