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Mineral dissolution kinetics as a function of distance from equilibrium – New experimental results

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ABSTRACT

We revisit a fundamental question in mineral dissolution kinetics, namely: *is the function of dissolution rate versus the distance from equilibrium continuous, or does the "switch" between two different reaction mechanisms cause a discontinuity, i.e., a kinetic bifurcation*? Based on new insight from experimental results, including direct observations of retreating crystal surfaces with vertical scanning interferometry (VSI), we present evidence that a discontinuity does indeed exist. Through a carefully designed near-equilibrium albite dissolution experiment, we show how a non-steady-state dissolution rate observed on a crystal surface reflects reactivity inherited from earlier episodes of undersaturation. This outcome forces us to re-think the common practice of extrapolating overall dissolution rates measured far-from-equilibrium to near-equilibrium conditions.

1. Introduction

A central problem in crystal dissolution kinetics involves two critical questions: (1) Can the rate's dependence on the difference in Gibbs free energy (ΔG_r, or its counterpart with respect to reaction progress, *A*, affinity) be described by a continuous function, and (2) can this dependence be described by a mathematical formalism based on the transition state theory (TST)? These questions have been at the center of our work on crystal and glass dissolution. A number of publications have addressed this issue over the last 20 years (crystal: Luttge, 2006; Beig and Luttge, 2006; Hellmann and Tisserand, 2006; glass: Icenhower et al., 2004a,b; Gin et al., 2008). Despite these efforts, no definitive answer, at least in the case of crystal dissolution, is as yet available.

Over this period several authors have measured dissolution rates of various silicate minerals, including gibbsite, kaolinite, smectite, labradorite, and albite (see Fig. 1) over a range of Gibbs free energies approaching equilibrium conditions (e.g., Nagy et al., 1991; Nagy and Lasaga, 1992; Burch et al., 1993; Gautier et al., 1994; Ganor et al., 1995; Oelkers et al., 1994; Devidal et al., 1997; Oelkers and Schott, 1999; Taylor et al., 2000; Berger et al., 2002; Hellmann and Tisserand, 2006; Hellmann et al., 2007). Most experiments exhibit a sigmoidal relationship between dissolution rate and saturation state. The explanation for this behavior is the fact that rates sufficiently far from equilibrium become independent of ΔG_r, thus establishing the so-called *dissolution plateau*. As equilibrium is approached dissolution rates decrease sharply over a small range of ΔG_r. Close to equilibrium the curve is approximately linear as rates approach zero along a shallow slope. Results published by Oelkers et al. (1994) typically exhibit a linear relationship with dissolution rates decreasing steadily as equilibrium is approached.

Recent experimental studies have focused specifically on the dissolution kinetics of albite ($NaAlSi_3O_8$). The most comprehensive long-term laboratory investigation is available from Hellmann (1994) and Hellmann and Tisserand (2006, Hellmann et al., 2007). While these studies are still in progress, the results of Hellmann and Tisserand (2006, Hellmann et al., 2007) are thus far self-consistent. A key component of our discussion here is their confirmation of highly non-linear, sigmoidal behavior of the albite dissolution rate at 100 and 150 °C and various pH values. However, a fundamental question remains unanswered: Does the sigmoidal behavior represent true steady-state conditions (*cf.* non-steady-state curves in Fig. 2), or does a discontinuity exist between two different reaction mechanisms? The answer to this question will determine the reliability of extrapolating the results of far-from-equilibrium experiments to predict rates near equilibrium.

There is recent convergence towards agreement with respect to the question of whether one or two reaction mechanisms control the dissolution kinetics of albite and other feldspars. In the past, discussion of this issue was based either on experimental observations (e.g., Berner and Holdren, 1979; Chou and Wollast 1984, 1985; Casey et al., 1988a,b; Burch et al., 1993; Gautier et al., 1994; Hellmann, 1994; Stillings and Brantley, 1995; Brantley and Stillings, 1996; Stillings et al., 1996; Alekseyev et al., 1997; Berger et al., 2002; Beig and Luttge, 2006; Hellmann and Tisserand 2006; Hellmann et al., 2007) or theoretical

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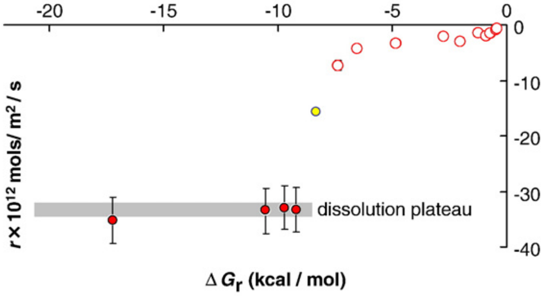

Fig. 1. Dissolution rate of albite, $T = 80$ °C, pH 8.8, taken from Burch et al. (1993). Datum in yellow was taken from Knauss and Wolery (1986) and recomputed by Burch et al. (1993) for 80 °C.

arguments (e.g., Helgeson et al., 1984; Amrhein and Suarez, 1988, 1992; Lasaga and Luttge, 2004a,b, 2005; Luttge, 2006; Zhang and Luttge, 2007, 2008a,b). However, although theoretical considerations have produced some strong arguments, their experimental confirmation has been weak and has left many in the field unconvinced. Our present study provides a definitive answer to this question. In order to further clarify and set the stage for these results, we shall first provide a brief review of our earlier arguments and position. For discussions in depth we refer the reader to the original publications.

