

## MeHCO<sub>3</sub><sup>+</sup> and MeCO<sub>3</sub> (Me = Ca and Mg) species in aqueous solution: Insights from quantum mechanical calculations

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The most stable, long-term storage mechanism for atmospheric CO<sub>2</sub> is the formation of carbonate minerals such as calcite (CaCO<sub>3</sub>), dolomite (Ca<sub>0.5</sub>Mg<sub>0.5</sub>CO<sub>3</sub>) and magnesite (MgCO<sub>3</sub>) [1]. Despite the importance of these mineralisation processes, little is known about the onset of CaCO<sub>3</sub> and MgCO<sub>3</sub> nucleation, mostly because the investigation of the first stages in the nucleation of metal carbonates presents many experimental challenges [2].

Here, we present a computational study aimed at investigating the formation, structure and solvation environment of the building blocks of CaCO<sub>3</sub> and MgCO<sub>3</sub> in water, and computing the formation of CaCO<sub>3</sub> and MgCO<sub>3</sub> oligomers under neutral and basic pH conditions.

First principle molecular dynamics simulations of Ca<sup>2+</sup>/CO<sub>3</sub><sup>2-</sup> and Ca<sup>2+</sup>/HCO<sub>3</sub><sup>-</sup> immersed in water show that the dominant building block of calcium (bi-)carbonate in aqueous solution is Ca[η<sup>1</sup>-(H)CO<sub>3</sub>](H<sub>2</sub>O)<sub>5</sub>, i.e. the preferred hydration number is five and the (H)CO<sub>3</sub> is coordinated to the Ca in a monodentate mode [2]. Starting from these monomers, the Gibbs free energies for the formation of the calcium bicarbonate species present in the early stages of the homogeneous nucleation process have been computed using a microsolvation-continuum method [3]. The results show that the formation of inter-molecular as well as intra-molecular calcium bicarbonate dimers is not spontaneous, indicating that the nucleation of calcium carbonate cannot occur through a homogeneous process when the major source of CaCO<sub>3</sub> in the aqueous environment are the calcium-bicarbonate ion pairs. The same methodology is then applied to investigate the structure and hydration environment of the monomers of Mg<sup>2+</sup>/CO<sub>3</sub><sup>2-</sup> and Mg<sup>2+</sup>/HCO<sub>3</sub><sup>-</sup>, and the mechanism of formation of magnesium carbonate clusters.

[1] Oelkers *et al.* (2008) *Elements* **4**, 333-337. [2] Rodriguez-Blanco *et al.* (2008) *Mineralogical Magazine* **72**, 283-286 [2] Di Tommaso & de Leeuw (2008) *J. Phys. Chem B* **112**, 6965-6975. [3] Di Tommaso & de Leeuw (2008) *GCA*, submitted.

## Nanoscale characterization of organic matter in modern stromatolites

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Laminated structures in the rock record constitute some of the oldest evidence for life on Earth, but the processes involved in the formation of stromatolitic lamination are still poorly understood. Modern Bahamian stromatolites have been proposed as a modern analogue for ancient forms; however, the textural component does not necessarily match that of Precambrian stromatolites. Thus, a new formation model for these ancient examples is needed. In this study, we investigated modern stromatolitic structures, which are growing in a hypersaline coastal lagoon, Lagoa Vermelha, Brazil. These modern examples are texturally more equivalent to their ancient counterparts. The identification of ancient microorganisms participating in the biomineralization processes remains difficult because fossil components are not easily recognizable or well preserved.

To determine if a metabolic signal is possibly preserved in the Lagoa Vermelha stromatolites, we have applied a high spatial resolution approach to characterize the organic matter enclosed in the carbonate laminae. Analytical transmission electron microscopy, plus electron energy loss spectroscopy (TEM-EELS), X-ray microscopy and scanning electron and laser microscopic studies were used to gain information about the biomineralization processes and associated metabolic mechanisms, such as photosynthesis, aerobic and anaerobic respiration, methanogenesis and fermentation. As reference substances for organic matter, we used extracellular substances from both free and attached to cells of sulfate reducing bacteria and cyanobacteria. Our results demonstrate that distinct patterns are observable, which can be used to interpret possible metabolic mechanisms involved in the formation of the carbonate laminae.