	Experiment title: Probing the early stages of silicate mineral dissolution with X-ray reflectivity: Insights into dissolution mechanisms relevant to CO₂ sequestration and chemical weathering	Experiment number: 32-03-723
Beamline: BM32	Date of experiment: from:12/03/14 to: 15/03/14	Date of report: 31/08/14 <i>Received at ESRF:</i>
Shifts: 9	Local contact(s): Jean-Sébastien Micha and François Rieutord	
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Overall context

This experiment is part of our commitment to study the mechanisms of nm-thick surface layer formation during the dissolution of silicate minerals, and their consequences for mineral reactivity. In recent studies (e.g. [Daval et al., 2011; 2013](#)), we showed that the formation of amorphous-rich silica layers on the surface of dissolving silicate minerals could dramatically impact their dissolution rate. However, open questions remain as to why these effects are not universal, since passivation was reported to be mineral-dependent or even crystallographic-face-dependent.

In the framework of the VALVE project (INSU-EC2CO, PI: D. Daval, co-PI: A. Fernandez-Martinez), one of our main objectives was to determine whether the passivating ability of such surface coatings was acquired early on during the dissolution process (i.e., as soon as silicate minerals contact aqueous solutions) or if passivation could be a time-dependent process, for which kinetic rate laws need to be determined.

To reach this goal, Ca-rich silicate minerals, and in particular, wollastonite (CaSiO₃), was selected as a model mineral because of (1) the thick amorphous coatings developed on its crystal faces and (2) its elevated dissolution rate, which allows probing the formation of amorphous coating on short timescales. *In situ* X-ray reflectivity (XRR) patterns were acquired as a function of time to evaluate the evolution of the thickness and density of the surface layers, while *ex situ* experiments run on crystals with orientations identical to the samples we used at ESRF allowed for the determination of wollastonite dissolution rate as a function of time. Taken together, these data provided unprecedented information about the intricate interplay between microstructural modifications of surface layers and mineral dissolution kinetics.

Experimental details

Wollastonite (CaSiO₃) and labradorite [(Na, Ca)(Al, Si)₄O₈] single crystals have been selected, cut following specific cleavage directions identified by electron backscattered diffraction (cf. Figs. 1a-b: wollastonite: (100); (010) and (001); labradorite: (001)), and polished prior to starting the XRR analyses. The development of silica layers was studied *in situ* by placing the crystal face in a home-made cell covered with a kapton dome (Fig. 1c) at room temperature. Acidic solutions (pH 2) have been chosen to run the experiments in order to favor the formation of thick Si-rich surface layers on short timescales. Because Fe was recently proposed to play a crucial role in rendering layers passivating (e.g. [Saldi et al., 2013](#)), additional experiments were run on all crystals with the same acidic solutions containing 5 mM of FeCl₃.

XRR patterns were acquired for 2θ angles ranging between 0 and 1° , with an X-ray beam wavelength of 0.0459 nm. Experiments were run for a maximum time of 8 hours. XRR patterns were taken every 20 minutes, to follow the structural changes associated with the dissolution process. The XRR patterns were subsequently fitted using Irena software (APS) to get the evolution of the thickness and density of the layers.

In addition, ongoing complementary experiments are run in our laboratory using cleavages with the same orientations as the ones we used at ESRF in order to monitor the release rate of Ca to the solution, and eventually relate the evolution of surface layer properties that we measured using XRR to the evolution of wollastonite dissolution rates as a function of time.

