

## Computer simulations of the interaction of bio-molecules with hydroxyapatite surfaces in aqueous environment

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In view of the importance of the hydroxyapatite/ collagen composite of both natural bone tissue and in synthetic biomaterials, we have employed a combination of electronic structure calculations based on the Density Functional Theory and Molecular Dynamics simulations to investigate the interaction with two major hydroxyapatite surfaces of the three amino acids that largely make up the collagen matrix, as well as a peptide strand of the same residues (glycine, proline and hydroxyproline).

We have performed full geometry optimisations of the hydroxyapatite surfaces with adsorbed amino acid molecules to obtain the optimum substrate/adsorbate structures and interaction energies, both *in vacuo* and in a liquid water environment. An aqueous environment is added through the explicit introduction of water molecules in the simulation of the dynamic behaviour. The calculations show that the amino acids, as well as the complete peptide are capable of forming multiple interactions with surface species, particularly if they can bridge between two surface calcium ions. The binding energies range from 291 kJ mol<sup>-1</sup> for glycine on the (0001) surface to 610 kJ mol<sup>-1</sup> for hydroxy-proline on the (01 $\bar{1}$ 0) surface. The large adsorption energies are due to a wide range of interactions between adsorbate and surface, including proton transfer from the adsorbates to surface OH or PO<sub>4</sub> groups. Similar to the amino acids, the Gly-Pro-Hyp peptide also binds more strongly to the hydroxyapatite (01 $\bar{1}$ 0) surface; indeed, in an aqueous environment only binding at this surface is thermodynamically favourable, which suggest that, in the presence of the collagen matrix, the hydroxyapatite crystal would grow more rapidly in the (0001) direction than in the (01 $\bar{1}$ 0) direction, in agreement with the naturally observed bone morphology.

## A thrust for early skeletal evolution provided by ocean chemistry

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The advent of biomineralization at the end of the Precambrian (~ 550 Myr ago) produced fundamental changes in biology, ocean chemistry and sedimentary rocks. Mineral skeletons are thought to have arisen as protective armours in response to an increase in predation pressure, or as a means to maintain cellular calcium below toxic levels in the face of increasing oceanic calcium concentrations. I describe and additional thrust for early skeletal evolution provided by oceanic chemistry. I reconstructed the CaCO<sub>3</sub> saturation state ( $\Omega_{\text{CaCO}_3}$ ) and total alkalinity (TA) of the ocean during the advent of biomineralization from the sedimentary distribution of calcified cyanobacteria. The calcification of cyanobacteria is dependent on the  $\Omega_{\text{CaCO}_3}$  of benthic cyanobacterial mats and the  $\Omega_{\text{CaCO}_3}$  of the overlying ocean. With a recently developed numerical model of  $\Omega_{\text{CaCO}_3}$  in cyanobacterial mats [1], the relative contribution of microbially-induced  $\Omega_{\text{CaCO}_3}$  shifts and ocean chemistry can be disentangled, providing some constraints on the carbonate system of the ancient ocean. This approach indicates that when the first skeleton-producing animals appeared and diversified, the CaCO<sub>3</sub> saturation state and the alkalinity of the ocean were extremely high. This agrees with paleogeographic reconstructions, the strontium isotope record of marine carbonates and the geological record of marine clays which indicate intense continental weathering at that time, implying large fluxes of dissolved calcium and bicarbonate to the oceans. In most marine organisms that build CaCO<sub>3</sub> skeletons, the rate of calcification is positively related to the CaCO<sub>3</sub> saturation state of ambient waters, to the concentration of bicarbonate, or both, implying that oceanic chemistry during the advent of biomineralization favoured CaCO<sub>3</sub> skeletogenesis. High continental weathering rates would have delivered also dissolved phosphate and silica to the ocean, favouring the development of phosphate and silica skeletons.

[1] Aloisi (2008) *Geochim. Cosmochim. Acta* **72**, 6037-6060.