52. *Arrangement of Micro-Crystals of Calcium Carbonate in Some Fossil Shells,* Glycymeris yessoensis SOWERBY.

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It is attempted to study the arrangement of micro-crystals of calcium carbonate in the fossil shells of *Glycymeris yessoensis* SOWERBY by means of X-rays. These fossil shells can be found in Japanese Islands in each of the successive geological formations beginning with Miocene up to the recent. Following seven specimens from different geological formations were examined; (1) Recent, (2) Upper Pleistocence, Susui, Tiba, (3) Lower Pleistocene, Honda, Tiba, (4) Upper Pliocene, Sanukimati, Tiba, (5) Lower Pliocene, Yasuda, Akita, (6) Lower Pliocene, Nagaya, Kanazawa, and (7) Miocene, Kenomaigawa, Hidaka.

Experimental.

It is revealed under microscope that these shells consist of three layers a, b and b' generally, each comprising fine stratifications, as shown in Fig. 1 and the relative thickness of the layers is modified to some extent for different parts of the shell.

A fine beam of X-rays is sent in the direction perpendicular to the specimen cut in the plane perpendicular to the shell surface through its central axis and the diffraction pattern is obtained on the photographic plate placed behind the specimen. The pattern is also obtained in the same way with the specimen cut in the plane parallel to the surface of the shell.

For producing X-rays, a metal tube equipped with copper-anticathode is used. Besides Cu-K radiation, a certain amount of W-L radiation is contained in the X-rays which is due to tungsten sputtered on the anticathode. In the present experiment, however, there is no difficulty in determining whether a certain diffraction ring or spot is due to Cu-K or to W-L.

The degree of dispersion of fibrous arrangement.

It is ascertained from the examination of the X-ray diffraction figures thus obtained that calcium carbonate in the shell of *Glycymeris yessoensis* SOWERBY is in the form of micro-crystals of aragonite and also that they are arranged in fibrous structure, the axis of which being in the direction perpendicular to the stratifications for each layer a, b or b' respectively, while the c-axis of the orthorhombic lattice of aragonite agrees in average with the axis of the fibre. It is to be noticed here that each diffraction spot is elongated along the circular arc with respect to the centre of the diffraction figure as shown in Fig. 11, which is a schematical sketch of the most prominent diffraction pattern due to (021) planes of aragonite lattice. This elongation indicates that a certain amount of fluctuations exists in the orientations of the c-axis of the aragonite lattice in the fossil shells. Thus, the degree of dispersion of these fibrous arrangement, i. e., the range of angle Φ, which the c-axes of aragonite crystals subtend with the axis of fibre (Fig. 12), is estimated for each fossils shells examined and are tabulated in the accompanying table.

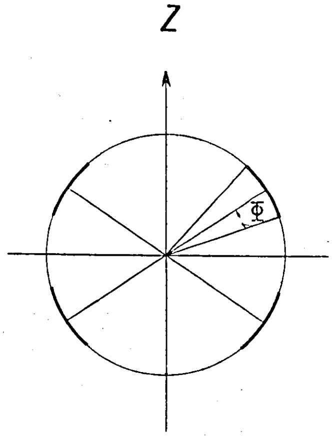

Fig. 11.
Z: Direction of the normal to the stratification.

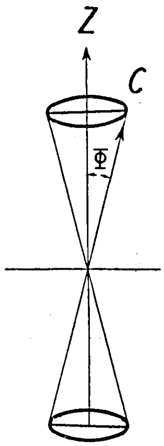

Fig. 12.
Z: Axis of fibrous structure.
C: C-axis of aragonite.

Table I.

Geological epochs and localities	Degree of dispersion of fibrous arrangement, Φ			I. (Middle layer)
	Inner layer	Middle layer	Outer layer	
Recent St. 645.	9°	8·5°		s
Upper pleistocene Du I, Susui, Tiba.	15	7·5		s
Lower pleistocene Honda, Tiba.	15·8	23		w
Upper pliocene Sanuki, Tiba.	22·5	11·5		ms
Lower pliocene Yasuda, Akita.		13	28°	m
Lower pliocene Nagaya, Kanazawa.		22	31·5	w
Miocene Kenomaigawa, Hidaka.		33	35	w

I: Intensities of the diffractions with smaller angles.
s, strong; m, medium; w, weak.

It is clearly seen that Φ becomes larger as the shell becomes older in geological age. The specimen from Honda which has an extraordinary large value of Φ may be looked upon as exceptional.

