Structure and relative stability of hydrous and anhydrous Ca-Mg carbonates from first-principle calculations

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Calcium and magnesium carbonates play an important role in the chemistry of the hydrosphere, lithosphere, atmosphere and biosphere. From a technological point of view, the precipitation of carbonates in industrial and domestic environments represents a problem in terms of process efficiency and maintenance costs.

The crystallisation and growth mechanisms of these compounds, as well as their structure and relative stability, are still a matter for investigation. In particular, relatively little data is available for the hydrated phases, due to limited natural occurrence and low stability. However, they may well play a role during the crystallisation and growth mechanism of the anhydrous phases (included Ca-Mg carbonate solid solutions) and in CO_2 sequestration, especially at low temperature [1-5]. Information regarding the formation of mixed calcium-magnesium carbonates is also pertinent to understanding the dolomite problem.

A comprehensive *ab initio* structural and thermodynamic study of calcium-magnesium carbonates and their hydrates will be presented. The good agreement between calculated and available experimental data attests to the validity of the applied computational approaches, namely Density Functional Theory in the present study.

[1] Nebel *et al.* (2008) *Inorg. Chem.* **47**, 7874-7879. [2] Tang *et al.* (2009) *J. Appl. Cryst.* **42**, 225-233. [3] De Angelis *et al.* (2007) *Amer. Mineral.* **92**, 510-517. [4] Vágvölgyi *et al.* (2008) *J. Therm. Anal. Calorim.* **94**, 523-528. [5] Davies *et al.* (1977) *Chem. Geol.* **19**, 187-214.

Nucleation of amorphous calcium carbonate: A combined theoretical and experimental perspective

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The nature of the nucleation of amorphous calcium carbonate is examined in the light of both recent experimental [1,2] and theoretical [3] results. While experiment demonstrates the existence of stable pre-nucleation clusters, followed by a nucleation event, computer simulations suggest that the free energy of adding ion pairs to amorphous calcium carbonate is exothermic regardless of size, which may indicate the absence of a barrier. How these two different sets of observations can be reconciled will be examined in this work through the use of molecular dynamics simulations of pre-nucleation calcium carbonate solutions.

In this presentation we will explore the use of computer simulation methods to try to unravel the complexities of the nucleation and growth processes for calcium carbonate. Central to this is the development of a force field that is accurately calibrated against experimental free energies [3] since failure to do so can result in qualitative errors for interfacial properties. Based on this we have explored the stability of ACC versus crystalline nanoparticles while accounting for the variable water content in the amorphous structure [4]. In the light of this, and new experimental results, we propose a model to explain the non-classical aspects of the nucleation mechanisms of calcium carbonate, the origins for which can be traced back to the interfacial properties.

[1] D. Gebauer *et al.* (2010), *Angew. Chem. Int. Ed.* 49, 8889. [2] D. Gebauer *et al.* (2008), *Science*, **322**, 1819. [3] P. Raiteri *et al.* (2010), *J. Phys. Chem. C*, **114**, 5997. [4] P. Raiteri and J.D. Gale (2010), *J. Am. Chem. Soc.*, **132**, 17623.