

Modelling the nucleation of hydroxyapatite at a collagen template

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The biomineral hydroxyapatite nucleates at an organic collagen matrix, which controls the growth process and eventual morphology of the apatite crystallites. An important but largely unresolved issue is the way in which nature controls the nucleation, growth and morphology of the inorganic crystallites and the function of the templating biomolecules, here collagen, in these reactions. However, as it is not yet possible to study directly, by experiment alone, the molecular mechanisms of biomineralisation processes, we have employed a combination of *ab initio* and classical Molecular Dynamics simulations to investigate the early processes of the nucleation of hydroxyapatite at a collagen template, by immersing a triple-helical collagen molecule in a stoichiometric solution of Ca²⁺, PO₄³⁻ and OH⁻ ions.

The average number of water molecules in the first hydration shells of the Ca ions and PO₄ groups from the classical MD simulations are all in excellent agreement between with the *ab initio* MD and experiment. Very quickly, a number of stable calcium phosphate (CaP) clusters form in solution, although preferential CaP formation occurs at the collagen matrix.

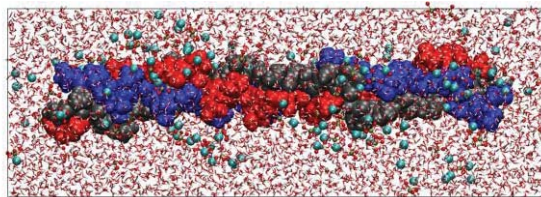


Figure 1: Graphical representation of the collagen triple helix in stoichiometric hydroxyapatite solution.

Electrostatic attractions are prevalent between calcium ions and oxygen atoms of the glycine and hydroxyproline residues, which were the starting point for the formation of the calcium phosphate clusters. At body temperature, calcium ions interact with water molecules to form stable complexes, but attracted by electrostatic forces, they coordinate to PO₄ ions and start forming clusters. Some phosphate ions form hydrogen-bonds with the hydroxy groups of hydroxyproline residues, whereas due to strong water-OH interactions most of the hydroxy ions stay in solution, although some become attached to calcium phosphate clusters. These results agree with suggestions that HA growth follows initial amorphous CaP formation.

Comparison of our results¹ with those of Kawska et al.² shows that fluoride ions inhibit calcium phosphate formation by competitively binding the Ca ions into calcium fluoride clusters.

[1] Almora-Barríos (2012) *Cryst. Growth Des.* DOI: 10.1021/cg201092s. [2] Kawska (2008) *Angew. Chem. Int. Ed.* **47**, 4982.

Geochemical modelling of long-term mineral alteration induced by the injection of CO₂ in a saline aquifer: the Ketzin site

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The assessment of expected long-term CO₂-induced mineral alterations of reservoir and cap rock is crucial to ensure the long-term stability of the storage project, and to evaluate the potential carbon trapping provided by mineralization. In the first European on-shore pilot site at Ketzin, nearby Potsdam, Germany, about 60,000 t of CO₂ were injected (as of February, 2012) in a saline aquifer in a Triassic sandstone at about 650 m depth. A rich set of analyses of pristine formation fluids [1] as well as mineralogical and geochemical composition of the reservoir rock [2] made possible a precise parametrization of the reference geochemical model.

Batch 0-D simulations including reaction kinetics were run using the speciation code PHREEQC under the assumption of a constant CO₂ pressure over the simulation time of 5,000 y. The pore pressure itself was found to have a negligible impact on mineral alterations, at least in the considered range of approximately 50 to 80 bar expected for the site. The reference simulation predicts the precipitation of kaolinite, K-feldspar, and plagioclase (represented by the end-member albite) which greatly compensate the partial dissolution of illite, Fe-rich chlorite, and anhydrite cement. Of all carbonate minerals included in the model (siderite, magnesite, calcite, and dolomite), siderite is the only one which precipitates in significant amounts, and thus contributes to mineral trapping. However, the precipitation of carbonates always starts after several hundreds years in the models.

To investigate the robustness of these results, different scenarios were run, each representing a different choice for primary and secondary minerals and different hypothesis for the parametrization of mineral reactive surfaces with respect to the reference model. The simulated results are quite variable, but the simulated total relative change in pore volume after 5,000 years was always below 2%. This can be considered irrelevant in terms of influence on the hydrodynamic properties of the rock. These results are confirmed by the observations from laboratory experiments on core samples exposed to CO₂.

[1] Würdemann et al. (2010) *CO₂SINK—From site characterisation and risk assessment to monitoring and verification: One year of operational experience with the field laboratory for CO₂ storage at Ketzin, Germany* **International Journal of Greenhouse Gas Control** 4(6), pp 938-951

[2] Förster et al. (2010) *Reservoir characterization of a CO₂ storage aquifer: The Upper Triassic Stuttgart Formation in the Northeast German Basin*, **Marine and Petroleum Geology** 27, 2156-2172.