The diffraction figure of the shell of Miocene, Hidaka, shows quite different features in comparison with those of other ones (Fig. 9, Fig. 10). A number of discrete Laue-spots are superposed which are due to single crystals of comparatively large dimensions, the largest one of which observed under nicol-microscope being as large as 0·5 mm in diameter. It is also remarkable that some traces of stratifications are kept still distinctly in this Miocene shell (Fig. 3, Fig. 4).

Diffractions with smaller angles.

There are some prominent diffractions with smaller diffraction angles, especially for the middle layer of the shell. They correspond to the molecular periodicity of about 8·4 Å in the direction perpendicular to (021) plane of aragonite crystal, and may probably be due to some biocolloidal matter deposited on the grain boundary of micro-crystals of aragonite in the course of growth of the shells. These diffractions with the smaller angles diminish in intensitiy as the shell becomes older as shown in the last column of the Table I.

Discussion.

In connection with the results described above, the following alternative explanations may be proposed.

First, it may be considered that the degree of dispersion of fibrous arrangement in *Glycymeris yessoensis* SOWERBY from different geological formations had been different in their original living states, or in other words, these fossil shells had not suffered any serious change so far as the arrangement of micro-crystals are concerned in spite of the long geological aging. Dr. Jinzo Tsutsumi[1)] examined the arrangements of calcium carbonate for a number of different species of living moluscan shells by means of X-rays and showed that the micro-crystals of calcite or aragonite are in fibrous arrangement, the degree of dispersion of which being a characteristic property for each species. In the present case, therefore, it may not be quite absurd to make such an assumption described above, although without any positive proof.

If we assume next, that the structure of the shells had been the same initially, then the observed changes in the diffraction figures may be looked upon as the effect of aging which the shells had suffered.

1) J. TSUTSUMI: *Memoirs Coll. Sci., Kyoto Imp. Univ.*, [A], **12** (1929), 199.

The shell has not an isotropic structure, but has distinct stratifications as shown above and the elastic properties should, accordingly, be different for different directions. Thus, if the shell with such a structure be put under external stresses, the heterogeneous strain will be developed within it even if the stress be hydrostatical. It is well known that when some polycrystalline metal sheet such as one of alminium is rolled, rearrangements of micro-crystals take place, with the result that a certain axis of the crystal lattice is arranged fibrously in the direction parallel to that of rolling. In the course of aging of fossil shells, nearly the same process of rearrangement of micro-crystals may take place.

There is still another possibility for explaining the rearrangement of micro-crystals in the shells even if any sensible effect of external stress had not existed; namely, if some reagent existing in the boundaries of micro-crystals that is capable of restricting the orientation of each of the micro-crystals to assume the fibrous arrangement, be lost gradually with time, then some disturbances may be expected to occur in the initial fibrous structure. The diminution in intensity of the diffraction with smaller angles described above may be in good accordance with these views. Recrystalizations may also be taken into account, such as seen in the shell of Miocene.

At any rate, it seems to be interesting that, at least with the shells examined in this paper, the age of the geological formations from which they are collected can be roughly estimated by means of some physical method.

The authors express their sincere thanks to Professor T. Terada for his kind suggestions and criticisms on this work, and also to Dr. Y. Otuka who placed the specimens of the fossils examined at our disposals.

52. エゾタマキガヒの化石介殼内に於ける微結晶の配列

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エゾタマキガヒの化石は最近の各地質時代の地層から得られるので，我々は其の介殼の中の微結晶の配列が化石の古さによつて如何に變化するものであるかを X-線によつて調べたのである．調べた標本は

（1） 現　代
（2） 上部洪積統（千葉縣酒々井）
（3） 下部洪積統（千葉縣瑿田）
（4） 上部鮮新統（千葉縣佐貫）
（5） 下部鮮新統（秋田縣安田）
（6） 下部鮮新統（石川縣長屋）
（7） 中　新　統（北海道慶能舞川）

からのものである．

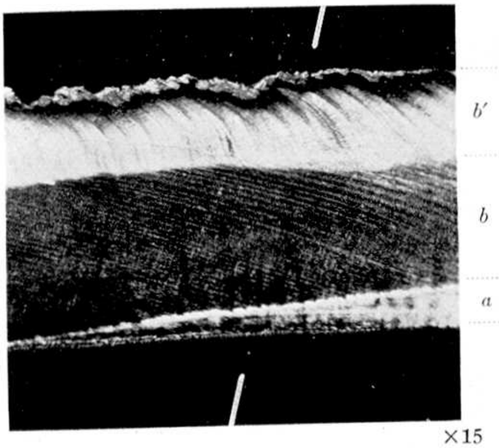
先づ顯微鏡下で見ると Fig. 1 の樣に介殼は一般に 3 つの層よりなり，その各々にこまかい縞がある事が解る．

