Role of pore scale heterogeneities on the localization of dissolution and precipitation reactions
Take home message:

To characterize and predict chemical processes (dissolution, precipitation, redox reactions, ...), it is necessary to take into account the coupled reactive-transport processes and the local structural and mineralogical heterogeneities.
Dissolution localization

Clogging mechanism

Role of undissolved grains on the localization

Precipitation localization
Methodology

GEOCHEMICAL PARAMETERS
- dissolution - precipitation
  Kinetics, pH, $P_{CO2}$, temperature...

STRUCTURAL CHANGES
- porosity, fluid-rock interface, tortuosity, ...

CHANGES OF TRANSPORT PROPERTIES
- permeability, diffusivity, ...

Log (Permeability, mD) vs. Log (Porosity)

2.2
2.0
1.6
1.4
-1.12
-1.08
-1.04
-1.00

0 20 40 60 80 100 120 140 160

Log (Porosity)
Methodology

Reservoir rock samples

Caprock samples

Cement samples

Reservoir rock samples
Methodology

Porosity along the sample, connectivity, pore size distribution, 3D visualization (X-ray microtomography)
Methodology

Porosity along the sample, connectivity, pore size distribution, 3D visualization (X-ray microtomography)

Density, connected porosity (triple weighing)
Methodology

- Porosity along the sample, connectivity, pore size distribution, 3D visualization (X-ray microtomography)
- Density, connected porosity (triple weighing)
- Diffusion coefficient (tracer test)
Methodology

- Electrical and sonic measurements (see Laura Martinez seminar)

- Porosity along the sample, connectivity, pore size distribution, 3D visualization (X-ray microtomography)

- Permeability, dissolution (varying pH, flow rate, solution)

- Density, connected porosity (triple weighing)

- Pore size distribution (water retention curve)

- Diffusion coefficient (tracer test)

+ Electrical and sonic measurements (see Laura Martinez seminar)
Methodology

20 – 200 °C
0.1 – 25 MPa
10⁻³ – 10³ mD
Dissolution localization

Clogging mechanism

Role of undissolved grains on the localization

Precipitation localization
Precipitation localization

Clogging mechanism

Dissolution localization

Role of undissolved grains on the localization

Precipitation localization
Limestone dissolution theory depending on flow and acidity conditions (Pe and Da numbers)

- Daccord, 1987
- Fredd and Fogler, 1998
- Golfier et al., 2002

Numerically validated for homogeneous media
CO₂ rich brine injection through porous limestone

**Experimental conditions**

- **Temperature (T)**: 100 °C
- **Pressure (P)**: 120 bar
- **Flow rate (Q)**: 1.14 ml/min

<table>
<thead>
<tr>
<th>Species (mmol L⁻¹)</th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1 000</td>
<td>1 000</td>
<td>1 000</td>
</tr>
<tr>
<td>Ca</td>
<td>8.25</td>
<td>9.37</td>
<td>10.0</td>
</tr>
<tr>
<td>Mg</td>
<td>0.16</td>
<td>0.19</td>
<td>0.21</td>
</tr>
<tr>
<td>Cl</td>
<td>1 000</td>
<td>1 000</td>
<td>1 000</td>
</tr>
<tr>
<td>CO₂ (mol L⁻¹)</td>
<td>0.8</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>PCO₂ (MPa)</td>
<td>10</td>
<td>6</td>
<td>2.5</td>
</tr>
<tr>
<td>pH</td>
<td>3.21</td>
<td>3.51</td>
<td>4.02</td>
</tr>
</tbody>
</table>

**Sample**

- Limestone from Mondeville (MDV) oolithic limestone
- Mg-calcite (1% Mg, 99% Ca)

- D1: Drying-out zone composed essentially of scCO₂
- D2: Aqueous zone (brine + dissolved CO₂)
- D3: Brine zone without CO₂

- Gouze and Luquot, 2011 JCH
Limestone dissolution theory depending on flow and acidity conditions (Pe and Da numbers)

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numerically validated for homogeneous media
Porosity changes

D1: Localization of the dissolution
   - formation of large wormholes

D2: Formation of ramified wormholes

D3: Homogeneous dissolution
Porosity changes

D1: Localization of the dissolution ► formation of large wormholes

D2: Formation of ramified wormholes

D3: Homogeneous dissolution
Temporal prediction of porosity change

\[
\bar{\phi}(t) = \bar{\phi}^{(0)} \left[ 1 + \bar{\mathcal{G}}^{(0)} wt \right]^{1/w}
\]

\[
\bar{\mathcal{G}} = \bar{r} S_r (1 - \Omega)
\]
The temporal prediction of porosity change is controlled by the initial values of the porosity and the reaction rate and an effective parameter that characterizes the dissolution regime.

