# Study of the Dissolution and Precipitation Mechanisms at the Pore-Scale Using Percolation Experiments and X-Ray Microtomography

/Linda Luquot (1\*), María García-Ríos (1), Tobias Roetting (2), Olivier Rodriguez (3), Philippe Gouze (4), Jesús Carrera (1)

(1) IDAEA-CSIC, calle Jordi Girona 18-26, 08034 Barcelona (Spain)

(2) UPC, calle Jordi Girona 31, 08034 Barcelona (Spain)

(3) Voxaya SAS, Cap Oméga, Rond-point Benjamin Franklin, CS 3952, 34960 Montpellier (France)

(4) Geosciences Laboratory, University of Montpellier, Place Eugène Bataillon, 34095 Montpellier (France)

# INTRODUCCIÓN

Precipitation and dissolution processes play a critical role during many geological processes, such as diagenesis. hydrothermal circulation. biomineralization, or CO2 sequestration (Buhmann & Dreybrodt, 1985; Hilgers and Urai, 2002; Kampman et al., 2014; Kaszuba et al., 2013; Lackner, 2003; Tenthorey et al., 1998). Precipitation and/or dissolution of minerals like calcite can cause significant changes in permeability and flow reorganization in reservoirs by altering the shape, size and connectivity of the pores, or the roughness of their Surface. Developing a full understanding of the feedbacks between geochemical reactions and flow and transport characteristics at the reservoir scale requires, as а preliminary, investigations of dissolution and precipitation mechanisms at the pore-scale.

Application of non-invasive methods has considerably increased experimental capability by giving access to a spatiotemporal (i.e. 4D) vision of the physicalchemical processes within the rocks. Among them, X-ray micro-tomography allows the visualization of 3D objects with a micrometer resolution. New information is now accessible, which provides a better understanding of the coupled thermo-hydro-mechanical and chemical processes and allows numerical models to be better constrained.

We present some applications of X-ray

micro-tomography to study changes of petrophysical properties (e.g. porosity, permeability, mineral surface area, etc.) and characterize geochemical processes (e.g. dissolution rate, precipitation processes) in different types of rocks in response to fluid-rock interactions.

Experimental observations will be discussed in regard to numerical modelling of flow and reactive transport.

#### METHODOLOGY

The experiments involve injecting the  $CO_2$ -rich brine (of known composition) at constant flow rate through cylindrical cores of 9 mm diameter (*D*) and 18 mm length (*L*) of different mineral composition (limestone, dolostone and sandstone samples). These experiments

were performed using different flowthrough benches depending on the rock permeability and the pressure and temperature conditions. These different benches are located in Montpellier University (France, Fig. 1) and in the CSIC-IDAEA in Barcelona (Spain). A complete description of the equipment and experimental protocol is given in Luquot & Gouze (2009), Luquot et al. (2012) and Luquot et al. (2014a).

The cores were imaged using XMT to characterize the pore space geometry. The XMT technique is an unmatched tool for producing non-destructive three dimensional images of rocks without any prior preparation. Data acquisition was performed at the ID 19 beamline of the European Synchrotron Radiation



**fig 1.** Scheme of the flow-through equipment used in this study. They are located in Montpellier University (France).

palabras clav	Procesos	а	Escala	de	Poros,	Permeabilidad,	key	words:	Pore	Scale	Processes,	Permeability,	Dissolution	and
Disolución y Precipitacion.						Precipitation.								

Facility (ESRF). Synchrotron X-ray tomography allows imaging of the sample with higher resolution comparing to other conventional 3D tomography techniques. XMT is based on the measurement of X-ray attenuation by the sample under investigation.

The images display attenuation represented by grayscale variations that depend on the thickness of the sample, the mineralogy, and the spatial variation of the rock matrix density.

# **RESULTS AND DISCUSSION**

#### **Limestone Dissolution**

A set of four reactive flow-through experiments at temperature T = 100 °C and total pressure P = 12 MPa was performed in limestone reservoir samples (Luquot & Gouze, 2009). By using various ranging from 0.7 to 10 MPa, these experiments mimic mass transfers occurring (1) near the injection well, where the brine is almost saturated with CO<sub>2</sub> (i.e.  $P_{CO2} \approx P$ ), and (2) at increasing distances from the injection well, where the fluid displays lower values and higher divalent cation concentrations due rock dissolution along the fluid pathway.

