

An AFM study of calcite dissolution in concentrated electrolyte solutions

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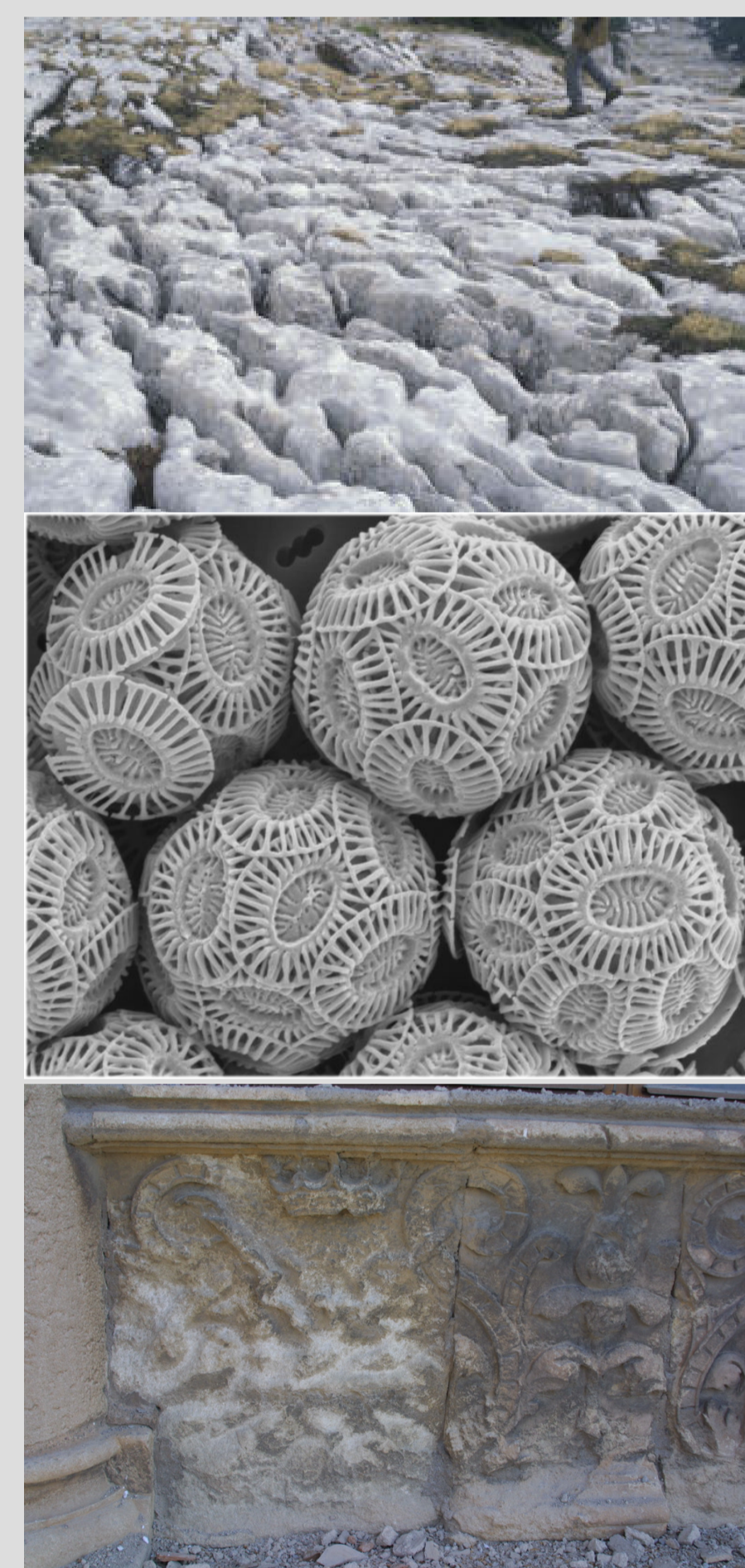
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Mineral dissolution: effect of ionic strength

The kinetics of dissolution of silicates and carbonates is critical for the geochemical cycle of many elements, Earth climate feedback and, ultimately, the evolution of the biosphere. In particular, the dissolution of calcite has attracted a great deal of research due to its paramount importance in a wide variety of processes such as rock-weathering, soil chemistry, and biomineralization

