

Probing reactivity at the calcite-water interface using computer simulation

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Carbonate minerals are of significant interest due to their relevance to both biomineralisation and potentially long-term carbon sequestration. Calcite, as the stable form of calcium carbonate at ambient conditions, represents arguably the most studied mineral of this group. Its morphology is typically dominated by the (104) basal plane and there have been extensive experimental studies of growth and dissolution at this surface, especially via atomic force microscopy [1,2], as well as the structure of the water-mineral interface [3,4].

In this study we examine the atomistic detail underlying the observations at longer length and time scales. Using molecular dynamics, based on a thermodynamically accurate force field [5], we examine the extent to which it is possible to probe the thermodynamics of individual growth events at the acute and obtuse steps on the calcite basal surface. Since the growth of calcite often occurs from solutions where the dominant species is bicarbonate rather than carbonate, the question of whether proton transfer occurs before or after addition of the anion to calcite will be discussed.

Given the considerable computational challenge of determining rates for reactions at the calcite-water interface, the possibility of predicting growth and dissolution via more approximate atomistic approaches will also be examined. Preliminary results suggest that the use of static calculations with a more approximate treatment of the water may be able to predict realistic rate constants. This will be shown to be a promising future direction that offers the possibility to connect atomistic detail with macroscopic experimental observations and existing growth models [6].

[1] Ruiz-Agudo & Putnis (2012) *Miner. Mag.*, **76**, 227-253. [2] Stack & Grantham (2010) *Cryst. Growth Des.*, **10**, 1409-1413. [3] Geissbühler *et al.* (2004) *Surf. Sci.*, **573**, 191-203. [4] Fenter *et al.* (2013) *J. Phys. Chem. C*, **117**, 5028-5042. [5] Raiteri *et al.* (2015) *J. Phys. Chem. C*, **119**, 24447-24458. [6] Nielsen *et al.* (2013) *Geochim. Cosmochim. Acta*, **115**, 110-114.