

Nanoscale imaging at the calcite-water interface: Implications for potential environmental remediation



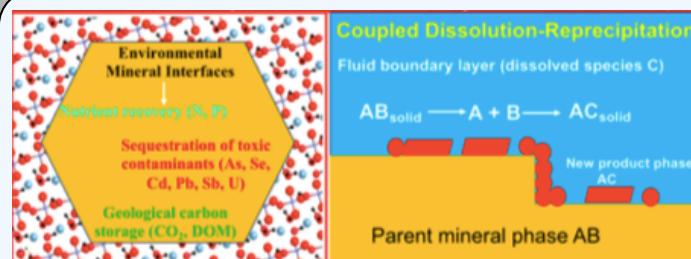
Christine V. Putnis^{1,2}

¹Institut für Mineralogie, University of Münster, Germany, ²Curtin University, Perth, Australia

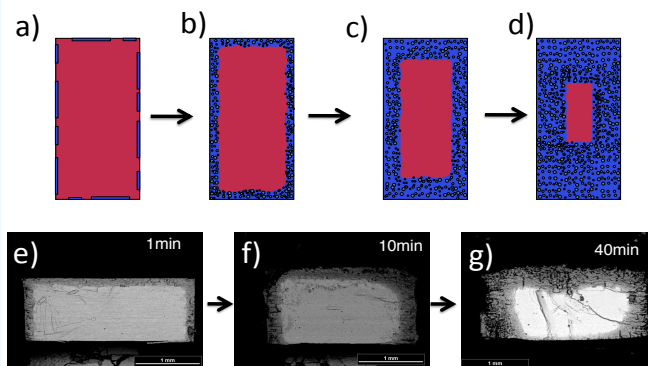
An aqueous fluid will induce some dissolution even in a highly insoluble phase, such as most minerals, producing an interfacial boundary layer of fluid that may be supersaturated with respect to one or more stable phases. One of these phases may then nucleate at the surface of the parent phase initiating an autocatalytic reaction that couples the dissolution and precipitation rate. In this pseudomorphic reaction, porosity forms in the product phase as a result of a volume deficit reaction.

Mechanism

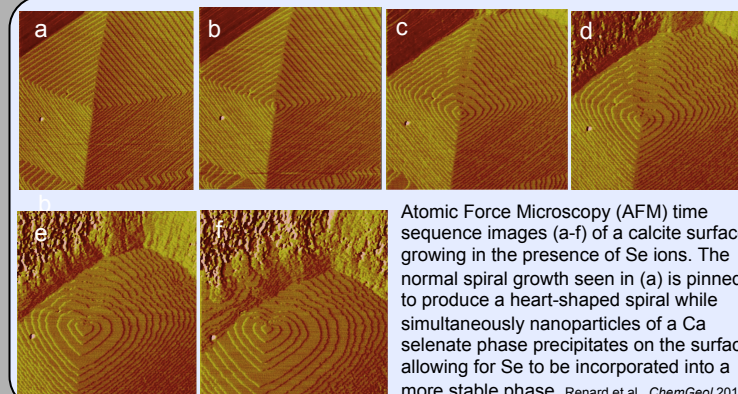
Reactions occur at the mineral-fluid interface so that one mineral may be replaced by another more stable mineral by an **interface-coupled dissolution-precipitation mechanism**.



The above diagrams indicate the mechanism of coupled dissolution and precipitation where the dissolution of a parent phase releases ions that can combine with ions in solution to form a new more stable product phase.



Above: a-d), diagram of a replacement sequence; e-g), BS-SEM images of the pseudomorphic replacement of a single crystal of KBr by KCl, showing the development of porosity in the K(Br,Cl) replacement rim. The final product is a pseudomorphic replacement of KBr by KCl.



Atomic Force Microscopy (AFM) time sequence images (a-f) of a calcite surface growing in the presence of Se ions. The normal spiral growth seen in (a) is pinned to produce a heart-shaped spiral while simultaneously nanoparticles of a Ca selenate phase precipitates on the surface allowing for Se to be incorporated into a more stable phase. Renard et al., *ChemGeol* 2013

Aqueous solutions contains As on calcite surfaces

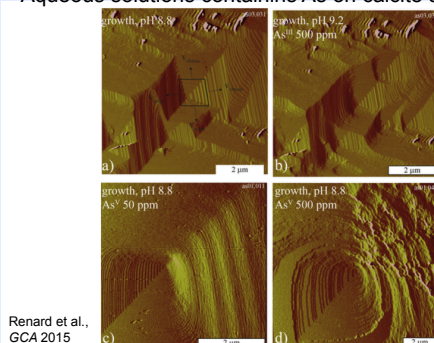
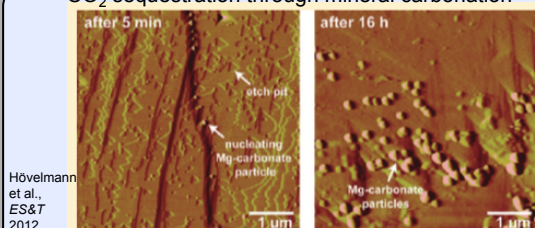


Fig. 4. AFM deflection images of the effect of arsenic during growth of calcite on the (10-14) cleavage surface. (a) Pyramidal hillock with acute and obtuse angles indicated and the corresponding step velocities v_{acute} and v_{obtuse} respectively. (b) Effect of As^{III} , 500 ppm is characterized by a slight rounding of the acute angle. (c) Effect of As^{V} , 50 ppm, characterized by a slight rounding of the acute angle. (d) Strong effect of As^{V} , 500 ppm, with the transformation of the pyramidal hillock morphology into tear shape by pinning the acute angle.

CO₂ sequestration through mineral carbonation



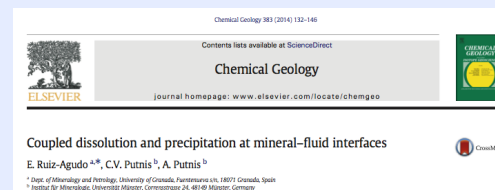
Hövelmann et al., *ES&T* 2012

AFM images of a brucite (Mg(OH)₂) surface in a carbonated water solution. The carbonate is captured in a new more stable Mg carbonate phase.

Summary:

Real-time imaging using *in situ* Atomic Force Microscopy (AFM) allows for initial mineral growth stages to be observed. When an aqueous solution containing toxic elements is in contact with a mineral surface such as calcite, a small dissolution of the calcite, releasing Ca²⁺ and CO₃²⁻ ions into the mineral-fluid interfacial solution, can result in the supersaturation and precipitation of a new product phase, that effectively sequesters the toxic element in that more stable solid phase.

These examples show that through coupled dissolution and precipitation, toxic elements, such as Se, As, Sb, Pb, heavy metals, may form stable new product phases that can precipitate on a calcite surface and hence be removed from the aqueous solution environment. This also includes excess phosphorus causing eutrophication of waters and CO₂ in the atmosphere.



Coupled dissolution and precipitation at mineral-fluid interfaces

E. Ruiz-Agudo ^{*,1}, C.V. Putnis ², A. Putnis ³

¹ Dept. of Mineralogy and Petrology, University of Granada, Spain

² Institut für Mineralogie, Universität Münster, Germany

The above review paper explains the conditions necessary for the coupling between dissolution and precipitation