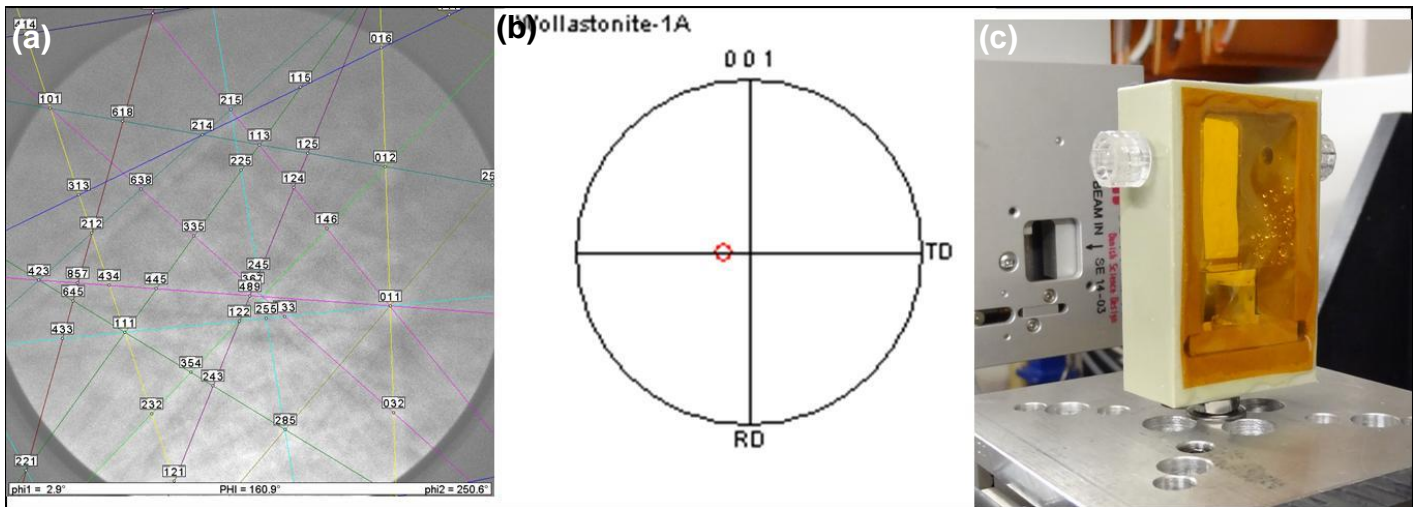


Fig.1. (a) and (b) Typical EBSD characterizations run for all cleavages used in this study prior to performing XRR experiments (here sample W3). Such a technique allows for the determination of crystal orientation (in this specific case, fairly close the (001) zone axis). (c) Picture of the home-made cell that we used for the XRR analyses.

Results

We'll organise the results, here, along two axes: (1) physicochemical properties of surface layers as a function of crystal orientation, aqueous solution composition and time, and (2) dissolution rates of the underlying silicate mineral.

Insights from XRR patterns

Labradorite

Unfortunately, the formation of surface layers on this mineral was either (1) too slow to be monitored by XRR on timescales compatible with the requirement of the experiments (< 10 h) or (2) accompanied by a high roughness that prevented its observation with XRR. While the formation of thick silica coatings was expected based on literature analysis, since previous studies have documented that nm-sized layers could be formed on labradorite over short timescales (e.g. [Hellmann et al., 2012](#)), we speculate that this result may stem from the anisotropy of the process: it is tempting to conclude that surface layers formed on (001) surfaces were particularly thin.

Wollastonite

The formation of surface layers has been observed on all samples, regardless of the crystal orientation. No obvious discrepancies was observed between the experiments run in Fe-free and those run in Fe-rich solutions, suggesting that in the specific conditions of our experiments, Fe does not impact the thickness and density of the surface coatings.

Regarding the physicochemical properties of the layers, we evidenced that they were dramatically impacted by crystal orientation, with faces (100) and (010) exhibiting similar behaviors (early loss of XRR patterns associated with the surface layers, which may be attributed to an important roughening of the surface). The results for face (001) are specifically detailed below, and can be summarized as follow: the XRR spectra continuously evolved with time all along the duration of the experiment (see Fig. 2a). Satisfactory fitting of the XRR patterns collected on this face was best obtained by supposing that two distinct layers formed on the surface of wollastonite. Interestingly, our fitting results suggest that the density of the surface layers continuously increased with time.

