論文内容の要旨

A study of fine structures of calcium carbonate crystals in mollusk nacre and their forming mechanism using FIB-TEM technique

（FIB-TEM 法を用いた軟体動物真珠層を形成する炭酸カルシウム結晶中の微細構造と形成機構に関する研究）

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Biominerals are produced as a result of the interaction between minerals and organic matrix, and often show interesting features which are not found in abiogenic minerals. They are widely found in nature, such as bone, teeth, shell, coral, fish otolith, etc. Among the biominerals, nacreous layer in mollusk shell has many unique properties in terms of mineralogical aspects, and a lot of studies about nacre have been carried out so far. This structure is composed of thin aragonite tablets intercalated with interlamellar organic sheets which are regularly spaced, and the *c*-axes of the aragonite tablets are always perpendicular to the lamination of nacre. At the growth front of gastropod nacre, aragonite tablets form a stacking structure, whereas the nacre of bivalve shows stepped surface and a brick wall structure. In this study, the nacre and fibrous aragonite layer which is the precursor of nacre were investigated. Particularly, I tried to clarify the detailed structure or growth mechanism of aragonite tablets in nacre. By using FIB-TEM technique, it was enabled to analyze specific regions in the shells.

An abiogenically synthesized aragonite crystal shows an acicular form elongated along the *c*-axis and expanded parallel to {110} twin planes (Fig. 1a). Concerning the fibrous aragonite layer in a gastropod, *Omphalius pfeifferi pfeiffer*, aragonite crystals nucleate at dimples formed on the outer calcite layer, and the *c*-axes of the aragonite crystals are gradually aligned perpendicular to the shell surface by the geometrical selections. Probably, the regulated crystal orientation of aragonite tablets in nacre is inherited from the fibrous aragonite layer. In the horizontal direction, a fan-like structure constituting this layer showed that many crystals are expanded radially from the center (Fig. 1b). Each crystal has twin relationship and is elongated to the twin plane. These mineralogical features are consistent with the abiogenic aragonite. In the fibrous aragonite layer of a bivalve, *Pinctada fucata*, similar feature was also observed (Fig. 1c).

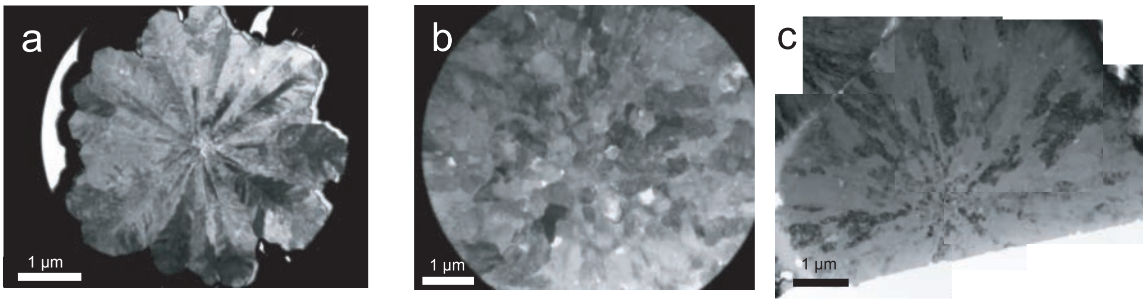

Fig. 1 Bright-field TEM images. (a) Cross section of acicular shaped aragonite crystal. (b, c) Plain-view specimens of fibrous aragonite layer in (b) a gastropod, *Omphalius pfeifferi pfeifferi*, and (c) a bivalve, *Pinctada fucata*.

On the other hand, the plain-view TEM observations commonly showed that a tablet in the nacreous layers of gastropod and bivalve is composed of a single crystal or several sectors separated by low angle grain boundaries (Figs. 2a and b). Electron diffraction acquired from these tablets basically showed single crystal patterns, and {110} twins are rare. Such mineralogical feature is different from abiogenic or other biogenic aragonite, for instance, that is the fibrous aragonite layer, shown in Fig. 1.

