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**Water Rock Interaction [WRI 14]****Fundamental controls of dissolution rate spectra: comparisons of model and experimental results**Andreas Lüttge \* <sup>a,b</sup>, Rolf S. Arvidson<sup>a</sup>, Cornelius Fischer<sup>a,b</sup><sup>a</sup>University of Bremen, MARUM and FB5, Bremen (Germany)<sup>b</sup>Department of Earth Science, Rice University (USA)**Abstract**

Real-time microscopic observations of reacting mineral surfaces have provided a significant advance in the understanding of mineral dissolution and growth. The kinetics of surfaces are often dominated by the distribution of defects, e.g., screw dislocations, that provide a critical means of sustaining step movement and kink creation that are fundamental to dissolution and growth processes. However, in natural settings, the discontinuities created by physical grain boundaries and contacts may constitute a critical contribution to “whole rock” reactivity, a point that has been recognized in the past. Because of the complex relationship between mineral surface characteristics such as area, roughness, and reactivity, this problem requires a modeling approach that examines the relationship between rate and surface morphology. This approach is relevant to the question of whether a critical size exists that is governed by surfaces kinetics, below which the reactivity of grains is dominated by contributions from boundary sites. We discuss these results in light of experimental observations of the statistical distribution of rates using the concept of rate spectra.

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*Keywords:* dissolution rate spectra, reactive surface area, and kinetic Monte Carlo simulations.**1. Introduction**

Over the past two decades, critical information of mineral surface topography and reactivity has been derived from direct observations using atomic force microscopy, optical interferometry, surface spectroscopy, and related instrumental approaches. Much of the AFM work on the dissolution of silicate and carbonate minerals has focused on defect-driven reactions, in which screw dislocations provide a critical mechanism for sustaining the movement of steps over the surface [1]. These investigations as a

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rule involve crystals having diameters of  $>1$  millimeter. However, it has also long been recognized that the edges of grains also provide a source of reactive sites [2]. In a perfect crystal with a cubic form, for example, it is obvious that the ratio of the total edge length to surface area increases with decreasing crystal size. This problem was recently introduced in terms of intrinsic variations in rate [3]; in this paper, we use this concept as a means of comparing model results with experimental observations.

The model described below generates a three dimensional Kossel-Stranski crystal in which all bonds are equivalent, and uses conventional kinetic Monte Carlo techniques to simulate the dissolution process. This powerful approach has provided significant insight into the relationship between dissolution kinetics and its morphological expression in terms of a crystal's surface morphology [4]. A key concept is that a heterogeneous distribution of sites exists on a reacting crystal surface (Fig 1A), with large differences in potential rates (attachment, detachment, diffusion, etc.) as a function of both immediate and long-range coordination (Fig 1B). Our purpose here is to examine the evolution of this distribution on the surface and its impact on overall reactivity.

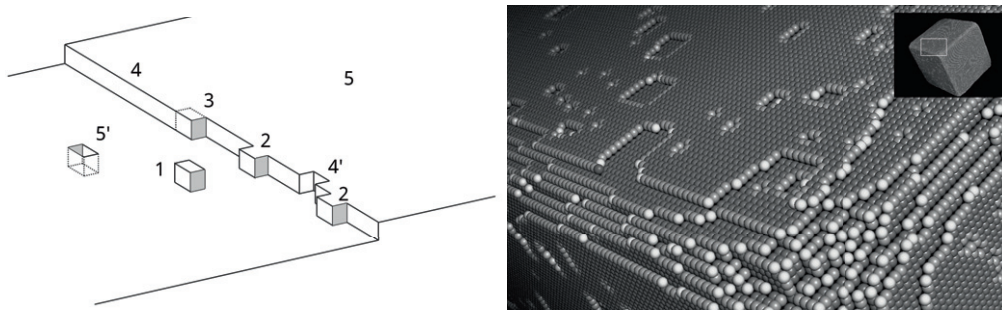


Fig. 1. Left: Simple schematic diagram of a 2D Kossel-Stranski crystal surface, showing principal sites: single-bonded atom (1), 2-bonded cluster or molecule sorbed to step edge (2), kink site (3), step edge (4), newly nucleated step vacancy or “double” kink (4’), terrace (5), and terrace vacancy (5’). Right: Detail of corner and monolayer pits of 3D Kossel-Stranski cubic crystal, showing terrace atoms, step edge sites, kink sites, and 2-bonded chains or clusters.

