

# A comprehensive stochastic model of phyllosilicate dissolution: Structure and kinematics of etch pits formed on muscovite basal face

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## Abstract

Accurate modeling of phyllosilicate dissolution kinetics is a complex problem involving recognition of the influence of structure, chemical composition, lattice defects, and surface topography on local and global dissolution mechanisms. Previous research has provided a wealth of experimental observations that illustrate the dominant role of etch pits in formation of the steps on the basal face of mica during the dissolution reaction. The shape of the etch pits bears important information on surface reactivity and dissolution rate anisotropy at given environmental conditions. In order to understand the influence of various kinetic factors on etch pit and step morphology, as well as the overall dissolution mechanisms, we have developed a new Kinetic Monte Carlo model simulating dissolution of these minerals. The model considers the effects of chemical composition, structural position, the number of first and second-order nearest neighbors and the steric hindrance of surface atoms on the etch pit morphology and step reactivity. We describe several complexity levels of the model which are characterized by the different ranges of the effects considered. These levels were developed in order to find the most optimal model capable of predicting experimentally observed etch pit morphologies. Our simulation results show that the models based on the sole consideration of the first coordination sphere in general can predict etch pit shape and orientation, while recognition of the site reactivity difference imposed by the steric factors helps us to explain the geometry of monolayer pit superposition. However, the distinction of the ledge and kink sites at all the experimentally observed surface steps is possible only with the use of the second-order neighbors. Based on these findings, we propose a mechanistic scheme explaining the role of the first and second-order coordination numbers in step stabilization and correct prediction of the etch pit structure.

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## 1. INTRODUCTION

Phyllosilicates are often distinguished as minerals that have unique dissolution mechanism due to their layered structure. The extreme difference in basal (001) and edge (*hk*0) face reactivity is typically cited as a primary explanation for the specific dissolution kinetics of these minerals (Turpault and Trotignon, 1994; Rufe and Hochella, 1999;

Bickmore et al., 2001; Hodson, 2006; Kuwahara, 2006, 2008). However, the occurrence of etch pits on basal faces undermines the general assumption of low (001) face reactivity (Patel and Tolansky, 1957; Patel and Ramanathan, 1962; Johnsson et al., 1992; Rufe and Hochella, 1999; Maurice et al., 2002; Brandt et al., 2003; Aldushin et al., 2006a,b; Shao et al., 2010, 2011; Kurganskaya et al., 2012). The presence of the etch pits provides a basic explanation for crystal dissolution mechanisms proceeding via the generation of steps at etch pit walls, their propagation and coalescence, and, thus, the gradual retreat of the

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dissolving surface (Lasaga and Luttge, 2001, 2003). Putative differences in reactivity of basal versus edge faces have little relevance to etch pits associated with  $c^*$ -oriented screw dislocations (Amelinckx, 1952; Baronnnet, 1972, 1975; Sunagawa and Koshino, 1975; Pandey et al., 1982). In addition, published data indicate that the layered structure is responsible for a range of other important kinetic effects in phyllosilicate dissolution. For example, the surface step, which typically has one atomic thickness in other minerals, is made of two or three atomic (tetrahedral and octahedral) layers in phyllosilicates (Rufe and Hochella, 1999; Brandt et al., 2003; Stübner et al., 2008). Another important phenomenon is the specific step interlacing, or “zigzag” patterns, caused by the interlayer rotation common for this class of minerals (Snowden-Ifft et al., 1993; Nagahara et al., 1994; Kuwahara et al., 1998, 2001; Aldushin et al., 2006b). Thus obtaining a more complete understanding of phyllosilicate dissolution mechanisms requires us to integrate the mechanisms common for all minerals and the specific influences of the layered structure. In our previous study (Kurganskaya et al., 2012) we discussed these issues in detail. Particularly, we used experimental observations of reacted surface topography to demonstrate that the step-wave model explains mechanisms of phyllosilicate dissolution. The differential “basal vs. edge” reactivity is not a unique feature characterizing sheet silicates since the other minerals have differential reactivity between the terrace, step and kink sites. We thus treated phyllosilicates in a very general way, explaining their dissolution through kink site and step propagation, step coalescence, etch pit growth and normal surface retreat. Although our previous experimental data demonstrated the structure of etch pits on (001) muscovite face, it was inadequate in describing smaller surface features. These smaller features are presumably influenced by kink site structures, mechanisms of dissolution at these sites, dissolution anisotropy within the mica layers, and etch pit morphology, all of which are integrated into our present model.

