Standard Project

Experimental Report template

Proposal title: Unravelling silicate surface ageing processes by combining X-ray reflectivity (XRR) with Grazing-incidence small-angle scattering (GISAXS): Insights into dissolution mechanisms relevant to chemical		**Proposal number:** 20141312
Beamline: BM32	**Date(s) of experiment:** from: 15/06/2015 to: 21/06/2015	**Date of report:** 15/09/2015
Shifts: 14	**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 is of primary importance for various processes ranging from chemical weathering and the C cycle to CO2 sequestration. Recently, the formation of silica layers at the mineral-water interface has been observed to control the dissolution kinetics of silicate minerals such as olivine[1] and diopside[2]. The same kind of amorphous silica coatings have also been observed on the surfaces of other minerals such as wollastonite[3] and anorthite[4] but with little to no effect on the dissolution rate has been evidenced. This series of *in situ* X-ray reflectivity (XRR) experiments aims at studying the very first stages of the dissolution process of selected silicate minerals, trying to ascertain the degree of cation leaching from the surface, the formation of a light, porous amorphous silica layer, and its eventual densification over time. We have performed the following experiments using different polished crystal faces of wollastonite (calcium silicate) and labradorite (calcium, sodium aluminosilicate) to probe the differences in the dissolution behaviour following the crystallographic orientation.

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

Wollastonite ($CaSiO_3$) and labradorite [$(Na, Ca)(Al, Si)_4O_8$] single crystals have been oriented by electron backscattered diffraction and cut along specific crystallographic directions ((100), (010) and (001) for wollastonite ; (001) and (110) for labradorite). 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 pH (pH = 2 and 4 for wollastonite, and pH = 1.5 and 3 for labradorite) have been circulated through the setup in order to favor the formation of Si-rich surface layers following different suspected mechanisms.