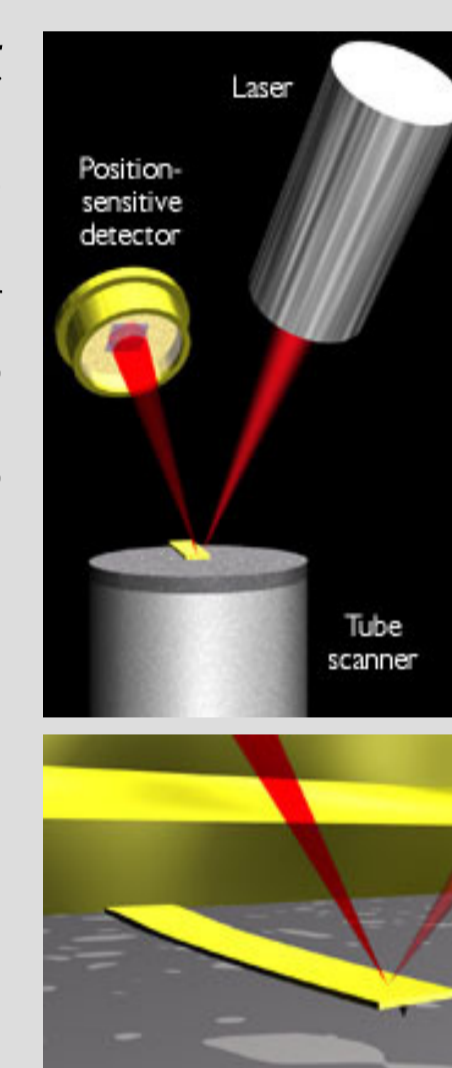
Knowledge of the kinetics of dissolution of minerals under different experimental conditions allows a better description of mineral-water interactions in many natural systems. Changes in mineral dissolution rates as a function of ionic strength (IS) are typically measured experimentally using NaCl or KCl as background electrolytes. Experimental studies have shown that the dependence of dissolution rate on IS is complex, and depends on the ionic species producing it. It is the aim of this research to assess the basic hypothesis that mineral dissolution in the presence of salts is governed by changes in solvent structure, surface hydration and ion solvation environment induced by electrolytes, following the model proposed by Kowacz and Putnis (2008) for the case of barite.



Atomic Force Microscopy (AFM)

AFM operates by measuring attractive or repulsive forces between a tip and the sample. Working in contact mode, the instrument lightly touches the sample with a tip at the end of a spring or *cantilever*. As a raster-scan drags the tip over the sample, a detector measures the vertical deflection of the cantilever, which indicates the local sample height (Baselt, 1986).

In recent years the study of mineral-water interactions has experienced a significant advance due to the use of *in situ* AFM. This technique has enabled nanoscale observations of mineral surfaces reacting with fluids, as well as real-time studies of the dissolution and precipitation of sparingly soluble minerals (Putnis et al., 1995; Shtukenberg et al., 2005).

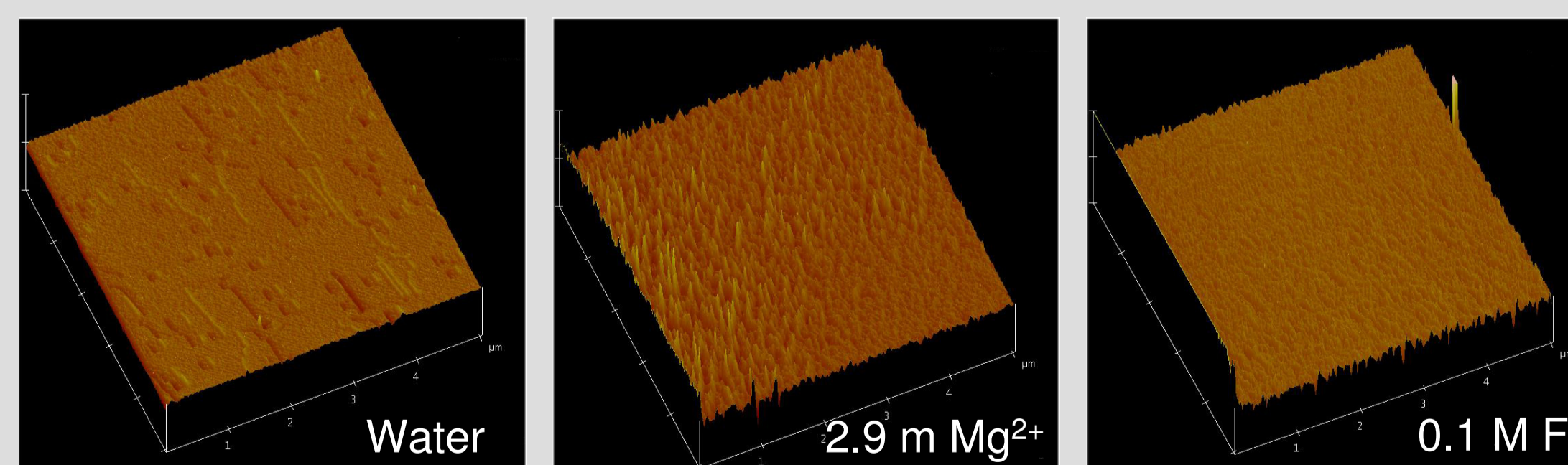


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Effect of electrolytes on calcite dissolution

