Modelling the nucleation of metal carbonates: The importance of the hydration shell in the monomer formation

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The process of homogeneous nucleation of crystals in an aqueous solution, involves the reaction of the hydrated cations $A^{a+}(H_2O)_n$ and and anions $B^{b-}(H_2O)_m$ to form the building units A_xB_y, the clusters $(A_xB_y)_n$ and possibly the critical cluster $[(A_xB_y)_{n*}]$, from which the spontaneous growth of the mineral occurs. An accurate knowledge of the solvation structure of the ions A^{a+} and B^{b-} and of their dynamical characteristics is therefore of fundamental importance to our understanding of the nucleation and growth of minerals from solution.

Here, we present a computational study aimed at investigating the structural and dynamical properties of the alkaline earth metal ions Mg^{2+}, Ca^{2+}, and Sr^{2+} and their (bi-)carbonate complexes in aqueous solution.

According to our simulations, the magnesium ion undergoes a significant contraction of its coordination sphere in the Mg $(H)CO_3^{(+)}$ aqueous complex [1], whereas calcium and strontium increase their average first shell coordination number when coordinated to HCO_3^- or CO_3^{2-} [2]. The analysis of the water exchange processes in the first and second coordination shells of the metal ions shows that the bicarbonate and carbonate ligands affect on the lability of the magnesium and calcium first hydration shells, whereas the influence of the heteroligand on the more flexible strontium solvation shell is negligible. Moreover, our sinulations are used to suggest the structures of the most stable metal bicarbonate and metal carbonates in aqueous solution.

Molecular dynamics simulations of *non*-associated solvent shared ion pairs Me^{2+}-X^- (Me = Mg, Ca and Sr; X = F, Cl and Br) in solution show that simple halide ions can change the structural and dynamical properties of the first and second hydration shell of Me^{2+}, and consequently affect the reactivity of the metal ions in solution.

[1] Di Tommaso & de Leeuw (2010) *Phys. Chem. Chem. Phys.* **12**, 894–901. [2] Di Tommaso & de Leeuw (2008) *J. Phys. Chem. B* **112**, 6965–6975.

Microbe-mineral interfaces in biofilms as seen by Atomic Force Microscopy combined with Raman and X-ray Spectroscopy

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Microbial mats are unique biogeochemical 'piazza', where geochemistry and biology interact at nanoscale. In this study we investigate microbe-mineral interactions in modern stromatolites from a hypersaline lagoon, Lagoa Vermelha, Brazil. Additionally, cyanobacteria from biofilms in hot springs and sediment cores have been imaged by high resolution microscopic and spectroscopic techniques. Raman scattering techniques have elicited significant interest for biomolecule detection as they provide several advantages over other spectroscopic techniques. Unlike IR and NMR, Raman signals are not affected by the presence of water, and Raman bands are much narrower than fluorescence bands. Till now, tip enhanced Raman Microscopy was not used for microscopically resolved chemical mapping of microbial mats. The maps (Fig. 1) reveal a link between the spatial pattern and the chemical composition.
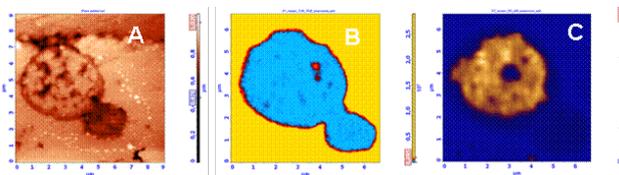

Figure 1: AFM image (A) and Raman confocal images ($\sim$1574 cm^{-1}(B), 345 cm^{-1}(C)).