# Do silicate dissolution rate constants really exist? Discussing the thermodynamic driving force of silicate dissolution

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Both laboratory and field studies have revealed an intriguing, yet unresolved invariant aspect of chemical weathering: in appearance, the reactivity of silicates decreases with time following a power law. This fundamental aspect is poorly accounted for by reactive transport simulations and challenges the reliability of long term predictions of chemical fluxes resulting from water-rock interactions. This emphasizes the need to shed light on the mechanisms that could account for these observations.

Here, I describe our recent findings regarding the impact of the spontaneous evolution of the physicochemical surface properties of dissolving silicates on their dissolution rates [1-3]. First, face-specific measurements of silicate dissolution anisotropy are combined with numerical simulations (cellular automata and kinetic Monte Carlo modeling) to demonstrate that the morphology of single crystals continuously evolves with the reaction progress [1]. This evolution is shown to result in an unexpected evolution of the effective function that relates the apparent silicate dissolution rate to the Gibbs free energy of dissolution. Second, we report on a series of spectroscopic and microscopic characterizations of altered silicate surfaces either weathered in the field (topsoil horizons of forested areas) or in well-controled laboratory experiments [2,3]. While the development of nm-thick amorphous layers covering the surface of silicates is ubiquitous, their transport properties are shown to evolve as the reaction progresses. Consequently, the driving force of the reaction switches from the difference of chemical potentials between the fluid and the silicate to the difference of chemical potentials between the fluid and the layer. We will discuss how this gradual switch is responsible for a gradual decrease of silicate dissolution rate, ultimately challenging the use of the conventional concept of “dissolution rate constant”.

[1] Pollet-Villard, M. *et al.*, *Geochim Cosmochim Ac* **2016,** *190*, 294-308; [2] Daval, D. *et al..*, *Geochim Cosmochim Ac* **2017,** *209*, 51-69; [3] Daval, D. *et al.*, *Earth Planet Sc Lett* **2018,** *498*, 226-236.