Brachiopod shell biomineralization: Stuctural and chemical characteristics

W.W. SCHMAHL[1], E. GRIESSHABER[2], R.D. NEUSER[2], T. PETTKE[3] AND U. BRAND[4]

[1]Department für Geo- und Umweltwissenschaften, LMU München, Germany (Wolfgang.W.Schmahl@rub.de)
[2]Department of Earth Sciences, Universität Bochum, Germany (Erika.Griesshaber@rub.de)
[3]Isotope Geochemistry and Mineral Resources, ETH Zürich, Switzerland (Thomas.Pettke@erdw.ethz.ch)
[4]Department of Earth Sciences, Brock University St.Cathrines, Ontario L2S 3A1, Canada (uwe.brand@brocku.ca)

Magnesian calcites of biogenic origin play an important role in geochemical processes such as diagenesis, calcification, cement formation/dissolution and seawater chemistry. These hard tissues are advanced materials which can be adressed as multi-scaled (from nanoscale to macroscale) biological composites (inorganic matter and biopolymers), where inorganic processes (e.g. crystallisation of calcite and thus shell formation) occur through biological meditation.

We have investigated the ultrastructure and chemical composition of the modern calcitic brachiopods *Megerlia truncata* and *Terebratalia transversa* with SEM, EBSD, microhardness indentation and LA-ICP-MS. The outer, primary shell layer can be regarded as a nanocrystalline thin film that forms a hard protective coating around the inner, much softer secondary shell layer that can be expressed as an organic/inorganic fibre composite. While the hardness of the nanocrystalline layer gives a mechanical protection against abrasives, the fibre composite material provides elasticity to the structure. The fibrous, curved growth of he secondary shell layer crystals occurs in arbitrary directions perpendicular to the <0 0 0 1> triad symmetry direction of calcite and is kmost likely obtained by simple confinement to a protein sheath. The curvature of the fibres is caused by rearrangements of the secreting cell array during growth, whereby the existing crystal lattice is not distorted. Thus a biologically meditated calcite crystallization is a purposeful process and seems to be significantly different to the inorganic crystallization of calcite. A strong decrease in microhardness is accompanied by distinct change in chemical composition from the primary or the outermost part of the secondary layer towards the innermost portion of the secondary shell layer. Thus, our measurements show that chemical and structural inhomogeneity occurs even in mordern brachiopods.

Amorphous oligomer nucleation and aggregation mechanism for biomineralization

NITA SAHAI [1,2] AND KATYA DELAK[2]

[1]Department of Geology and Geophysics, 1215 West Dayton Street, University of Wisconsin, Madison, WI 53706, USA (sahai@geology.wisc.edu)
[2]Department of Chemistry, 1101 University Avenue, University of Wisconsin, Madison, WI 53706, USA (kdelak@geology.wisc.edu)

Among the distinguishing features of biominerals are their unique morphologies compared to their inorganically grown counterparts. The involvement of organic macromolecules is widely acknowledged, usually, in a template-directed mechanism. Epitaxial matching or stereochemical control is sought between the functional groups on the macromolecule and atom positions or crystal dimensions in the mineral, and may operates in the case of biogenic $CaCO_3$ growth [1]. Similar epitaxy may be more difficult to find in other biominerals such as hydroxyapatite in bones and teeth, and the biogenic amorphous silica of diatoms, sponges and radiolaria.

We present, here, an alternative mechanism for biomineralization. First, specific functional groups locally promote nucleation of amorphous oligomers. Multiple functional groups along the macromolecule then promote aggregation of the oligomers to form a solid phase that may, subsequently, undergo phase transformation to the final form if the ultimate biomineral is crystalline (e.g. bone-apatite).

We have examined biomimetic amorphous silica precipitation. We used ^{29}Si NMR to follow the kinetics of monoamine- and polyamine-catalyzed organosilicate hydrolysis and polymerization, and SEM to examine the amorphous silica morphologies produced. The amines represent the active portions of silica-precipitating enzymes. Results suggest that monoamines and polyamines promote organosilicate hydrolysis and polymerization via a S_N2 nucleophilic mechanism, where a hypervalent silicon reactive intermediate may exist [2, 3]. Subsequent silica oligomer aggregation is promoted by cooperative, steric effects of neighboring amine functionalities on the polyamines [2]. Aggregation is promoted by macromolecular conformation, without a strict requirement for epitaxial matching.

References

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