Transport properties of interfacial Si-rich layers formed on silicate minerals during weathering: Implications for geothermal purposes

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The dissolution of silicate minerals is of primary importance for various processes ranging from chemical weathering to CO_2 sequestration. Whether it determines the rates of soil formation, CO_2 uptake and its impact on climate change, channeling caused by hydrothermal circulation in reservoirs of geothermal power plants, durability of radioactive waste confinement glasses or geological sequestration of CO_2, the same strategy is commonly applied for determining the long term evolution of fluid-rock interactions. This strategy relies on a bottom-up approach, where the kinetic rate laws governing silicate mineral dissolution are determined from laboratory experiments. However, a long-standing problem regarding this approach stems from the observation that laboratory-derived dissolution rates overestimate their field counterparts by orders of magnitude, casting doubt of the accuracy and relevance of predictions based on reactive-transport simulations.

Recently[1], it has been suggested that taking into account the formation of amorphous Si-rich surface layers (ASSL) as a consequence of mineral dissolution may contribute to decrease the large gap existing between laboratory and natural rates. Our ongoing study is aimed at deciphering the extent to which ASSL may represent a protective entity which affects the dissolution rate of the underlying minerals, both physically (passivation) and chemically (by promoting the formation of a local chemical medium which significantly differs from that of the bulk solution). Our strategy relies on the nm-scale measurement of the physicochemical properties (diffusivity, thickness and density) of ASSL formed on cleavages of a model mineral (wollastonite) and their evolution as a function of reaction progress.

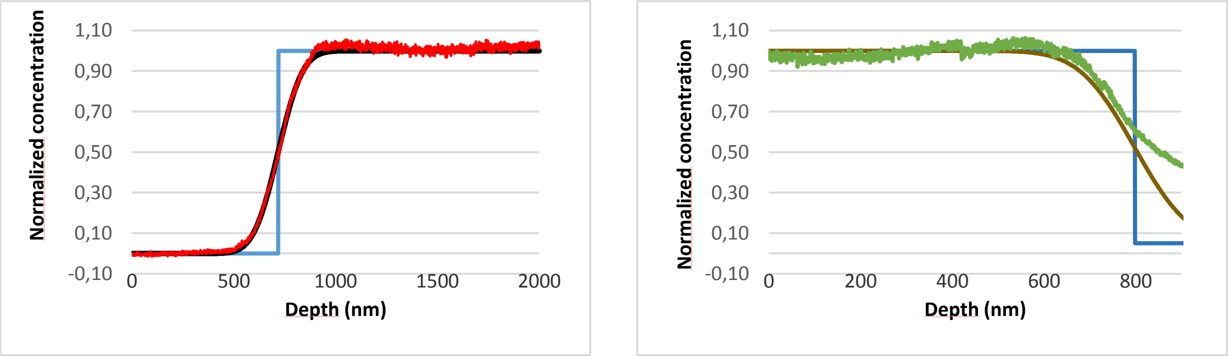

Figure 1. Measured and simulated profiles of (left) Ca/Si and (right) S/Si ratios obtained on a (010) wollastonite cleavage reacted for 50 h in an acidic solution (pH = 2). On the left hand-side, the blue solid line represents the schematic Ca/Si ratio measured by TEM, to be compared with the red solid line measured by nanoSIMS. The larger imprint of the ion beam on the rough surface is responsible for an artefactual broadening of the actual Ca/Si profile. Such a broadening can be accurately fitted by convoluting the signal with a Gaussian function. The same function is used to convolute the simulated S/Si profile (solid blue line) obtained through diffusion modeling. The diffusion coefficients are eventually adjusted such that the generated profile (brown solid curve) match to the measured profile (green solid line). Applying such a method for different time durations allowed us to evidence a gradual decrease of the diffusivity of the layer for most crystallographic directions, also termed as ‘ageing’.