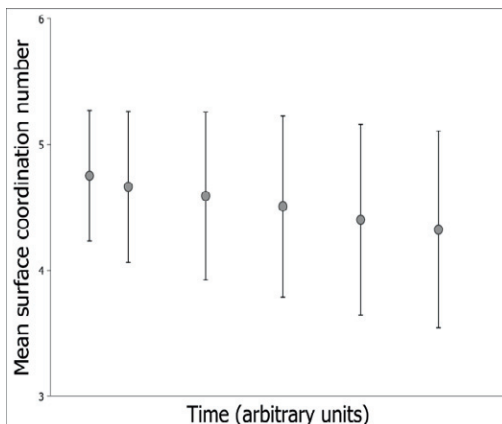


Fig. 2. Model results showing the decrease in mean atomic coordination number as stable areas of the surface are consumed, with increasing dispersion.

## 2. Modelling results

The kinetic Monte Carlo simulation shown here considers two fundamental processes: attachment/detachment of surface atoms and their surface diffusion. These two processes are parameterized by activation energies that are linearly related to local coordination numbers, and thus give rise to a Boltzmann distribution in rates. During the simulation, the progressive loss of material from the surface results in the secular evolution of site distribution. This evolution has two key consequences. First, preferential attack of grain boundaries results in the loss of stable terrace sites, decreasing the mean coordination number (Fig. 2). In addition, there is also an *increase* in the diversity of remaining sites. These

two trends are illustrated graphically in the sequence of Fig. 3. Here the material loss and synchronous increase in surface roughness is shown at time steps corresponding to 5, 10, 20, 30, 40, and 50 percent of dissolved mass.

### 3. Experimental results

We investigated the material release during dissolution from a dense fine-grained rock (micrite) that is composed of a multitude of grains. The heterogeneous dissolution of simple grain surfaces, as expressed in the simulation shown above, is also observed in these complex materials.

Dissolution of micrite results in a surface topography that is fundamentally different from those of an etched single crystals [3]. Here we investigate the evolution of dissolution rate spectra of micrite in more detail: a polished micrite surface reacted for up to four hours at pH 4.7. Initially the surface shows height deviations in the range of about 0-200 nm below the smooth “zero” plane (Fig. 4, dashed line, 0h). After an initial dissolution period of one hour, a more complex surface height distribution was observed. This height distribution can be converted into a rate spectrum that provides information about the rate distribution, characterized by a single asymmetric peak with a significant shoulder. This shape indicates heterogeneous material release from the surface. After three hours of reaction, the rate spectrum has evolved to a narrower peak; however, the shoulder at the right side (higher rates) of the distribution is still preserved, indicating two persistent kinetic modes. The rate distribution after four hours of reaction changes fundamentally: The rate spectrum is characterized by a comparatively broad peak of simpler shape, indicating the existence of a large variability of surface reactivity. This observation is consistent to the result shown in Fig. 2: the progressive divergence in rates.

