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Revisiting classical silicate dissolution rate laws under hydrothermal conditions

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Introduction

Prediction of reaction kinetics of fluid/rock interactions represents a critical issue for several geological and engineering concerns, including geothermal systems. 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-spar and plagioclase, while promoting the precipitation of secondary phases, such as calcite and/or Al-(hydr)oxides (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.

Moreover, it is noteworthy that in several geothermal systems such as the one of Soultz-sous-Forêts, the circulation of aqueous fluids induces only modest modifications of their chemical composition, which slightly deviates from an equilibrium state. Therefore, fluid-rock interactions take place at close-to-equilibrium conditions, where the rate-affinity relations are poorly known and intensively debated (see e.g. Schott et al., 2009).

Therefore, the prediction of the kinetics of dissolution and precipitation reactions at play during fluid/rock interactions, their coupling, their temporal evolution and their evolution in close-to-equilibrium conditions represents a critical issue for evaluating the efficiency of a geothermal site, as well as the prediction of its long-term evolution.

In the context of the geothermal power station of Soultz-sous-Forêts, we identified three major issues that we are currently addressing:

(1) Determining the kinetic feedback effects induced by dissolution/precipitation processes in a geothermal reservoir;
(2) Investigating the dissolution of the main cleavages of K-spar (one of the prevalent primary minerals in the reservoir) in order to decipher the impact of crystallographic orientation and microstructural surface modifications on its dissolution kinetics;
(3) Proposing a relation between K-spar dissolution rate and the Gibbs free energy of reaction (ΔG) over a wide range of ΔG conditions.

Our global objective is (i) to produce a more comprehensive model of the evolution of the reactive surface of silicate minerals and (ii) to account for the effect of various ΔG conditions on mineral dissolution rate in order to modify reactive transport codes and ultimately improve the predictive ability of geochemical simulations.

1) Effect of secondary coatings on mineral dissolution rates

Heterogeneous precipitation of secondary phases may prevent a direct contact between the bulk fluid and the surface of the dissolving minerals, thereby limiting their dissolution (e.g. Velbel, 1993; Daval et al., 2009). Up to now, a substantial body of classical experimental works dedicated to determining the kinetics of fluid/mineral interactions were run on crushed single mineral powders, either monitoring dissolution or precipitation, without investigating the coupling between these reactions. Moreover, the decrease of the reactive surface of the primary phases is not accounted for in most of the geochemical codes that we are aware of. However, it is noteworthy that in geothermal contexts, fluid circulation occurs in fractures where primary silicates are covered with secondary coatings, raising the question as to what the actual “reactive surface” is.

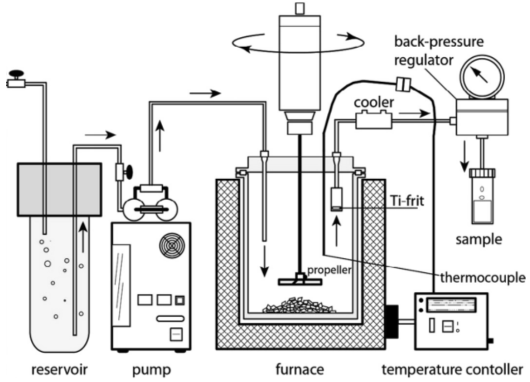

Figure 1: Schematic illustration of the experimental setup used for experiments dedicated to investigate the effect of secondary coatings (adapted from Saldi et al., 2013).

Our experimental strategy consists in dissolving fresh crushed K-spar powders, and comparing their dissolution rates with those of powders previously coated with secondary minerals. First of all we designed an experimental protocol allowing the development of various K-spar powders artificially coated with a layer of secondary phases. The experiments are purposely carried out at 180 °C in a mixed-flow reactor under conditions where aluminum is poorly soluble (Fig. 1, adapted from Saldi et al., 2013).

By modifying the composition of the inlet fluid, the flow rate and the reaction time we are able to synthesize mineral coatings on the surface of K-spar grains for which we can control and characterize the proportion of coated K-spar (using SEM image processing), as well as the mineralogical composition and thickness of the coating (using FIB-TEM methods) (Fig. 2).

