



Mechanisms influencing micron and nanometer-scale reaction rate patterns during dolostone dissolution



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ABSTRACT

Water–rock interactions often involve the dissolution of a primary mineral and the precipitation of a new secondary phase. Many of the mechanisms governing such coupled reactions can only be observed directly using high resolution imaging techniques. In this study, atomic force microscopy was used to examine dolostone dissolution at the nanometer and micron scale at different pH conditions in the range 3.5–4.5. During the experiments, a secondary Mg-rich phase comprising nano-scale particles forms on the surface. Importantly, the precipitate does not significantly inhibit dissolution of the dolostone, and although the overall rates of surface retreat are highly dependent on pH, similar mechanisms are found to govern the evolution of the surface. At all pH values, high dissolution rates are observed at etch pits and along grain boundaries, resulting in rate spectra (probability density functions of reaction rates) that are often highly asymmetric and skewed towards higher values. A model based on extreme value theory performs well at capturing the long tails characteristic of the asymmetric distributions, indicating a possible route towards predicting rate spectra in dissolving rocks.

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1. Introduction

The formation of soils, the evolution of landscapes, and the erosion of buildings and monuments are all influenced by the rate of rock weathering. Importantly, the rates of these processes are often controlled by water–rock interactions acting over a wide range of spatial and temporal scales. These interactions typically lead to the dissolution of the minerals comprising the rock, with different mechanisms resulting in varying rates over the mineral surface. For example, reaction at perfect crystal faces is thought to be much slower than reaction at point defects, crystal lattice dislocations, or microfractures (Schott et al., 1989, 2012). Importantly, as some regions dissolve more rapidly than others, such varying rates can lead to an increase in surface roughness and surface area. Complicating matters further, the dissolution of primary minerals in rocks is often accompanied by secondary phase precipitation. This secondary precipitate can coat the surface of the dissolving phases, reducing the effective contact area between the primary mineral and fluid phases, thereby acting to increase the degree of heterogeneity in surface reactivity. Thus, the formation of secondary phases is intricately linked to the dissolution of primary phases (e.g., White and Brantley, 2003; Maher et al., 2006; Ganor et al., 2007; Maher et al., 2009; Zhu and Lu, 2009; Emmanuel and Aque, 2011). However, due to the fact that these secondary phases are often nanometer-size, direct imaging of the way in which they form, and determining how they impact primary mineral dissolution, represents a significant challenge.

In recent years, high resolution in situ imaging techniques, such as atomic force microscopy (AFM) and vertical scanning interferometry (VSI), have been used extensively to study reacting mineral surfaces (e.g., Lüttge et al., 1999, 2003; Dove et al., 2005; Bisschop et al., 2006; Arvidson and Lüttge, 2010; Ruiz-Agudo and Putnis, 2012; Daval et al., 2013; Levenson and Emmanuel, 2013). These techniques provide images of the surface that can be used to calculate quantitative maps of surface dissolution patterns, and to express dissolution rates as probability density functions or reaction rate spectra (Fischer et al., 2012; Lüttge et al., 2013). Crucially, such analyses can help to identify the mechanisms controlling surface reactions in different geological materials. For example, small crystal size and the resulting high density of grain boundaries could lead rocks to behave very differently to individual large crystals; in fact, high resolution studies have indeed shown that micritic limestone can dissolve much faster than calcite spar crystals (Fischer et al., 2012; Lüttge et al., 2013).

In contrast to the relatively large number of studies that have examined minerals that dissolve congruently, the application of in situ imaging techniques to systems exhibiting both primary mineral dissolution and secondary phase precipitation has so far been limited (e.g., Urosevic et al., 2012). Moreover, no such studies have yet explored the behavior of coupled mineral dissolution–precipitation in actual rock samples. One of the obstacles usually associated with exploring coupled reactions in rocks is that the minerals most often involved – silicates – react at very slow rates at near-ambient conditions, so that changes are difficult to observe at the time scales of standard laboratory experiments. However, one rock type that reacts much more rapidly, and which could potentially serve as an analogue for other systems, is

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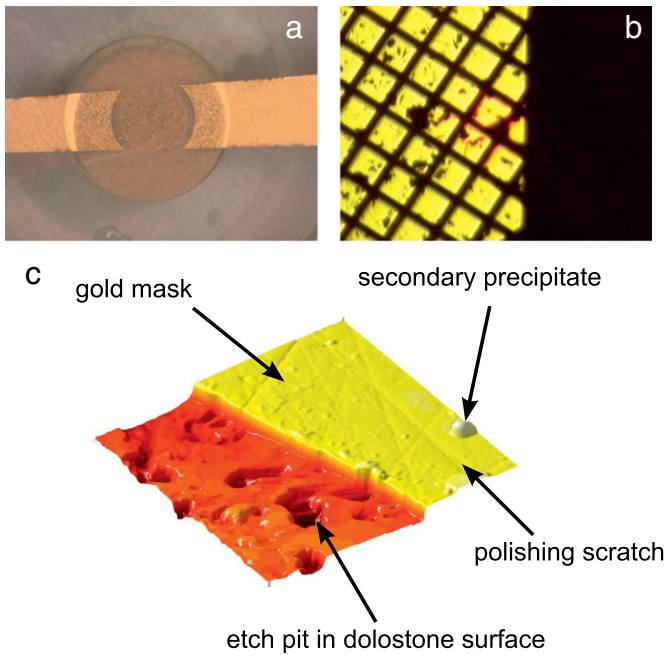