\[ \bar{\phi}(t) = \bar{\phi}^{(0)} \left[ 1 + \bar{\varphi}^{(0)} \frac{wt}{w} \right]^{1/\nu} \]

\[ \frac{\partial \phi}{\partial t} \]
Temporal prediction of reactive surface changes

3 surface calculating techniques

From data analyses

\[ S_r = \frac{\bar{\vartheta}}{\bar{r}(1-\Omega)} \]

Using porosity relations

\[ S_r(t) = \frac{S_r^{(0)}}{1 + \vartheta^{(0)}wt} \]

From X-Ray Microtomography

\[ \Delta S_r = \alpha \cdot \Delta S_{XMT} \]

Hypotheses

\[ \bar{r} \]
\[ \bar{\vartheta} \]
\[ \bar{\Omega} \]

\[ S_r(t) = S_r^{(0)} \left( \bar{\phi}(t) / \bar{\phi}^{(0)} \right)^w \]

\[ \bar{\phi}(t) = \bar{\phi}^{(0)} \left[ 1 + \bar{\vartheta}^{(0)}wt \right]^{1/w} \]

\[ \alpha = \frac{S_r^{(0)}D^3}{S_{XMT}^{(0)}D^3} \]
Reactive surface area decreases

\[
S_r(t) = S_r^{(0)} \left( \frac{\bar{\phi}(t)}{\bar{\phi}^{(0)}} \right)^w
\]

\[
S_r = \frac{\bar{\vartheta}}{\bar{r}\left(1-\Omega\right)}
\]

Temporal prediction of reactive surface changes
Validation by XMT

~ 5 m²

\[ S_r^{(0)}_{XMT} \]

\[ S_{r(0)} D3 \]

\[ S_{r(0)} D2 \]

\[ S_{r(0)} D1 \]

elapsed time (minute)

\[ \Delta S_{XMT} (m^2) \]

\[ z (mm) \]

D3

D2

D1
Validation by XMT

\[ S_r^{(0)}_{XMT} \]

\[ S_r^{(0)}_{D1} \]

\[ S_r^{(0)}_{D2} \]

\[ S_r^{(0)}_{D3} \]

\[ \psi^{(0)} = 41\% \]

\[ \Delta S_{XMT} \text{ (m}^2\text{)} \]

\[ \text{elapsed time (minute)} \]

\[ \sim 2 \text{ m}^2 \]
Validation by XMT

\[ S_r^{(0)}_{XMT} \]

\[ S_r^{(0)}_{D3} \]

\[ S_r^{(0)}_{D2} \]

\[ S_r^{(0)}_{D1} \]

\[ \psi^{(0)} = 12\% \]

\[ \Delta S_{XMT} (m^2) \]

\[ \sim 1 \text{ m}^2 \]

\[ \text{elapsed time (minute)} \]
Relation $k - \phi$

$$k(t) = k_0 (\phi(t) - \phi_c)^n$$

- One simple relation for each dissolution processes
- 3 dissolution processes = 3 $n$ values
Conclusions on limestone reservoir study

- Experimental bench and protocol allow calculating $\phi(t)$ and $Sr(t)$

- We propose a simple non-linear model to predict porosity ($\phi$) and reactive surface ($Sr$) changes

- We show that a single $k-\phi$ relation characterizes each experiment

- Both $\phi$ (or $Sr$) results and $k-\phi$ results show that initial conditions control the parameters changes (i.e. the properties of the injection fluid)
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Can we apply all these observations to every limestone samples?
Four percolation experiments.
Oolitic limestone composed of micro- and macroporosity.

Luquot et al., 2014 Transp. Porous Media
Four percolation experiments. Oolitic limestone composed of micro- and macroporosity.

Temperature (100 °C), pressure (12 MPa), and flow rate (5 cm$^3$ h$^{-1}$), $PCO_2$ (from 0.034 to 3.4 MPa).