Results for  $P_{CO2}$  = 10 MPa show nonuniform dissolution features associated with transport-controlled mass transfer, while reaction-controlled uniform dissolution is observed for  $P_{CO2}$  = 2.5 MPa. The experiment with  $P_{CO2}$  = 6 MPa allows investigating in detail the transition from transport to reactioncontrolled dissolution. Conversely, the experiment reproducing conditions far from the injection well ( $P_{CO2}$  = 0.7MPa), shows a decrease of porosity triggered by the precipitation of Mg-rich calcite.

For all the dissolution experiments, the time-resolved porosity  $\phi(t)$  can be modeled by a simple non-linear equation including parameters that characterize the dissolution regime triggered by the reactivity of the inlet fluid (measured by the Damköhler number. Da). Furthermore, all dissolution experiments display power scaling between permeability (k) and porosity ( $\phi$ ) with distinctly different scaling exponents characterising the reactivity of the fluid percolating the sample. independently from the decrease with time of the reactive surface area. It is shown also that

dissolution at moderate positive values of Da seems the most efficient to increase permeability and promote a rapid spreading of the reaction front, while inducing minimal modification of the porosity in the vicinity of the  $CO_2$ injection well.

These results can be used to parameterize the  $k - \phi$  function for modeling the earliest dissolution processes occurring in the vicinity of the reaction front. Moreover a non-linear relationship between the reactive surface area and the porosity is proposed to predict the evolution of the reactive surface area during the dissolution process (Fig. 2).

# Dissolution, Precipitation and Redox Reaction in a Rich Chlorite and Zeolite Sandstone Sample

Mineral storage is the more secure technology for  $CO_2$  storage, but requires the presence of high concentration of divalent cations in the pore-fluid. Results from  $CO_2$  percolation experiments through chlorite/zeolite-rich sandstone samples from the Pretty Hill Formation (Otway Basin, Australia) are presented.

The dissolution of the laumontite (7 wt.%) and chamosite (7 wt.%) are the potential sources of calcium, iron and magnesium required for carbonate precipitation. The percolation experiment was setup to reproduce, at laboratory scale, the in situ temperature and pressure conditions (T = 95 °C and P = 10 MPa).

The fluid injected at constant flow rate is a rock-equilibrated brine subsequently enriched in  $CO_2$  up to partial pressure of 6 MPa.

We observe feldspars, laumontite and chamosite dissolution, kaolinite and silica precipitation and a noticeable sink of  $CO_2$  in the sample which is attributed to the precipitation of both amorphous carbon due to the reduction of  $CO_2$  and Fe-rich carbonate (Fig. 3). Permeability decreases of about one order of magnitude due to the localization of the kaolinite precipitation in the main flow paths, while porosity increases.

The high reactivity of this sandstone makes this reservoir a valuable target for  $CO_2$  mineralization, but the associated permeability decrease may limit the injection rate and the spreading of the  $CO_2$  in the reservoir.

### Pore Clogging Mechanism and Permeability Decrease During Limestone Dissolution

Rock dissolution induces changes in texture (porosity, pore-size distribution, or tortuosity) which modify multiphase transport properties flow and diffusion coefficient, (permeability, retention curve). Therefore. characterizing those changes is essential for understanding flow and transport during and after the CO2 injection because they can affect the storage capacity, injectivity, and trapping mechanisms.



fig 2. Reactive specific surface area versus elapsed time for experiments D1 (circles), D2 (squares) and D3 (diamonds). (Luquot & Gouze, 2009).



**fig 3.** TEM image of the chlorite fibres and precipitated magnesite surrounded by amorphous and poorly crystallized carbon. On the left: Chemical analysis associated with the TEM image, A: magnetite chemical analysis, B: carbon chemical analysis and C: chamosite chemical analysis. Raman spectra of precipitated carbon near chlorite compared with epoxy-resin spectra and disordered carbon spectra (Luquot et al., 2012).

We report seven dissolution experiments performed on four limestone samples by injecting water with pH ranging from 3.5 to 5.0 (Luquot et al., 2014a). Sample porosity, diffusion coefficient, and poresize distribution were measured before and after each rock attack, which was repeated twice on three of the samples. Permeability was monitored continuously and chemical samples evaluate were taken to calcite dissolution. We find that overall porosity increases over time as expected. But the increase is nonuniform along the sample. At the samples inlets, large pores increase significantly while small pores remain unchanged, which is consistent with wormhole initiation. However, the size of largest pores is reduced at the outlet, which we attribute to clogging by particles dragged from the inlet (Table 1). As a result, the overall permeability is reduced. Particle dragging is unlikely during supercritical CO<sub>2</sub> storage because head gradients are small, but may be expected in the case of dissolved CO<sub>2</sub> injection or during well stimulation by acid injection. Our results imply that dissolution is highly localized, which will result in a significant increase in capillary trapping.

