Synthetic Dissolution Rate Spectra

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Many natural processes and technical applications require our ability to provide a reliable prediction of crystal surface reactivity. This reactivity is not a material constant. Instead, the existence of intrinsic variability in surface reactivity has been concluded from a multitude of experimental investigations [1]. Consequently, single rate constants and homogeneous surface area normalization are problematic constraints for the explanation and prediction of surface reactions.

The concept of rate spectra has been recently introduced [2]. This concept includes and quantifies the individual contributions to the overall rate and, thus, analyzes heterogeneous surface reactivity. Rate spectra are used to evaluate rate distribution data that are based on direct surface analysis using data collected by, e.g., atomic force microscopy or vertical scanning interferometry.

In this contribution we connect the rate spectra concept for the first time with results from kinetic Monte Carlo (KMC) simulations. We apply temporal sequences of KMC results of crystal dissolution. The heterogeneity of surface rates causes shape differences of rate spectra. Thus, the KMC technique can be used to produce synthetic rate spectra. We analyze the evolution over time of rate spectra systematically for the specific impact of crystal defects, e.g., the size and density of screw dislocations. This allows us to gain deeper insight into the mechanistic interpretation of rate spectra.

The propagation of step waves and the coalescence of etch pits cause the geometric complexity and dynamic of a crystal surface. A critical result is the evolution of less vs. more reactive surface sections. Synthetic rate spectra show the temporal stability of such surface sections and their impact on the overall evolution of surface reactivity with important applications towards evolution of pore systems and permeability as a function of surface reactivity.

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