FORMATION OF CARBONATES TROUGH THE BIOMINERALIZATION PROCESSES: NANO- SCALE AGGREGATION ROUTE

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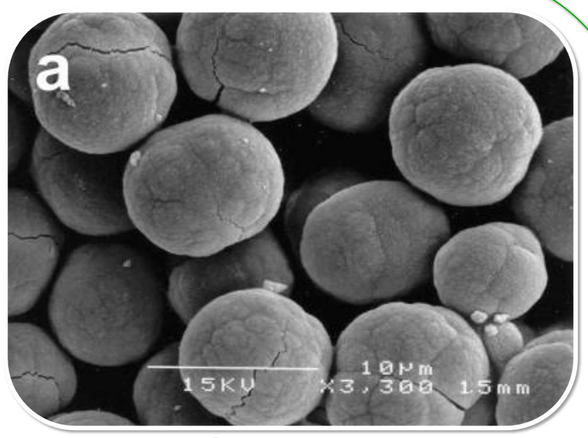
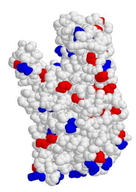
Introduction:
Different organic macromolecules play a significant role in initial crystallization and growth of carbonate solids. Several studies have shown that even the small differences in their amino acid sequence can govern the formation of different calcium carbonate polymorphs with unusual hierarchically organized morphologies. Two similar nano-aggregation processes are presented ; one involved in biomimetic formation of carbonates in a laboratory and another one in the formation of aragonitic stuctures of corals in nature.

CALCIUM CARBONATE BIOMINERALS IN NATURE:



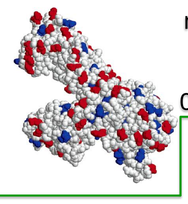
Calcite

Vaterite



Canavalia ensiformis

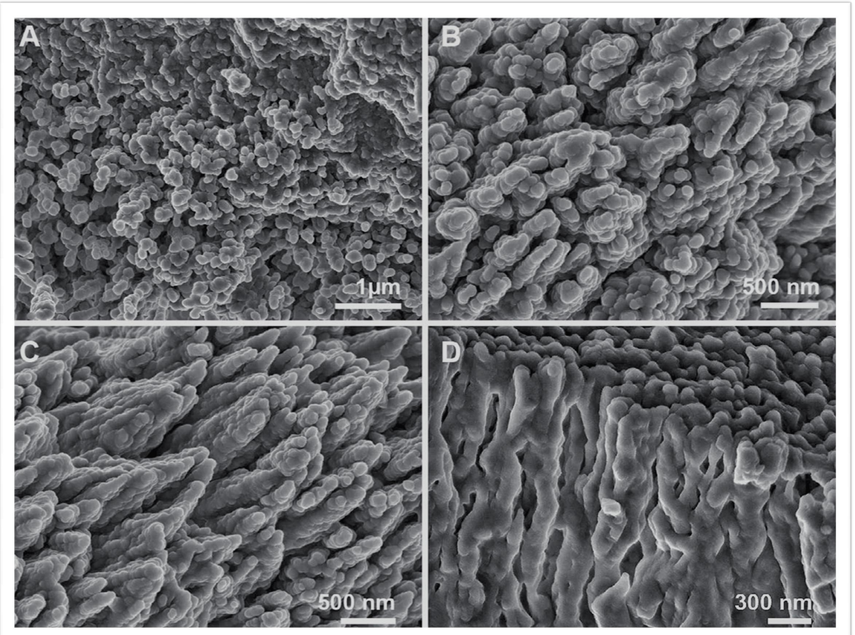
Bacillus pasteurii



The solution was aged under the same experimental conditions at 25 °C for 120 min. Solution contains 0.5 mol dm^{-3} urea, 0.2 mol dm^{-3} $CaCl_2$, and 0.5 g cm^{-3} urease from:

either

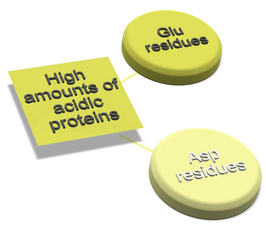
The difference in polymorphs may be explained with the properties of proteins involved in the process of biomineralization; they have various amounts of acidic amino acids with the rich carboxylic character (especially Asp and Glu acids) [1-3]. *Bacillus* urease has more acidic aminoacids: possible reason why its preferential polymorph is vaterite.

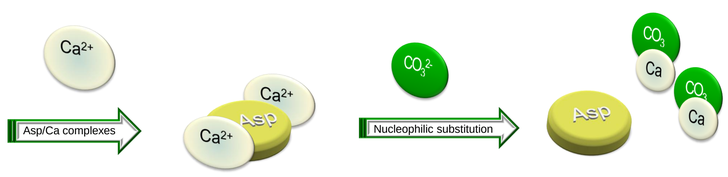


FESEM photomicrographs: different types of morphology on the septal unit surface within the calyx: submicrometre-sized, nearly spherical crystallites (A), transitional forms of elongated cone structures built up of submicrometre - sized particles (B,C), and elongated aragonite fibres (D). (Figure from [4]).