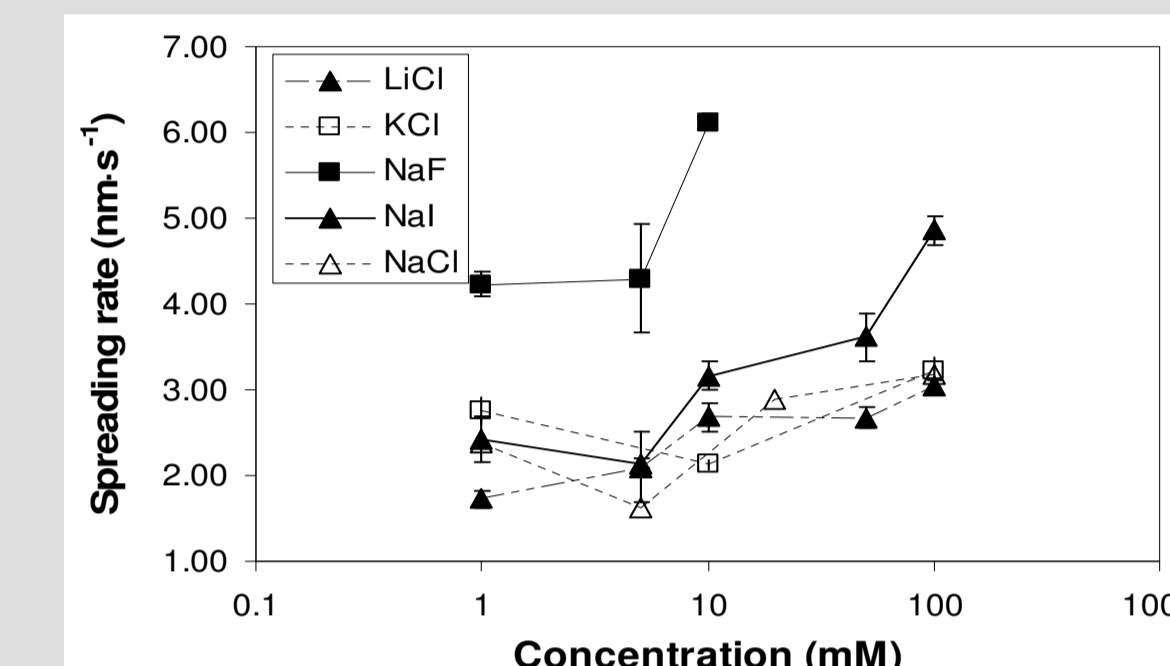
(a) Etch pit nucleation: role of ions with high charge density

We observed a general increase in etch pit depth and density with increasing F⁻ or Mg²⁺ concentration. Ions with high charge density (Mg²⁺, Mn⁺, F⁻) are able to adsorb onto calcite surfaces and compete for surface hydration water. The strong ion-surface interaction and the fact that such ions can disrupt the surface hydration layer can lead to surface destabilization, and ultimately favor 2D nucleation of etch pits, increasing the dissolution rate.



(b) Effect of electrolytes on dissolution kinetics

Calcite dissolution rates at low IS decrease with increasing ion separation in solution (decreasing ion pairing) and thus, with increasing stabilization of water orientation in cation hydration shell.