用ひた X-線は Cu-K 線であるが，對陰極に着いてゐるタングステンによる W-L 線も少しは混じて居る．然しこれは邪魔にはならない．X-線寫眞は Fig. 5～Fig. 10 に示した通りのもので，これによつて此の介殼の中では各層ともに，霰石の微結晶が集つたものであつて，其の C 軸が前述の縞目に略垂直に揃つて並んでゐる所謂纖維構造をなしてゐる事が解つた．但し寫眞で見られる樣に X-線廻折像は圓弧に沿つて延びて居るが，之は Fig. 12 に示した通り C 軸の方向に Φ だけの不同がある事を示すのである．Fig. 11 の如くにして此の Φ を寫眞から讀み取り表にしたものが Table I である．表で明らかなる樣に Φ の値は古い化石程大きくなつて居る．換言すれば纖維構造の規則正しさが次第に失はれて行くのである．

尙注意すべきは，霰石による廻折像以外に中心點近くに別の廻折像がある事で (Fig. 6)，これは 8·4Å と云ふ大きい間隔を持つた格子面に相當するから恐らく霰石の微結晶の間にある何等かの Biocolloid に由來するものであらう．此の廻折像の强度は古い化石程弱い．

以上の事柄を說明するには色々な方法があらう．第一に今日化石として產するエゾタマキガヒは，それが生きてゐた時から旣に微結晶の配列に於いて現生のものと違つて居たとしても差支ない．第二に斯樣な方向性を持つてゐる介殼が永い間地下に埋れて地壓を受けて居る間に微結晶の配列が變化して來ると云ふ事も考へられる．又第三には微結晶の間に何か Biocolloid があつて，その作用によつて微結晶が纖維構造を保つて居るのが，介殼の死後此の有機物質が次第に分解して仕舞つて微結晶の配列を束縛する事が出來なくなる爲，纖維構造の規則正しさが失はれて行くと考へても差支ない．この考は前述の中心角の小さい廻折像が地質年代と共に强度が弱くなる事ともよく協調する．

說明方法は何れにせよ，少くともエゾタマキガヒではその地質年代の古さが此の樣な物理的方法で，凡そ判定されるのは注意すべき事と思はれるのである．



×15

Fig. 1. Structure of the shell of recent. Between crossed nicols.

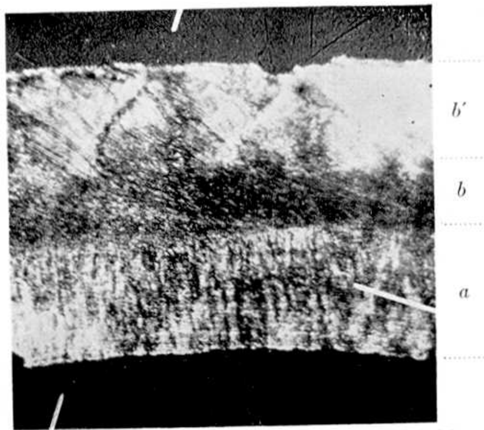


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Fig. 2. The shell of lower pliocene. Between crossed nicols.

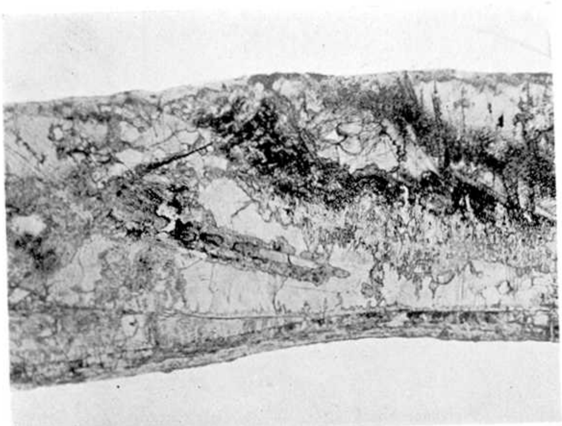

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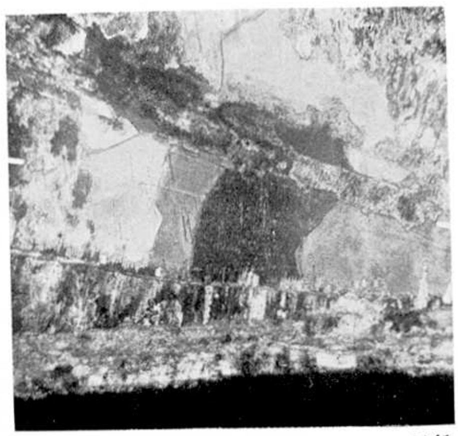
Fig. 3. The shell of miocene.



×41

Fig. 4. Single crystals developed in the shell of miocene. Between crossed nicols.

