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Kinetic Monte Carlo modeling of calcite dissolution kinetics

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Rhombohedral carbonates form ideal minerals for coupling experimental observations and modeling of surface-controlled kinetics. Calcite has a large and growing database of bulk and surface thermodynamic properties and a relatively simple bulk structure. Numerous studies have demonstrated that step velocities and the interaction of impurities during dissolution (Fig. 1) and growth reflect the basic anisotropy of the cleavage surface. This steric control must derive from differences in the potential energy of attachment offered by specific kink sites, and how the population and distribution of these sites and diffusing species varies as the surface evolves. However, the use of Kinetic Monte Carlo (KMC) techniques to simulate this behavior has involved relatively abstract treatments of the (104) surface itself, using kink and step velocities but not energy distributions [1,2]. Here we present a new KMC model parameterized by bond energies for the calcite cleavage surface, and use this model to simulate basic reactions at the surface during dissolution.

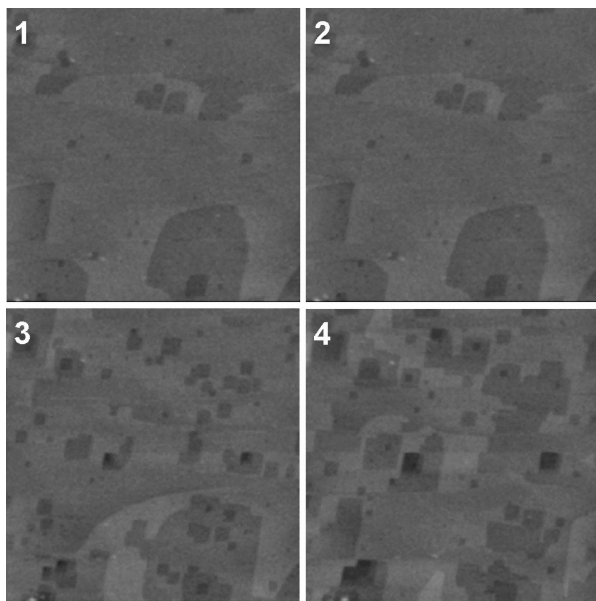


Figure 1. Increase in calcite etch pit density after Mg^{2+} introduction to $NaHCO_3$ solution (AFM sequence).

References

- [1] McCoy J. M. and LaFemina J.P. (1997) *Surface Science* **373**, 288-299.
 [2] Williford et al. (in press) *J. Crystal. Growth*, doi:10.1016/j.jcrysgro.2003. 10.015.

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Computer modelling of apatite/water and apatite/quartz interfaces

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Computer simulation techniques have been employed to study solid/liquid and solid/solid interfaces of apatite minerals. Simulations of apatite thin films at a range of α -quartz surfaces show how the strength of adhesion between thin films of apatite material and silicate surfaces is crucially dependent upon both the orientation of the film relative to the substrate and the nature of the substrate surface. Although the unrelaxed quartz surface is more reactive towards the apatite film, the more regular thin film structures grown at the pre-relaxed quartz surfaces lead to more stable interfaces. Hence, the nature of the substrate surface before attachment of the film is more important in determining the structure and stability of the resulting interface than the initial reactivity of the substrate and/or the degree of bonding between the two materials across the interfacial. In addition, film growth at the unrelaxed quartz surface is energetically increasingly unfavourable, whereas growth at the pre-relaxed surface is calculated to continue beyond the first layer and we predict that the apatite thin films will form local domains of both (2×2) as well as clockwise and anti-clockwise $(2 \times 2)R120^\circ$ adsorbate layers. The effect of hydration of the quartz surface is to make the interfacial energies less dependent on the rotation of the thin film with respect to the underlying substrate surface.

Molecular Dynamics simulations of the incorporation of fluoride into hydroxy-apatite show that fluoride ions are easily incorporated from solution into the surface of hydroxy-apatite ($\Delta E = -193 \text{ kJmol}^{-1}$), but that they do not segregate into the bulk crystal beyond approximately 10 \AA . The hydroxy groups, which remain aligned in the c-direction in the bulk material due to the formation of pairs of OH groups, are found to reverse randomly in the surface region when a vacuum interface is introduced. This surface region shows considerable relaxation and reconstruction of the calcium and phosphate sub-lattices, leading to the disintegration of the OH pairs and hence their re-orientation. However, when the vacuum is filled with water, the surface relaxation is less extensive and the hydroxy groups remain aligned, although surface OH groups dissolve into the water. When surface OH groups are replaced by fluoride ions, this fluoride remains in the crystal lattice and further anchors surface calcium ions. As such this surface fluoride prevents the onset of apatite dissolution, although the fluorapatite layer is only superficial.