The final step consists in comparing the dissolution rates of coated and uncoated K-spar powders. Reactive transport simulations will be run using solely (1) the dissolution rate of uncoated powders and (2) measured values of coating diffusivity, thickness and size as input parameters to evaluate whether classical reactive transport codes can be satisfactorily used to predict the dissolution rate of coated powders without any further refining parameter.

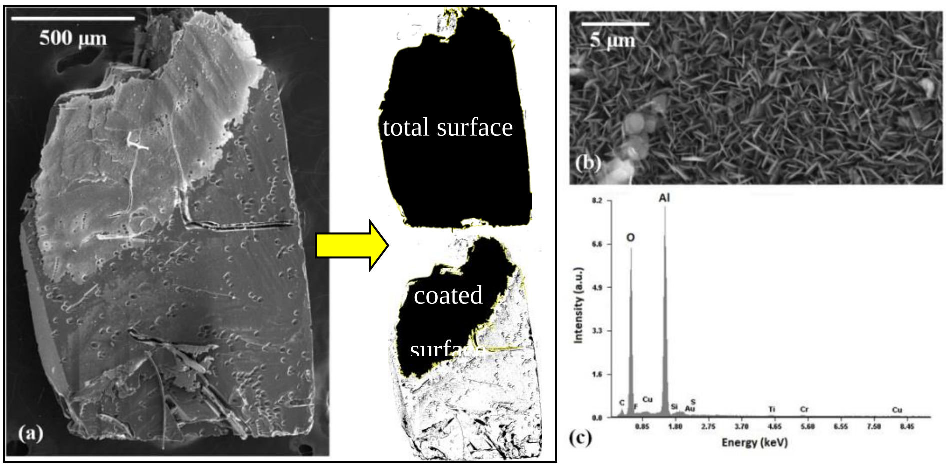

Fig. 2 : SEM analyses of a K-spar grain after experiment in an acidic solution at 180 °C. (a) Image of the grain. Its surface is partially covered with boehmite (AlO(OH)). Grayscale thresholding allows for the determination of the proportion of the grain which is actually covered by secondary minerals (b) Close-up the coating. (c) EDX spectrum of the coating.

2) Effect of crystallographic orientation of K-spar dissolution kinetics

In 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 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. 3 and e.g. Smith et al., 2013). These results cast doubt of the relevance of a surface model based on shrinking particles.

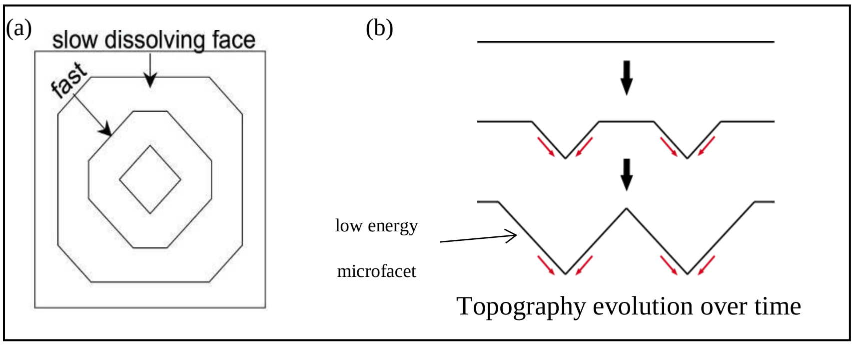

Fig. 3: Schematic evolution of (a) crystal morphology and (b) surface topography over time. While the most reactive faces tend to vanish over time at the grain scale, an opposite trend may take place at the µm-scale on each face. Depending on the prevailing mechanism, one can expect either an apparent increase or a decrease of mineral reactivity over time.

