



Simulation of surface dynamics during dissolution as a function of the surface orientation: Implications for non-constant dissolution rates



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ABSTRACT

An important problem in geochemistry is the understanding of how changes occurring on a surface during dissolution affect the variability of measured dissolution rates. In this study a new approach to study the effect of surface dynamics on dissolution rates is tested by coupling experimental data with a numerical model that simulates the retreat of surface profiles during dissolution. We present specific results from the simulation of dissolution of fluorite surfaces. The equations that determine the retreat of a surface are based on experimentally obtained equations that relate the retreat rate of a surface to a single variable, the crystallographic orientation of the surface.

Our results show that depending on the starting orientation, different types of topography are developed, similar to those observed experimentally. During the initial dissolution phase, changes of topography are rapid and associated with fast dissolution rates. The progressively slower dissolution rates are coupled with the development of surface segments with orientations that dissolve at a slower rate. Consequently, the overall retreat rate of a profile decreases during the simulation, and tends to a near-constant value. The results show a close relationship between dissolution rates, surface orientation and surface dynamics, which suggests that the dissolution rate of a specific mineral phase is not constant but varies with dissolution time and surface structure. This variability needs to be considered in the evaluation of experimentally derived dissolution rates, future dissolution experiments, and predictive kinetic models of dissolution.

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1. Introduction

Predictive dissolution models and an in-depth understanding of dissolution processes are needed in many areas of geochemistry such as the nuclear waste disposal industry (e.g. Gambrow et al., 2011), weathering (e.g. Brantley et al., 2008), mineral replacement reactions (e.g. Putnis and Austrheim, 2010) and environmental remediation (e.g. Putnis and Ruiz-Agudo, 2013). In general, dissolution is a process characterized by the breaking of bonds between atoms or clusters of atoms on a surface and the atoms in the bulk of the crystal. This is followed by the release of the surface atoms or clusters into solution, and consequent change of the surface structure where the atoms were released. The preferential dissolution of kink sites relative to steps and of steps relative to

terraces makes dissolution a dynamic process that continuously changes the surface in terms of area and reactivity (Fischer et al., 2012; Godinho et al., 2012, 2014a; Lasaga and Lüttge, 2001; Lüttge, 2005). This suggests that the traditional method of calculating dissolution rates normalized to an overall surface area (Brantley et al., 2008; Lasaga, 1981; Oelkers and Schott, 2009) should result in a variation of dissolution rates with dissolution time. Furthermore, the stochastic nature of dissolution, i.e. each surface site has some probability to be released into solution, and the existence of different surface sites characteristic of each surface orientation suggest that dissolution rates are not a constant for a single crystal phase (e.g. Arvidson et al., 2003; Fischer et al., 2012; Godinho et al., 2014a; Lüttge et al., 2013).

The dissolution processes of minerals have been extensively studied using different approaches. For example, direct observations of dissolution using atomic force microscopy or optical profilometry frequently focus on the study of cleavage surfaces with low density of defects (e.g. Cama et al., 2010; Ruiz-Agudo and

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Putnis, 2012). In classical dissolution experiments, powders with a high surface area/volume ratio and a high density of high energy sites are dissolved and the dissolution rate is monitored through the fluid chemistry. In contrast to such experiments, surfaces found in nature commonly present irregular topographies either as stepped surfaces, pores or grain boundaries (Anbeek, 1992; White and Brantley, 2003; Yanina et al., 2006). The variety of surfaces present on the starting material used in each study has been suggested to contribute to the discrepancies of several orders of magnitude of measured dissolution rates for the same mineral phase (e.g. Emmanuel and Ague, 2011; Moore et al., 2012; Yoo and Mudd, 2008).

Numerical modeling has been used to improve our ability to predict dissolution rates and study dissolution mechanisms (Lüttge et al., 2013; Stack et al., 2013 and references therein). Ideally the simulations should account for the atomic interactions between surface atoms and of these atoms with atoms in the fluid phase. This is possible using for example molecular dynamics (Stack et al., 2012, 2013). However, due to computational time restrictions, this technique is limited with regard to finite duration of dissolution and size of the modeled system. To simulate dissolution of areas that can be related to macroscopic systems simpler algorithms need to be used. This can be achieved by using a theoretical simplification relative to the atomic scale, as used in kinetic Monte Carlo methods. For example, using an algorithm in which the detachment of a surface site has a specific probability based on the number of near-neighbour sites or the energy of the site (Cama et al., 2010; Kurganskaya and Lüttge, 2013; Lasaga and Lüttge, 2001). Alternatively, the equations governing the numerical model can be set based on experimental results. Different models have been developed to simulate the development of etch pits or the macroscopic shapes of crystals caused by dissolution (Alekseev et al., 2002; Lüttge, 2005; Smereka et al., 2005; Snyder and Doherty, 2007).