# Role of Mobile and Immobile Zone on Reaction Processes

The Heletz structure has been selected as a test site for a prospective  $CO_2$ reservoir and for the MUSTANG European project injection experiment based on the analysis of the available geological, geophysical and borehole data from various areas of Israel. The Heletz area is located in the Southern part of the Mediterranean Coastal Plain, about 7 km from the sea shore. The target layer is composed of sandstone, has a thickness of around 20 meters and is located at a depth of 1500 m.

Flow-through laboratory experiments of CO<sub>2</sub>-rich brine were performed to evaluate the chemical processes occurring in the Heletz site.

The Heletz sandstone rock is poorly consolidated and has a high porosity (around 23%) and connectivity. We four flow-through performed experiments at in situ storage conditions  $(T = 60^{\circ}C, P = 15 \text{ MPa}, P_{C02} = 1.8 \text{ MPa}).$ The injection flow rates were 0.05 and 0.30 mL.min-1. Two different brine solutions were used, both representative of the Heletz reservoir native water. The first one was a synthetic brine of the Heletz reservoir (closed to seawater). The second one was the first one equilibrated with gypsum.

The results show an increase in permeability for all the percolation experiments whatever the flow rate and the brine solution were. This is explained by the dissolution of ankerite, dolomite and feldspar. We observed that the permeability increase is higher and faster for high injection flow rate than for low flow rate. Precipitation of gypsum occurred as a secondary phase gypsum-equilibratedduring brine injection. Secondary clay minerals precipitation was also observed near feldspar dissolution (Fig. 4).

Modeling these experiments is a nontrivial task, as some chemical processes are local in space. Reactive transport

Pore Size Radius (µm)	L1	L2	L3	L4
Before dissolution experiments				
> 102.27	0.56%	0.55%	0.53%	0.53%
34.99-102.27	4.48%	4.40%	4.22%	4.25%
10.23-34.99	7.05%	6.93%	6.65%	6.68%
3.14-10.23	21.16%	20.81%	19.94%	20.06%
1.29-3.14	27.77%	27.31%	26.17%	26.32%
0.48-1.29	26.06%	25.62%	24.56%	24.70%
< 0.48	12.92%	14.38%	17.93%	14.46%
After the dissolution experiment	ts, in flow direction			
> 102.27	2.61%	3.85%	8.24%	6.81%
34.99 - 102.27	5.60%	3.90%	4.91%	3.84%
10.23 - 34.99	12.05%	4.00%	5.57%	6.00%
3.14 - 10.23	9.98%	10.02%	9.25%	12.57%
1.29 - 3.14	27.53%	25.01%	15.79%	13.85%
0.48 - 1.29	27.32%	26.46%	43.15%	47.33%
< 0.48	14.91%	26.76%	13.09%	9.60%
After the dissolution experiment	ts, in the opposite of the flow	direction		
> 102.27	4.56%	5.76%	10.52%	6.82%
34.99 - 102.27	5.29%	6.50%	7.15%	7.53%
10.23 - 34.99	19.30%	13.88%	15.10%	22.37%
3.14 - 10.23	19.43%	9.90%	12.07%	14.53%
1.29 – 3.14	14.14%	23.43%	14.96%	15.94%
0.48 - 1.29	28.98%	29.63%	31.43%	26.15%
< 0.48	8.30%	10.90%	8.77%	6.66%

 Table 1. Pore-Size Distribution Before and After the Two Dissolution Experiments (in Flow Direction and in the Opposite) for Samples L1, L2, L3, and L4 (Luquot et al., 2014a).

#### macla nº 20. julio '15 revista de la sociedad española de mineralogía



fig 4. SEM image of Kaolinite, gypsum and saponite precipitation near ankerite and K-feldspar dissolution.

models have been performed in order to understand and reproduce the observed processes. We have used a water mixing approach which uses the mass mixing between mobile fraction and/or immobile zones. The approach relies in the fact of not transporting species or components, but the containing waters. This allows decoupling chemistry from calculation solute transport modelling.



