

MINERAL CHEMISTRY

How minerals dissolve

Local surface processes drive calcite dissolution

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During mineral growth and dissolution, material (in the form of atoms, molecules, complexes, or clusters) is transported through water to or from the mineral surface. Even in a solution that is at equilibrium with respect to a given mineral, there is transport to and from the surface. Although this equilibrium transport is in balance over large scales, the rates of this transport can vary locally depending on the energy landscape of the mineral surface (1). On page 1330 of this issue, Laanait *et al.* (2) present an elegant way of measuring and visualizing how dissolution rates vary across the calcite surface with time and with dissolution mechanism.

Calcite (CaCO_3) is the main long-term sink for carbon (3) and is one of the most abundant minerals in Earth's surface environment. It is therefore of prime importance in the global carbon cycle. It also

helps to regulate the chemistry of aquatic environments (4), scavenges trace and heavy metals (5), and records paleoenvironmental conditions (6). One of the remaining challenges is the accurate prediction of how calcite dissolution rates vary and evolve (1). This is vital, for example, for preventing calcite dissolution in historic limestone and marble buildings and artifacts. This knowledge may also help to increase oil and gas yield from carbonate rock reservoirs.

Following numerous macroscopic investigations of calcite dissolution with traditional methods (4), in the past decade research has zoomed in on the microscopic scale. In particular, atomic force microscopy (AFM) and interferometry have been instrumental for the direct observation of calcite dissolution mechanisms and the quantification of their kinetics (5). As in the current work (2), AFM and interferometry studies of calcite dissolution are performed on cleaved surfaces and have revealed a range of dissolution processes (see the figure). How far out of equilibrium a solution is will control which mechanism dominates calcite surface dissolution (1, 5). Laanait *et al.*

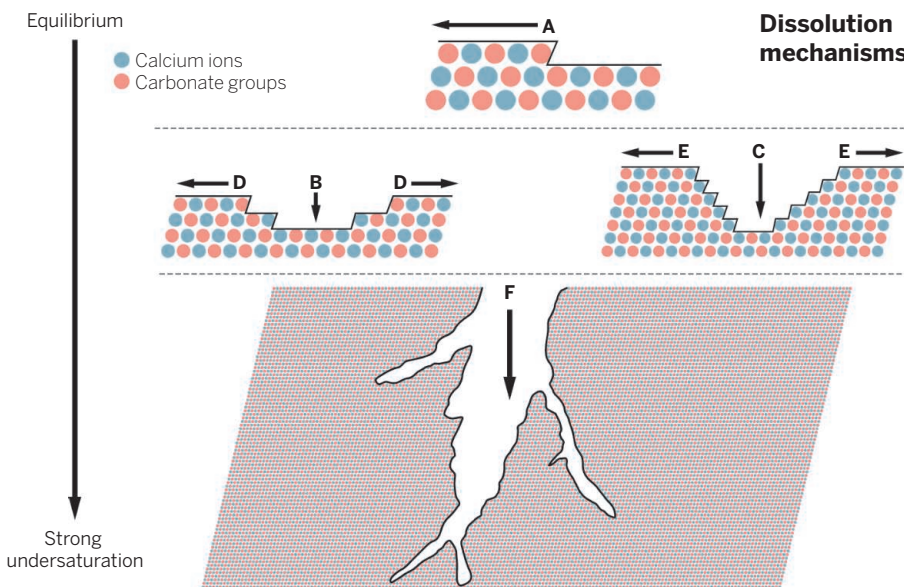
also report the formation of “wormholes,” which occur in carbonate rocks upon CO_2 injection (7) but have not previously been shown using AFM.

Calcite dissolution studies by AFM have generally been performed in cells flushed with fluid of a constant composition. In contrast, Laanait *et al.* used the reaction of an intense x-ray beam with water close to the calcite surface. Radicals formed through this reaction drive fluid compositional changes that subsequently cause calcite dissolution. By varying x-ray beam intensity and exposure time, they could vary fluid composition and thereby scan a range of dissolution mechanisms and rates.

The lowest dissolution rates they report for etch-pit spreading are generally in good agreement with those reported using AFM (5), but the rates vary strongly and asymmetrically and can be almost five times as fast as those typically observed using AFM. These higher rates may be caused by the interaction of radicals in the fluid with the calcite surface or by energetically induced reactions caused by the x-ray beam. However, rate variability and oscillations between the fastest- and slowest-dissolving surface structures do not correlate with radical concentration (compare Fig. 4 with fig. S8). Variability in dissolution rates has been reported previously (1). Currently, distribution rate spectra are used instead of single-rate laws to simulate this variability. Laanait *et al.* now show quantitatively how calcite dissolution rate spectra evolve with surface structure, time, and dissolution mechanism.

The quantitative imaging technique that enabled revealing these large local variations in dissolution rate is known as particle image velocimetry (PIV). This technique has been used for a few decades (8) to determine the flow of suspended particles; Laanait *et al.* adapted it to map dissolution front velocities at the surface from surface x-ray microscopy. Combining PIV with time-resolved surface analysis techniques including AFM and interferometry will ultimately reveal the evolution of mineral surface dissolution rates over longer time scales and over a wide range of natural conditions. ■

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Calcite dissolution mechanisms. Calcite may dissolve through retreat of preexisting atomic steps at the calcite surface (A) (9), formation of new shallow (B) and deep (C) etch pits (10), widening of shallow etch pits (D) (11), and (E) trains of surface steps (stepwaves) that originate at deep etch pits (1, 12). The number of etch pits formed depends on the number and type of imperfections in the surface. Shallow etch pits nucleate at surface defects and—if the solution is far enough out of equilibrium—also at defect-free sites (9). In contrast, deep etch pits form at crystal lattice imperfections referred to as screw dislocations (1). Laanait *et al.* also report “wormholing” in unstable reaction fronts (F).

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