A multi-scale approach to study mineral dissolution: Kinetic Monte Carlo models and experimental observations

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Introduction

Dissolution kinetics of minerals is a challenging problem to study. The major challenge is the chemical complexity of any natural reactive system incorporating a large amount of species both in the fluid phase and at the solid surface. The structural and chemical complexity of minerals naturally leads to a large number of possible reactive surface groups. It is thus not possible to treat dissolution as detachment of a single “surface complex” controlling the overall dissolution rate. In the past, the conventional approach has been to describe dissolution kinetics solely on its functional dependence on environmental parameters, e.g. saturation index or pH value. However, this approach has produced discrepancies of several orders of magnitude in “rate constants” measured in different laboratories. This problem is described in detail as an intrinsic rate variance stemming from the complexity of reactive surface structure together with a large number of possible dissolution scenarios [1,2]. Our goal is to develop the next generation of dissolution models capable of capturing dissolution mechanisms at different scales, and identifying the sources of rate variance.

Methods

Kinetic Monte Carlo (KMC) method is a stochastic approach to simulate the temporal development of a reactive system. Detachment of surface groups is performed as a series of reactive events whose probabilities are defined by surface group (atom or molecule) dissolution rate. This rate is a thermally activated process calculated as a function of local site coordination. We developed KMC models for three contrasting types of minerals: phyllosilicates, characterized by layered crystal structure, quartz, representing a 3-D framework of covalent Si-O bonds, and carbonates, representing ionic crystals. Each model is characterized by a level of complexity sufficient to reproduce experimental observations acquired by Vertical Scanning Interferometry (VSI) and Atomic Force Microscopy (AFM) techniques.

Results and Discussion

Our experimental observations using Vertical Scanning Interferometry (VSI) demonstrated that basal faces of mica dissolve via formation of etch pits and their interaction [3]. This finding contradicts the conventional view of phyllosilicate dissolution as a process taking place only at grain edges while basal faces remain intact. AFM measurements showed that etch pits develop a specific crystallographic shape, indicating consistent differences in the velocities of steps moving in different crystallographic directions. We developed a series of KMC models testing various hypotheses regarding controls on site reactivity until we reproduced experimental observations [4].

Dissolution mechanisms of quartz at the molecular level have been previously studied using ab initio methods and experimental AFM observations at the nano and micro-scales [cite?]. Quartz crystals have energetically distinct stable faces. Each face is characterized by a different dissolution mechanism, corresponding etch pit shapes, and surface topography. We developed four KMC models, incorporating various details of site coordination, and compared performance of each model by verifying simulations against experimental data [5]. A striking finding of the model results is the sensitivity of simulated dissolution patterns to model complexity and parameters for prism and pinacoid faces, versus corresponding insensitivity of the rhombohedral faces. This dependence shows the important contribution of surface-water interface bonding network prevailing on both prism and pinacoid faces to the overall dissolution mechanism.
Calcite is an attractive mineral to study, because specific step velocities are fast enough to permit collection of a large number of observations over short periods of time, but slow enough to be captured by a conventional AFM. Thus a large amount of kinetic data for calcite can be found in literature. A remarkable observation is the 2-3 of magnitude variation of dissolution rates [6]. We applied a parameterized KMC model to simulate dissolution of calcite in real time and identify the sources of spatio-temporal rate variance [7]. As it has been found in experiments [8], most of the material flux is attributed to the concave steps formed at the intersection of straight steps. The analysis of surface normal retreat showed a strong dependence of dissolution rate on type and availability of defects.

Conclusions

A combination of Kinetic Monte Carlo method and microscopic experimental observations can be used as a powerful technique to iteratively test various hypotheses about dissolution mechanisms and controls. We have found that both first and second order coordination spheres have crucial importance for site reactivity on mica and quartz surfaces. The bonding network between mineral and fluid phases might affect dissolution kinetics of quartz. A proper parameterization of KMC models makes it possible to understand spatio-temporal rate variance and identify its contributors by using calcite as a case study.

References