



Experiment title: Iron speciation in high pressure high temperature H ₂ O-CO ₂ fluids in contact with crystalline siderite and /or magnetite	Experiment number: HS 2628	
Beamline: BM30b	Date of experiment: from: 8/12/2004 to: 15/12/2004	Date of report: 25/02/05
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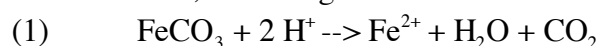
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Geological context

We have carried out a first series of experiments to study the reactivity of FeCO₃ siderite in water under acidic conditions up to 1000 bar and 300°C, according to reaction:



In deep geological storage context, the quantity of CO₂ that cannot be sequestered as carbonate is directly related to the concentration of Fe²⁺ in the fluid. We have measured, for the first time under hydrothermal conditions, the dissolution of siderite in water by monitoring *in situ* the concentration of Fe²⁺ at different pressures, temperatures and pH. First data on speciation of Fe in the relevant fluids have also been recorded.

Experimental details

High pressure-high temperature XAFS spectroscopy analyses were performed at the Fe K-edge, using an X-ray cell developed at the Laboratoire de Cristallographie (Grenoble). A total of six experiments were performed: (a) FeCl₂ (0.05M) + HCl (0.1M), (b) FeCl₂ (0.05M) + HCl (0.1 M) + NaCl (1M); (c) FeCl₂ (0.05M) + oxalic acid (0.05 M) used as a source of CO₂ above 150°C; (d) siderite + HCl (0.1M); (e) siderite + HCl (0.1 M) + NaCl (1M); (f) siderite + oxalic acid (0.05 M). In each experiment, data were obtained at different temperatures along isobars up to 300°C and 1000 bar.

Results

The experiments with FeCl₂ provide reference data for both Fe²⁺ concentration and speciation in solutions under high pressure and high temperature: in figure 1, there is a clear temperature dependence of the Fe local solvation structure. The presence of NaCl (1M) was shown to have no major effect on speciation.

The solubility results can be adequately fitted with available thermodynamical data, provided that the specific heats of compounds involved in reaction (1) be adjusted. Precise refinements on solubility data could

further provide important constraints on thermodynamic parameters of reaction (1). In particular, a tentative increase in solubility of siderite, unexpected for carbonates, that was measured between 100°C and 300°C (figure 2, left) can be modelled with an adequate set of specific heats.

The kinetics of siderite dissolution in HCl (0.1 M) was determined at 300 bar and 100°C (figure 2, right). NaCl apparently decreased the dissolution of siderite, a behaviour which remains to be explained using thermodynamical parameters and a fine analysis of the spectroscopic data on Fe speciation in the fluid. In the case of dissolution of siderite in oxalic acid solutions, two regimes should be considered: (1) a low temperature regime ($T < 150^\circ\text{C}$), below decomposition temperature of oxalic acid, where dissolution is lower than in HCl solutions at the same conditions (at 100°C, a concentration of 9mmol of Fe^{2+} is measured compared to 30mmol in HCl solutions); 2) a high temperature regime ($T > 200^\circ\text{C}$) where a decrease of solubility is observed (<4mmol at 250°C). This decrease can be attributed to the presence of carbon dioxide which is a weaker acid than oxalic acid.

Perspectives

These first results are encouraging; a publication is in preparation. Longer acquisition time spectra would be important for determining the exact speciation of Fe^{2+} in those $\text{H}_2\text{O}-\text{CO}_2-\text{Cl}$ fluids. It would be desirable to better control the activity of CO_2 which is a key parameter in the dissolution reaction. The use of oxalic acid decomposition as a source of CO_2 is a limiting factor because of the equivalent low partial pressure of CO_2 available (we estimate a maximum PCO_2 of 3 bar in our experiments). A direct loading of $\text{CO}_2/\text{H}_2\text{O}$ mixtures at ambient temperature would be a good method to control and vary this parameter, essential for appropriate modelling of these reactions.

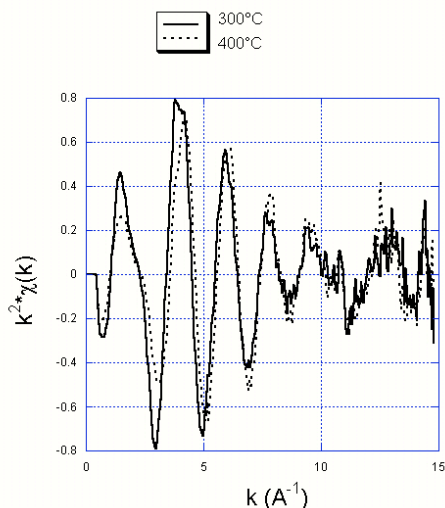


Figure 1: EXAFS oscillations of 0.05M FeCl_2 solutions at 300 bar (300 and 400°C).

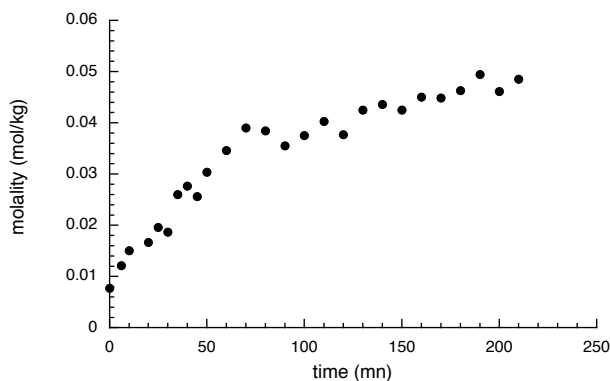
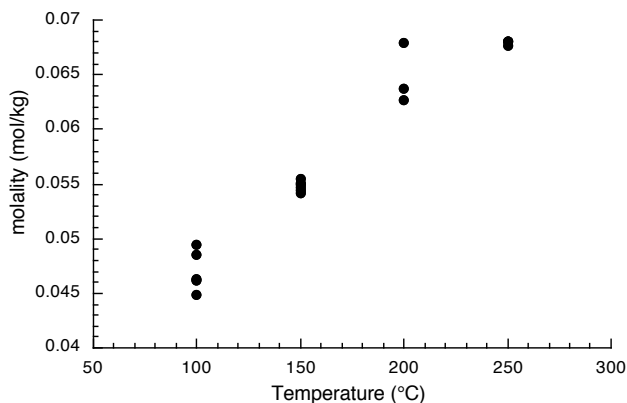


Figure 2: Left: Evolution of Fe^{2+} concentration in the fluid at 300bars as a function of temperature. Right: Concentration of Fe^{2+} (in mol/kg) at 300bar-100°C as a function of time.