

## Experiment Report Form



<b>Experiment title:</b> <i>Effect of alkalinity on the kinetics of olivine serpentinization</i>	<b>Experiment number:</b> ES-91	
<b>Beamline:</b> ID27	<b>Date of experiment:</b> from: 06 Feb 2014      to: 11 Feb 2014	<b>Date of report:</b>  <i>Received at ESRF:</i>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr Volodymyr Svitlyk	
<b>Names and affiliations of applicants (* indicates experimentalists):</b> *Muriel ANDREANI, LGL, UMR 5276, ENS et Univ. Lyon 1 *Isabelle DANIEL, LGL, UMR 5276, ENS et Univ. Lyon 1 *Jean-Philippe PERRILLAT, LGL, UMR 5276, ENS et Univ. Lyon 1 *Hervé CARDON, LGL, UMR 5276, ENS et Univ. Lyon 1 *Maria PENS, LGL, UMR 5276, ENS et Univ. Lyon 1		

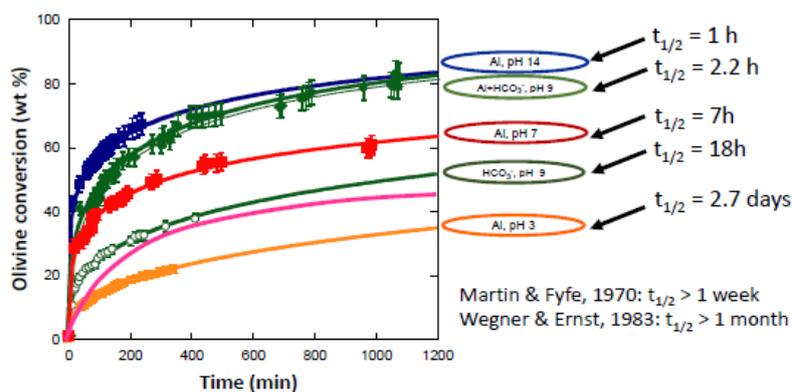
### Report:

The objective of this experiment was to measure the kinetics of olivine alteration (hydration and/or carbonation) in basic and/or bicarbonate-enriched fluids, such as those circulating within the oceanic lithosphere at mid-ocean ridges. Previous experiments ([1] and data from Exp. HS-4586) highlighted the important role of Al in accelerating the kinetics of olivine hydration in near neutral pH conditions. We wanted here to test the effect of pH on the role of Al, running experiments with and without Al. We used a low-P diamond anvil cell able to reproduce the chosen T-P conditions (T=200°C or 350°C, and P=0.2 GPa) and to allow in-operando follow up of reaction with XRD.

A total of eleven experiments have been run for 4 to 23 h. Nine was run using an olivine powder as the starting material, one an orthopyroxene powder and one an olivine+orthopyroxene powder, for comparison. All of them contained solutions made of 0.5M NaCl with either aluminium and 0.4 M NaHCO<sub>3</sub>, or with 0.4 M NaHCO<sub>3</sub> alone. pH was buffered to reach values of 3, 7, 9 or 14. All experiments worked very well and we did not encountered technical difficulties related to the beamline.