The formulation of a KMC model for mineral dissolution based on elementary surface reactions (e.g., atomic attachment, detachment, and surface diffusion) has a relatively short but successful history. Blum and Lasaga (1987) used KMC methods to define dissolution rates in the presence of a strain field induced by dislocations. They used a simple cubic or Kossel model to reveal the mechanisms of etch pit formation around screw dislocations and the formation and movement of steps at various saturation states. Although such simple models can predict general dissolution mechanisms they lack the kinetic insight of important chemical and structural effects specific for certain minerals. Thus, Wehrli (1989) proposed a KMC model for the dissolution of oxides with complex compositions. More than a decade later, Lasaga and Luttge (2004a,b) formulated a general KMC model, with kink site-based dissolution rate laws applied to very simple AB and  $A_3B$  crystal structures. Despite their simplifications, these studies demonstrated the capabilities of the KMC method to extract important mechanistic information, e.g., statistics of the reactive sites, rate dependence on saturation state, the effect of net activation energy, and more. Particularly, the  $A_3B$

model served as a precursor template for the study of albite dissolution. Zhang and Luttge (2008, 2009a,b) expanded this basic model by introducing complete feldspar structures and studied the dissolution mechanisms of the entire plagioclase series. Their work addressed order–disorder influences on dissolution rate, the influence of Al concentration in plagioclase feldspars, saturation state dependencies, and temporal evolution of feldspar nanograin morphology and reactivity. Meakin and Rosso (2008) made another significant advance in the KMC modeling era showing the ability of this method to study dissolution at the bigger scales. They used up-to-date efficient algorithms to simulate dissolution of a large ( $4000 \times 4000$  surface sites) pitted surface of Kossel crystal and demonstrated the possibility of using various dislocations in the model. Reaching these scales allow us to access dissolution mechanisms of complex rough surfaces having multiple step sources.

Each of the surface reactions considered in these models (dissolution, surface diffusion and adsorption) can be viewed as an integrated result of the bond breaking and formation taking place at any given surface site, and can be characterized as a “site-centered” approach. An alternative “bond-centered” method, based on the explicit incorporation of bond-breaking-forming reactions in the simulation algorithm, has also been developed. According to this approach, a “reactive event” performed at each iteration step can be either bond breaking or formation, instead of departure or arrival of molecules from and to surface lattice sites as it simulated using “site-centered” method. In 1995, Lasaga had introduced such a model for kaolinite dissolution, where the bond hydrolysis reactions were used instead of dissolution or molecular detachment reactions mentioned above. The results demonstrated that kaolinite dissolves through a layer-by-layer mechanism. It is important to note that the latter mechanism differ from the stepwave mechanism of micas described by Kurganskaya et al. (2012). In contrast, Nangia and Garsion (2009) developed another method in which they utilized the reactive potential function to calculate the probabilities of bond breaking-forming reactions. An important breakthrough was the consideration of the influence of long-range order effects of second and third order neighbors on the dissolution probabilities. The strong influence of site topology effect on dissolution rate from surface sites was previously demonstrated already by using electronic structure calculations (Pelmenschikov et al., 2000; Criscenti et al., 2006). Although these “bond-centered” models provide more realistic and accurate results than the “site-centered” models, molecular detachment becomes an extremely rare event due to the large number of bond-healing reactions competing with the hydrolysis reactions (Pelmenschikov et al., 1992). As a consequence, the typically simulated time-scale and system size are too small to be compared to microscopic observations of surface features and measured dissolution rates. Moreover, simulations involving small systems (such as nanoclusters or nanograins) do not capture all spatiotemporal variability of surface reactivity that is inherent to natural and synthetic crystals (Luttge et al., 2013).

In contrast, the “site-centered” approach allows us to simulate dissolution of crystal surfaces that are large enough to produce at least etch pits that are commonly

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