In this contribution, we test whether a simple conceptual model that relates dissolution rates to the surface orientation, which has been shown to be directly related to the atomic structure of the surface (Godinho et al., 2014a), is sufficient to explain the experimental observations that show (a) dissolution rates are not constant though time, and (b) the structure of the initial surface determines the time dependent development of topography. To do this we use a simple numerical model to investigate the coupling between dissolution rates, surface orientation and surface topography during dissolution. Other environmental factors, such as solution composition or temperature are not considered, i.e. are assumed to remain constant in comparable experiments. In the presented model, we simulate the development of topography on a two dimensional profile over fluorite surfaces with different orientations and test its validity by comparison with experimental results. The novelty of this simulation approach is that the governing equations used to calculate the local dissolution rates were determined experimentally (Godinho et al., 2012) and only dependent on the orientation of a surface. Our results show that the dissolution rate of a mineral phase cannot be a single value for a specific dissolution condition (e.g. temperature, fluid composition). Instead, dissolution rates vary due to the continuous change of the surface structure during dissolution.

2. Conceptual model

The numerical model described here is based conceptually on the general model for dissolution of polycrystalline materials presented in Godinho et al. (2012, 2014a). This model is based on experimental results which showed that, during dissolution of fluorite, stable surfaces tend to persist, and high energy sites, such as steps, are progressively removed (Godinho et al., 2012). The preferential

release of atoms from less stable sites exposes more stable surfaces, causing systematic changes of topography and the progressive stabilization of the surface. The topography developed is dependent on the initial density and type of steps and the inclination of the surface relative to its closest stable plane (Godinho et al., 2011, 2012, 2014a, 2014b). Both factors are directly related to the surface orientation (Maldonado et al., 2013). Experiments show that after an initial very dynamic stage during which a high increase of roughness and fast decrease of dissolution rates occur, the surfaces tend to an approximately constant topography that is specific for each initial orientation. The continuously smaller changes of topography are caused by a progressively less dynamic surface. Furthermore, experiments showed that the progressive variation of topography is associated with an increase in surface area. Contrary to classic dissolution theory (Brantley et al., 2008; Lasaga, 1981; Schott et al., 2009), it was shown that the increase in surface area can result in the decrease of the overall dissolution rate (Godinho et al., 2014a).

To understand the dynamics of dissolution it is important to distinguish between two types of steps, here referred to as “atomic scale steps” and “macro scale steps” (Godinho et al., 2014a; Maldonado et al., 2013). Atomic scale steps are formed by the interception of two stable planes {001} and/or {111}. The atoms at the steps have a lower coordination number, thus are more likely to dissolve. When one atomic scale step is removed by dissolution a larger area of the terrace is exposed. As dissolution progresses, the density of this type of steps decreases and consequently the dissolution rate also decreases. The so-called macro scale steps are also formed by the intercept between the stable planes, thus preferential dissolution also occurs at these sites. Larger terraces exist on both sides of a macro scale step, forming a persistent source of instability from where atomic scale steps emanate to the terraces (Godinho et al., 2014a; Lasaga and Lüttge, 2001). Examples of this type of step are the top of a topographic peak formed during dissolution, the edge of a pore and a grain boundary.

3. Numerical implementation

3.1. Model set-up

We have implemented our model using the open-source modeling platform Elle (Bons et al., 2008; Jessell et al., 2001; Piazzolo et al., 2010, <http://microstructure.info/elle>). Elle was originally designed to simulate the evolution of a 2D microstructure, which is defined in a XY coordinate system according to the given governing equations. Elle is based on a data structure that can describe a polycrystalline material using a two dimensional network of nodes (Fig. 1). Grains are represented by closed polygons defined by nodes connected by straight segments. Each polygon can have independent attributes that may determine the behaviour of the nodes during the simulation. For example, a polygon can be defined as representing a crystal of predefined crystallographic orientation (polygons II–III), while an adjacent polygon may be defined as a fluid (polygon I) (Fig. 1). If two adjacent polygons have different orientation, then the dividing nodes represent a grain boundary (dashed lines) and can be given a specific distinct behaviour. The model has horizontal wrapping meaning that a node on the $X = 1$ boundary (right side in Fig. 1) is connected to a node on the $X = 0$ boundary (left side in Fig. 1). Elle has been used to study the macro scale topographical developments during stylolite formation resulting from liquid – solid interactions (Ebner et al., 2009; Koehn et al., 2004, 2007).

Dissolution of a surface is simulated by the retreat of the solid–liquid interface specified in the model. During the simulation, the

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