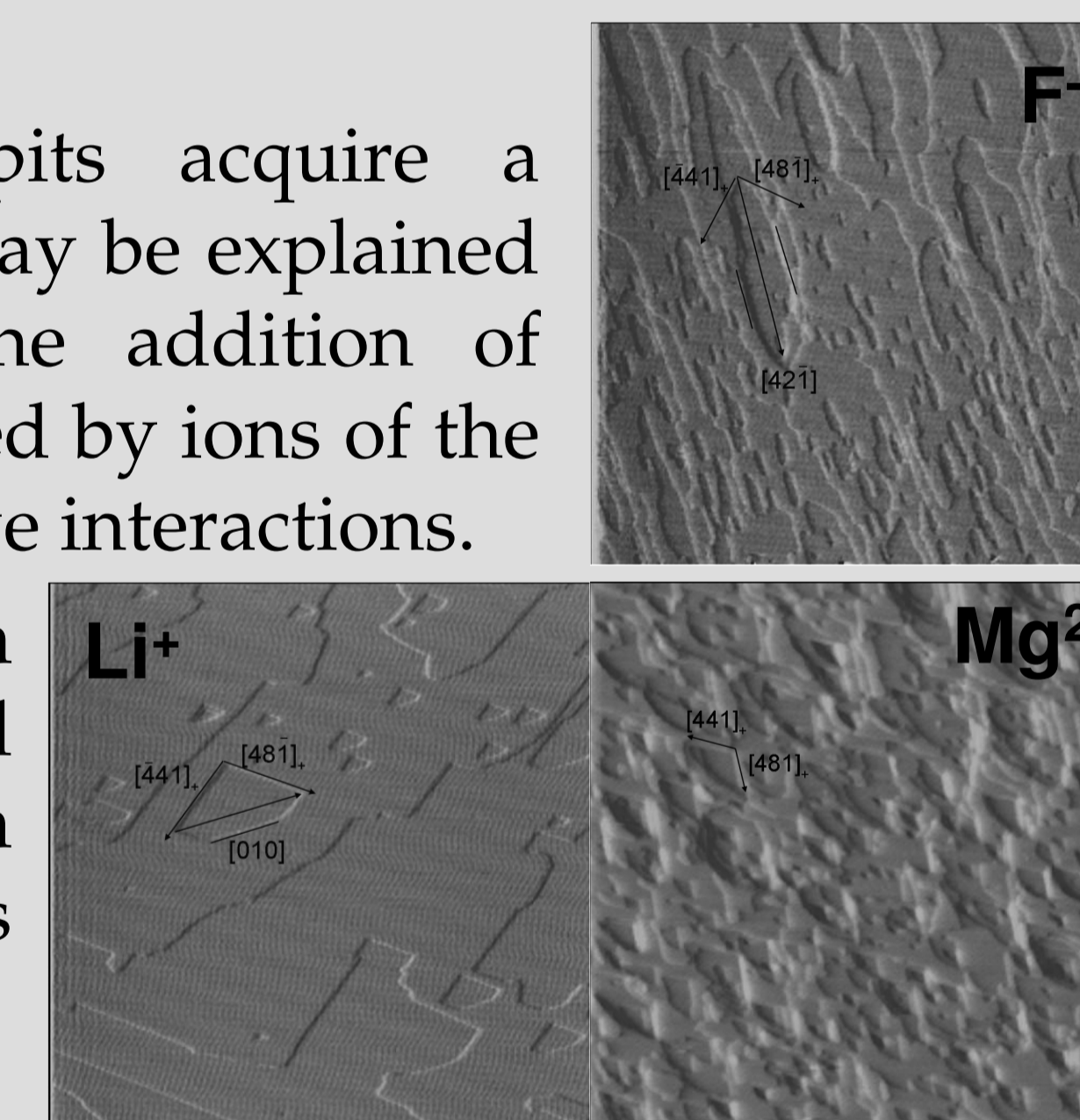


This trend is opposite to that found for barite and can be explained in terms of hydration entropies considering the differences in hydration characteristics of calcium and barium ions. At high IS dissolution kinetics increase with decreasing water affinity of the background anion (NaF>NaI>LiCl≈KCl≈NaCl). However, the ability of F⁻ to compete for surface hydration water may enhance calcite dissolution.

(c) Changes in etch pit morphology

In the presence of NaF, etch pits acquire a pseudo-hexagonal appearance. This may be explained by increasing ion hydration by the addition of electrolytes that stabilizes steps bonded by ions of the same sign due to reduction of repulsive interactions.

When dissolution occurs in solution containing Li⁺ or Mg²⁺, preferential incorporation of ions on selected etch pit corners modifies etch pit shape as observed in the figures.



Scale of the AFM pictures: the side of the image is 5 μm

Experimental set-up

Calcite {104} surfaces were used as substrates and freshly cleaved prior to each experiment. Six saline systems were used in the *in situ* Atomic Force Microscopy (AFM) dissolution experiments: NaF, NaCl, NaI, LiCl, KCl and MgCl₂. Ca-free saline solutions in concentrations ranging from 0.01 mM to saturation flowed continuously at 50 mL h⁻¹ from a syringe to a fluid cell containing the sample crystal

References

- Baselt, D. (1993) The tip-sample interaction in atomic force microscopy and its implications for biological applications. Ph.D. thesis
- Kowacz, M., Putnis, A. (2008) The effect of specific background electrolytes on water structure and solute hydration: Consequences for crystal dissolution and growth. *Geoch. Cosmoch. Acta* 72 4476-4487
- Putnis, A., Junta-Rosso, J.L. and Hochella, M.F. Jr. (1995) Dissolution of barite by a chelating ligand: An atomic force microscopy study. *Geoch. Cosmoch. Acta* 59, 4623-4632
- Shtukenberg, A. G., Astilleros, J.M. and Putnis, A. (2005) Nanoscale observations of the epitaxial growth of hashemite on barite (001). *Surf. Science* 590, 212-223