

Standard Project

Experimental Report template

Proposal title: Microstructural modifications of dissolving silicate minerals: bridging the gap between laboratory and field rates		Proposal number: 32-02-800
Beamline: BM32	Date(s) of experiment: from: 29/06/2017 to: 04/07/2017	Date of report:
Shifts: 12	Local contact(s): Jean-sebastien Micha (email: micha@esrf.fr)	Date of submission:

Objective & expected results (less than 10 lines):

Amorphous silica-rich surface layers (ASSLs) formed at the interface between silicate materials and reacting fluids are known as one of the controlling factors of the dissolution rate of primary silicates. However, the factors governing the formation of ASSLs are still largely unknown. Here, we suggested to combine recent developments in the use of vertical scanning interferometry (VSI) and synchrotron-based X-ray reflectivity (XRR) to directly follow the in-situ development of ASSLs and evolution of their physical properties over time. We investigated the effects of pH, SiO₂(aq) concentration and temperature, crystallographic orientation, and temperature, on the layer thickness, density and reactivity as well as their impact on the dissolution of the primary mineral. We expected to gain insights into the dynamics of ASSL formation depending on the fluid composition, and especially, the impact of the fluid composition on the evolution of ASSL density, which was supposed to be a major rate-controlling factor of silicate reactivity.

Results and the conclusions of the study (main part):

Labradorite [(Na, Ca)(Al, Si)₄O₈] single crystals have been oriented by electron backscattered diffraction and cut along specific crystallographic directions ((001) and (010)). They have been subsequently polished to 250 nm grade prior to starting the XRR analyses. The monitoring of *in situ* development of silica layers has been enabled by a home-made experimental setup, initially designed to reach up to 80 °C in a kapton flow-through cell (Fig.1). Acidic solutions at several pHs have been circulated through the setup in order to favor the formation of Si-rich surface layers following different suspected mechanisms.

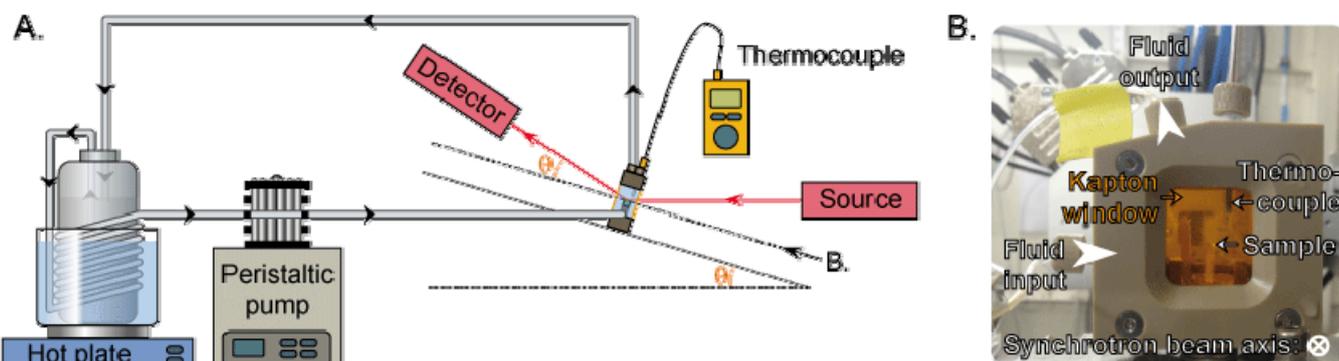


Figure 1. Overview of the experimental setup (A) and front view of the flow-through cell designed for *in situ* experiments (B). Fluid temperature within the cell was verified with a thermocouple. Taken from [1].

We estimated an increasing dissolution rate of labradorite with temperature, following an apparent energy of activation energy of $\sim 57 \text{ kJ}\cdot\text{mol}^{-1}$, while no significant anisotropy of dissolution could be detected by comparing (001) and (010) faces. Both labradorite and ASSL dissolution rates decreased as circum-neutral pH conditions were approached. High SiO₂(aq) concentrations resulted in (i) decreased apparent rates, while far-from-equilibrium conditions were maintained in the bulk fluid, and (ii) in overall increase of ASSL density (Fig. 2).

