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Review

Biogenic and synthetic high magnesium calcite – A review ☆

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ABSTRACT

Systematic studies on the Mg distributions, the crystal orientations, the formation mechanisms and the mechanical properties of biogenic high-Mg calcites in different marine organisms were summarized in detail in this review. The high-Mg calcites in the hard tissues of marine organisms mentioned generally own a few common features as follows. Firstly, the Mg distribution is not uniform in most of the minerals. Secondly, high-Mg calcite biominerals are usually composed of nanoparticles that own almost the same crystallographic orientations and thus they behave like single crystals or mesocrystals. Thirdly, the formation of thermodynamically unstable high-Mg calcites in marine organisms under mild conditions is affected by three key factors, that is, the formation of amorphous calcium (magnesium) carbonate precursor, the control of polymorph via biomolecules and the high Mg/Ca ratios in modern sea. Lastly, the existence of Mg ions in the Mg-containing calcite may improve the mechanical properties of biogenic minerals. Furthermore, the key progress in the synthesis of high-Mg calcites in the laboratory based on the formation mechanisms of the biogenic high-Mg calcites was reviewed. Many researchers have realized the synthesis of high-Mg calcites in the laboratory under ambient conditions with the help of intermediate amorphous phase, mixed solvents, organic/inorganic surfaces and soluble additives. Studies on the structural analysis and formation mechanisms of thermodynamically unstable biogenic high-Mg calcite minerals may shed light on the preparation of functional materials with enhanced mechanical properties.

1. Introduction

Many organisms can form functional materials with amazing mechanical properties by combining inorganic minerals with organic macromolecules in complex hierarchical micro- and nano-structures (Meyers et al., 2008). Mg is a very common additive in biogenic carbonate and phosphate minerals. It has become customary to divide marine calcites into low- and high-Mg calcite based on a boundary of 3–4 mol% $MgCO_3$, which is representative of the least soluble Mg–calcite phase (Azmy et al., 2011; Carpenter and Lohmann, 1992, 1995; Chave, 1954; Mackenzie et al., 1983; Morse et al., 2006). High-Mg calcite crystals with Mg contents higher than 10 mol% are a thermodynamically unstable phase of calcium carbonate under ambient conditions (Raz et al., 2000). However, high magnesium calcites with magnesium contents varying from 4 to 45 mol% exist in many marine organisms such as foraminifera (Boussetta et al., 2011; Ries, 2010), echinoids (Berman et al., 1990; Chave, 1954; Pilkey and Hower, 1960), red corals (Finch and Allison, 2008; Floquet and Vielzeuf, 2012), red corallina algae (Floquet and Vielzeuf, 2012; Stanley et al., 2002), and calcareous serpulid worms (Neff, 1969; Tanur et al., 2010) in modern sea. The mechanical properties of Mg containing calcite biominerals are reported to be greatly enhanced in comparison to geologic calcite (Moureaux et al., 2010; Wang et al., 1997). The mechanical properties are strongly related to the Mg content in the minerals based on both the experimental results from synthetic (Kunitake et al., 2012) and biogenic Mg-bearing calcite minerals (Kunitake et al., 2013; Ma et al., 2008; Moureaux et al., 2010), and the theoretical calculations (Elstnerova et al., 2010).

Recently, Ries reviewed a series of experiments that explored the effect of seawater Mg/Ca ratio on the biomineralization of extant representatives of the marine calcifying taxa, animals, and bacterial biofilms (Ries, 2010). The Mg/Ca ratio of biogenic calcite of marine invertebrate organisms such as foraminifera and mollusk shells have been successfully used to determine seawater temperature due to the partitioning of Mg during calcification (Elderfield and Ganssen, 2000). On the contrary, it was proposed that the presence of a significant ontogenetic effect on Mg incorporation in foraminifera can potentially offset Mg/Ca-based temperature reconstructions (Duenas-Bohorquez et al., 2011; Groeneveld and Chiessi, 2011; Haarmann et al., 2011).

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A few key questions related to biogenic high-Mg calcites have attracted scientists' interests for a long time. How do marine organisms produce this kind of thermodynamically unstable phase under ambient conditions while the synthetic high-Mg calcite is often obtained under high temperature and high pressure? How do the organic molecules influence the Mg/Ca ratio in biominerals? What is the role of Mg in the biogenic high-Mg calcites? How to synthesize high-Mg calcite in the laboratory under ambient conditions? We would address these questions in this review. In comparison to Ries's review (Ries, 2010), we mainly focus on two parts: biogenic and synthetic Mg-containing calcites with high Mg contents. Organisms composed of low magnesium calcite such as Brachiopods (Cusack et al., 2008; Foster et al., 2008), isopods (Neues et al., 2007), decapods (Seidl et al., 2011), and mollusk (Dauphin, 1999; Freitas et al., 2009) with Mg contents less than 4 mol% will not be addressed in this review. Important research studies on some modern high-Mg calcite secreting organisms such as sea urchin and sea star (Echinodermata), coralline red algae (Rhodophyta), red coral (Octocorallia), calcareous sponges (Calcarea), and calcareous serpulid worms (Polychaeta), will be summarized herein. In the first part, we describe important research progress on the Mg distribution, crystal orientation, formation mechanism and mechanical properties of biogenic high-Mg calcites formed in marine organisms. In the second part, the preparation of high-Mg calcites under ambient conditions in aqueous solution or mixed solvents in the presence of soluble additives, on organic/inorganic surfaces, and via solid transformation process is summarized.