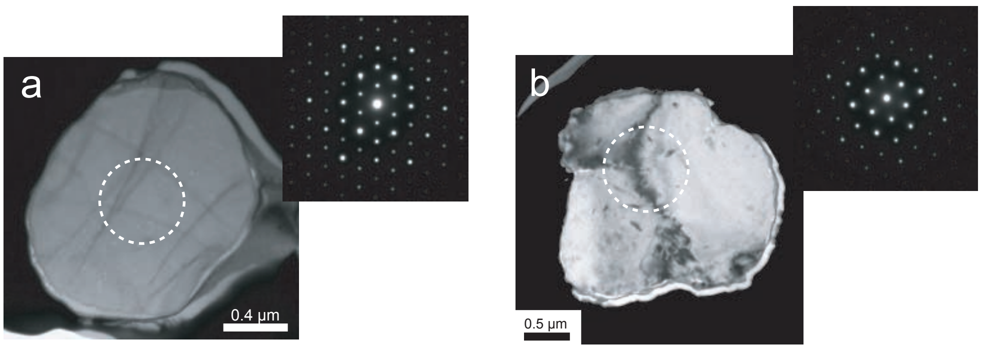

Fig. 2 TEM images of tablets in a gastropod, *Haliotis discus hannai*, and electron diffraction patterns acquired from the circles, respecitively. (a) An elliptical shaped tablet, and (b) a distorted shaped tablet separated by low angle grain boundaries.

Moreover, at the initial stage of formation of a tablet in a gastropod, *Haliotis discus hannai*, one to a few seed crystals were observed at the top of the stacking structure (Fig. 3a). Analysis by TEM clarified that each seed crystal is connected with the underlying tablet through a large hole of the interlamellar organic sheet (Figs. 3b-e). In nacre of a bivalve, *P. fucata*, seed crystals located around the boundaries between the underlying tablets are also connected by the holes. Hence, it is understood that an aragonite tablet in gastropod and bivalve nacre is formed from these one to a few seed crystals, which probably reflect the number of the sectors. The location of the holes of the interlamellar organic sheet may differentiate the growth process of nacre between gastropod and bivalve. Probably, the less twin structure of tablets originates from the process that fibrous aragonite layer containing high density of twins passes through the hole of the interlamellar organic sheet. As a future subject, it is needed to investigate the mechanism of how the holes in the interlamellar organic sheet are produced accurately at the specific regions of the nacreous structures.

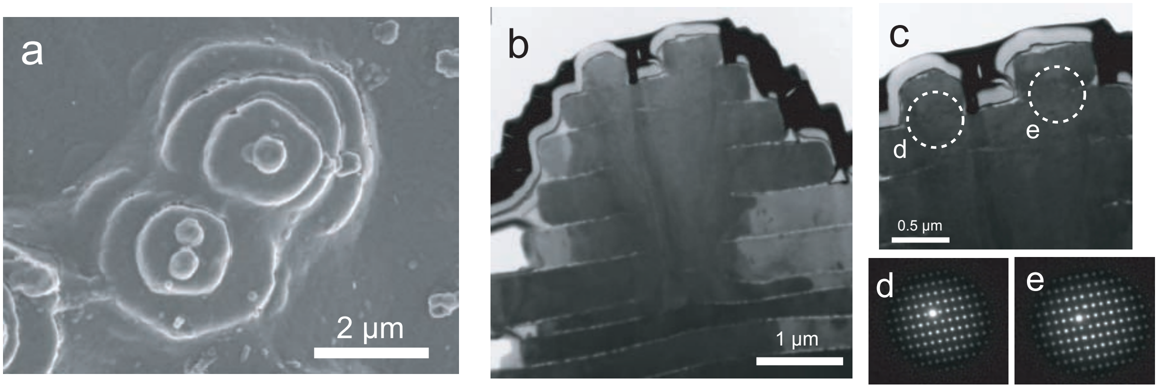

Fig. 3 (a) SEM image of stack structures in a gastropod, *Haliotis discus hannai*, having seed crystals at their tops. (b) TEM image of cross section of a stack having two seed crystals. (c) Magnified TEM image of cross section in (b) around the top. (d, e) Electron diffraction patterns acquired at the circles in (c).