Polyaspartate as a stereochemical switch for controlling the growth and morphology of calcite

S. ELHADJ[1], E. SALTER[2], P.M. DOVE[1], A. WIERZBICKI[2] AND J.J. DE YOREO[2]

[1]Dept. of Geosciences, Virginia Tech, USA (elhadj@vt.edu, dove@vt.edu)
[2]Dept. of Chemistry, Univ. South Alabama, USA
[3]Dept. Chemistry and Material Sciences, LLNL, USA

The controlled synthesis of biominerals involves active constraints on growth processes that result in functional structures beyond what is possible by passive growth in inorganic systems. Using proteins as nucleation templates or growth modifiers, studies are largely aimed at understanding the crystal phase that forms, along with the resulting local and macroscopic structures. As a result, numerous studies show that proteins regulate the type of $CaCO_3$ polymorphs generated, as well as their morphologies and orientation. Effectiveness of these proteins can be linked to their peptide sequences and structures. However, the mechanisms by which primary and secondary protein structure characteristics affect crystal growth are only beginning to be understood.

Polyaspartate domains are a dominant feature of proteins associated with biogenic carbonates. These biomolecules are implicated in modifying crystal morphology through specific interactions with step edges. In this study we find that polyaspartates, Asp_n, introduced to solutions during calcite growth exhibit binding selection between obtuse and acute steps that is chain-length dependent. Shorter Asp_1 and Asp_2 favour interactions with acute steps while $Asp_{4,5,6}$ favour the obtuse. This crossover between Asp_2 and Asp_4 is expressed in differential roughening and rounding of the acute and obtuse steps as evidenced by *in situ* force microscopy images.

Using semi-empirical quantum mechanical modeling of polyaspartate-calcite binding energies, we independently determine that the crossover occurs at n=2 and is caused by a switch in the dehydration energy penalty of binding a given polyaspartate to acute versus to obtuse steps depending on its length. Step velocity measurements demonstrate that the linear increase in binding energy with aspartate chain length produces an exponential decrease in the aspartate concentration that gives complete growth inhibition. Using a step adsorption model, from fitted data, we find that complete inhibition of step growth is achieved for a fixed fractional coverage of step edges by all Asp_n studied here. Step rounding due to favourable changes in step interaction energies with Asp_n generates growth in new directions, enabling changes in hillock morphology. These findings suggest a mechanism by which primary structure in peptides may directly control crystal shape and point to role of solvation in controlling interaction energies.

Mechanisms of formation of plants bioliths

A.L. KOVALEVSKII[1], O.M. KOVALEVSKAYA[1] AND S.I. PROKOCHUK[2]

[1]Geological Institute, Siberian Branch of Russian Academy of Sciences. Ulan-Ude, Russia (koval@gin.bsc.buryatia.ru)
[2]Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences. Irkutsk, Russia (psi@igc.irk.ru)

Complex research of plants bioliths by physico-chechemical, chemical and mineralogical by methods let speak about some mechanisms of their formation. The main ones are accumulation processes of chemical elements on biological membranes, which are physiological barriers on migration ways of intercellular plants juice. In addition physico-chemical mechanisms of solution evaporation from surfaces have been established. The most intensive mineralization of plant tissue is connected with many-year evaporation concentration from porous medium to atmosphere through a surface of tree trunk barks and stumps The objects of our plants biomineralization research are different organs and tissues of pine (*Pinus silvestris*), common birch (*Betula platyphyla; B. verrucosa*), Dahurica and Siberian larch (*Larix dahurica*, *L. sibirica*), Siberian fir (*Picea obovata Ledeb*), Siberian fir (*Abies sibirica*), tremble aspen (*Populus tremulus*), goat willow (*Salix carpea*). The main are external loping layers of their trunk bark. These bioobjects are characterized by non-barrier accumulation, linear-proportionally to concentration in rootinhabited zone of some ore chemical elements forming "large" bioliths 50-500 µm suitable for research by general mineralogical methods. Au bioliths concentrations on the main biological membranes, which are separation borders between bark, bast and wood, have been established for all 7 investigated tree families wood plants in Siberia. The most important border is the xylem (sap-wood) separation surface, on which there is a rising flow from roots to leaves, and phloems (bast), on which there is a descending flow of solutions. Received data prove that enlargement of Au bioliths in wood and bark consisting of bast and bark is of different mechanisms. In bast and especially in bark Au particles fall out from chelated solutions and grow under conditions of evaporation concentration of microbioliths number on the borders: "alburnum – bast" and to a less extent "bast–trust bark". Adsorption mechanisms of less intensive radial flow, mainly mineral solutions from alburnum to trees ore are apparently to predominante in wood.