



# 1 Isotopic and geochemical characteristics to monitor fluid-rock interactions, following a small scale CO<sub>2</sub> injection

**N. Assayag (1,3), J. Matter (2), M. Ader (1,3) and P. Agrinier (1,3)**

(1) Centre de recherches sur le stockage géologique du CO<sub>2</sub> Total Schlumberger IPGP, Paris, France, (2) Lamont Doherty Earth Observatory, Columbia University, (3) Laboratoire de Géochimie des Isotopes Stables, I.P.G.P, Paris, France (assayag@ipgp.jussieu.fr)

Carbon dioxide geological storage in deep aquifers is one of the most promising alternatives to reduce CO<sub>2</sub> emissions to the atmosphere. In this context, CO<sub>2</sub> geological storage, via geochemical trapping, would be achieved according to three mechanisms sequentially ordered: solubility, ionic and mineral trapping. The mineral trapping is the most permanent and thus secure form of geochemical trapping but it is the slowest mechanism since the in-situ dissolution rates of e.g. Ca, Mg silicate minerals are slow (Gunter et al., 2004). Studies related on CO<sub>2</sub>-fluid-rock interactions showed that the chemistry of formation water and rock mineralogy of the reservoir play a determinant role on the efficiency of the CO<sub>2</sub>storage. Gunter et al. 2000

In order to investigate the extent of in-situ CO<sub>2</sub>-fluid-rock reactions relevant to the effectiveness of CO<sub>2</sub>sequestration, 3 single well push-pull tests (1 blank test “non reactive test” and 2 CO<sub>2</sub> tests “reactive test”) were performed in a basaltic rock aquifer at the Lamont-Doherty Earth Observatory test well site, New York. It includes an instrumental borehole of a total depth of 304 m, which cuts through most of the section of the Palisades sill and into the Newark Basin sediments.

Using a straddle packer system, a test solution was injected (“pushed”) in a hydraulically isolated and permeable zone, at a depth interval located between the Palisades sill (chilled dolerite) and the underlying Newark Basin sediments (metamorphosed

sediments). Conservative chemical and/or isotopic tracers ( $\text{NaCl}$ , D,  $^{18}\text{O}$ ) were added to the test solution. For the  $\text{CO}_2$  tests, the test solution was additionally equilibrated with a  $\text{CO}_{2(g)}$  partial pressure (1 and 8 bars). After an incubation period (ranged between 1 and 3 weeks), the test solution/background water mixture was continuously pumped back (“pulled”) from the hydraulically isolated zone. Physico-chemical parameters were measured ex-situ (pH, temperature, electrical conductivity) and sealed samples were collected for isotopic ( $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) and chemical (DIC, major ions) analyses.

For the blank test, the injection of a  $\text{CO}_2$  non-saturated fluid reveals only a mixing process between the background water and the injected water and, the invariance of the fluid compositions confirms the non-reactivity of this test. For the  $\text{CO}_2$  tests, the variations of the chemical and isotopic fluid compositions are due to two main processes: (1) mixing between the background water and the injected water and (2)  $\text{CO}_2$  reactivity (reactions of the dissolved  $\text{CO}_2$  with the surroundings rocks and  $\text{CO}_2$  degassing (for the fluid equilibrated with the higher partial pressure)). The main consequence of the  $\text{CO}_2$  reactivity was the dissolution of carbonate minerals (fracture fillings) and to a lesser extent the dissolution of primary minerals such as Ca, Mg silicates from the basalt. The release of alkaline earth metals by the acid neutralization reaction sets the stage for the subsequent formation of new, secondary carbonate minerals, and therefore for the mineral trapping of  $\text{CO}_2$  (Matter et al., 2006).