Controlled morphogenesis of amorphous silica and its relevance to biosilicification

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ABSTRACT

Biogenic biosilica displays intricate patterns that are structured on a nanometer-to-micrometer scale. At the nanoscale, it involves the polymerization products of silica, apparently mediated by the interaction between different biomolecules with special functional groups. In this paper, using tetraethyl orthosilicate [TEOS, Si(OCH2CH3)4] as a silica source, phospholipid (PL) and dodecylamine (DA) were introduced as model organic additives to investigate their influence on the formation and morphology of silica in the mineralization process. Morphology, structure, and composition of the products were characterized using a range of techniques including FESEM, TEM, SAXRD, TG-DTA, solid-state 29Si NMR, FTIR, and nitrogen physisorption. The FESEM and TEM analyses demonstrate that increasing PL concentrations at constant DA content leads to the formation of siliceous elongated structures. Localized enlargement can also be observed during further growth of elongated structures, displaying some features of the earliest recognizable stage of valve development in diatoms. In addition, in the presence or absence of PL, a series of control experiments using ammonia instead of DA show that no elongated structures are obtained, suggesting that the formation of elongated silica structures results from the cooperative interactions between PL and DA molecules. Because both organic amines (e.g., long-chain polyamines, LCPA) and phospholipid membranes (e.g., silicalemma) are of special importance for biosilicification in diatoms and sponges, our results imply that phospholipids are involved in the formation of organic aggregates, and thus influence the amines-mediated silica deposition. As such, our results may provide a new insight into the mechanism of biosilicification.

Keywords: Biosilica, phospholipids, organic amine, biomimetic mineralization, biosilicification

INTRODUCTION

Biomineralization is a process by which living organisms produce organic/inorganic composites, often to harden or stiffen existing tissues (Lowenstam and Weiner 1989; Sigel et al. 2008). Approximately 80% of these organic/inorganic structures are crystalline (Weiner and Addadi 1997; Addadi et al. 2003). Silica (biosilica) is the second-most abundant constituent of biominerals after carbonate (Lowenstam 1981; Perry and Keeling-Tucker 2000), and biosilica always consists of glassy amorphous solid (Schröder et al. 2008). Biosilica has attracted much attention because of its unique morphologies and hierarchical structures, fascinating mechanical properties, and potential applications in many fields (e.g., Round et al. 1990; Sumpner et al. 2003; Sumpner and Brunner 2006; Losic et al. 2009).

Understanding biomineralization requires elucidation of the underlying cellular and molecular biological processes. It is especially important to determine how organic molecules (such as proteins, polysaccharides, and lipids) can be involved in the formation of specific mineral substructures. Phospholipids, often in the form of bilayer structures, have been commonly involved in natural biomineralization processes (e.g., Lowenstam and Weiner 1989). In particular, phospholipids as important membrane constituents of biological vesicles are commonly involved in delineating reaction compartments for the crystallization of biominerals (e.g., Gorby et al. 1988; Collier and Messersmith 2002; Bäuerlein 2003; Anderson et al. 2005). The isolation and structural determination of phospholipids from biosilicification organisms including sponges and diatoms have been reported (e.g., Djerassi and Lam 1991; Early et al. 1996; Genin et al. 2008; Ivanisevic et al. 2011). For example, the sponge cell membrane is unique in terms of its lipid diversity, and Ivanisevic et al. (2011) suggest that lysophospholipids could play an important role in sponge embryogenesis and morphogenesis. Phospholipid membrane was also found to surround hexactinellid spicules and delimit the confined space where silicification occurs (Uriz 2006).

Silica deposition in diatoms is also a membrane phenomenon. It occurs within a specialized compartment known as the silica deposition vesicle (Sumpner and Kröger 2004), whose membrane, called the silicalemma, consists of a typical lipid bilayer (Chippino and Volcani 1977; Bäuerlein 2003). In recent decades, various organic and biological molecules have been successfully separated and identified from cell-wall extracts of diatoms. Organic amines (long-chain polyamines, LCPAs) extracted from diatoms can induce in vitro precipitation of spherical silica particles under physiological pH conditions (Kröger et al. 2000). However, the spheres obtained in these biomimetic experiments are not seen in the smooth, elongated girdle bands or raphe of diatoms (Reimann et al. 1965). This means that additional factors must come into play to shape biosilica (Davis and Hildebrand...