



**Experiment title: Rôle du CO<sub>2</sub> sur le transport du fer dans des fluides crustaux mixtes H<sub>2</sub>O-CO<sub>2</sub> en conditions hydrothermales métamorphiques: étude par spectroscopie d'absorption X.**

**Experiment number:**  
30-02-898

**Beamline:**  
BM30b

**Date of experiment:**  
from: 08/04/08 to: 15/04/08

**Date of report:**  
23/07/09

**Shifts:**  
21

**Local contact(s):**  
Denis Testemale

*Received at ESRF:*

**Names and affiliations of applicants (\* indicates experimentalists):**

**D. Daval\* – IPGP, Paris**

**F. Guyot\* – IMPMC, Paris**

**D. Testemale\* – Institut Néel**

**G. S. Pokrovski\* – LMTG, Toulouse.**

## 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, Daval et al., in prep.). In the present experiment, we investigated the speciation of iron(II) and the solubility of magnetite in hydrothermal solutions containing large amounts of CO<sub>2</sub>. Indeed, in natural metamorphic fluids, large quantities of carbon dioxide are frequent. It is thus of critical importance to get speciation and thermodynamical 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 500 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.
- Solution dissolved FeCl<sub>2</sub> (50 mmol) + HCl (100 mmol). XAS spectra of this solution were acquired at 500 bar from 30 to 450°C.
- same solution but we added silver oxalate pellets. Indeed, we decided not to load CO<sub>2</sub> with aqueous oxalic acid as indicated in the proposal, but with solid silver oxalate (AgOx), and increase the temperature up to the thermal decomposition of the oxalate (Boldyrev, 2002) at approx. 150°C. We acquired XAS spectra from 30 to 450°C. AgOx quantities were adapted so that we have 20% CO<sub>2</sub> in the solution, after decomposition.

- dissolution of a single crystal of magnetite in an HCl solution (100 mmol) at 500 bar from 30°C to 450°C.
- dissolution of a single crystal of magnetite in Na<sub>2</sub>CO<sub>3</sub> solutions (1M, pH=11.47) at 500 bar from 30 to 400°C.
- dissolution of a single crystal of magnetite in HCl (0.1 M) solutions + solid AgOx (in quantity so that we have 20% CO<sub>2</sub> in the solution).

## Results

We'll organise the results, here, along two axis: speciation of iron(II), and solubility of magnetite. But first, one word about AgOx. This method appears to be reliable. We'd like to acknowledge here the high-quality support from H. Müller (ESRF, Chemical lab. facility), who synthesized AgOx powder and conducted the purity analysis. Once the temperature is set above the thermal decomposition value, CO<sub>2</sub> is liberated in the solutions (whether it stays there is something we want to check in a near future by Raman spectroscopy). Weighing of the pellets of AgOx before and after experiment indicates that all the CO<sub>2</sub> available is liberated from solid. In figure 1, a MEB image of a pellet recovered from one experiment is shown: EDX analysis confirmed that it is pure Ag, in the form of a 'dendritic foam' as it is visible in the figure.

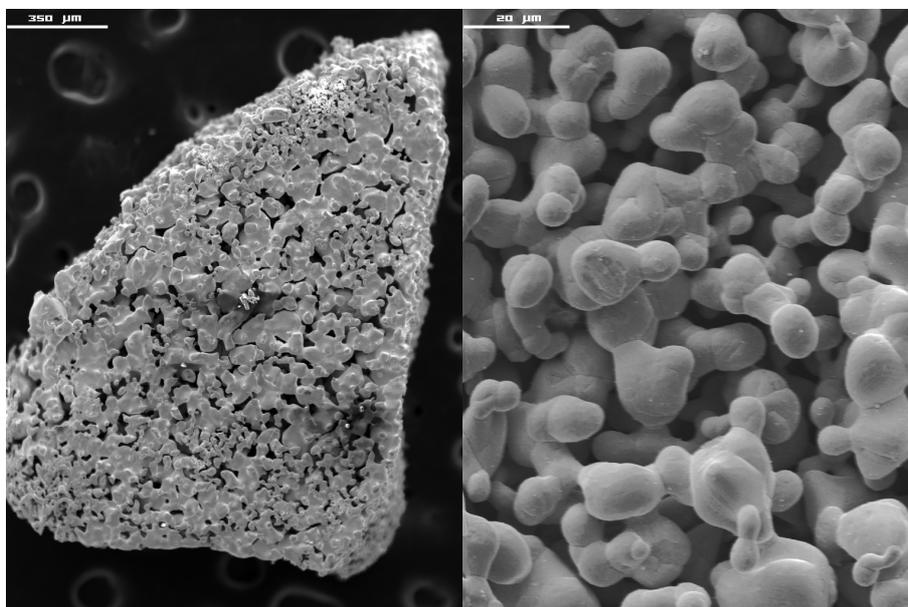


Figure 1: MEB image of an AgOx pellet (after total loss of CO<sub>2</sub>) recovered from an experiment. The global shape of the initial millimetric pellet is conserved (left, the white scale in the top left corner corresponds to 350 μm), and the microscopic 'dendritic texture' of pure Ag is visible (right, the white scale in the top left corner corresponds to 20 μm).

