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Beyond the conventional understanding of water–rock reactivity

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ABSTRACT

A common assumption is that water–rock reaction rates should converge to a mean value. There is, however, an emerging consensus on the genuine nature of reaction rate variations under identical chemical conditions. Thus, the further use of mean reaction rates for the prediction of material fluxes is environmentally and economically risky, manifest for example in the management of nuclear waste or the evolution of reservoir rocks. Surface-sensitive methods and resulting information about heterogeneous surface reactivity illustrate the inherent rate variability. Consequently, a statistical analysis was developed in order to quantify the heterogeneity of surface rates. We show how key components of the rate combine to give an overall rate and how the identification of those individual rate contributors provide mechanistic insight into complex heterogeneous reactions. This generates a paradigm change by proposing a new pathway to reaction model parameterization and for the prediction of reaction rates.

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1. Introduction

Recent experimental results have shown conclusively that the conventional “mean rate” approach is deceptive and fails to provide predictive power for reaction rates of even simple mineral phases under carefully controlled conditions (Arvidson et al., 2003; Daval et al., 2013; Fischer et al., 2012a; Wolthers, 2015). Regardless of the mineral type, the resulting uncertainty for interpretation or prediction of material fluxes is two to three orders of magnitude under identical or similar chemical conditions (e.g., Arvidson et al., 2003; Avery and Benning, 2008). The reason for this uncertainty is simple: The results of concurrently acting reaction mechanisms may not be quantified using a simple normal distribution of the overall rate. The assumption of a mean rate implies the occurrence of a single reaction mechanism and thus precludes determination of mechanistic explanation of reaction kinetics. As a consequence, the use of mean reaction rates may be misleading for predictions related to management of nuclear waste management (Ewing, 2015; Hellmann et al., 2015) or reservoir rock evolution (Taylor et al., 2010). On the positive side, however, the measurable heterogeneity of surface reaction rates is key to mapping concurrently acting reaction mechanisms, which are the kinetic signature of processes at the atomic scale (Luttge et al., 2013b). The analysis of spatially-resolved measured dissolution or precipitation flux maps describes the overall range of reactivity and the spatial heterogene-

ity of surface reactivity. The statistical analysis of flux map data in the frequency domain, using the spectral distributions of rate contributors, allows us to understand how reaction rates vary in time and space. Consequently, this information has been integrated in the concept of “rate spectra” (Fischer et al., 2012a). Subsequently, several applications of this statistical analysis based on the rate spectra concept have been published (e.g., Emmanuel, 2014; Emmanuel and Levenson, 2014; Fischer et al., 2015, 2014).

The application of reactive transport models requires parameters that describe the reaction kinetics of solid materials. Approximating these by the “mean reactivity” approach is incorrect (Luttge et al., 2013b; Pollet-Villard et al., 2016; Wolthers, 2015), and the variations in reaction rate in space and time need to be taken into account. The spectral distribution, i.e., the shape and amount of rate contributors, reflects the material’s reactivity and provides a method for modeling the full complexity of reaction rates. In this study, we utilize the dissolution of polycrystalline calcite as an example of how to identify and use such parameters for future applications.

2. Materials and methods

2.1. Experimental setup

A polished calcite marble sample (Lasa, Italy) (Unterwurzacher and Obojes, 2012) was partially masked with a gold layer of 550 nm thickness using the physical vapor deposition (PVD) technique (Mahan, 2000). The chemically-inert masked surface section

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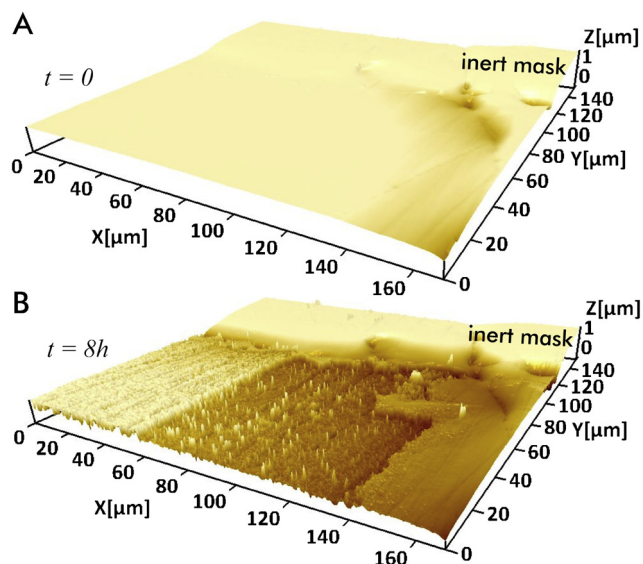


Fig. 1. Surface maps of reacted calcite marble surface before (A) and after (B) a reaction period of 8 h. The inert gold mask (upper section) was used as a reference height datum for height difference calculations.

served as a height reference for height difference calculations after dissolution reactions. Dissolution experiments were performed in a flow-through cell. The fluid volume in the cell was 300 μL . The volumetric flow rate was 30 mL/h, and the reaction period was 8 h. We used a 2.2 mMol Na_2CO_3 solution, equilibrated with air to obtain constant pCO_2 at pH 9.2 for dissolution experiments. Experimental settings similar to those in many calcite dissolution studies in literature were used in order to provide comparable results (Arvidson et al., 2003; Chou et al., 1989; Liang et al., 1996; Morse and Arvidson, 2002; Sjöberg, 1978).

