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Does crystallographic anisotropy prevent the conventional treatment of aqueous mineral reactivity? A case study based on K-feldspar dissolution kinetics

Marion Pollet-Villard[a,*], Damien Daval[a,b], Philippe Ackerer[a], Giuseppe D. Saldi[b], Bastien Wild[a], Kevin G. Knauss[b], Bertrand Fritz[a]

[a] Laboratoire d'Hydrologie et de Géochimie de Strasbourg, Université de Strasbourg/EOST, CNRS, 67084 Strasbourg, France
[b] Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

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Abstract

Which conceptual framework should be preferred to develop mineral dissolution rate laws, and how the aqueous mineral reactivity should be measured? For over 30 years, the classical strategy to model solid dissolution over large space and time scales has relied on so-called kinetic rate laws derived from powder dissolution experiments. In the present study, we provide detailed investigations of the dissolution kinetics of K-feldspar as a function of surface orientation and chemical affinity which question the commonplace belief that elementary mechanisms and resulting rate laws can be retrieved from conventional powder dissolution experiments. Nanometer-scale surface measurements evidenced that K-feldspar dissolution is an anisotropic process, where the face-specific dissolution rate satisfactorily agrees with the periodic bond chain (PBC) theory. The chemical affinity of the reaction was shown to impact differently the various faces of a single crystal, controlling the spontaneous nucleation of etch pits which, in turn, drive the dissolution process. These results were used to develop a simple numerical model which revealed that single crystal dissolution rates vary with reaction progress. Overall, these results cast doubt on the conventional protocol which is used to measure mineral dissolution rates and develop kinetic rate laws, because mineral reactivity is intimately related to the morphology of dissolving crystals, which remains totally uncontrolled in powder dissolution experiments. Beyond offering an interpretive framework to understand the large discrepancies consistently reported between sources and across space scales, the recognition of the anisotropy of crystal reactivity challenges the classical approach for modeling dissolution and weathering, and may be drawn upon to develop alternative treatments of aqueous mineral reactivity.

Keywords: Orthoclase; Dissolution; Kinetic rate laws; Gibbs free energy; Crystallographic orientation; Dissolution anisotropy

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1. INTRODUCTION

Chemical weathering spontaneously affects most solids including building and industrial materials (e.g. Nicoleau et al., 2013; King et al., 2014; Hellmann et al., 2015), biomaterials (e.g. Derry et al., 2005) or geomaterials (e.g. Lasaga and Lüttge, 2001). Accordingly, mineral dissolution drives a series of fundamental processes of industrial (e.g. CO_2 sequestration (Knauss et al., 2005; Saldi et al., 2015), enhanced geothermal systems (Fritz et al., 2010)), biological (e.g. nutrient supply, see Lower et al., 2001) and geologic (e.g. carbon cycle Maher and Chamberlain, 2014) relevance. For most of these fields and in particular, in Earth

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[*] Corresponding author.
E-mail address: polletvillard@unistra.fr (M. Pollet-Villard).

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sciences, two main approaches have been commonly applied to model the fate of chemical weathering at large space and time scales. The first category of models relies on a phenomenological, top-down strategy where empirical relations between mineral dissolution and effective external forcing parameters such as temperature or runoff are used (Berner, 1990). Since the early 90s, this approach has been gradually superseded by reactive transport models, where mineral reactivity is accounted for via kinetic rate laws derived from dissolution experiments carried out on powdered single-crystals. This strategy now fuels most simulations of fluid-mineral interactions (see e.g. Knauss et al., 2005; Fritz et al., 2010; Beaulieu et al., 2012; Maher and Chamberlain, 2014).

Compared to the top-down approach, the bottom-up strategy is often praised for its presumably greater reliability. Because experiments are conducted on powdered materials under well-defined conditions, it is often claimed that the resulting kinetic rate laws supposedly reflect the underlying elementary dissolution and precipitation mechanisms (Schott et al., 2009), rendering the corresponding fluid-mineral simulations more robust.

