



	Experiment title: Iron speciation in high pressure high temperature H₂O-CO₂ fluids in contact with crystalline siderite and/or magnetite.	Experiment number: ME-1314
Beamline: ID-26	Date of experiment: from: 27/10/05 to: 01/11/05	Date of report: 14/09/06 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Sigrid Eeckhout	
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Geological context

The form of CO₂ sequestration that offers the more stable and long term storage capabilities is the mineral sequestration of CO₂ under the form of carbonates in deep geological reservoirs. For this reason, and because this carbonatation process is similar to the natural weathering of basic and ultra basic rocks of major importance in the cycle of carbon, it is essential to conduct studies on water-rock interactions in high temperature and high pressure conditions. In this framework, our groups already conducted a successful series of experiments on the kinetics of dissolution of siderite (cf Exp. Rep. HS-2628, and [1] for final results). The purpose of the present experiment was to apply a similar method to the dissolution of magnetite Fe₃O₄ in similar conditions, for the reason that magnetite could be a major source of iron ions necessary for the carbonatation of CO₂. Another reason makes also this study of critical interest: the need to study the aqueous redox equilibria Fe(II)/Fe(III) in the solution in contact with dissolving magnetite, which are little known in such conditions.

Experimental details

X-ray Absorption Spectroscopy experiments were conducted in the following conditions:

- dissolution of a magnetite monocrystal, in the presence of 0.1 mol/kg of HCl, 300 bar, 4 temperatures: 100°C, 150°C, 200°C, 250°C. Experiment A.
- dissolution of a magnetite monocrystal, in the presence of 1 mol/kg of HCl, 300 bar, 3 temperatures: 100°C, 75°C, 150°C. Experiment B.

All these experiments are time-resolved in order to derive kinetics properties and laws whenever possible [1]. In order to be able to determine the solubility of magnetite, the Fe concentration had to be determined. The ID26 setup does not allow reproductive and reliable measurements of the transmitted signal which is usually used for that purpose. Consequently we had to establish an experimental protocol to achieve it from the fluorescence signal itself (of very good quality on ID26). For that matter, calibrated iron solutions of known concentrations were measured in the same experimental detection geometry as the dissolution measurements (5, 15, 50 and 100 mmol/kg of Fe and 0.1 and 1 mol/kg of HCl), and abaque were established that were used to determine the Fe concentration from the fluorescence intensity, in the magnetite dissolution experiments A and B.

Results

The evolution of the Fe concentration is summarized in **Figure 1** for both experiments A and B, as a function of time. Dissolution rates were derived from these data and allow the determination of activation energies: respectively 72.3 and 83.3 kJ/mol \pm 20 kJ/mol. These values indicate a surface limiting process, most likely the complexation of surface species by the aqueous proton [1].

The next step of the analysis is to derive a kinetics law from this dataset, as it was done in the case of siderite dissolution (Exp. Rep. HS-2628). This part is not finalized yet.

The last important result from this study concerns the speciation and oxydation state of the aqueous iron dissolved from magnetite. This aspect of the results is complexified by an apparent oxydation of aqueous Fe under the intense x-ray beam. But we can still infer that, as shown in **Figure 2**, the stable oxydation state of aqueous Fe is +2 in the experiment A and +3 in experiment B. This seems to indicate that in the case of low pH (B), the acidity is sufficient to ensure the solvation of Fe(III) ions, although in the more basic experiment A, Fe(II) is the main species due to a probable concentration of Fe(III) in a non soluble hydroxide phase.

Perspectives

There are several tracks to be followed in continuation of this work. First, additional solubility/kinetics data are needed, in other pH and T conditions, in order to be able to establish a solid kinetics model for dissolution of magnetite. Then, the understanding of redox equilibria and the determination of the pH domain of stability for the different oxydation states need further consideration and experimental work. Finally, in order to obtain dataset necessary for the modelization of the CO₂ sequestration, other minerals reactivity are to be studied: in particular the mafic Fe-bearing mineral olivine is of particular importance.

References

1. F. Dufaud, Thèse de l'Institut de Physique du Globe de Paris (2006).

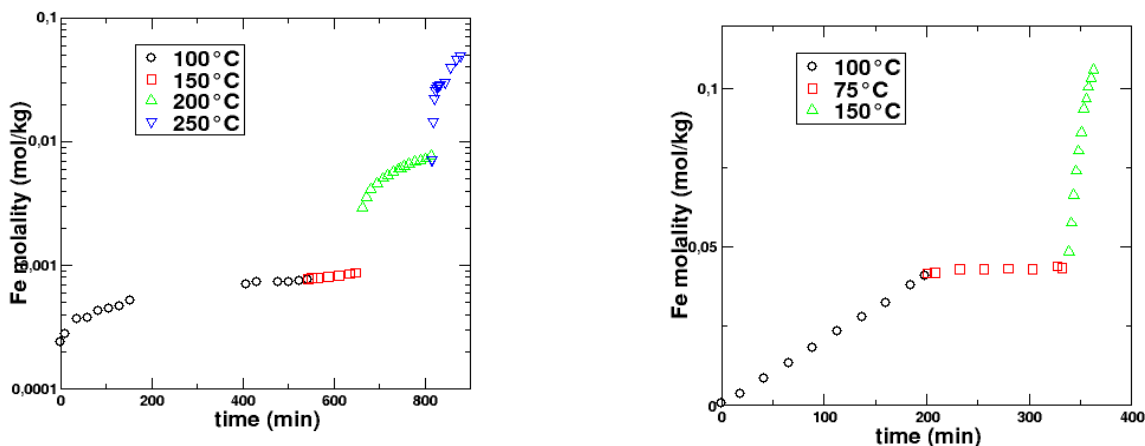


Figure 1: Iron molality determined from the fluorescence signal in experiment A (left) and B (right).

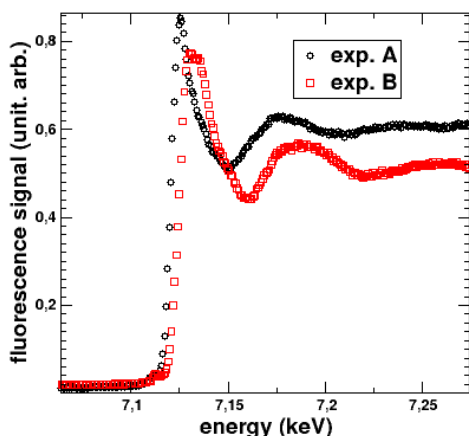


Figure 2: Spectra of stable aqueous iron species in experiment A and B: from the edge position and the shape of the spectra, it is clearly visible that Fe(II) is stable in experiment A, respectively Fe(III) in experiment B.