



**Experiment title: Dissolution of olivine and serpentine in hydrothermal aqueous solutions: speciation and solubility of iron by X-ray absorption spectroscopy. Application for mineral sequestration of CO<sub>2</sub>.**

**Experiment number:**  
HE-2957

<b>Beamline:</b> BM30b	<b>Date of experiment:</b> from:29/10/08 to: 04/11/08	<b>Date of report:</b> 25/02/10
<b>Shifts:</b> 18	<b>Local contact(s):</b> Denis Testemale	<i>Received at ESRF:</i>

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*This work is subject of a manuscript: Fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) dissolution kinetics determined by X-ray absorption spectroscopy, Damien Daval, Denis Testemale, Nadir Recham, Jean-Marie Tarascon, Julien Siebert, Fabrice Brunet, Isabelle Martinez and François Guyot, Chemical Geology, submitted.*

## Geological context

This experiment is part of our commitment to the study of iron speciation and its transport properties in hydrothermal conditions. In previous studies, we investigated the speciation of iron(II) in chloride brines (Testemale et al., 2009a), and the dissolution of iron minerals in conditions relevant to the mineral sequestration of CO<sub>2</sub> (Testemale et al., 2009b, Guyot et al., 2007, experiments HS2628, ME1314). In the present experiment, we investigated the speciation of iron(II) and the solubility of fayalite in dilute HCl or acetate buffered hydrothermal solutions. It is thus of critical importance to get speciation, thermodynamical and kinetics data in these conditions, in order to be able then to model the transport of iron in natural fluids (by use of geochemical codes).

## Experimental details

The usual procedure was used for generating the HP/HT conditions (autoclave developed at Laboratoire de Cristallographie, CNRS, Grenoble and used routinely on the FAME beamline).

Several experimental runs were conducted:

- measurement of the transmission of pure water at 300 bar (working pressure during the whole experiment) from 30 to 500°C. The purpose of such a measurement is the calibration of the temperature by determining the water density (from the transmission of the sample) and comparing it with theoretical values (NIST chemistry webbook). We already encountered at this stage the usual difficulty of experiments at the Fe K-edge: the transmitted signal is very weak.
- dissolution of a pellet of fayalite in an HCl solution (100 mmol) at 300 bar from 30°C to 100°C.

- dissolution of a pellet of fayalite in acetate buffered 2M solution at 300 bar from 30°C to 100°C.

## Results

We'll organise the results, here, along two axis: speciation of iron(II), and solubility of fayalite.

### Fayalite solubility:

Fayalite solubility was determined by measurement of Fe molality as a function of time. The method used was similar to all our previous studies. But in this experiment, we optimized the fluorescence measurement (geometry of the experiment fixed, measurement of standard solution, calibration of molality by transmission measurement) so that we were able to determine the Fe molality by measuring the fluorescence signal at one energy (above the edge). The benefit from this method is that the time precision of our kinetics study is not limited anymore by the time length of an EXAFS scan (movements of the monochromator), and it was thus possible to obtain smooth dissolution curves, especially in the very first moments of the dissolution. The rate constants can thus be derived with better precision. Then, classical XANES and EXAFS scans were acquired to derive the speciation of Fe in solution (see below). An example of this methodology is given in figure 1.

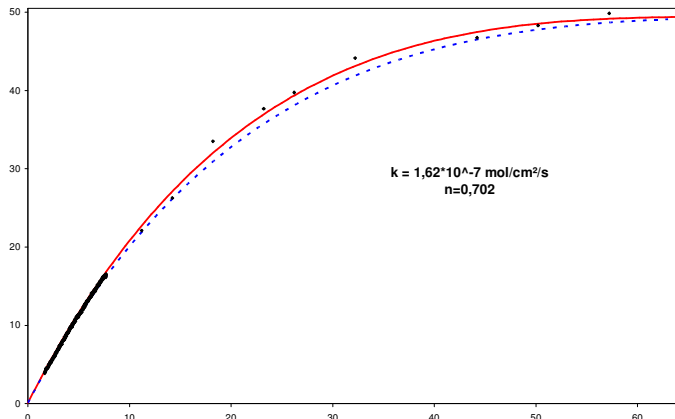


Figure 1: measurement of Fe molality (in mmol) as a function of time (in minutes), for the case of fayalite dissolution at 300bar/65°C in 0.1m HCl solutions. Single energy fluorescence measurement is used at the beginning of the experiment giving a very small time step, we then switched to classical XANES acquisition (after ~10 minutes): the time step is larger but speciation information is then available.

