

# Iron in hydrothermal fluids: fundamental geochemical processes studied by synchrotron radiation

In the present economic and ecological context, two primordial fields of research in Earth Sciences are (i) developing methods for sequestration of CO<sub>2</sub> in mineral form as stable carbonate rocks and (ii) understanding the formation of metal-ore deposits in view of the prospecting of new, mineable resources. A common aspect of these two research fields is understanding the complex processes of dissolution/precipitation of rocks in aqueous fluids.

Experimental information about the elements dissolved in a fluid phase at high temperatures and pressures are needed: their speciation (i.e. their chemical and structural form) and their thermodynamics data (i.e. the stability of the different species present as a function of temperature, pressure, salinity). To obtain such information, we have developed a new methodology based on the use of X-Ray Absorption Spectroscopy.

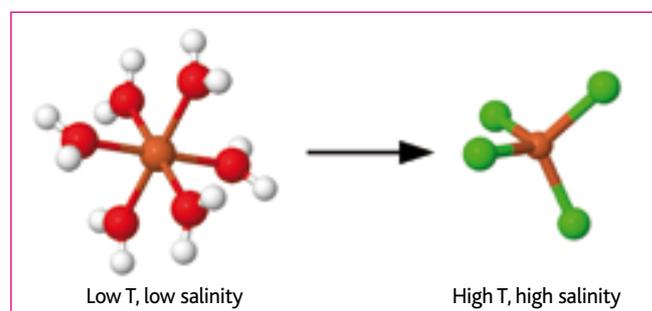
We use a dedicated, high pressure autoclave designed and developed at the Néel Institute by R. Argoud. The autoclave is equipped with beryllium windows for X-Ray absorption and fluorescence spectroscopy measurements. It is installed on FAME (the French Absorption spectroscopy beamline for Material and Environmental sciences) at the European Synchrotron Radiation Facility in Grenoble. This experimental development allows us to cover a large domain of the phase diagram (pressures 1-2000 bars, temperatures 30-600 °C, densities down to 0.1 g.cm<sup>-3</sup>), corresponding to conditions existing in the real Earth. Since iron is both a typical and an ubiquitous element in the Earth's crust and mantle, we have investigated using this instrument the fate of aqueous iron in hydrothermal (i.e. high temperature and pressure) conditions.

First we explored the speciation from ambient up to supercritical conditions (500°C, 500 bar), as a function of temperature and chlorinity of the solutions (i.e. the quantity of dissolved chlorine ions).

The near edge X-Ray Absorption spectrum is very sensitive to the local environment of solvated iron. Recent theoretical progress in ab initio calculations of the X-Ray Absorption Near-Edge Structure (XANES) using Finite Difference Method (FDMNES) calculations allowed us to interpret the spectral signature of the iron complexes and to observe their transition from octahedral hydrated species Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> to tetrahedral chlorinated species FeCl<sub>4</sub><sup>2-</sup> (see figure). This investigation was performed in collaboration with Adelaide University & CSIRO (Australia).

Secondly, we studied the dissolution/precipitation reaction of siderite (FeCO<sub>3</sub>) in hydrothermal conditions, a model reaction for an essential step in proposed methods to sequester CO<sub>2</sub> as metal carbonates. In nature, this corresponds to the final step of carbonation (transformation to carbonate) once Fe<sup>2+</sup> is released in solution by earlier dissolution of other iron-bearing rocks, such as the silicates widely present in the Earth's crust and mantle. Measuring in situ the X-ray transmission of the carbonate solution, we determine iron concentration and we derive kinetics parameters and thermodynamics data such as dissolution rate constants, activation energies, dependence on pH and chlorinity. Simultaneously, the iron speciation was also determined by X-Ray fluorescence spectroscopy.

This work, done in collaboration with the Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC, Paris) on a model dissolution reaction, provides an overall set of speciation, thermodynamics & kinetics data. Data of this kind is essential for geochemical modeling. Through our current national and international collaborations, we are extending these methods to other aqueous geochemical systems (Cu, Co, Ga, Au, Ag, etc.).



Observed changes of iron speciation in saline aqueous solution. At low chlorine concentration and/or low temperature, Fe<sup>2+</sup> ions are hydrated by 6 water molecules in an octahedral symmetry; in high salinity and/or high temperature (i.e. hydrothermal) conditions up to 500°C, Fe<sup>2+</sup> ions are coordinated by 4 chloride ions Cl<sup>-</sup> in a tetrahedral symmetry.

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## FURTHER READING

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