**fig. 5.** Scheme of the multi-rate mass transfert model taking into account mobile and immobile zone.

# CONCLUSIONS

For all these different examples, permeability and porosity changes in the samples are attributed to dissolution and precipitation processes. These dynamic processes are constrained by monitoring permeability changes as well as measuring mass fluxes and sample pore structure changes. Due to the nondestructive nature of XMT imaging, the geochemical changes in the pore microstructure can be estimated. The complexity of different dissolution paterns, from ramified wormhole formation to more homogeneous dissolution, were observed during limestone dissolution (Fig. 6).



fig 6. Representation of the nodes of the main components of the skeleton, i.e., parts of the skeleton coinciding with connected components of the void space that were exposed to dissolution at macroscopic scale. The color map corresponds to the radius of the largest sphere centered at each node inscribed inside the void space (brightest points correspond to largest radii, logarithmic scale in voxel unit) (Luquot et al., 2014b).

We observed that precipitation reactions were also highly controlled by the surface heterogeneity and the local transport mechanism. Precipitation reaction was highly localized, usually in low fluid renewal zone where the transport was controlled by diffusion in immobile zones.

When dissolution and precipitation reactions occurred, the permeability change was usually different from that of only dissolution. In many cases, the dissolution reaction was faster and the volume of dissolved mineral was higher than the volume of precipitated mineral. Consequently, the permeability always increased with or without precipitation reactions. Nevertheless, some delay in permeability increase has been observed when precipitation occurred compared with similar experiments performed under the same experimental conditions (same flow rate, temperature and pressure) but without precipitation (only dissolution) (Fig. 7).



**fig 7.** Variation in fracture permeability vs. the number of equivalent fracture volumes (time/residence time  $\tau$ ) for the limestone (dashed lines) and sandstone (solid lines) experiments. Q = 1 mL/h (green line), Q = 5 mL/h (red and pale red lines) and Q = 60 mL/h (black and grey lines). k(t0) indicates initial fracture permeability (Garcia-Rios, 2015).

#### ACKNOWLEDGEMENTS

Linda Luquot was funded by the Juan de la Cierva fellowship (MINECO, Spain). This study was financed by the MUSTANG (European project Community's Seventh Framework Programme FP7/2007-2013 under grant agreement number 227286) and PANACEA project (European the Seventh Framework Community's Programme FP7/2007-2013 under grant agreement number 282900).

#### REFERENCES

Buhmann, D. & Dreybrodt, W. (1985): The kinetics of calcite dissolution and precipitation in geologically relevant situations of karst areas. 1. Open system. Chem. Geol., 48, 189-211.

- Garcia-Rios, M. (2015): Dissolved COé effect on the reactivity of the Hontomin reservoir rocks (limestone and sandstone), Universidad Politecnica de Catalunya, 178 p.
- Hilgers, C. & Urai. J.L. (2002): Experimental study of syntaxial vein growth during lateral fluid flow in transmitted light: first results. Journal of Structural Geology, 24, 1029-43. DOI: 10.1016/s0191-8141(01)00089-x.
- Kampman, N., Bickle, M., Wigley, M., Dubacq, B. (2014): Fluid flow and CO2-fluid-mineral interactions during CO2-storage in sedimentary basins. Chem. Geol., **369**, 22-50. DOI: 10.1016/j.chemgeo.2013.11.012.
- Kaszuba, J., Yardley, B., Andreani, M. (2013): Experimental perspectives of mineral dissolution and precipitation due to carbon dioxide-water-rock interactions. in: DJ DePaolo, DR Cole, A Navrotsky, IC Bourg, (Eds.). Geochemistry of Geologic CO2 Sequestration. Reviews in Mineralogy and Geochemistry, 153-88 p.
- Lackner K.S. (2003): A Guide to CO2 sequestration. Science. **300**, 1677-8.
- Luquot, L. & Gouze, Ph. (2009): Experimental determination of porosity and permeability changes induced by massive injection of CO2 into carbonate reservoirs. Chem.Geol. DOI:10.1016/j.chemgeo.2009.03.028.
- Luquot, L., Andreani, M., Gouze, Ph., Camps, P. (2012): CO<sub>2</sub> percolation experiment through chlorite/zeolite-rich sandstone from Pretty Hill formation - Australia. Chem. Geol. DOI:10.1016/j.chemgeo.2011.11.018.
- Luquot, L., Roetting, T., Carrera. J., (2014a): Characterization of flow parameters and evidence of pore clogging during limestone dissolution experiments. Water Resources Research. **50**.
- Luquot, L., Rodriguez, O., Gouze, Ph. (2014b): Experimental characterization of porosity structure and transport properties changes in limestone undergoing different dissolution regimes. Transport in Porous Media. DOI: 10.1007/s11242-013-0257-4.
- Tenthorey, E., Scholz, H., Aharonov, E., Léger, A. (1998): Precipitation sealing and diagenesis 1. Experimental results. J. Geophys Res., 103, 23951-67.