Our results indicate that the diffusivity of nm-thick ASSL formed on wollastonite surface is ~10^6 times smaller than that reported for an aqueous medium, as estimated from the monitoring of the progression of a tracer in nm-thick ASSL by means of nanoSIMS analyses (Fig. 1). However, estimated diffusion coefficients remain up to 20 orders of magnitude greater than those corresponding to solid-state diffusion, indicating that such ASSL were not formed through a solid-state transformation of wollastonite. In addition, the estimation of diffusion coefficients of the tracer for samples recovered after two different time durations indicates that such a diffusion coefficient may decreases with time. This result may be explained by the spontaneous evolution of the density of ASSL, which increased as the dissolution reaction proceeds, as shown from modeling of time-resolved *in situ* X-ray reflectivity spectra obtained on the dissolving surfaces (Fig. 2).

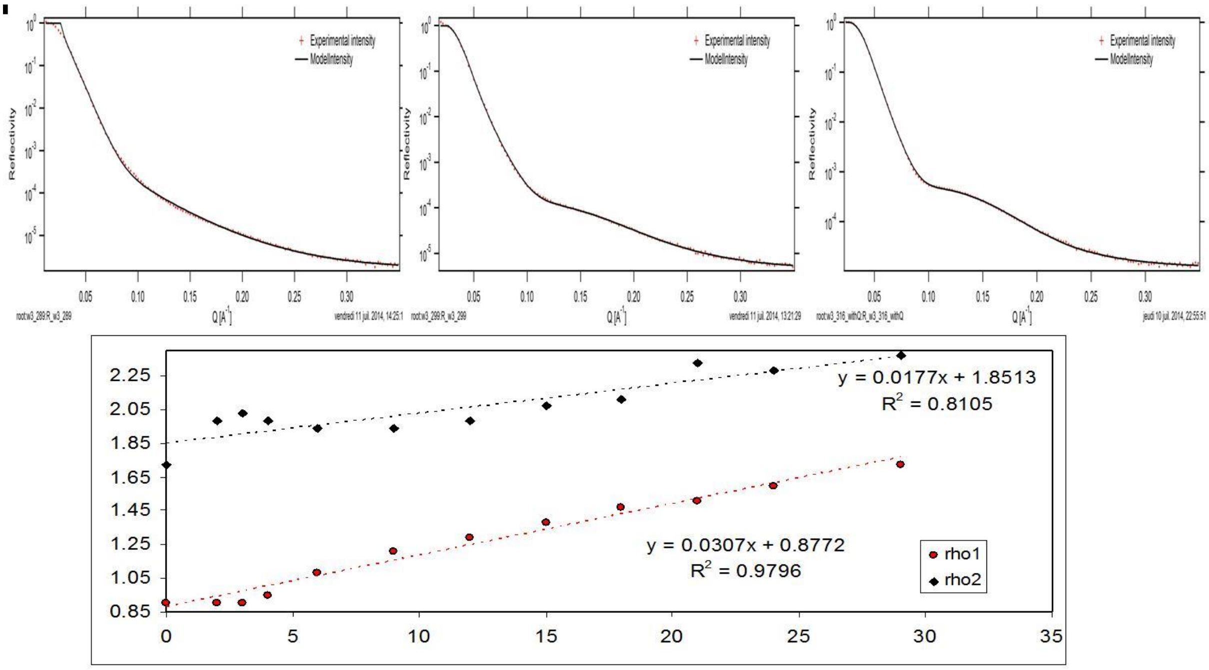

Figure 2. (top) Time-resolved evolution of the XRR patterns for a (001) wollastonite cleavage, (pH = 2, *T* = 20 °C). After 4h, the modification of the XRR pattern testified from the formation of layers on the surface of wollastonite. (bottom) Fitting of the XRR spectra revealed that the density of the surface coatings increased with time. Such an evolution may explain the slight decrease of wollastonite dissolution rate that we measured from *ex situ* experiments run on the cleavage.

Because silicates are among the most prominent rock-forming minerals that one can find in fractured granite impacted by fluid circulation, the present work on a model mineral such as wollastonite is thought to be relevant for unravelling the rate-controlling processes which influence the chemical composition of circulating fluids in the reservoir of geothermal plants. Overall, these results emphasize the need for the recognition of the importance of the interfacial fluid/mineral medium for adequately modeling the dissolution kinetics of silicate minerals relevant for environmental concerns.

[1] Daval, D. et al.., 2013. *Geochim Cosmochim Acta* **107**, 121-134.