Effect of the crystal structure anisotropy on k-feldspar dissolution kinetics in hydrothermal conditions

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Introduction

Feldspar minerals are part of the most abundant minerals in the Earth crust. Predicting their long term evolution dissolution represents a critical issue for several geological and engineering concerns. For example, in the context of the Soultz-sous-Forêts enhanced geothermal system (Alsace, France), the pumping of hot water and exploitation of heat at surface may provoke a partial re-equilibration of the aqueous fluid composition, and re-injection of cooled water at depth may favor the dissolution of the main rock-forming minerals of the reservoir (such as K-feldspar) while promoting the precipitation of secondary phases (Fritz et al., 2010). The relative intensities of primary mineral leaching and secondary phase formation significantly affect porosity and permeability of the reservoir, thereby influencing its hydraulic performance and the efficiency of the geothermal site.

To determine the long term evolution of fluid/rock interactions in natural environments, the common strategy consists in investigating experimentally, the influence of different parameters (pH, temperature, concentration of cations, deviation from equilibrium….) on dissolution rates in conditions in which dissolution is relatively fast (high temperature, far-from equilibrium conditions…) to be measured. Then, resulting kinetic rate laws are implemented in geochemical codes which are ultimately used to make an extrapolation to field conditions. With this method, five orders of magnitude are reported between the laboratory-based silicate weathering rates and those measured in field (White and Brantley, 2003).

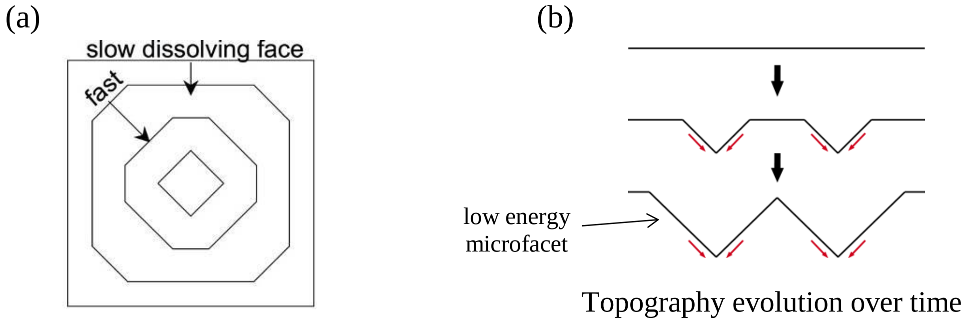

Fig. 1: Schematic evolution of (a) crystal morphology and (b) surface topography over time. While the most reactive faces tend to vanish over time at the grain scale, an opposite trend may take place at the µm-scale on each face. Depending on the prevailing mechanism, one can expect either an apparent increase or a decrease of mineral reactivity over time.

In actual reactive transport codes, the evolution of surface area is related to the amount of dissolving mineral through a shrinking core model. The dissolution is considered as to be isotropic. However, recent studies suggest that some faces could dissolve up to 1,000 times faster than other (Daval et al., 2013). Besides, etch pitting is responsible for the development of microfacets less energetic (i.e. less reactive) during long-term dissolution (see Fig. 1 and e.g. Smith et al., 2013). These results cast doubt of the relevance of a surface model based on shrinking spheres.

The aim of this study is to quantify the impact of K-feldspar anisotropy on dissolution rates in order to develop a more comprehensive model of the evolution of the reactive surface of silicate minerals. Our global objective is to propose alternate kinetic rate laws which could in turn be implemented into reactive transport codes and ultimately improve the predictive ability of geochemical simulations.