To investigate the effect of crystallographic orientation of K-spar dissolution kinetics, single-crystals of K-spar are oriented using electron back-scattered diffraction (EBSD) (Fig. 4a), cut, polished, and the starting topography is measured using vertical scanning interferometry (VSI). Our experimental protocol consists in dissolving such crystals in an apparatus which allows for the creation of a non-wetted, unreacted reference surface (Fig. 4b). After alteration, the surface retreat is determined using VSI, which allows for a direct measurement of the face-specific dissolution rate (Figs. 4c-d).

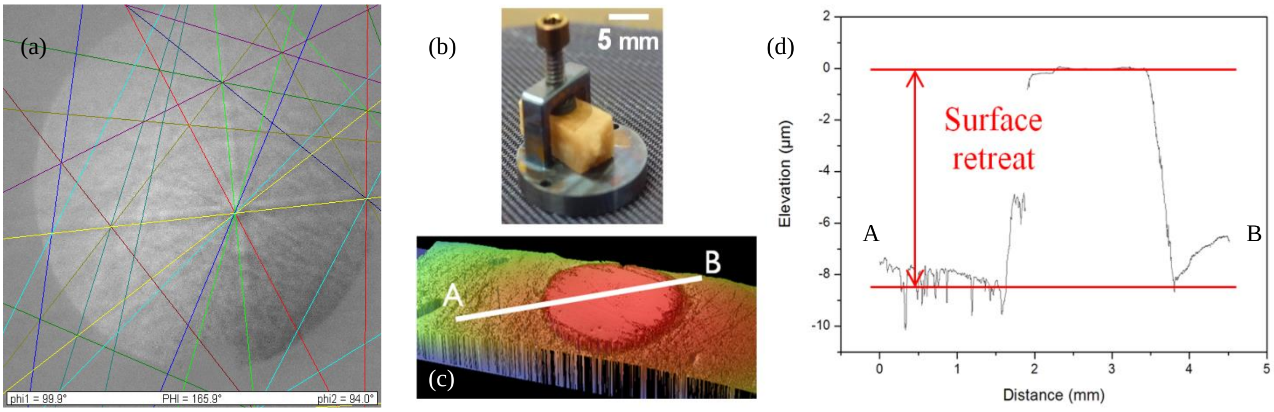

Fig. 4: Face-specific measurements of K-spar dissolution rate. (a) EBSD pattern of one of the cleaved crystals that has been prepared (here face (10-1)). (b) K-spar crystal mounted on a Ti-jig as designed by Daval et al. (2013). Pressure is applied via a screw on a Viton disk, creating a non-wetted reference area. The crystal is subsequently altered in a mixed-flow reactor at 180°C, in a synthetic basic solution. (c) and (d) after reaction, the K-spar crystal is recovered and the nanotopography of the surface (here, face (10-1)) is monitored using VSI. The measurement of the surface retreat allows one to determine the dissolution rate of the mineral.

Our ongoing experiments confirm that K-spar dissolution is an anisotropic process. For instance, among the different faces that have been studied so far, we found that the (10-1) face dissolves up to ten times faster than the slowest (001) faces (Fig. 5a).

