



	Experiment title: Spéciation et solubilité du fer dans des solutions aqueuses hydrothermales en présence de magnétite, d'olivine et d'orthopyroxène. Application à la séquestration géologique du CO ₂ .	Experiment number: 30-02-821
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Geological context

In the research program on mineral sequestration of CO₂, time-resolved studies dedicated to fluid-rock interactions are essential. Magnetite (Fe^{II}Fe^{III}₂)O₄ is an accessory host solid phase (the most reactive host candidates are basic and ultra-basic rocks), but is likely to release critical amounts of dissolved iron in the fluid, iron which is a reactant for the carbonation of carbon dioxide. Furthermore, magnetite may play a major role in the redox control of the system. For those reasons, we studied the dissolution of magnetite in hydrothermal conditions, as a function of pH, temperature and the nature of ligands in presence (the roles of sulfate and chloride ligands were quantitatively compared).

Methodology

Our methodology is based on *in situ* x-ray absorption spectroscopy (XAS) on synchrotron sources. For that purpose, we use an high-pressure/high-temperature cell (Testemale et al., 2005) that allows, in the same run, the determination of iron molality in the fluid in contact with a monocrystal of magnetite, the kinetics of this dissolution, and the measurement of X-ray absorption spectra at the iron K-edge (see figure 1). The latter is a strong point of this method: the speciation and oxidation state of dissolved iron can be inferred from these x-ray absorption spectra.

Kinetics modelling was performed using the geochemical code CHESS (Mines de Paris, Van der Lee et al.).

Experimental details

The experimental conditions that we studied are:

- dissolution of a monocrystal of magnetite (8 mg) in a 3.14 M HCl solution (pH_{25°C} = 0.25).

Temperatures investigated: 30, 65, 100, 150, 200, 250 and 300°C at 300 bar.

- dissolution of a monocrystal of magnetite (6 mg) in a 2.5 M H₂SO₄ solution (pH_{25°C}=-0.27).
Temperatures investigated: 30, 65, 100, 150, 200, 250 and 300°C at 300 bar.

Solubility and speciation were both determined through the fluorescence signal of the solution acquired by the Canberra setup of the FAME beamline.

Results

Three main results were derived from this experiment: the solubility of iron in the solution, as a function of time, the congruence of the reaction (relative quantities of Fe(II) and Fe(III) in the solution), and the speciation of dissolved iron as a function of the ligands present in the fluids. Examples of these results (for sulfuric acid solutions) are visible in figure 1 (Fe solubility) and table 1 (stoichiometry of the dissolution). Similar results are obtained for chloridric acid solutions).

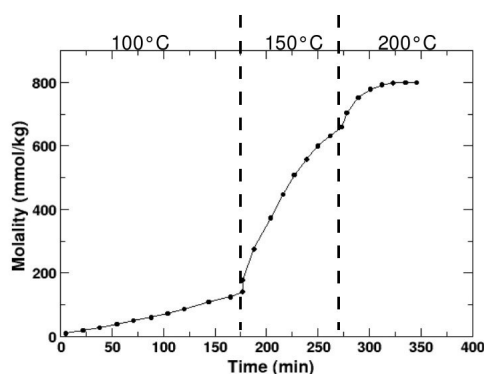


Figure 1: Total iron molality (Fe^{II} and Fe^{III}), as a function of time, in a 2.5M sulfuric acid solution. For each point, we acquired a XAS spectrum from which the speciation is determined.

	30	65	100	150	200	250	300
Fe(II) (T)	0,00	0,00	0,12	0,33	0,38	0,76	0,87
Fe(III)	0,00	0,43	0,82	0,61	0,63	0,24	0,13
Fe(III) window	1,00	0,57	0,06	0,06	0,00	0,00	0,00
ratio Fe(II)/Fe(III)	n.d	0,00	0,15	0,54	0,60	3,10	6,52

Table 1. Results of linear combination of standard spectra of Fe(II)-sulfate and Fe(III)-sulfate species. Window is the contribution of iron from the Be windows of the autoclave. The theoretical ration of a congruent dissolution is 0.5. From 250°C and above, the ratio is larger than 0.5, corresponding to the precipitation of Fe₂SO₄₃.

These results are part of the PhD work of Damien Daval (IPGP, and ENS Paris) (Daval, 2007; Guyot et al., 2007) and a forthcoming publication is in preparation.

Perspectives

These results, combined with previous studies on siderite dissolution (Testemale et al., 2008), give strong support to our methodology which provides in situ data on solubility, kinetics and speciation in hydrothermal conditions. In the framework of CO₂ sequestration in natural reservoirs, the necessary orientations of future studies are:

- similar time resolved solubility analysis of other minerals (especially olivines and orthopyroxenes which could not be studied in this experiment, due to time constraints), coupled with geochemical modelling.
- similar solubility and speciation studies of iron-bearing minerals, in the presence of organic siderophores, that could authorize higher pH.

References

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