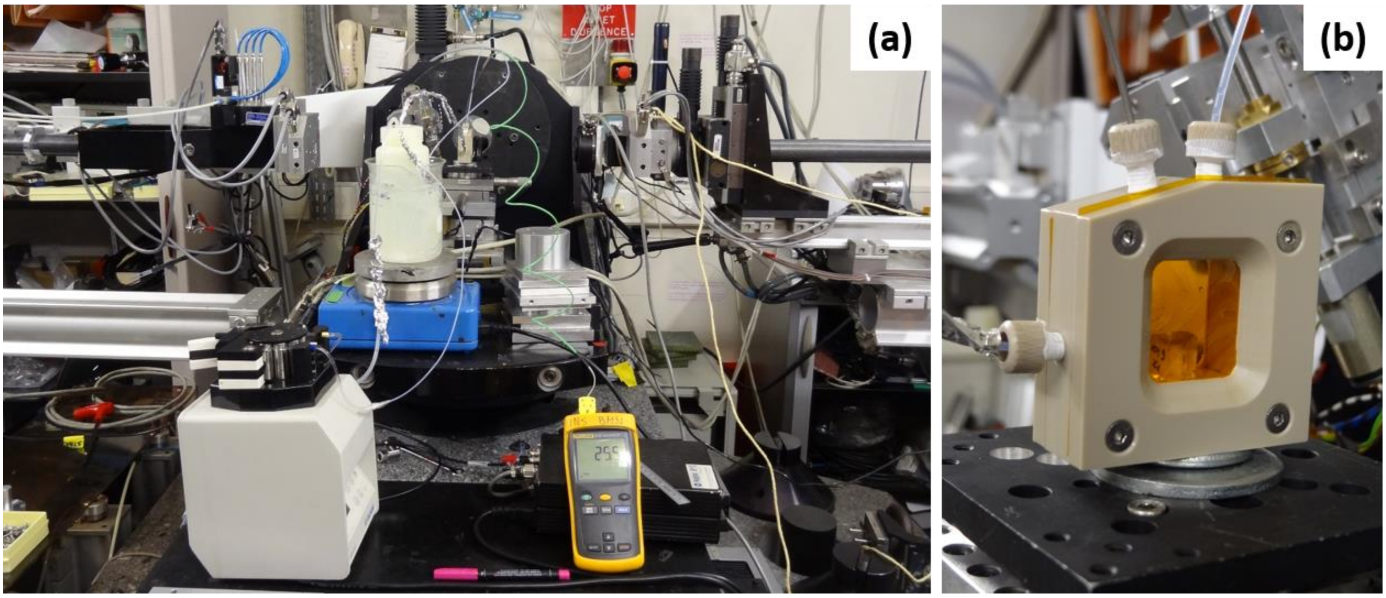

Figure 1 : (a) Picture of the experimental setup used for *in situ* XRR experiments. (b) Close-up of the home-made flow cell.

Regarding wollastonite, this session has enabled to confirm densification trends observed in our previous set of experiments (See experimental report of experiment number 32-03-723). At room temperature, under acidic conditions (pH = 2), the density of the surface layers has continuously increased with time. Further refinement of the obtained XRR spectra is still underway.

Amorphous Si-rich surface layers (ASSLs) were observed on labradorite samples thanks to significant improvement of data acquisition procedure. Indeed, convection of the fluid inside the cell and polymer dilatation due to temperature have lead us to systematically perform a sequence of alignment of the beam prior to measurement. The dataset has been fitted with *Motofit* plugin for *IgorPro* software. As shown on Figure 2, satisfactory fittings were obtained by using a double-layer model. A densification of the layer similar to that observed on wollastonite samples has been monitored for labradorite samples at 60°C in pH = 1.5 HCl solution (Fig. 3). Eventhough the experimental setup did not enabled us to reach temperatures higher than 60°C for reasons regarding signal stability, our results can be correlated to recent evidences for ageing reported on labradorite mineral at 80°C [5]. Interestingly, the behaviour of labradorite at pH = 1.5 and T = 60°C is similar to the one observed at pH = 3, T = 80°C. No significant anisotropy in terms of reactivity nor layer textural properties could be observed between (001) and (110) crystal orientations. However, further data refinements are still under progress on these aspects.

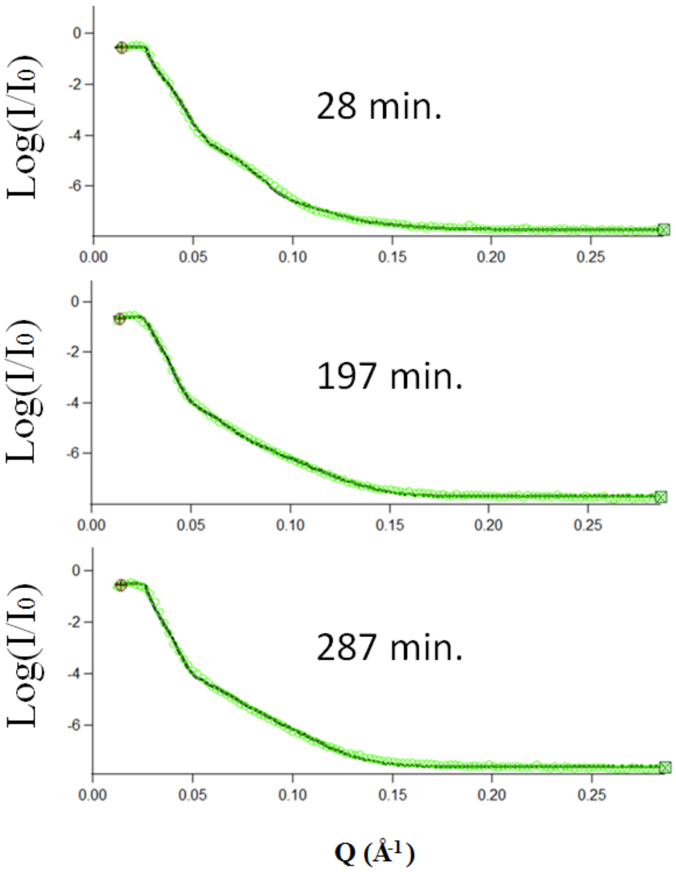

Figure 2 : Time-resolved evolution of the XRR patterns (green circles) and associated fits (black lines) obtained for labradorite dissolution at 60°C in pH = 1.5 HCl solution.