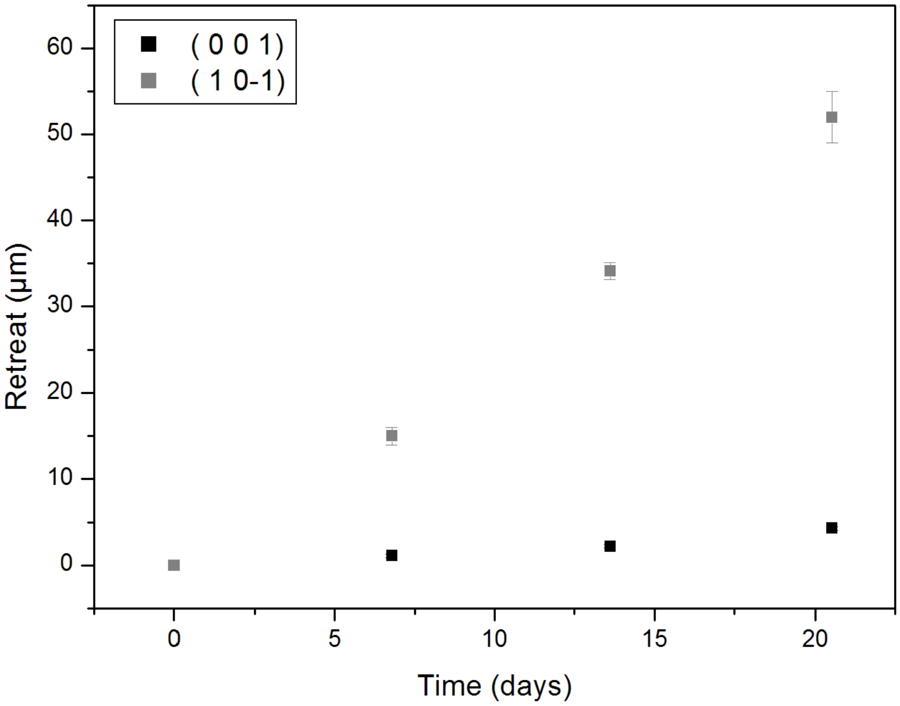

Fig. 5: Plot showing the surface retreat measured on (001) and (10-1) K-spar faces during an alteration experiment run in a mixed-flow reactor at 180°C with a basic solution. A ten-fold factor between the dissolution rates of these two faces can be seen, attesting to the anisotropic nature of K-spar dissolution.

In addition, the formation of etch pits on the surface during its alteration has been evidenced on all of the different faces that have been studied so far (Fig. 6). This complex evolution of the surface topography as well as the dissolution anisotropy at the crystal habit scale are at odds with the shrinking core model implemented in most of geochemical codes. Current work is directed to ascertaining the reasons for the observed features, based on a detailed analysis of K-spar crystallography.

The ultimate objective of this study is to modify the surface function implemented in geochemical codes so that they not only account for a modification of the *quantity* of reactive surface, but also on their '*quality'*. It is expected that such modifications will improve the predictive ability of simulations of water-rock interactions.

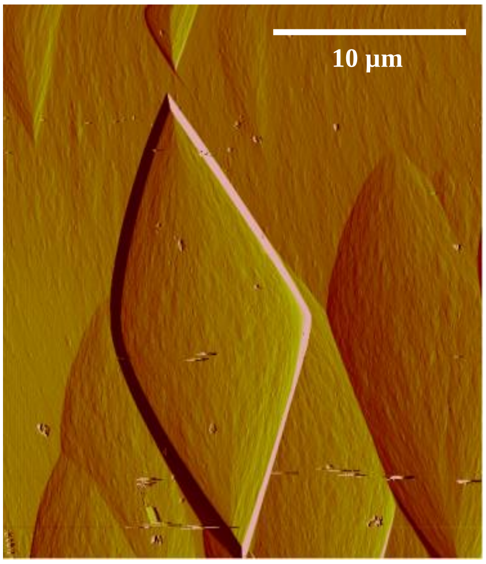

Fig. 6: Typical AFM image (deflection mode) of (001) K-spar surface reacted for 43 hours in a mixed-flow reactor at 180 °C.

3) Close-to-equilibrium reaction rates

As mentioned above, 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 $\Delta[c]/[c]$ ratio is below the quantification limit of the ICP-AES). To circumvent this problem, we are following an innovative approach, where the mineral dissolution kinetics is determined by monitoring directly the surface retreat during dissolution (cf.

protocol described in Fig. 4). This will allow us to propose a relation between K-spar dissolution rate and the Gibbs free energy of reaction (ΔG) over a wide range of ΔG conditions.

Our preliminary results seem to evidence that the relation between K-spar dissolution rate and ΔG differs from the transition state theory currently implemented into geochemical codes.

Conclusions

Investigating water-rock interactions in new directions is requested to go beyond the long-standing problem of bridging the gap between laboratory and field estimates of chemical weathering rates (White and Brantley, 2003). Taken together, the new findings that will be detailed during this workshop show promise as a means for improving the accuracy of geochemical simulations.

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