Driving mineral dissolution studies towards new directions: applications to geothermal concerns

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The chemical weathering of rocks represents a fundamental step in the geochemical cycle of many elements. Interactions between aqueous fluids and rock-forming minerals play a central role in many major engineering, environmental, and geological processes. Whether it determines the rates of soil formation (Godderis et al., 2006), soil fertility and nutrient availability (White and Brantley, 1995), CO_2 uptake and its impact on climate change (Beaulieu et al., 2012), durability of radioactive waste confinement glasses (Frugier et al., 2008) or geological sequestration of CO_2 (Knauss et al., 2005), the same bottom-up strategy has been so far applied for predicting the long term evolution of fluid-rock interactions. This strategy relies on (i) the experimental determination of the kinetic rate laws governing the dissolution of silicate minerals, which is based on experiments performed on freshly crushed single minerals immersed in synthetic solutions, and (ii) the implementation of such laws into reactive transport codes. Nowadays, this methodology represents a standard approach in hydro- and biogeochemistry for predicting the chemical weathering rates of rocks.

Although such rate laws are expected to predict the reactivity of silicate minerals over large spatial and temporal scales, their application generally require substantial adjustments to predict the reactivity of silicate minerals for durations as short as a few weeks, and in volumes as low as a liter (e.g. Daval et al., 2011). More generally and since the pioneering work of Paces (1983), it has been widely accepted that the laboratory-derived dissolution rate laws drastically overestimate the weathering rates measured in natural settings (up to 6 orders of magnitude, see details in White and Brantley, 2003), thereby casting doubt on the accuracy of reactive transport simulations. Among the impacted application fields, geothermal systems represent a context where the accurate knowledge of the elemental fluxes involved in water-rock interactions is absolutely crucial: the pumping of hot water and the exploitation of heat at surface may provoke a partial re-equilibration of the aqueous fluid composition, while 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 the porosity and permeability of the reservoir, thereby impacting its hydraulic performance and the efficiency of the geothermal site.

Reconciling laboratory- with field-derived rates has been at an impasse for many years, and for a growing amount of scientists, this endeavor will probably remain unsuccessful as long as the strategy to evaluate and describe mineral dissolution kinetics is not revisited in depth (e.g. Lüttge et al., 2013). In an attempt to bridge the gap existing between laboratory- and field-determined mineral dissolution rates, we recently embarked into a research program aiming at investigating some novel *intrinsic* and *extrinsic* factors which may help understanding the abovementioned kinetic discrepancies. An *intrinsic* factor is a parameter that depends on the evolution of the properties of the reacting minerals as a function of their extents of dissolution. Conversely, *extrinsic* factors encompass all kind of parameters dealing with the immediate environment (e.g. fluid composition, temperature, presence of biota, etc.). In this presentation, we review each of the tasks that we are currently following to better constrain the influence of intrinsic and extrinsic factors on the variability of mineral dissolution rate:

- Dealing with *intrinsic* factors, our efforts focus on the mechanisms of *'ageing'* of mineral surfaces. Such a work is motivated by the growing number of studies based on field analyses emphasizing that the dissolution rate of a given silicate is negatively correlated with the 'substrate age' regardless of the weathering context (e.g. Taylor et al., 1995, White et al. 1996, White and Brantley, 2003, Maher et al., 2004, Fantle and DePaolo, 2006, Porder et al., 2007). However, the molecular mechanisms underpinning the apparent decrease of mineral reactivity remain poorly understood. In that respect, our investigations are two-fold:

(1) probing the temporal evolution of the transport properties of the nm-sized amorphous silica-rich layers which have been documented for decades to form on silicate surface (see Hellmann et al., 2012 for a thorough study). The combined use of microscopic (e.g. transmission electron microscopy, TEM) and spectroscopic synchrotron-based techniques (e.g. X-ray reflectivity) enables determining the evolution of the microstructural and physical properties (e.g. density, diffusivity) of the surface layers, in conjunction with the evolution of the reactivity of the underlying silicate mineral;

(2) unraveling the effect of the modification of crystal habit as a function of mineral dissolution, due to the anisotropy of the crystal structure. Recent studies (e.g. Godinho et al., 2012, Smith et al., 2013) suggested that as the dissolution reaction proceeds, the proportion of low energy microfacets increases, thereby decreasing the overall mineral reactivity. This task will be briefly explained in our presentation, and is further developed in the PhD work of Pollet-Villard et al. (this conference).

- Dealing with *extrinsic* factors, our work is intended to investigate the intricate interplay existing between mineral reactivity, mineral surface microstructure and associated microbial communities. While it has been recently shown (e.g. Rogers and Bennett; 2004, Uroz et al., 2012) that the bacterial communities from bulk soil differed from that of targeted minerals (also termed *'mineralosphere'*), little is known regarding (1) the mineralosphere characteristics in hydrothermal contexts and (2) its dynamic evolution as a function of mineral reactivity. We will briefly show our strategy to address this issue, which could impact the kinetics of water-solid interactions in different compartments of the hydrothermal loop of geothermal systems.

Taken together, these novel research axes are expected to improve our home-made reactive transport codes that have long been used to model fluid-rock interactions in the context of the Soultz-sous-Forêts geothermal system (Fritz et al., 2010).

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