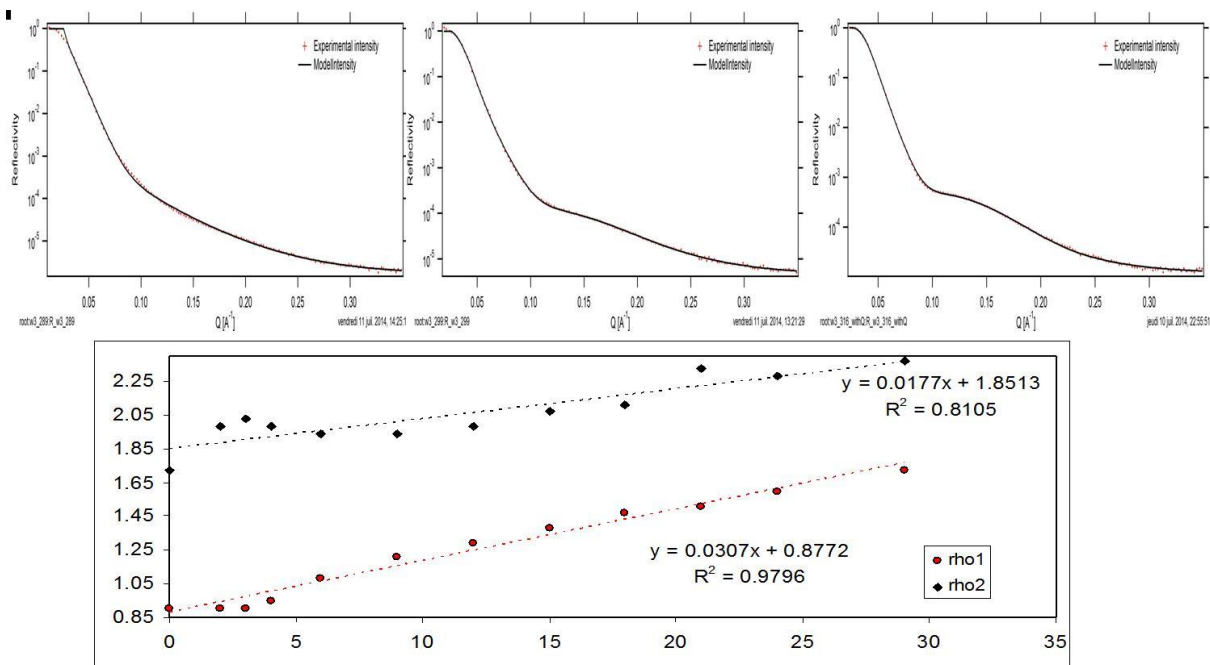


Fig. 2. (top) Time-resolved evolution of the XRR patterns for sample W3 ((001) face, pH = 2, $T = 20\text{ °C}$). After 4h, the modification of the XRR pattern testified from the formation of layers on the surface of wollastonite. (bottom) Fitting of the XRR spectra revealed that the density of the surface 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.

Additional information obtained from *ex situ* experiments

Interestingly, *ex situ* experiments run on a wollastonite crystal oriented following the same direction ((001)) revealed a slight decrease of wollastonite reactivity as a function of time. Taken together, these results suggest that denser coatings are less permeable and are more prone to affect the transport of ions from and to the wollastonite surface.

A final comment that can be made is that, curiously, XRR patterns of most of the initial, supposedly pristine, wollastonite cleavages obtained prior to immersion in aqueous solutions showed that surface layers already existed prior to starting the experiments. This may be due to weathering of the samples during the polishing process that we used. It is noteworthy that such layers apparently vanished right away after immersion of the wollastonite cleavages in the aqueous solutions.

Conclusions/Perspectives

The present study strengthens the idea that ageing is a mechanism which deserves further attention, as it dramatically impacts surface layer density in conjunction with silicate mineral reactivity. This study paves the way for future investigations in a similar direction, as such effects are not incorporated into classical reactive transport codes, which overestimate the actual rate of silicate mineral dissolution.

Future studies should be directed to ascertain which parameters influence the kinetics of surface layer densification. Combining techniques which probe at the same time the density and the porosity of the layers would ultimately confirm the link which exists between nm-scale structural changes of surface layers and silicate mineral reactivity. In addition, higher temperature experiments and/or experiments run in other crystallographic directions should be carried out for labradorite, as our preliminary experiments were not conclusive regarding the formation of surface layers.

Finally, modified polishing methods will be applied to get rid of the starting surface layers, even though it is likely that they did not affect the subsequent evolution of surface layers, as they apparently vanished as soon as the crystals were immersed in aqueous solutions.

References

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