Biomineralization of sea urchin teeth

Yurong MA (✉) and Limin Qi

Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry, Peking University, Beijing 100871, China

The sea urchin tooth, which is composed almost entirely of Mg-enriched CaCO₃, is of particular interest as a model for the study of biomineralization process due to its amazing mechanical toughness and hardness. Our recent work on the formation process, the crystal composition and orientation, and the mechanical properties of sea urchin tooth are summarized in this paper. First, transmission electron microscopy images and electron diffraction patterns, as well as crystal overgrowth experiments, show that the highly convoluted primary plate-lamellar needle complex grows into a single crystal of calcite from a transient amorphous precursor phase in the sea urchin tooth. Amorphous calcium carbonate exists in the center of both the primary plates and the needles, even though the surfaces are already well crystallized. Second, X-ray photoelectron emission spectromicroscopy demonstrates that the needles, primary plates, and polycrystalline matrix crystals are all aligned. And there are two alternating crystal orientations in the stone part of the sea urchin tooth. Microbeam X-ray diffraction patterns further prove the existence of the two crystal orientations in sea urchin tooth. The c axes of calcite in the two oriented crystals are only a few degrees from each other. Third, the mechanical properties of sea urchin tooth grinding tip were studied by nanoindentation. The polycrystalline matrix has a higher elastic modulus and hardness than single crystalline needles and plates. It is proposed that the grinding capability of the tooth can be attributed to the small and uniform sizes of the polycrystalline crystals, their high Mg contents, and the two co-orientations of single crystals and polycrystalline structure. The improved understanding of the biomineralization process of sea urchin tooth and the relations between their structures and mechanical properties may shed light on the design of mechanical grinding and cutting tools with tunable properties.

Keywords sea urchin tooth, biomineralization, high Mg calcite, amorphous precursor, crystal orientation

1 Introduction

Biomineralization is the process by which living organisms secrete inorganic minerals in the form of skeletons, shells, teeth, bones, etc. [1–4]. The biomineralization processes in nature have produced a lot of delicate biominerals with complex morphologies in several hierarchical levels and may thus own superior optical, electric, magnetic, and mechanical properties. The ability of the sea urchin tooth to grind down limestone is one of the most amazing paradigms in the field of biomineralization since both the tooth and the rock are composed almost entirely of calcite. Sea urchin has been an important experimental model for over a century, and vertebrates share many specific features of embryonic development with sea urchin. There is a special issue on the sea urchin genome on Science in 2006 [5]. The impressive ability of sea urchin tooth is certainly related to the structure of the whole tooth and especially the organization of the materials that make up the mature end, that is, the grinding tip of the tooth. The sea urchin tooth has been investigated extensively in order to understand the unique structural
features that enable it to function so effectively as a grinding tool in the past 60 years [6–13]. The major structural elements of the sea urchin tooth are single crystalline primary plates and needles composed of low Mg calcite (5–13 mol% Mg) and Mg-enriched calcite (40–45 mol% Mg) polycrystalline matrix confined to the stone part of the tooth. The latter has higher hardness and elastic modulus and is located in its central part, which is right at the grinding tip [9]. The polycrystalline matrix calcite crystals are enriched with very high percent of Mg, and thus, they were referred to as “protodolomite” [14], even though the structure corresponds to disordered Mg calcite.

Generally, the investigation on the biomineralization of sea urchin teeth involves the roles of proteins played in the mineralization, the mineral deposition process during the mineralization, and the structural and mechanical characteristics of the teeth. Since the biomineralization process is strongly related to the proteins in the biominerals, Veis et al. have done a lot of work on the extraction, purification, and analysis of the proteins in the sea urchin tooth in the recent years [8,11,13,15]. Mann et al. identified 138 proteins in the matrix of tooth powder, which is the most comprehensive list of sea urchin tooth matrix proteins available at present [16]. Other than the studies on the proteins in the tooth, the mineralization process, and the structural analysis are also very important parts in the biomineralization of sea urchin tooth. It has been shown that the plates and needles in the sea urchin tooth are being all aligned such that a whole tooth behaves like a single crystal based on X-ray diffraction [7] or as two crystals with a small angular offset based on polarized light microscopy [6]. Many questions concerning the nucleation, the crystal growth, and the orientation of the different single crystal needles and plates in sea urchin tooth still remain. Moreover, it is appealing to reveal what features of the tooth contribute to its superior mechanical properties as self-sharpening grinding tool. In this paper, our recent investigations on the mineral deposition process [17], the crystal composition and orientation [18], and the relations between the structures and the mechanical properties [19] of sea urchin teeth are reviewed.

2 Mineral deposition process [17]

The length of the plumula stage in the tooth of the sea urchin Paracentrotus lividus is about 4 mm. The plumula stage is arbitrarily divided into three stages: I, II and III. The three stages are schematically shown in Scheme 1, together with the main skeletal elements of the tooth. The plumula stage I, has a

Scheme 1 Left: A whole tooth. Middle: Schematic representation of the stages of growth of the sea urchin tooth. Arrows show the direction of observation at different growth stages from the forming tip at the plumula stages (I, II, and III) to the Shaft (IV). Right: The stages of formation of the major skeletal elements that make up the plumula (stages I, II, and III) and keel in the shaft (stage IV). PP: primary plate; LNC: lamellar needle complex. Figure was reprinted with permission from Ref. [17].