

Standard Project

Experimental Report

Proposal title: Microstructural modifications of dissolving silicate minerals: a step forward to studying superficial weathering		Proposal number: 20151388
Beamline: BM32	Date(s) of experiment: from: 29/06/2016 to: 04/07/2016	Date of report: 15/09/2016
Shifts: 18	Local contact(s): Dr. Jean-sébastien MICHA, Dr. François RIEUTORD	Date of submission:

Objective & expected results (less than 10 lines):

The dissolution of silicate minerals constitutes a key step in various natural and industrial processes such as carbon cycling over geological time scales¹ or CO₂ sequestration². More and more experimental evidences point towards a control of silicate mineral dissolution rates by interfacial processes, especially the formation of amorphous silica surface layers (ASSLs), that have been demonstrated to control the dissolution rate over a wide range of silicate minerals³⁻⁶. In particular, recent experiments conducted at ESRF on wollastonite have unravelled the control of the dissolution rate on specific cristallographic orientations by the densification of ASSL¹⁸. This series of *in situ* X-ray reflectivity (XRR) experiments investigates the very first stages of the dissolution process of labradorite feldspar, a representative constituent of the continental crust. It aims at probing the properties of surface layer in the course of their development and their impact on dissolution rates, depending crystallographic orientation. This requires overcoming experimental limitations met in previous experiments (see below).

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 (001) and (010) crystallographic planes. 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, whose design was improved to reach up to 80°C in a kapton flow-through cell (Fig.1). Acidic solutions at several pH values covering a wide range of dissolution regimes precedently studied at the macroscopic scale (pH = 1.5, 2.5, 3 and 4) have been circulated through the setup in order to favor the formation of Si-rich surface layers with different expected passivating properties.

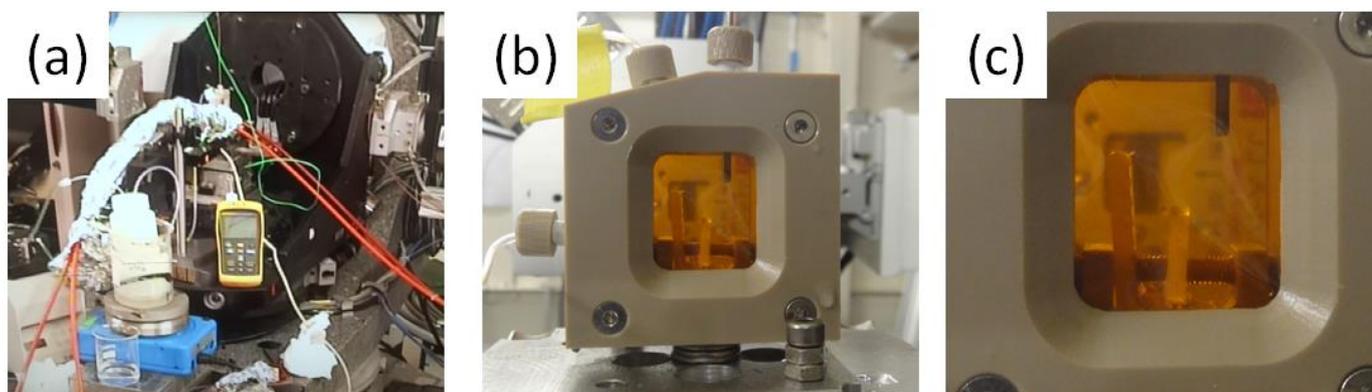


Figure 1 : Picture of the experimental setup used for *in situ* XRR experiments(a). Close-up view of the home-made flow cell (b) and of the upgraded sample holding system (c).

Amorphous Si-rich surface layers (ASSLs) were observed *in situ* on labradorite samples in the course of their

formation. Significant improvements brought to the sample holder (Fig. 1c), enabled to overcome previous limit of 65°C due to convection of the fluid inside the flow-through cell (see experimental report of experiment number 32-03-723 and 32-03-777). The temperature of 80°C was reached, enabling direct comparison with existing data of labradorite passivation at the macroscopic scale⁶. All experimental conditions tested in this study led to the development of ASSLs at the mineral fluid interface. Their properties such as thickness, density and roughness were successfully retrieved by fitting procedure with *Motofit* plugin for *IgorPro* software using a single-layer model (Fig. 2a).

