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Twin density of aragonite in molluscan shells characterized using X-ray diffraction and transmission electron microscopy

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ABSTRACT

{110} twin density in aragonites constituting various microstructures of molluscan shells has been characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM), to find the factors that determine the density in the shells. Several aragonite crystals of geological origin were also investigated for comparison. The twin density is strongly dependent on the microstructures and species of the shells. The nacreous structure has a very low twin density regardless of the shell classes. On the other hand, the twin density in the crossed-lamellar (CL) structure has large variation among classes or subclasses, which is mainly related to the crystallographic direction of the constituting aragonite fibers. TEM observation suggests two types of twin structures in aragonite crystals with dense {110} twins: rather regulated polysynthetic twins with parallel twin planes, and unregulated polycyclic ones with two or three directions for the twin planes. The former is probably characteristic in the CL structures of specific subclasses of Gastropoda. The latter type is probably related to the crystal boundaries dominated by (*hk*0) interfaces in the microstructures with preferred orientation of the *c*-axis, and the twin density is mainly correlated to the crystal size in the microstructures.

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1. Introduction

Molluscan shells can be called “master” biominerals. Owing to their elaborated and regulated microstructures, molluscan shells attain extremely higher toughness against fracture than the same minerals of geological origin [1,2]. The crystalline phases of calcium carbonate forming molluscan shells are mainly calcite and aragonite. Calcite is thermodynamically the most stable phase at the ambient temperature and pressure [3], but aragonite is also common in many shells, though it has a stability field at a high pressure [4].

It is well known that geological, biogenic and synthetic aragonite crystals contain {110} twins [5,6] which are easily identified using polarized optical microscopy and, if the twins are microscopic, using transmission electron microscopy (TEM). Generally the crystal size of aragonite shells is so small that the observation of the twins has been performed mainly by TEM. The {110} twins were reported in various shell structures consisting of aragonite; in the crossed-lamellar (CL) microstructures [7–14], larval shells [15,16], ligament of shell [17], shell spikes [18], gastropod nacre [19], etc. mainly by using TEM. However, the twinning is not a ubiquitus feature in the aragonite shells. For instance, {110} twins are seldom in aragonite plates of the nacreous layer near the growth front of gastropod shells [20]. Accordingly, quantitative comparison of {110} twin density in aragonite may be informative to consider the formation mechanism of various shell microstructures. For this purpose, probably characterization by only TEM is not sufficient to obtain convincing, quantitative results because the areas observable in TEM are so limited. Recently we proposed a method to evaluate {110} twin density in aragonite from the peak widths of specific reflections in the X-ray diffraction (XRD) pattern and reported the results for several biogenic aragonite specimens [21]. According to computer simulation, existence of {110} twins influences unevenly the peak widths of individual reflections of aragonite. Conversely, the difference of the peak widths between specific reflections can be used to estimate twin density in the specimens. In this study, we focus on molluscan shells consisting of aragonite, estimate the twin

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density using XRD, observe the twin structures by TEM, and discuss the origins of {110} twins of aragonite in molluscan shells. Several geological aragonites were also investigated similarly for comparison.

2. Materials and methods

2.1. Aragonites of molluscan shells and of geological origin

Aragonites in molluscan shells were collected to cover various shell microstructures and classes in mollusks, including those investigated in our previous work [21]. They are represented in Table 1.

The CL structure is the most common microstructure consisting of aragonite and is adopted in four out of the six living molluscan classes (Bivalvia, Gastropoda, Polyplacophora and Scaphopoda). The nacreous structure with oriented aragonite plates is another common one, constituting the inner layers of shells of representatives of the classes Bivalvia, Gastropoda, Cephalopoda and, to a minor extent, Monoplacophora. In total nine and six species were analyzed for the CL and nacreous structures, respectively. Besides these two microstructures, the homogeneous structure, which forms the inner layer of several bivalve shells, the aragonite prismatic structure of the outer layer of *Anodonta*, and the myostracum of *Mizuhopecten* were investigated. Geological aragonite samples from various occurrences were selected from the collection of The University Museum, The University of Tokyo (Table 1). Besides, brown-colored large prismatic aragonite from Morocco, which is commercially prevalent, was selected as a geological sample.