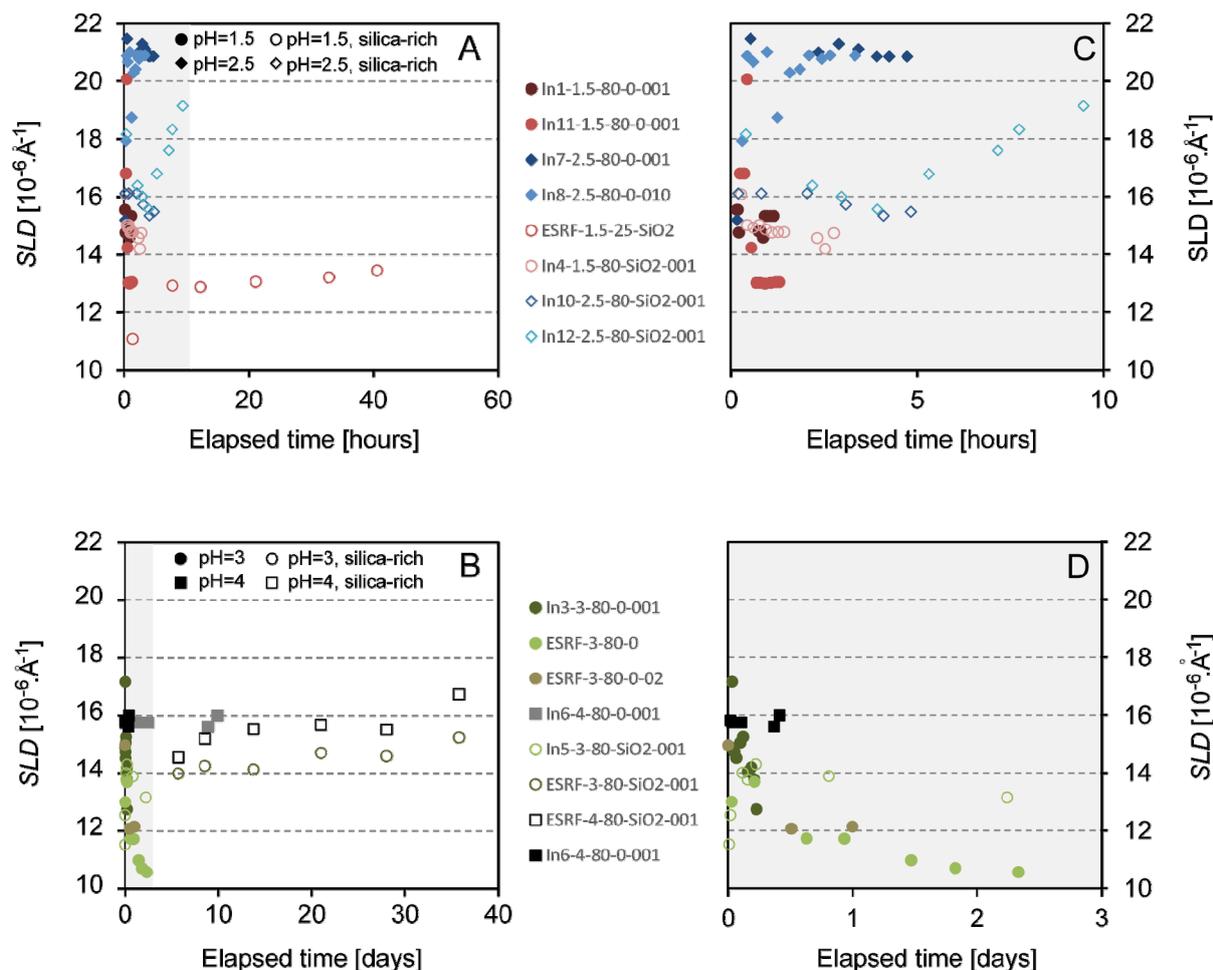


Fig.2. Temporal evolution of layer density, as measured by X-ray reflectivity for experiments at $\text{pH} \leq 2.5$ (A, C) and $\text{pH} > 2.5$ (B, D). Open data points correspond to experiments conducted with fluids saturated with respect to amorphous silica. C and D correspond to close-up views of the regions indicated by the shaded areas on plots A and B, respectively. All experiments were conducted at 80°C with the exception of experiment ESRF-1.5-25-SiO2 (red open circles in panel A), conducted at 25°C . Taken from [1].

Overall, our study highlighted the importance of ASSLs and their properties on the dissolution process, and more generally the discrepancy that may exist between bulk fluid conditions, generally probed and reported, and those actually operating at the interface with the primary phase being dissolved, which are of primary relevance for a number of environmental settings or certain industrial processes but are still largely unknown.

Justification and comments about the use of beam time (5 lines max.):

This session represented our fourth attempt to monitor the kinetics of ASSL formation on dissolving Ca-bearing silicates. While the very first session (March 2014) essentially paved the way towards the design of the fluid cell, the 3 subsequent beam times unravelled the kinetics and mechanisms of ASSL formation on wollastonite and labradorite, resulting in the publication of 2 studies [1, 2]. Possible future attempts may be directed to ascertain the extent to which biota, which is ubiquitous in natural settings, impacts the kinetics of such a process.

Publication(s): The first publication directly results from this proposal. The second one results from our two previous beamtimes (cf. reports from A32-02-789 and A32-02-777).

[1] Wild, B., Daval, D., Micha, J.-S., Bourg, I. C., White, C. E., Fernandez-Martinez, A. (2019) Physical properties of interfacial layers developed on weathered silicates: a case study based on labradorite feldspar. *The Journal of Physical Chemistry C* **123**, 24520-24532. <https://doi.org/10.1021/acs.jpcc.9b05491>

[2] Daval, D., Bernard, S., Rémusat, L., Wild, B., Guyot, F., Micha, J.-S., Rieutord, F., Magnin, V., Fernandez-Martinez, A. (2017) Dynamics of altered surface layer formation on dissolving silicates. *Geochimica et Cosmochimica Acta* **209**, 51-69. <https://doi.org/10.1016/j.gca.2017.04.010>