2.2. Surface topography analysis and calculation of rate maps

After each reaction step, the surface topography was analyzed using vertical scanning interferometry (VSI). This method is capable of analyzing sample surface height changes in the range of 1 nm using a Mirau interferometry system (Luttge et al., 1999), thus making the method suitable to track minute changes in material flux from reacting surfaces. We applied a ZeMapper interferometer system (manufacturer: Zometrics, Tucson, AZ) equipped with five interferometry objectives (Fischer et al., 2012b). Measurements were performed using white-light mode. Before and after the dissolution experiment, the sample surface topography was measured by VSI including both a masked and a reacted surface portion (Fig. 1). Using the inert surface section as a height reference, a height difference map was calculated. The height difference (dz) per reaction time (dt) of each (x, y) map point contains information about the height retreat velocity (dz/dt). The material flux map was used to calculate the rate map by dividing each (dz/dt) value by the molar volume $V_m = 36.9 \text{ cm}^3/\text{mol}$. Comparisons to mean reaction rates were calculated by using the mean height retreat of all dz (x, y) values and, subsequently, the mean retreat velocity and rate according to the above-mentioned protocol.

2.3. Kinetic Monte Carlo simulations

We applied a kinetic Monte Carlo (kMC) code for simulation of the dissolution of a simple cubic KOSSEL-type crystal (Kurganskaya et al., 2014). The model is based on the Bortz–Kalos–Lebowitz (BKL) algorithm (Bortz et al., 1975). The model includes periodic boundary conditions. The contrast in reactivity was introduced by

the defect type and density, i.e., screw dislocations and point defects. The defects were randomly seeded by using uniformly distributed random numbers for their center (x, y) coordinates. The simulation of the reaction starts with the opening of hollow cores at screw dislocations, followed by lateral and vertical etch pit growth (Burton et al., 1951; Lasaga and Luttge, 2001). At point defects, however, the pit grows only laterally. The evolution of surface roughness is controlled by the superimposition of etch pits. The iteration steps are defined by the number of dissolved blocks. The respective reaction time increment, Δt_i , between the ($i - 1$)th and i th events is calculated as a reciprocal sum of all N probabilities P of surface reactions normalized by the reaction attempt frequency, ν , i.e., the fundamental frequency (Blum and Lasaga, 1987; Pelmenschikov et al., 2001), that we set to 10^{12} :

$$\Delta t_i = \frac{1}{\nu \cdot \sum_{j=1}^N P_j}$$

This allows for the tracking of the reaction progress and the analysis of the overall rate as well as the kink and step site densities in time units. The model settings included constant bond strength conditions ($\Phi = 4$, normalized to kT units). We used SPIP 5.0.5 software for the visualization of the simulations' results that are presented as surface maps, material flux maps, and histograms. We used the height information from the pristine model surface for height difference map calculations.

3. Results and discussion

3.1. Reaction rate map and rate spectra analysis

First, we investigated the spatial distribution and quantitative heterogeneity of dissolution rates. Fig. 2A shows a map of the dissolution rate distribution of a polycrystalline calcite, i.e., a marble rock sample. A masked sample section served as a height reference with no dissolution. Reaction time was 8 h at pH = 9.2 in a flow-through experiment. The map shows three calcite grains that exemplify the overall rate range and the spatial distribution of the material flux of the reacted material. The first section [1] shows almost no surface normal retreat but locally enhanced dissolution rates. The highly-reactive spots are of uniform dimension and show a characteristic spatial distribution. Conversely, the second map section [2] shows a clearly elevated surface normal retreat. Additionally, and similar to [1], locally elevated material flux is observed at surface pits. Note the enhanced reaction rate at the coalescing surface pits of grain 2 close to the grain boundary on the right side. The third grain [3] is characterized by a moderate surface-normal retreat rate. No deep etch pits are visible as a source of elevated reaction rates. Fig. 2B quantifies these observations statistically in a rate spectrum. It shows the relative frequency of all rate contributions of map sections [1–3]. The measured rate range is about 2.5 orders of magnitude, from 0.003 to $0.7 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$. The overall rate is the integral of all rate contributions (dotted line) and shows a complex multi-modal shape. Consequently, the deconvolution of the rate spectrum informs about the modes of the rate distribution. The modes are the major contributors to the overall rate. The identification of such contributors and the analysis of their shape, i.e., height and width, inform about the governing mechanisms that control the reactivity of the rock grains (Table 1). Arvidson et al. (2003) provide a thorough compilation of calcite dissolution rates from literature data over a wide range of the pH. Similar to our experimental conditions, the reported rate variability at pH = 9 is about $0.03\text{--}10 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$. The highest rates of this compilation at about $10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ reflect the enhanced reactivity of calcite powder (Sjöberg, 1978) that is explained by the much higher

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