From these measurements, rate constants and pH exponents are derived and allow establishing the kinetics law of fayalite dissolution in this temperature and pH range.

$$R_{net} = k_0 \exp(-E_a / RT) a_{H^+}^n$$

with  $\log(k_0) = 0.17 \pm 0.63$  ;  $E_a = 45.1 \pm 4.2 \text{ kJ.mol}^{-1}$  ;  $n = 0.74 \pm 0.08$ .

It is important to mention that this  $R_{net}$  is normalised to geometric surface area.

### Iron speciation:

The in situ measurement of XANES spectra and their analysis (by comparison with our previous studies, Testemale et al. 2009a) lead to the conclusions that iron is mainly hexahydrated in HCl 0.1m solutions for temperature below 100°C. In figure 2, portions of XAS spectra (the white line and the first EXAFS oscillations) of two solutions (with or without acetate) are plotted. Their similarity and XANES ab initio calculations (not shown here) indicate that the acetate ligation is done with two acetate ions, each bonded to iron through one oxygen atom. This complexation is at the origin of the increased dissolution of fayalite.

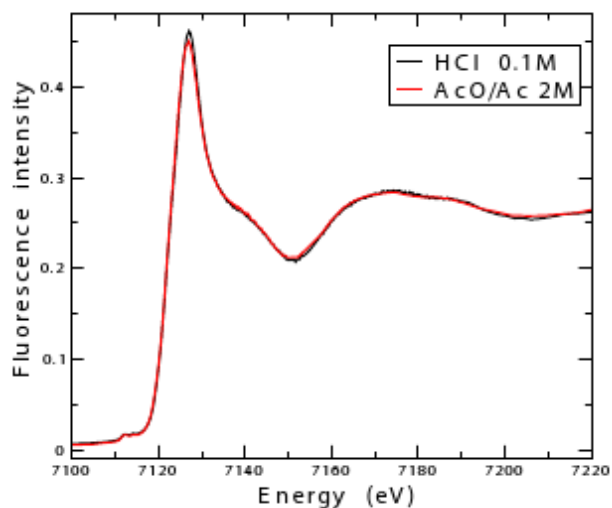


Figure 2: XAS spectra of 2 solutions: HCl 0.1M at 300 bar/50°C, and acetate buffered solution at 300bar/65°C. The two very similar spectra are an indication of a very close Fe speciation.

## Conclusions/Perspectives

This study comes after years of experimental and methodological development through our collaboration, especially for dissolution studies of Fe-bearing minerals. The combination of high sensitivity (a few mmol), kinetics precision (smooth curves to derive rate constants), availability of speciation (through measurements of XANES spectra), large experimental volumes (which allow the use of large monocrystals or pellets as starting materials and the post-experimental recovery of solutions) and large P/T range reachable are all very positive elements for such studies. We thus plan to leverage this expertise and apply it on other minerals relevant to water/rock interactions in the crust, or to the same minerals (siderite, fayalite, etc.) but in different temperature and pressure conditions.

## References

Guyot, F. et al., (2007) *Goldschmidt Conference Abstracts, Geochim. Cosmochim. Acta* A365 (2007).

Testemale, D., Brugger, J., Liu, W., Etschmann, B., and Hazemann, J.-L.: In-situ X-ray Absorption Study of Iron(II) Speciation in Brines up to Supercritical Conditions, *Chem. Geol.* 264, 295–310, 2009a.

Testemale, D., Dufaud, F., Martinez, I., Bénézech, P., Hazemann, J.-L., Schott, J., and Guyot, F.: An X-Ray Absorption study of the dissolution of siderite at 300 bar between 50°C and 100°C, *Chem. Geol.* 259, 8–16, 2009b.