1) Experimental strategy

To investigate the effect of crystallographic orientation of K-spar dissolution kinetics, single-crystals of K-spar were oriented using electron back-scattered diffraction (EBSD), cut, polished, and the starting topography was measured using vertical scanning interferometry (VSI). Our experimental protocol consisted in dissolving such crystals in an apparatus which allows for the creation of a non-wetted, unreacted reference surface (Fig. 2a). After alteration in a mixed-flow reactor (Fig. 2b) at 180°C in a synthetic alkaline solution, the surface retreat was determined using VSI, which allows for a direct measurement of the face-specific dissolution rate (Fig. 2c). Measurements were carried out under a large range of Gibbs free energy (ΔG_r) in order to determine, for each face, the evolution of the dissolution rate with the deviation from equilibrium.

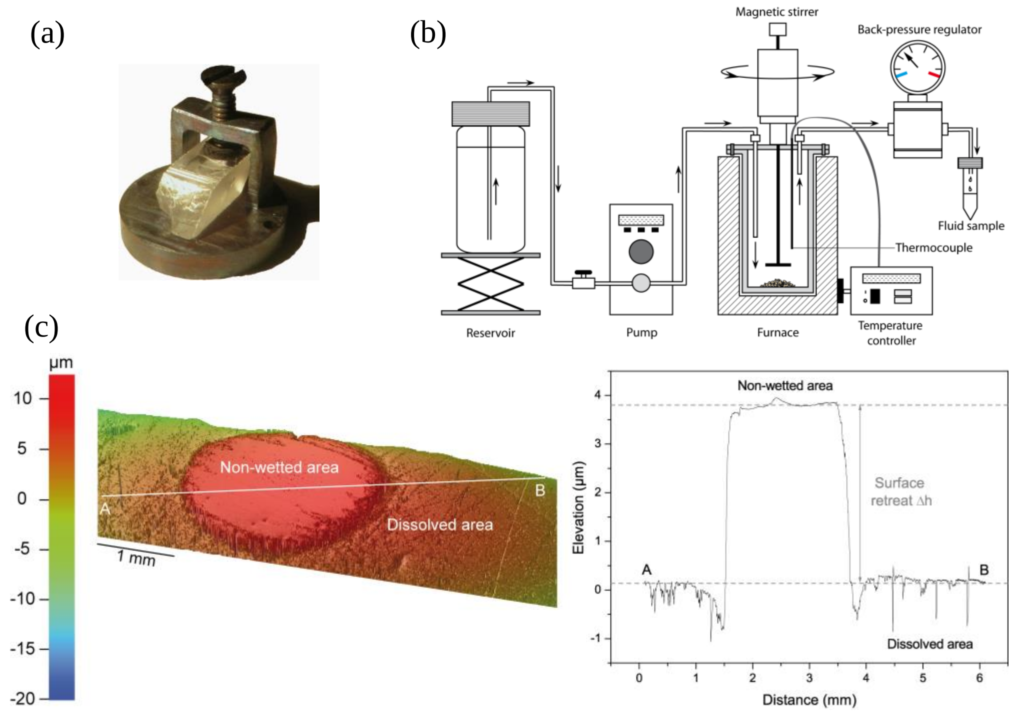

Fig. 2: Face-specific measurements of K-spar dissolution rate. (b) Oriented K-spar crystal mounted on a Ti-jig as designed by Daval et al. (2013). Pressure was applied via a screw on a Viton disk, creating a non-wetted reference area. (b) The crystal was subsequently altered in a mixed-flow reactor at 180°C, in a synthetic alkaline solution. (c) After reaction, the K-spar crystal was recovered and the nanotopography of the surface (here, face $(\bar{1}\mathbf{11})$) was monitored using VSI. The measurement of the surface retreat allows for the determination of the dissolution rate of the mineral.

2) Results and discussion

a. Far from equilibrium dissolution rate

A typical result of dissolution experiments monitored with the surface retreat is shown in Fig. 3a. This figure represents the evolution of surface retreats for three different faces ((001), $(\bar{1}01)$ and $(\bar{1}\bar{1}1)$) as a function of time. Since the surface retreat increases linearly with time: the dissolution rate is constant over time for each face. Besides, we see that the (001) face is ten times slower than the two other faces. This is an example of a non-negligible dissolution anisotropy.

