The role of amino acids as simple models of organic matrix molecules participating in calcium carbonate biomineralization

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Introduction

Calcium carbonate is the main inorganic component of biominerals in most of invertebrate organisms. It appears either, in a form of specific polymorph (calcite or aragonite), hydrate or as amorphous phase. However, it was found that calcitic skeletal elements regularly contain small amounts of proteins which are either, incorporated or adsorbed onto the crystals. It has been shown previously that isolated fragments of proteins extracted from mineralised tissue, or their synthetic macromolecular analogues, exert a significant influence on the morphology and crystal structure of calcium carbonate when precipitated in the appropriate model systems. In addition, it is known that the in vitro formation of specific crystal modifications is typically determined by parameters such as temperature or initial supersaturation, as well as by the presence of inorganic or organic additives.

The aim of this research is to investigate a possible distortions caused by the incorporation of selected amino acids into the calcite crystal lattice. At that, the amino acids are selected as simple models of biomacromolecules supposed to be responsible for nucleation, growth and transformation of calcium carbonates in biominalerising systems. For that purpose amino acids (AA) having distinct chemical and physical properties were selected.

Experimental

Experimental conditions

- $\theta = 25^\circ C$
- $0 < c(AA) / \text{mmol dm}^{-3} < 75$

Spontaneous precipitation

- $c(\text{CaCl}_2) = 10 \text{ mmol dm}^{-3}$
- $c(Na_2CO_3) = 10 \text{ mmol dm}^{-3}$
- $\text{pH} = 10.7$
- $c(\text{MgCl}_2) = 5 \text{ mmol dm}^{-3}$
- $c(\text{NaHCO}_3) = 5 \text{ mmol dm}^{-3}$
- $\text{pH} = 7.9$
- $A(\text{seed}) = 0.55 \text{ m}^2 \text{ dm}^{-3}$

Results

SPONTANEOUS PRECIPITATION

Polymorphism (FT-IR / PXRD)

Crystallographic distortions of the calcite lattice

PXR

EPR

- $Mn^{2+}$ probe - synchrotron X-ray absorption in calcite lattice
- measuring the distortion
- $(\delta/\Delta) = 2 \cdot 10^{-3}$ mmol dm$^{-3}$

Typical EPR spectrum of calcite/crystal labeled with Mn$^{2+}$

CRYSTAL GROWTH KINETICS

- The Langmuir adsorption constants ($K_L$) are calculated from growth kinetic data and used as an indication of extent of organic/inorganic interaction
- The results of structural (PXR, EPR) and growth kinetic data indicate that amino acids interaction with calcite surface increase in the order:

Conclusion

- Ala and Phe: no influence on polymorphic composition (calcite/vaterite)
- Ser, Tyr, Asn, Lys, Asp:
  - at lower additive concentration: vaterite is dominant phase (inhibition of calcite growth?)
  - at higher additive concentration: calcite dominant phase (different morphology)
- Model system: calcite precipitates in a form of regular rhombohedral crystals
- Addition of AAs caused the changes of morphology (stepped calcite crystals)
- The strongest effect caused by the Asp addition (rosette-like calcite crystals)