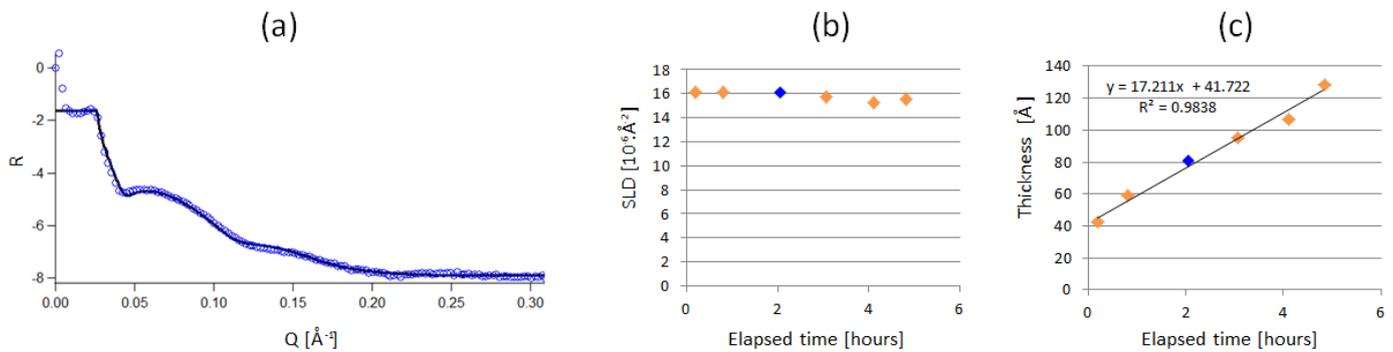


Figure 2 : XRR data (blue) and associated fit (black) realized with Motofit plugin on Igor Pro software (a), evolution of SLD (b) and layer thickness (c), obtained from fit. Data point in blue corresponds to the result of fit presented in (a). Data obtained from an experiment conducted at 80°C in a fluid saturated with respect to amorphous silica at pH = 2.5 on (001) labradorite polished cleavage.

As shown on Fig. 3, experiments conducted in fluid saturated with respect to amorphous silica yield lower rates than their counterparts in non-saturated fluids. This first order control of aqueous silica level on the labradorite dissolution rate is characteristic of mineral surfaces covered with passivating ASSL observation^{3,7-10} and confirms the impact of the surface layer on the rate of this silicate mineral. Note a progressive increase of this effect as pH conditions approach neutrality. A detectable decrease of the rate of layer thickening could be detected in the course of the experiment conducted at pH = 3 in saturated fluid on (001) cleavage. This might correspond to the expected passivation effect.

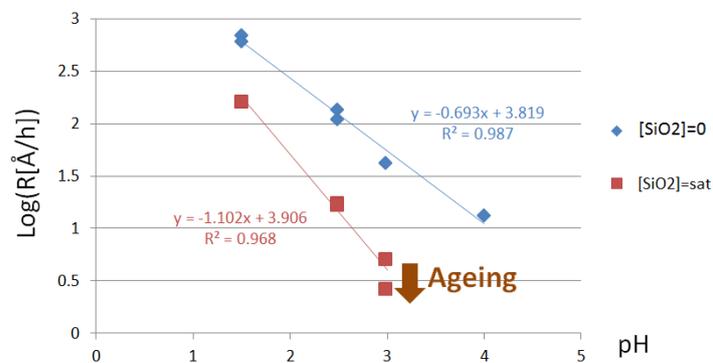


Figure 3 : Summary of layer formation rates obtained according to pH and saturation of the fluid. Points obtained at pH = 3 in saturated fluid (red squares) with higher and lower rate values correspond to the beginning and the end of this experiment respectively. They may correspond to the passivation of the surface due to ageing process.

However, contrary to what was expected, no clear densification of the surface layer could be detected at $\text{pH} > 1.5$ (see e.g. Fig. 2b). In the same time, the rate did not strictly decrease on the time span investigated here in any experiment that has been treated so far, as indicated by a linear relationship between layer thickness and elapsed time (as displayed e.g. in Fig. 2c). This indicates that longer maturation time might be required for the layer to densify, as reported in comparable process of ageing of silica sols¹¹, or of the maturation of amorphous precursors to secondary phases, such as pseudoboehmite or pregibbsite gels¹²⁻¹⁵, and ultimately exhibit passivation properties.