2.2. Analyses of {110} twin density using XRD

Our previous study [21] demonstrated that the influence of {110} twins on the full width at half-maximum (FWHM) of reflection peaks in the powder XRD pattern is different among individual reflections. Reflections with hkl where $k \neq h$ or $k \neq 3h$ (as the aragonite crystal is orthorhombic, indices to be considered in powder XRD can be greater than or equal to zero) are significantly broader than those with hhl or hkl where $k=3h$. Hence the difference of FWHMs between hkl ($k \neq \neq h$ or $k \neq \neq 3h$) and $h'h'l'$ reflections (D-FWHM$_{hkl-h'h'l'}$) with close Bragg's angles can be a measure to estimate the twin density in the specimen [21]. We expect that other factors such as impurity elements like Sr or coherent domain size that influence FWHM can be almost ignored by taking the difference of FWHM for two reflections, if we select the two reflections sufficiently close in their 2θ positions. For this purpose, FWHM must be measured precisely, and reflections with a sufficient intensity and not overlapped by other reflections should be used. We selected two pairs of reflections, 021, 111 and 211, 221, in order to increase the reliability of the analysis. According to the simulation results described in the previous report [21], the value of D-FWHM$_{211-221}$ is expected to be twice that of D-FWHM$_{021-111}$ for a certain twin density.

The shells or aragonite crystals were crushed into powders using an agate mortar and a pestle. If the shells are multilayered with different microstructures, layers other than those of interest were removed using a router and a rotating file. The dimple of the holder made of glass was filled up with the aragonite powders for XRD. XRD patterns were collected using both a PANalytical X'Pert PRO MPD or a Rigaku RINT-2000 Ultima diffractometer system with a Cu X-ray tube, an Ni filter, and a silicon strip X-ray detector [22]. Consistency of the data obtained using the different diffractometers was confirmed by the measurements of the same sample; 0.5° divergence slit, 1° anti-scatter slit and 10 mm mask confining the beam width were adopted. A continuous scan rate of ca. 0.6–1.0° (2θ) min^{-1} was adopted in the 2θ regions containing the reflections of interest. The contribution of CuKα_2 to the measured patterns was subtracted using the programs attached to the XRD instruments with the assumption that the intensity ratio of CuKα_1 to CuKα_2 was 2:1. After the subtraction, the FWHM for the reflections was measured using a self-made program by which the peak height and 2θ positions at the half-maximum in the left- and right-sides of the peak were determined by fitting 5–10 data points around the three positions (the peak, left and right 2θ positions) to polynomial equations using the least-square method.

Table 1
The shell and geological samples investigated in this study.

Molluscan shells		
Microstructure	Class	Species
Crossed-lamella	Scaphopoda	*Fissidentalium metivieri*
	Polyplacophora	*Acanthopleura japonica*
	Gastropoda	*Cellana toreuma*
		Lottia dorsuosa
		Conus betulinus
		Coniglobus mercatorius
	Bivalvia	*Meretrix lamarckii*
		Glycymeris glycymeris
		Callista chione
Nacre	Gastropoda	*Haliotis discus*
		Turbo cornutus
	Bivalvia	*Pinctada fucata*
		Atrina pectinata
	Cephalopoda	*Nautilus pompilius*
Homogeneous layer	Bivalvia	*Meretrix lusoria*
		Yoldia eightsi
Prism	Bivalvia	*Anodonta cygnea*
Myostracum	Bivalvia	*Mizuhopecten yessoensis*
Geological aragonite		
No. or name	Morphology	Occurrence
70193[a]	Aciculum	Deposit from hot spring
70096[a]	Aciculum	Deposit from hot spring
70087[a]	Lath	Veins in serpentinite rock
70738[a]	Hexagonal prism	Limestone cave
70807[a]	Hexagonal prism	Volcanic origin
Morocco	Hexagonal prism	Unknown

[a] Collections of The University Museum, The University of Tokyo.

2.3. TEM observations

TEM specimens were prepared using a Hitachi FB-2100 focused ion beam (FIB) with a micro-sampling system or dispersing shell powder on a holey carbon film supported by a copper microgrid, depending on the purpose of the observation. TEM observation was performed using a JEOL JEM-2010 TEM operated at 200 kV. Most TEM images and selected-area electron diffraction patterns were recorded using a Gatan ES-500W side-mount CCD camera. SEM observation was also conducted for some specimens, using a Hitachi S-4500 scanning electron microscope with a field-emission electron gun operated at 2–5 kV. Pt–Pd film was coated to obtain electron conductivity.

3. Results

3.1. Evaluation of the twin density from XRD

Fig. 1 shows the differences of FWHMs between 021 and 111 reflections (D-FWHM$_{021-111}$), and between 211 and 221 (D-FWHM$_{211-221}$) for all specimens investigated. For several species two or three individuals were available and data from them were plotted in the figure to consider the variance by the individuals. As mentioned

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