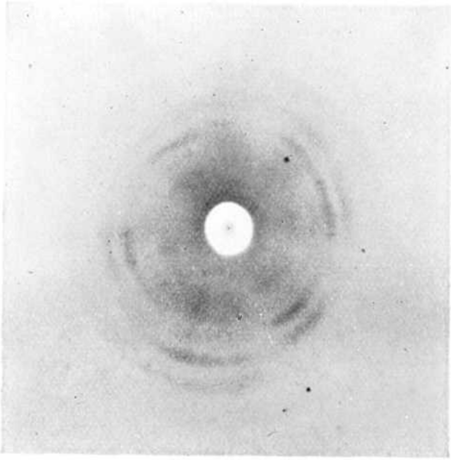


Fig. 5. Specimen 1. Inner layer.

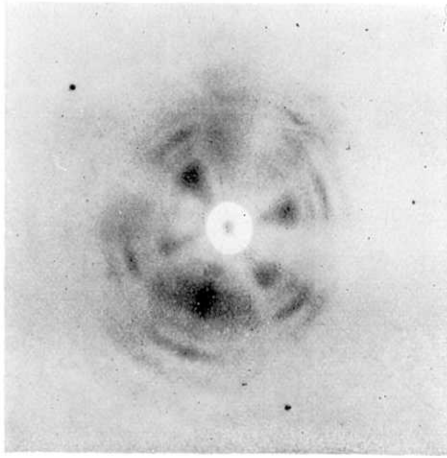


Fig. 6. Specimen 1. Middle layer.

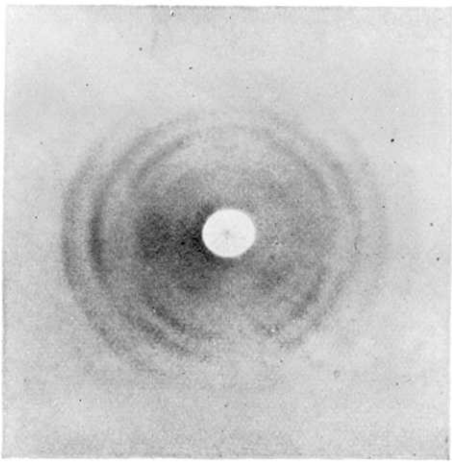


Fig. 7. Specimen 6. Inner layer.

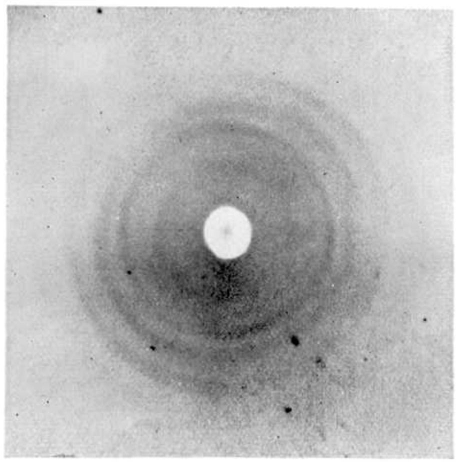


Fig. 8. Specimen 6. Outer layer.

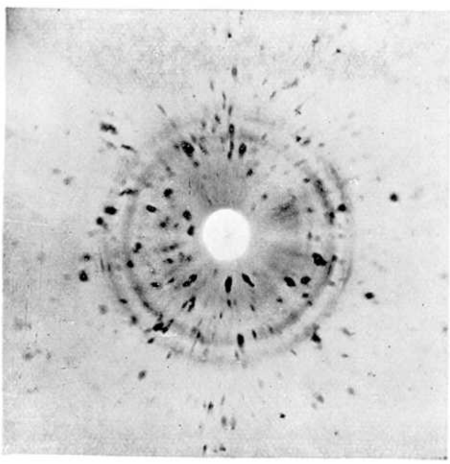


Fig. 9. Specimen 7. Inner layer.

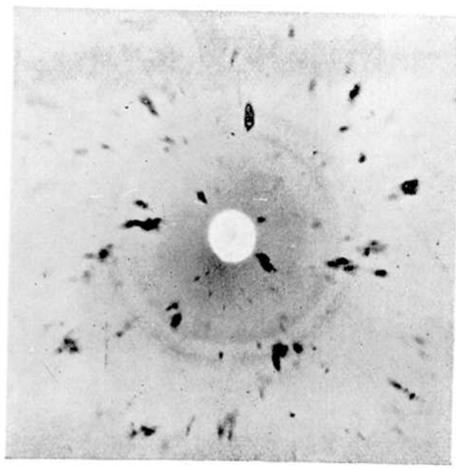


Fig. 10. Specimen 7. Outer layer.

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