### Iron speciation:

In figure 2, portions of XAS spectra (the white line and the first EXAFS oscillations) of solutions at 500 bar/450°C, with and without CO<sub>2</sub> are plotted. The effect is slight but visible: in the presence of CO<sub>2</sub> and chloride ions, the spectra are different from solutions with chloride ions (same quantity) and no CO<sub>2</sub>. The evolution of the spectra with temperature (not shown) are typical of the chlorination of iron (Testemale et al., 2009ab), thus it looks that in the presence of carbon dioxide, the chlorination is more advanced (a rough estimation would be an advance of 50°C). The observation is similar at 500°C (not shown).

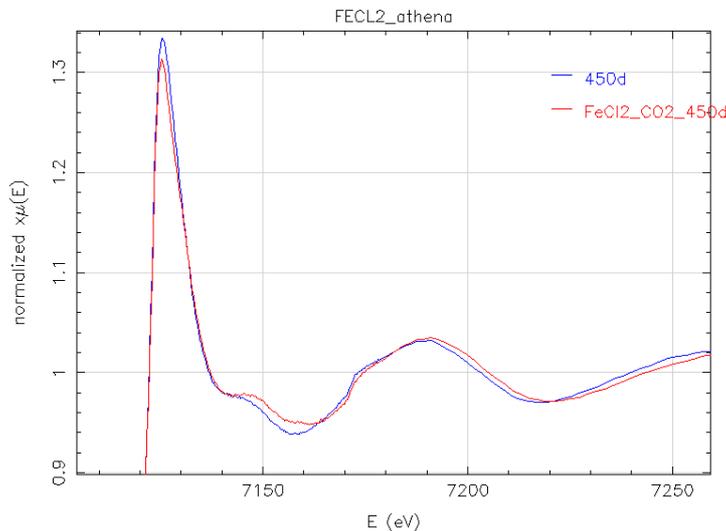


Figure 2: XAS spectra of 2 solutions at 500 bar/450°C, one with CO<sub>2</sub> (red), the other without (blue).

### Magnetite solubility:

In acidic conditions (HCl 100 mmol), magnetite dissolves up to [Fe]= 30 mmol (at 250°C, and the iron molality is then stable around this value for higher temperatures). This is in agreement with previous measurements of magnetite solubility we conducted in similar conditions (see experimental report ME-1314, and Daval et al., in preparation), where an iron concentration of 50 mmol was measured at 250°C (but with different crystals with probably different reactive surfaces). In the presence of aqueous carbonates (solution Na<sub>2</sub>CO<sub>3</sub> 1M), in basic conditions, magnetite does not dissolve. A more correct way to put things is: iron concentration is below our detection limit, which is approx. 2 mmol (=100ppm). The observation of the crystal that was recovered after the experiment indicates that there was very limited (if not absent) interaction of the mineral and the solution. The presence of carbonates in solution does not drive a preferential dissolution of magnetite. This is in agreement with thermodynamical calculations (code HCh and CHESS) that we conducted in parallel.

In the presence of AgOx, no iron is detected in solution (i.e., below the detection limit): the dissolution of magnetite seems to be inhibited by the presence of carbon dioxide in the solution. The signal from a secondary iron mineral is measured (possibly hematite, redish mineral). Furthermore, the EDX-MEB analysis on the recovered magnetite crystal demonstrated an additional superficial (microscopic) deposition of an Al-Si-phyllsilicate phase (not shown here).

### **Perspectives**

The perspectives are manifold:

- first we mentioned that we plan to monitor the suitability of our setup (internal cell) in the presence of dissolved gas: in order to check whether the liberated CO<sub>2</sub> remains in the cell, Raman experiments need to be conducted in situ. This is planned in the next future.
- although on the technological side: the deposition of an Al-Si mineral indicates the possibility of a small contamination of the solution (Al comes from the alumina pistons used in the internal cell: they will be replaced by inert glassy carbon pistons in the next experiments; where does Si come from?).
- then, there seems to be a valid speciation effect. This needs to be investigated further (by varying the relative amounts of species in solutions: larger carbon dioxide concentration, different chloride concentrations).
- finally, this inhibition of magnetite in presence of carbon dioxide needs confirmation. This would be a very interesting effect (in the framework on sequestration of CO<sub>2</sub>: stability of the host minerals) but has to be supported by laboratory experiments (determination of the solubility of magnetite in autoclave systems, as in LMTG, Toulouse). This is planned in the next future.

## References

Boldyrev, V. V.: Thermal decomposition of silver oxalate, *Thermochimica Acta* 388, 63–90, 2002.

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.