In addition to their technical simplicity, measurements of bulk dissolution rates became widespread and conventional because of the conceptual framework in which the corresponding kinetic rate laws have been developed. Application of the transition state theory (TST) initially developed for elementary reactions in homogeneous media to overall dissolution processes in heterogeneous media was proposed in the early 80s (Aagaard and Helgeson, 1982), and subsequently coupled to surface complexation models (SCM), paving the way to the SCM/TST framework (Schott et al., 2009). A fundamental and appealing implication of applying this conceptual framework is that the complexity of heterogeneous chemical reactions is boiled down to the isotropic dissolution of a given solid, justifying the conventional measurement of bulk dissolution rates, and pushing to the background any potential crystallographic control on the reaction rate and rate law.

Arguably, the SCM/TST framework has succeeded in describing the dissolution of materials with simple chemistry and fairly high symmetry space-groups, such as simple metal oxides or hydroxides (e.g. Schott et al., 2009; Ohlin et al., 2010 and references therein). However, the detailed mechanisms and corresponding dissolution rate laws for more complex materials such as silicates are still a source of lively debate (e.g. Burch et al., 1993; Oelkers et al., 1994; Gautier et al., 1994; Lasaga and Lüttge, 2001; Hellmann and Tisserand, 2006; Beig and Lüttge, 2006; Hellmann et al., 2010; Gruber et al., 2014). More broadly, rate data collected via the conventional approach have long been shown to diverge from their field counterparts (White and Brantley, 2003), revealing inconsistencies of orders of magnitude for most minerals, even at the laboratory scale (Fischer et al., 2014), which questions the reliability of rate models developed on such datasets. As a matter of fact, aside from a limited number of studies which managed to reconcile experimental and field data at specific sites (e.g. Maher et al., 2009), upscaling laboratory results to the field without adjustments of several modeling parameters has essentially remained an elusive goal.

The source for the above-mentioned discrepancies remains an open question: aside from identified complicating factors including aqueous transport-limitations (Ruiz-Agudo et al., 2012; Laanait et al., 2015) or passivation by surface layers (Daval et al., 2011, 2013), a handful of recent studies has pointed out that mineral surfaces do not homogeneously and isotropically react with aqueous fluids (Godinho et al., 2012, 2014; Daval et al., 2013; Fischer et al., 2014; Laanait et al., 2015). Although crystallographic control of aqueous mineral reactivity has been suggested for decades (e.g. Gratz et al., 1991), the lack of quantitative data coupled to the potential problems inherent to the difficulties associated with modeling of anisotropic dissolution (such as tracking mineral texture over time in reactive transport codes), the heterogeneity and anisotropic nature of the dissolution process has long remained overlooked. In fact, the recognition that atomic ordering primarily impacts solid reactivity is relatively new, essentially resulting from the advent of microscopic, spectroscopic and computational methods allowing one to probe heterogeneous reactions at the molecular-level (e.g. Yanina and Rosso, 2008; Bandstra and Brantley, 2008; Kubicki et al., 2012; Daval et al., 2013; Lüttge et al., 2013; Kurganskaya and Lüttge, 2013; Fenter et al., 2014). Taken together, these recent observations motivated the present study, aimed at clarifying the validity and limitations of the conventional protocol commonly used to measure and upscale mineral dissolution rates.

Below, we provide measurements of K-feldspar (orthoclase, $KAlSi_3O_8$) dissolution, considered as a model mineral. Orthoclase was selected because of (1) its chemical composition and low-symmetry space-group, which substantially deviate from simple oxides/hydroxides for which the SCM/TST model putatively applies, (2) the fairly large dataset related to the bulk dissolution kinetics and dissolving surface structure of orthoclase (see Gautier et al., 1994; Fenter et al., 2014 and references therein) and feldspars as a whole (Beig and Lüttge, 2006; Hellmann and Tisserand, 2006; Hellmann et al., 2010) and (3) undoubtedly, the relevance of feldspar dissolution for major processes such as atmospheric CO_2 drawdown through continental weathering of silicates (Kampman et al., 2009). As opposed to previously applied methods (e.g. Gautier et al., 1994; Hellmann and Tisserand, 2006) and following the pioneering measurements of Lüttge et al. (1999), our study benefited from the use of vertical scanning interferometry (VSI) technique to monitor orthoclase dissolution kinetics as a function of surface orientation and chemical affinity, which represents the driving force for any chemical reaction and is consequently the most fundamental parameter to be investigated.

2. MATERIALS AND METHODS

2.1. Sample characterization and preparation

The starting material is a natural orthoclase single crystal from Afghanistan. No minor phases were detected with