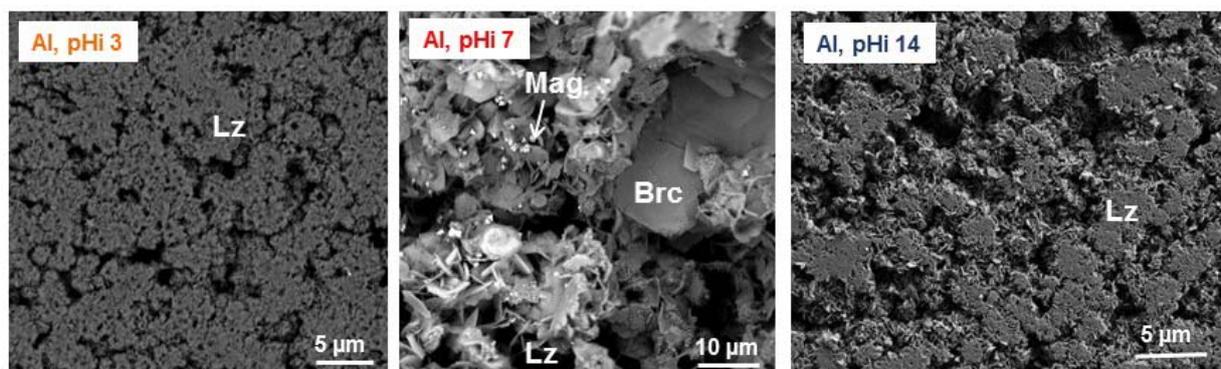
Data were treated using Le Bail method to refine cell parameters of the main identified phases (olivine/pyroxene and serpentine +/- carbonate and magnetite). Then the Rietveld method was used to quantify the proportion of each phase as a function of reaction advancement. These transformation-time data have been analysed in the Avrami's theory of nucleation and growth [2,3] to retrieve transformation rates, activation energies. Experiments displayed very different kinetics depending mainly on the pH value; the

fastest one occurring at highest pH with Al, showing half time of reaction as short as one hour. Most experiments went close to completion at 340°C (>80 % conversion) except those run at acidic pH. Test run on orthopyroxene allowed us to identify the contrasted effect of Al on olivine and pyroxene under neutral conditions at least. It complements our previous data (Exp. HS-4586) and allowed us to publish an article on the role of Al on the kinetics of those 2 minerals [4: Pens et al., Chem. Geol. 2016]. All these data have been treated and discussed in the PhD manuscript of Maria Pens, who defended in July 2016 [5: available online at : <https://www.theses.fr/196685818>]. A second article is under preparation but its submission has been delayed due to the need of 4 additional experiments to discriminate the role of basic pH (buffered by NaOH) versus the one of carbonate ions at high pH. We are currently running the experiments in the lab.



**Figure 1** : Evolution of the olivine conversion to lizardite (+/- magnetite) during the different reactions. Calculation of the half time reaction show the increase of the kinetic with pH in presence of Al. Even without Al, the presence of bicarbonate in solution increases the rate of olivine conversion compared to previously published data in similar conditions but pure water [6, 7]

SEM characterization of sample products were also realized (Figure 2). They revealed that serpentine, variably enriched with Al, is by far the dominant mineral formed under all conditions. Minor phases such as brucite ( $Mg(OH)_2$ , magnetite or carbonate (in  $NaHCO_3$  solutions) only occur at neutral or slightly basic conditions (pH 7 and 9; Fig. 2).



**Figure 2** : SEM images of the reaction products in presence of Al as a function of pH. Lizardite is more developed at high pH.

## References

- [1] Andreani M., Daniel I., Pollet-Villard M., 2013. Aluminium speeds up the hydrothermal alteration of olivine. *American Mineralogist*, 98, 1738-1744.
- [2] Avrami, M., 1939. Kinetics of phase change, *J. Chem. Phys.*, 7, 1103-1112.
- [3] Perrillat, JP, 2008 Kinetics of high-pressure mineral phase transformations using in situ time-resolved XRD in the Paris-Edinburgh cell: a practical guide for data acquisition and treatment, *Min. Mag.*, 72, 683-695.
- [4] Pens M., Andreani M., Daniel I., Perrillat J-P., Cardon H., 2016. Contrasted effect of aluminum on the serpentinization rate of olivine and orthopyroxene under hydrothermal conditions. *Chemical Geology*, 441, 256-264.
- [5] Pens M., Etude expérimentale de l'altération hydrothermale des roches ultrabasiques, PhD thesis, Université Claude Bernard Lyon 1, defended on July 11th 2016. Supervised by I. Daniel and M. Andreani.
- [6] Martin, B., Fyfe, W.S., 1970. Some experimental and theoretical observations on the kinetics of hydration reactions with particular reference to serpentinization. *Chem. Geol.* 6, 185-202.
- [7] Wegner, W.W., Ernst, W.G., 1983. Experimentally determined hydration and dehydration reaction rates in the system  $MgO-SiO_2-H_2O$ . *Am J Sci* 283, 151-180.