Fig. 1. Dolostone samples with partial gold mask: (a) optical microscope image of a 5 mm diameter dolostone sample embedded in a plexiglass disk; (b) optical microscope image showing gold islands and dark criss-cross pattern of the exposed dolostone surface; the small triangular structure near the center of the image is the AFM cantilever; (c) 3D rendition of a $10\ \mu\text{m} \times 10\ \mu\text{m}$ AFM scan of the dolostone surface at the end of an experiment ($\text{pH} = 4.0$; $\Delta t = 70\ \text{min}$). The yellow area represents the gold mask, while darker reddish regions represent the dissolved dolostone surface. The bumps on the gold surface are a Mg-rich secondary phase. Using the polishing scratches visible through the gold mask, a reliable datum can be determined that can be used to obtain accurate dissolution maps. Horizontal and vertical scales are equal.

dolostone. Under mildly acidic conditions dolomite – the dominant mineral comprising dolostone – dissolves (Busenberg and Plummer, 1982; Chou et al., 1989; Gautelier et al., 1999; Pokrovsky et al., 1999; Lüttge et al., 2003) with a nano-scale secondary Mg-rich precipitate, most likely a hydrated magnesium carbonate phase, forming on the

surface within minutes of contact with fluid (Urosevic et al., 2012). Thus, dolostone could provide an excellent model for determining the influence of secondary precipitates on the dissolution of primary minerals under laboratory conditions.

The primary objectives of this study were twofold: (i) to examine the surface dissolution patterns on dissolving dolostone surfaces, and (ii) to determine the surface evolution rates under different fluid conditions. To achieve this, atomic force microscopy was used to image polished dolostone samples at different pH conditions ranging from 3.5 to 4.5. The dissolution patterns and calculated rate spectra in these experiments are used to assess the mechanisms controlling surface retreat, and the suitability of a statistical model to describe rate spectra is explored. Finally, the implications the results have for other geological systems are assessed.

2. Methodology

2.1. Experimental methods

To determine the way a dolostone surface dissolves when in contact with reactive fluids, a series of experiments were carried out on samples collected from the predominantly dolomitic Late Cretaceous Weradim Formation exposed in outcrops on the Givat Ram campus at the Hebrew University of Jerusalem in Israel. Grain size in the collected samples is typically $10\text{--}20\ \mu\text{m}$, and porosity is estimated from digitized optical microscopy images to be around 20%. Mineralogy of the samples was determined from X-ray diffraction to be $\sim 99\%$ dolomite and $\sim 1\%$ calcite.

To obtain high resolution in situ images of the mineral dissolution process, atomic force microscopy was used (Veeco Multimode 8 AFM with a NanoScope V controller and NanoScope version 8.15 software). The experimental protocol employed a 5 mm diameter core of dolostone embedded in a plexiglass disk, which was polished by hand until smooth using a diamond-impregnated textile (Policloth; Fischer). Following polishing, the sample was rinsed with deionized water and wiped with ethanol. To create a surface that would serve as a datum in the experiments, a Transmission Electron Microscopy (TEM) grid was first attached to the polished surface; a thin film deposition system was then used to apply a 10 nm layer of titanium, followed by a 140 nm thick layer of gold. Finally, the TEM grid was removed to

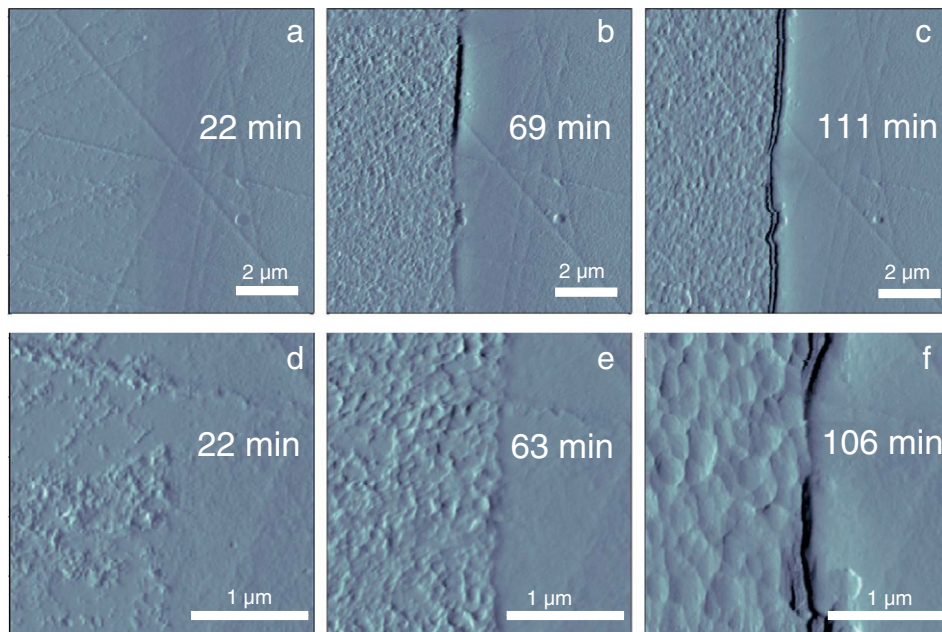


Fig. 2. AFM scans (Peakforce error signal) of an experiment carried out at $\text{pH} = 4.5$ at different times after fluid injection: (a) 22 min; (b) 69 min; (c) 111 min; (d) 22 min; (e) 63 min; (f) 106 min. In each image, the smooth region to the right of the field was masked in gold. The Peakforce error signal can be used to create pseudo 3D images of the surface, and is similar to deflection error in contact mode or amplitude error in tapping mode.

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