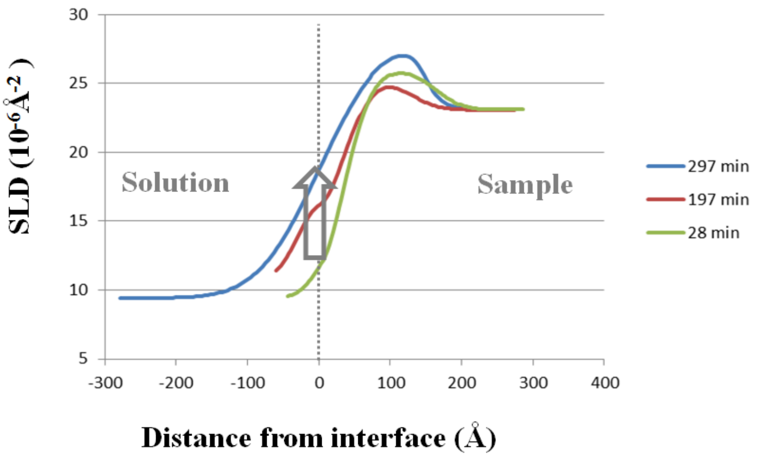

Figure 3 : Scattering length density (SLD) calculated for fits presented in Figure 2 as a function of distance from interface. Dotted line indicates the theoretical interface. Note the increase of the SLD as reaction proceeds indicated by the grey arrow.

Eventually, we have curiously found out that XRR patterns of most of the initial, supposedly pristine, labradorite cleavages obtained prior to immersion in aqueous solutions showed that a surface layer already existed prior to starting the experiments. This may be due to weathering of the samples during the polishing process that we used.

On the whole, the present study demonstrates that interfacial mechanisms may be key to understand bulk measurements of fluid-mineral interaction. This study has revealed the first clues for an unexpected evolution of amorphous layers formed on two silicate minerals, namely labradorite and wollastonite. It therefore opens the way to future investigations in this field as further characterisations are still needed to link ASSL density to the reaction

rate. In addition, higher temperature experiments that could not be completed with the present setup are still required to allow a comparison with existing kinetic data.
Finally, modified polishing methods that were sucessfully applied to wollastonite in this series of experiment will be extended to labradorite preparation to avoid any doubt regarding potential starting surface layers.

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

In this session, part of the beam time has been dedicated to the evaluation of ASSL porosity by GI-SAXS. These early tests have suggested that the nature of the samples produced requires them plus the detector to be both placed under vacuum to produce satisfying measurements. This information will be taken into account in future experiments on similar samples.

Publication(s):
None

Cited literature:

[1] D. Daval, O. Sissmann, N. Menguy, G.D. Saldi, F. Guyot, I. Martinez, J. Corvisier, B. Garcia, I. Machouk, K.G. Knauss, and R. Hellmann, Chem Geol **284**, 193 (2011).
[2] D. Daval, R. Hellmann, J. Corvisier, D. Tisserand, I. Martinez, and F. Guyot, Geochim Cosmochim Ac **74**, 2615 (2010).
[3] D. Daval, I. Martinez, J. Corvisier, N. Findling, B. Goffe, and F. Guyot, Chem Geol **265**, 63 (2009).
[4] G. Jordan, S.R. Higgins, C.M. Eggleston, S.M. Swapp, D.E. Janney, and K.G. Knauss, Geochim Cosmochim Ac **63**, 3183 (1999).
[5] B. Wild, D. Daval, G. Imfeld, G.D. Saldi, K.G. Knauss, Goldschmidt Conference (2014).