



## Revisiting classical silicate dissolution rate laws under hydrothermal conditions

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In the context of geothermal energy, the relative intensities of primary mineral leaching and secondary mineral precipitation can affect porosity and permeability of the reservoir, thereby influencing its hydraulic performance and the efficiency of the geothermal power station. That is why the prediction of reaction kinetics of fluid/rock interactions represents a critical issue in this context.

Moreover, in several geothermal systems such as the one of Soultz-sous-Forêts (Alsace, France), the circulation of aqueous fluids induces only modest modifications of their chemical composition. Therefore, fluid-rock interactions take place at close-to-equilibrium conditions, where the rate-affinity relations are poorly known and intensively debated [1].

To describe more precisely the dissolution processes, our strategy consists in investigating the dissolution of the main cleavages of K-spar minerals (one of the prevalent primary minerals in the reservoir of Soultz-sous-Forêts geothermal system) over a wide range of Gibbs free energy ( $\Delta G$ ) conditions. The aims are to decipher the impact of crystallographic orientation and microstructural surface modifications on the dissolution kinetics and to propose a relation between K-spar dissolution rate and  $\Delta G$ .

Our experimental work relies on a coupled approach which combines classical experiments of K-spar dissolution monitored by aqueous chemical analyses (ICP-AES) and innovative techniques of nm- to  $\mu\text{m}$ -scale characterization of solid surface (SEM, AFM, VSI) [2].

Our results confirm that K-spar dissolution is an anisotropic process: we measure a tenfold factor between the slowest and the fastest-dissolving surfaces. Moreover, the formation of etch pits on surfaces during their alteration has been evidenced on all of the different faces that have been studied. This complex evolution of the surface topography casts doubt of the relevance of a surface model based on shrinking particles and represents a possible cause of an apparent modification of silicate dissolution rate over time.

In addition, we evidenced that the relation between K-spar dissolution rate and  $\Delta G$  depends on the crystallographic orientation of the altered surface, and differs from the transition state theory currently implemented into geochemical codes. Importantly, this theoretical curve overestimates the dissolution rates measured in close-to-equilibrium conditions.

Taken together, the new findings show promise as a means for improving the accuracy of geochemical simulations.

[1] Schott, J., Pokrovsky, O. S., and Oelkers, E. H., 2009. *The Link Between Mineral Dissolution/Precipitation Kinetics and Solution Chemistry*. *Rev Mineral Geochem* 70, 207-258.

[2] Daval, D., Hellmann, R., Saldi, G. D., Wirth, R., and Knauss, K. G., 2013. *Linking nm-scale measurements of the anisotropy of silicate surface reactivity to macroscopic dissolution rate laws: New insights based on diopside*. *Geochim Cosmochim Acta* 107, 121-134.