Beig and Luttge (2006) based their discussion on an experimental investigation of the surfaces of two albite samples with VSI (vertical scanning interferometry) and AFM (atomic force microscopy). These observations and corresponding rate measurements showed that two albite samples exposed to identical reaction conditions could exhibit distinctly different dissolution rates. This difference was significant, between 1.5 and 2 orders of magnitude.

Their discussion was based on the well established BCF theory (Burton et al., 1951; Cabrera et al., 1954; Cabrera and Levine, 1956) and the so-called stepwave model introduced by Lasaga and Luttge (2001, 2003). In order to explain their observations, Luttge (2006) and Beig and Luttge (2006) proposed that the observed difference in rates is the direct consequence of a change in dissolution mechanism. According to the BCF theory a critical free energy value is required to open etch pits at line defects such as screw dislocations. Only if this critical value is reached can pre-existing hollow cores (Frank, 1951) open up into etch pits (see discussion below). The stepwave model explains that the pit walls are the source for steps that emanate from the outskirts of the pits and travel across the crystal surface. In this way, the crystal dissolves rapidly layer by layer. This important reaction mechanism has also been confirmed with AFM methods for a variety of minerals, including feldspars (Beig and Luttge, 2006) and carbonates (e.g., Luttge et al., 2003; Arvidson et al., 2003, 2006; Vinson and Luttge, 2005); we have also observed this mechanism in sulfates as well (Fewless and Luttge, unpublished data). Although this description is a simplification of the complex process of crystal dissolution, it describes the fastest and therefore rate-controlling mechanism quite well. In contrast, at near-equilibrium conditions the difference in free energy is insufficient and hollow cores cannot open into pits. The critical source for stepwaves is therefore missing. Under these conditions the dissolution mechanism is driven primarily by point defects and dissolution on pre-existing edges and corners. Although absolute rates will obviously vary from mineral to mineral, it is clear that this latter mechanism is much slower than the stepwave mechanism.

Luttge (2006) conducted the following thought experiment. He assumed that the two different reaction mechanisms (I) and (II) exist to dissolve a given crystal surface with two different rates [*rate*(I) and *rate*(II)] (Fig. 2). At near-equilibrium conditions mechanism (I) operates alone. The reaction rate is slow and lacks the formation of

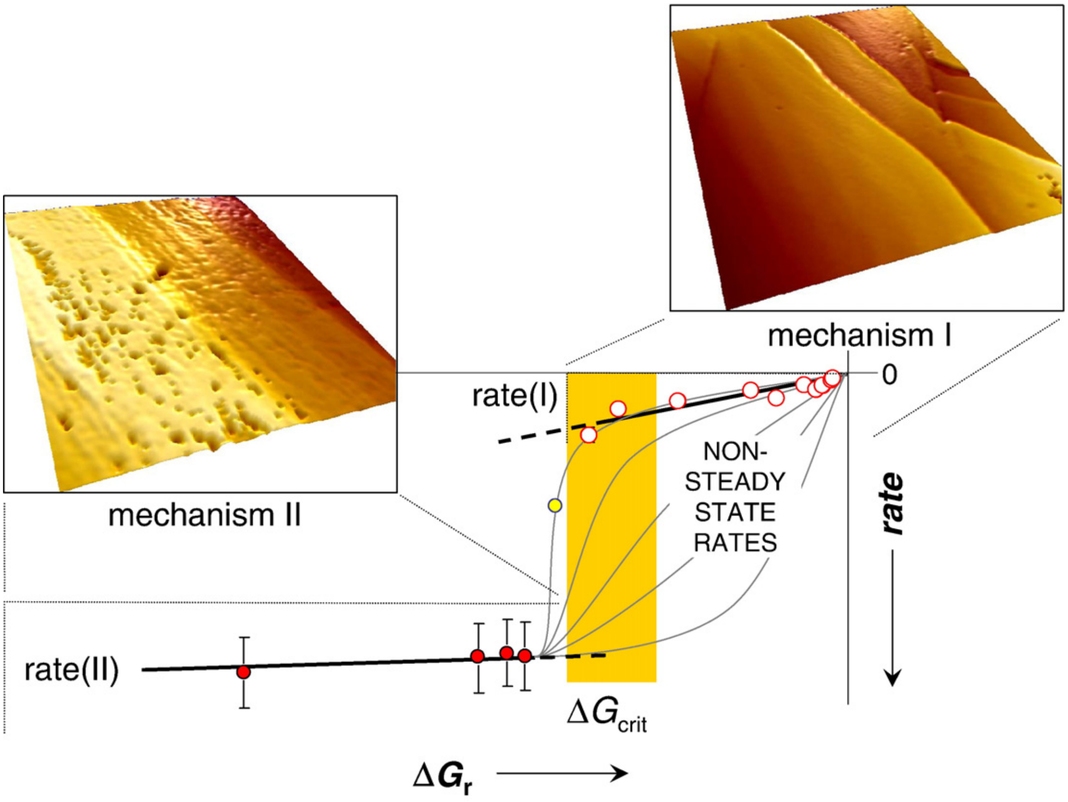

Fig. 2. Dissolution pathways of albite, $T = 80$ °C, pH 8.8. A reproducible, steady-state rate, for which ΔG_r is a necessary and sufficient predictor, does not exist in the “transition” region between *rate*(II) and *rate*(I). Instead, rates observed in this near-equilibrium domain of ΔG_r that are greater than the linear trend of *rate*(I) may be variable and non-steady state in nature, depending on previous fluid–mineral interaction.