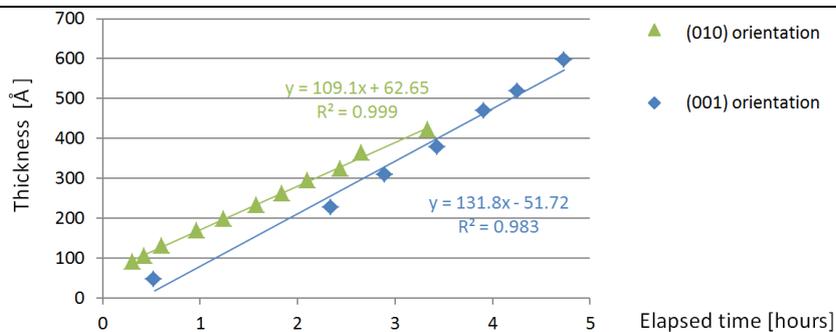


Figure 4 : evolution of layer thicknesses obtained from fit of XRR data. Data were obtained from experiments conducted at 80°C in non-saturated fluid at pH = 2.5 on (010) [triangles] and (001) [diamonds] labradorite polished cleavage.

Another surprising result was obtained by comparison of the evolution of layer thickness in between different cristallographic orientations (Fig. 4). Indeed, no significant anisotropy could be evidenced between results obtained between (001) and (010) cristallographic orientations at pH=2.5, which is at odds with recent work conducted on feldspar minerals in the absence of surface layers¹⁶. If these results are confirmed, they would further support the importance of the control of mineral dissolution by ASSLs in the context of mineral chemical weathering by acidic fluids. This would therefore open new considerations on mineral weathering processes according to the alteration context (soil profile, geothermal circulation, etc.).

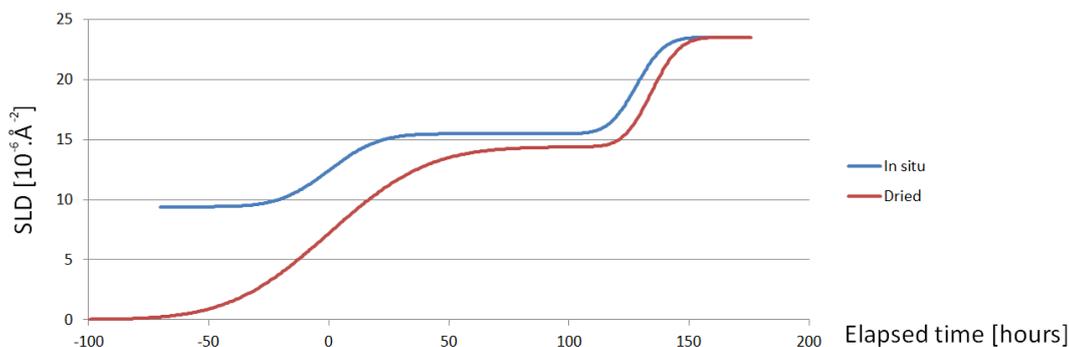


Figure 5 : SLD profiles obtained before (blue) and after (red) drying in an experiment conducted at 80°C in a fluid saturated with respect to amorphous silica at pH = 2.5 on (001) labradorite polished cleavage.

Further measurements were conducted on dried samples issued from selected modalities at the end of the dissolution step. As displayed on Fig. 5, dehydrated layers were slightly less dense than when measured *in situ*. This decrease of the density, most probably resulting from dehydration and expansion of the layer, came along with an increase of thickness and rugosity that was attributed to tensile strain/capillary pressures involved in the drying step¹⁷.

Our observations confirmed the occurrence of surface layers on all of the initial labradorite cleavages, supposedly pristine, as previously reported (*cf.* experimental report of experiment number 32-03-777). This layer was determined by linear regression to be 43.82 Å-thick on average. This initial surface feature was most probably generated during the polishing process, despite the use of a modified method successfully applied on Wollastonite samples (*cf.* experimental report of experiment number 32-03-777). The polishing step is unfortunately unavoidable in order to obtain XRR-grade mineral samples.

On the whole, the present work stretches previous experimental limits opening the way to the study of low-reactivity minerals representative of the continental crust, such as feldspars. This study confirmed previous results regarding the importance of ASSL in the process of dissolution of this category of silicate minerals. Of note is the anticipated increase of this effect in acidic solution as pH approaches neutrality (Fig. 3), forecasting the relevance of such mechanisms in the field. This study reveals a possible importance of the minimum ageing or maturation time required for the layer to exhibit passivating properties. This hypothesis necessitates further experiments involving *in situ* XRR investigations on samples reacted over longer time spans to be confirmed. Eventually, interesting observations were enabled regarding the cancellation of the face-specificity in mineral reactivity by interfacial layers, or the effect of dehydration on the properties of ASSLs. These early results, however, also require to be supported by further investigations.

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

The beam time allocated to the experiments was well balanced to the needs. It enabled to perform the *in situ* follow up of all of the scheduled experiments.

Publication(s):

Daval, D., *et al.* Dynamics of altered surface layer formation on dissolving silicates, submitted in *Geochimica et Cosmochimica Acta*

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