2. Studies on the biogenic high-Mg calcite minerals

2.1. Mg distributions in biogenic high-Mg calcites

In this part, we mainly emphasize the characterizations of biogenic Mg-containing calcites from Echinodermata such as

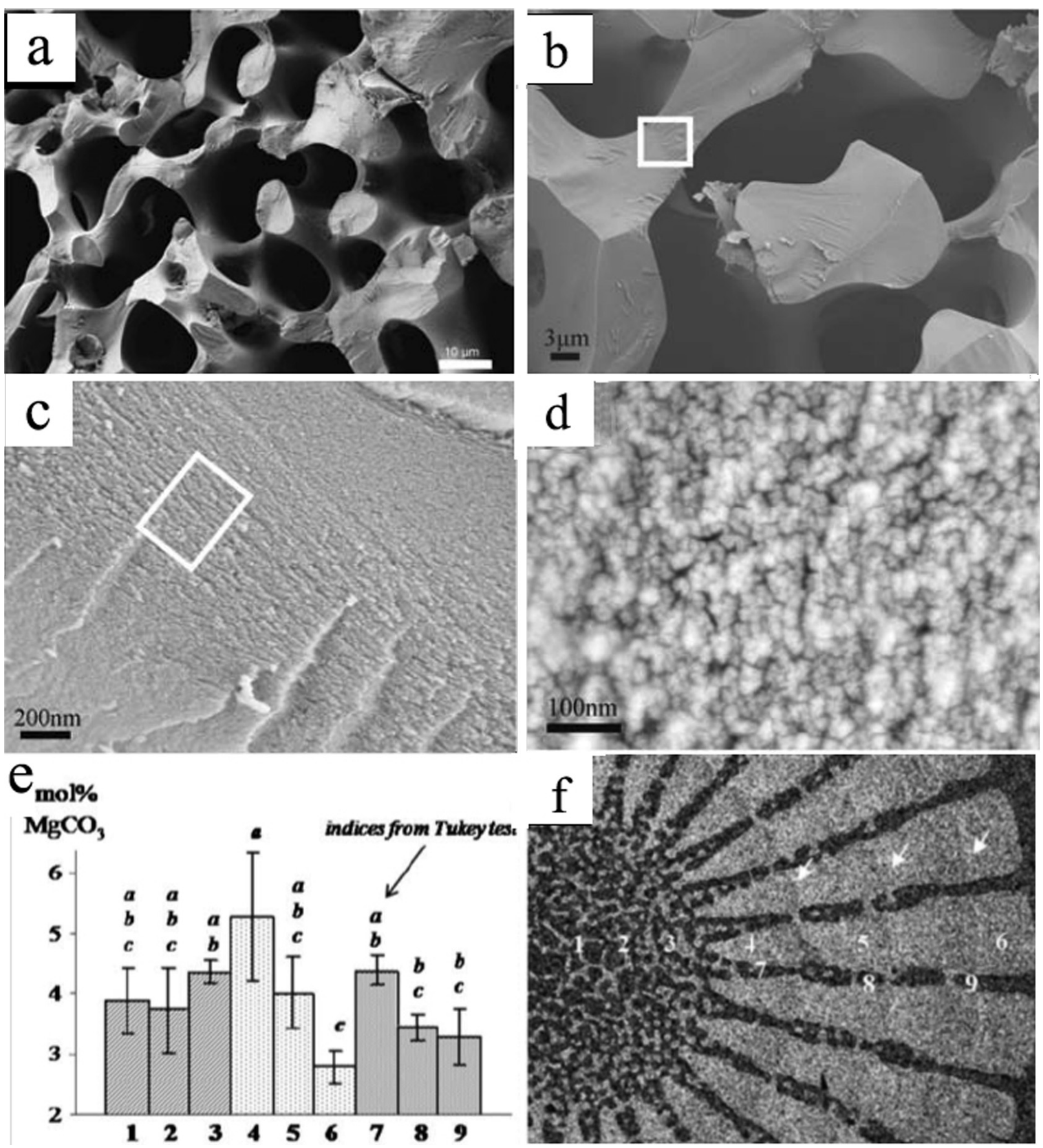

Fig.1. SEM images and EDX analysis for the transverse cross section of sea urchin spines. (a–d) Fracture surfaces of a sea urchin spine shown at different magnifications under SEM. (e, f) $MgCO_3$ distribution in transverse sections of *P. lividus* spine. (e) Mg concentration in transverse regions measured by EDX analyses, localization of analyses is indicated in (f). (f) EDX mapping of a transverse cross section of a sea urchin spine, 1–3: stereom; 4–6: septa; 7–9: transverse bridges. Reprinted with permission from (Moureaux et al., 2010; Seto et al., 2012).