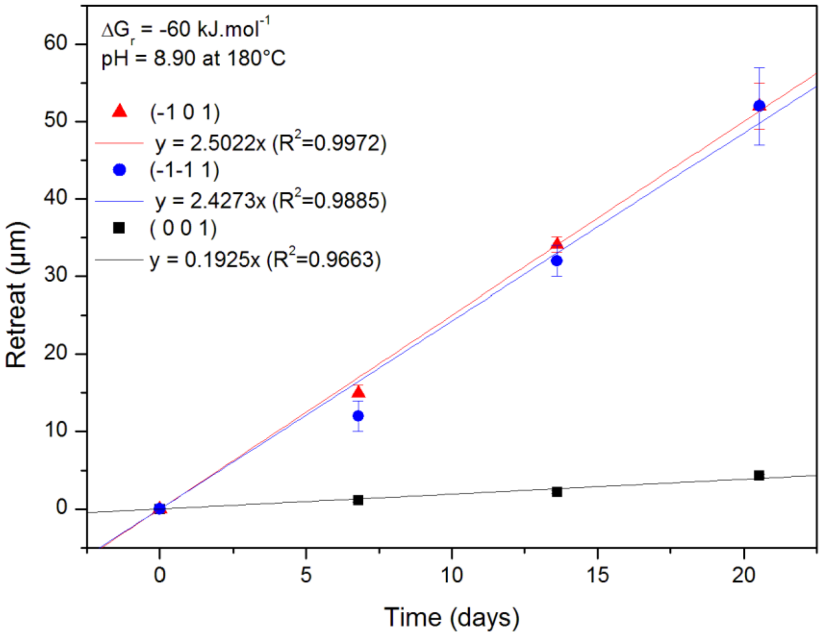

Fig. 3: Surface retreat monitored as a function of time with VSI during an experiment carried out at pH 8.9 at 180°C (ΔG_r) = -60 kJ.mol^{-1}). A ten-fold factor between the dissolution rate of the slowest and fastest faces can be seen, attesting to the anisotropic nature of K-spar dissolution.

Current geochemical codes use a single dissolution rate value to describe mineral dissolution kinetic. Our results give rise to the question of the signification and the relevance of this value. Indeed, if the dissolution rate depends on the crystallographic orientations of the mineral, it seems to be unreasonable to use a single, isotropic dissolution rate constant in models.

b. Relation between the dissolution rate and the Gibbs free energy of the reaction

In several geothermal systems, fluid-rock interactions occur at conditions which can be referred to as ‘close-to-equilibrium conditions’, in a Gibbs free energy range where the relations between dissolution rate and chemical affinity are poorly known and unreachable through conventional approaches based on the measurement of the concentrations of cations released during dissolution (because the concentration of cations released during the course of dissolution is negligible compared to the electrolyte background concentration). Such measurements are made possible using our protocol described in Fig. 2, allowing us to propose a relation between K-spar dissolution rate and the Gibbs free energy for the 6 different crystallographic orientations studied.

Our results evidence that the relation between K-spar dissolution rate and ΔG_r differs from the transition state theory currently implemented into geochemical codes. In addition, this relation depends on the crystallographic orientation of K-spar mineral (Fig. 4). As for the far-from-equilibrium dissolution rate, this result highlights that using a unique theoretical rate law to describe dissolution rate as a function of ΔG_r remains highly questionable.

Conclusion

The dissolution anisotropy at the crystal habit scale as well as the complex evolution of the surface topography are at odds with the shrinking core model implemented in most of geochemical codes. In addition, the relation between the dissolution rate and ΔG_r for a mineral seems to depend on crystallographic orientations expressed in the mineral morphology. These results challenge our understanding of dissolution mechanisms and evidence that the dissolution anisotropy plays a fundamental role in these mechanisms.

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