

論文の内容の要旨

Study of biogenic calcite regulated by intracrystalline organic molecules (結晶内有機分子に制御された生物起源 カルサイトに関する研究)

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Biogenic mineralized tissues, biominerals, contain not only inorganic constituents but also an organic phase, which contributes to their superior properties to geological minerals. Such biominerals as organic–inorganic composites have been attracting a lot of attention for potential applications to functional materials over the decades. The organic phase in biominerals can be classified into *intercrystalline* and *intracrystalline* organic molecules (abbreviated as OMs in this study), both of which play important roles in biomineralization processes. Compared with the intercrystalline OMs, the intracrystalline OMs have been scarcely investigated because of the difficulty of dealing with them. Here I show that intracrystalline OMs induce defect-rich microstructures in calcite crystals constituting outer layers of mollusk shells, mainly by using recent electron microscopic techniques. Although geological calcite readily cleaves owing to its intrinsic crystal structure, biogenic calcite overcomes this mechanical weakness by

occluding OMs inside crystals. Elaborate interaction between crystals and intracrystalline OMs invests the distinctive characters of biogenic calcite.

First, the prismatic structures of two bivalve shells, *Pinctada fucata* and *Atrina pectinata*, were crystallographically inquired. Scanning electron microscopy observation revealed the existence of membranous and net-like OMs that are insoluble in ethylenediaminetetraacetic acid, inside the prisms of *Pinctada*. The insoluble OMs were observed as bright Fresnel contrasts in under-focused transmission electron microscopy images, which were confirmed as organic phase by electron energy-loss spectroscopy. Defect-rich sub-grain structures with small-angle misorientation are induced by the insoluble OMs, which results in gradual orientation change over the crystals. Furthermore X-ray diffraction measurements demonstrated that great local lattice strain is caused by the defect-rich structure. In contrast, the insoluble OMs in *Atrina* are shaped like thin fibers and have no influence on the crystal structure. Consequently the calcite crystals of *Atrina* exhibit a defect-free single-crystalline feature.

I also analyzed the calcite crystals in the outer layers of other bivalve (*Pteria penguin* and *Crassostrea nippona*) and gastropod shells (*Haliotis discus hannai* and *Collisella dorsuosa*). Both bivalve and gastropod shells have a defect-rich structure similar to *Pinctada*, which is generated by reticulated organic membranes. Nanoindentation tests indicated that the defective microstructure contributes to inhibiting the propagation of cleavages along {104} planes of calcite, implying that diverse mollusks improve the mechanical strength of their shells owing to the defect-rich structure.

In previous studies, synthetic calcite crystals are monolithic single-crystalline

even though insoluble OMs are incorporated into the crystals. Hence I examined the influence of intracrystalline soluble OMs on crystal microstructure. Calcite crystals were synthesized *in vitro* in the presence of soluble OMs extracted from the prisms of *Pinctada* and *Atrina*. The resulting crystals containing the soluble OMs from *Pinctada* displayed a defective structure, whereas the crystals contain few defects in the case of the OMs from *Atrina*. These results are comparable with the characters of actual shell structures. Therefore it is concluded that not only insoluble OMs but also soluble OMs participate in forming the defect-rich structure.

On the basis of these results, I propose the following mechanism by which intracrystalline OMs regulate the microstructure of calcite crystals constituting outer layers of mollusk shells (Figure).

1. An organic framework is constructed by insoluble OMs, which include not only intercrystalline OMs but also subsequent intracrystalline OMs. Intercrystalline and intracrystalline OMs are typically shaped like thick sheets/walls and thin membranes/networks, respectively.
2. Soluble OMs are bound to the framework of insoluble OMs.
3. Calcite crystals are formed inside the framework, as the soluble OMs interact with crystals.
4. The intracrystalline OMs are incorporated into the crystals, which causes small-angle misorientation and generates a defect-rich structure.

The defect-rich structure induced in the crystals improves the mechanical properties of biogenic calcite by inhibiting propagation of cleavages. Such understanding of the

formation mechanism of the organic–inorganic composite biominerals gives hints for manufacturing structural materials at low cost.

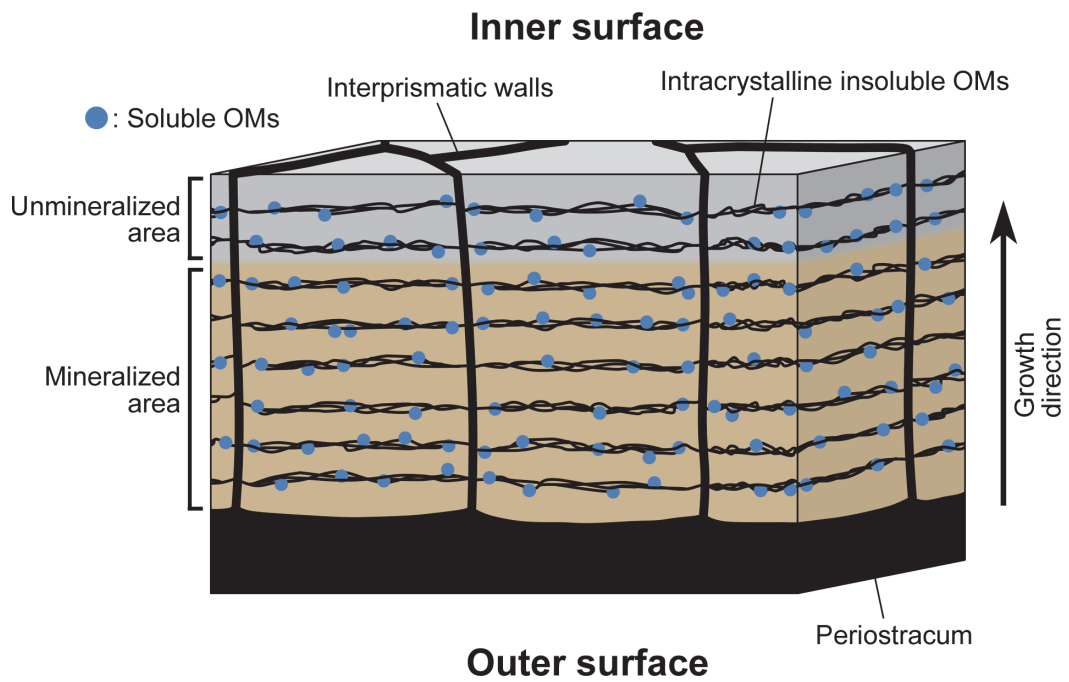


Figure. Schematic illustration of the prismatic structure, showing the mechanism by which intracrystalline OMs regulate the microstructure of calcite crystals constituting outer layers of mollusk shells. Soluble OMs are bound to the intracrystalline insoluble OMs and affect the crystal growth and structure.