Coral *Cladocora caespitosa* has oriented, fine-scale growth of aragonite structures, organized in a hierarchical way. With the control of organic matrix, nanosized spherulites are formed in the centers of calcification; on that basis the small nanosized units gradually constructs aggregated and oriented cone-cluster assemblies which subsequently change their morphology because of the coalescence processes.

The later stages have both; spherulitic crystallites of nanoparticles and elongated fibers, with the transition phase of elongated aragonitic cones from sub-micrometer particles among them. Bioinformatic analysis showed that they have 35% of Asp and Glu amino acids; Ala and Gly are next most abundant amino acids with 15 to 40% of the amino acid content [4].



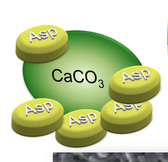


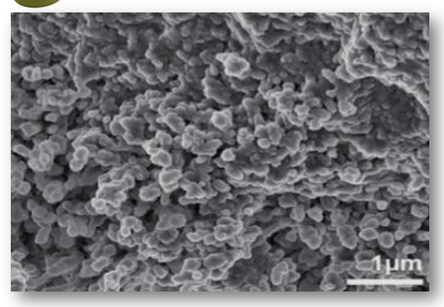
These complexes serve as an organic template and provide preferential sites for nucleation; they interact with carbonate precipitates from the surroundings and facilitate the formation and growth of crystals [1,4].

Carboxyl group of acidic amino acids can bond with Ca^{2+} and form Ca^{2+}/Asp or Ca^{2+}/Glu multi-carboxyl chelate complexes.

Limited growth of the crystal

NANO-SCALE AGGREGATION ROUTE

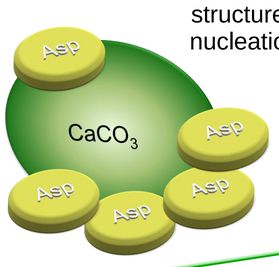




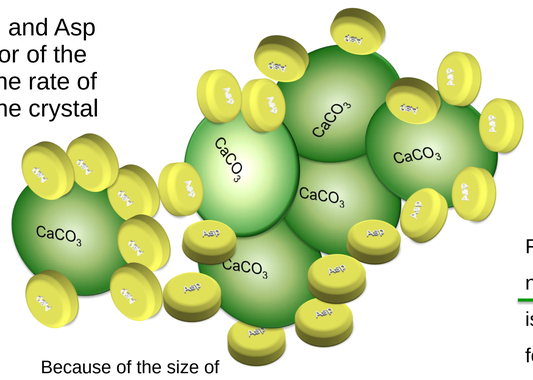
FESEM photomicrographs:

Morphology of the septal unit surface within the calyx: submicrometre-sized, nearly spherical crystallites

Porous vaterite forms and Asp serves as a stabilizator of the structure; it increase the rate of nucleation and limits the crystal growth.

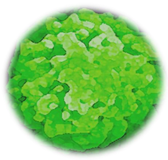


Fusion



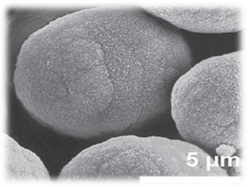
Because of the size of nanoparticles, interactions can be correlated with the ion interactions.

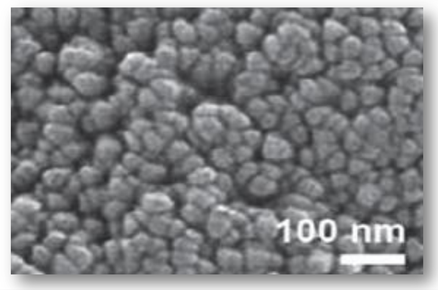
Particle aggregation and accumulation



Nanoparticles aggregate in clusters during the collisions = base for the submicrometar pseudospherical calcite growth.

Formed nanoparticles have negative surface charge that is transferred to the newly formed nanoclusters.





Vaterite particles obtained by the enzyme-catalyzed decomposition of urea by urease [6].).

In the process of nano - aggregation there are three major factors involved:
1. proteins that control the nucleation;
2. inhibition effects of ions on the solid compound growth;
3. hierarchical aggregation of nanoparticles.

*sheme adapted according to [5]

Vaterite is not the only factor that inhibits the growth of calcite; in the case of enzymatic decomposition of *Canavalia* urease if the solution contains proper concentration of magnesium ions it changes the thermodynamic conditions by interacting with calcite nanocrystals; there is a formation of transient amorphous calcium carbonate and inhibition of further calcite growth [1].

This research indicates that even a small change in the amino acid sequence or influence of diverse ions can signifficantly change final properties of biocrystals.

Conclusion:
The importance of nano - scale aggregation processes in the formation of biogenic and inorganic colloid – sized particles is obvious. Understanding these mechanisms sheds light on the non – conventional formation of carbonate mineral phases, a situation commonly encountered in natural systems.

References and acknowledgement:
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