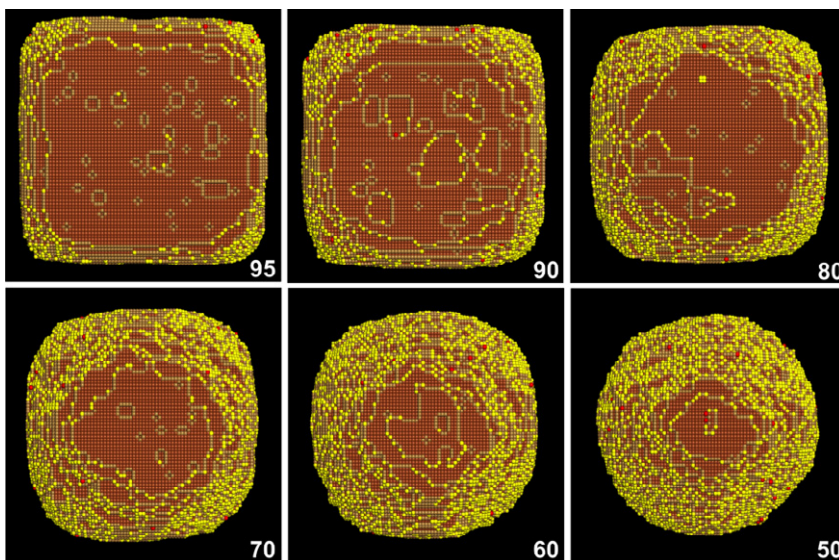


Fig. 3: Kinetic Monte Carlo results using  $\Phi/kT$  and  $\epsilon_D$  equal to 4 (corresponding to single bond hydrolysis activation energy and diffusion, respectively).

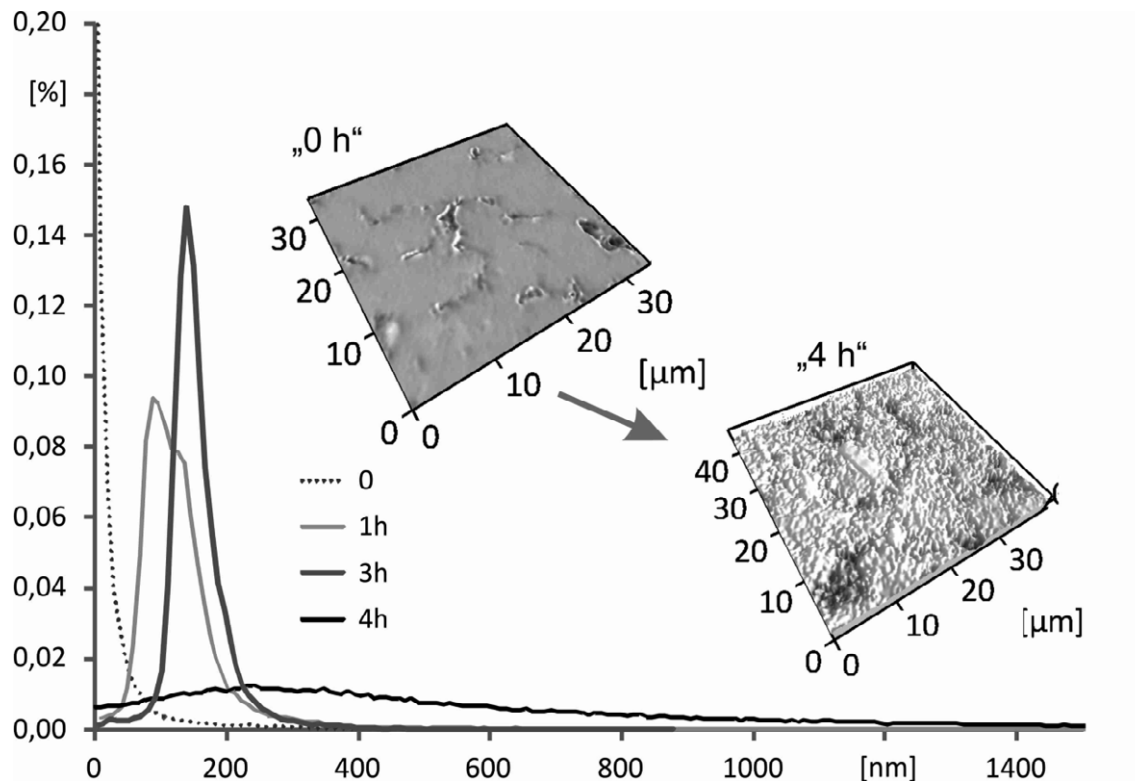


Fig. 4: Sample height retreat spectra (resulting in rate spectra) of dissolving micrite after 0, 1, 3, and 4 hours. For illustration, vertical scanning interferometry (VSI) surface topographic maps graphically show the change in roughness between initial and final time steps.

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