Same Pe number than experiment on samples D.
Same Da number for P1 and D3 (homogeneous dissolution)

<table>
<thead>
<tr>
<th></th>
<th>Ca (mmol/L)</th>
<th>Cl (mmol/L)</th>
<th>Na (mmol/L)</th>
<th>CO$_2$ (mmol/L)</th>
<th>$PCO_2$ (MPa)</th>
<th>$pH_{cal}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1.08</td>
<td>935</td>
<td>952</td>
<td>202</td>
<td>3.4</td>
<td>3.49</td>
</tr>
<tr>
<td>P2</td>
<td>1.153</td>
<td>971</td>
<td>973</td>
<td>20.5</td>
<td>0.34</td>
<td>4.38</td>
</tr>
<tr>
<td>P3</td>
<td>1.125</td>
<td>956</td>
<td>959</td>
<td>10.1</td>
<td>0.17</td>
<td>4.68</td>
</tr>
<tr>
<td>P4</td>
<td>1.08</td>
<td>1011</td>
<td>1002</td>
<td>2.0</td>
<td>0.034</td>
<td>5.41</td>
</tr>
</tbody>
</table>

D3 CO$_2$ partial pressure (homogeneous dissolution)
Flow-transport parameters

- Permeability increased noticeably during experiments P1 and P2.
- The increase of permeability during experiment P3 was smaller.
- Conversely, the P4 experiment was characterized by a decrease of permeability.
Flow-transport parameters

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- The increase of permeability during experiment P3 was smaller
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Nodes of the main components of the skeleton

P1: One preferential wormhole with higher pore diameters in the main skeleton branch than in the different ramified skeleton branches.

P2: At the sample inlet, three preferential flow paths were initiated instead of two during P1.

P3: During experiment P3, different preferential flow paths developed at the sample inlet, suggesting an evolution toward a homogeneous dissolution regime.

P4: Homogeneous dissolution. No wormhole.
Porosity changes

Part 1

Micro porosity increases

Particles accumulation

Strong gradient along $z$

Micro porosity decreases

Micro porosity increases
$k-\phi$ relationship

P1, P2: high $n$ value (dominant wormhole, large pore diameter). The ratios (after/before) of the number of skeleton tips of the macro-porous phase were high, denoting new ramifications at macro-scale favoring permeability increase.

P3: the $n$ factor is quite low (homogeneous dissolution).

P4: Permeability decreases (pore clogging mechanism). Micro-porosity increase induced an increase of the quantity of small pore diameters which controlled the permeability decrease (decrease of the hydraulic diameter of the throats).
Conclusions

- All experiments display $k \propto A\phi^n$ type law with $n$ increasing with the potential dissolution rate (here determined by the $P_{CO_2}$).

- But the initial pore structure (connectivity, reactive surface/pore volume ratio, etc) seems to be an important factor controlling this laws.

Luquot et al., 2014 Transp. Porous Media
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Conclusions

- At low values of $PCO_2$ the differential dissolution of the cement and the grains forming the limestone induce sustainable detachment / displacement / accumulation of particles producing negatively correlated $k-\phi$ laws.

Luquot et al., 2014 WRR
Mangane et al., 2013 GRL
Noiriel et al., 2009, Chem. Geol.
Luquot et al., 2014 Transp. Porous Media
Precipitation localization

Clogging mechanism

Role of undissolved grains on the localization

Precipitation localization
More than particles dragging, sometimes, some grains remain in the sample as “undissolved” grains. These grains can be dragged and clog the system but also influence the dissolution localization.
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- Inert silicate grains in the sandstone experiments favored more extended dissolution structures.
- Limestone dissolution tended to be localized (wormhole), whereas sandstone dissolution tended to be extended (uniform).

The volume of dissolved rock was larger in the sandstone experiments than in the limestone ones.

What happens when the undissolved mineral is a porous matrix (skeleton)?

Claystone sample

CO$_2$-rich brine injection at various flow rates

$Q = 0.2$ mL.h$^{-1}$

$Q = 1$ mL.h$^{-1}$

$Q = 60$ mL.h$^{-1}$

Constant permeability

CO₂-rich brine injection at various flow rates

- Face dissolution
- Face dissolution to wormhole formation
- Wormhole to homogeneous dissolution

*Davila PhD thesis, 2015*
CO$_2$-rich brine injection at various flow rates

- Face dissolution
- Face dissolution to wormhole formation
- Wormhole to homogeneous dissolution

*Davila PhD thesis, 2015*
CO$_2$-rich brine injection at various flow rates

Clay skeleton keep the initial fracture aperture and thus the hydraulic aperture

Conclusions

Importance of the secondary minerals:

- undissolved grains: more homogeneous dissolution, increase of the reaction rate, permeability increase not so fast

- clusters (clay skeleton): permeability remains constant, dissolution processes more and more slowest due to the diffusion zone

See PhD thesis of Maria Garcia-Rios and Gabriela Davila and associated articles

What happens if precipitation reaction occurs in this type of rock? How the transport can control precipitation reaction?
CO$_2$-rich gypsum equilibrated brine injection at various flow rates

permeabilities decrease

CO$_2$-rich gypsum equilibrated brine injection at various flow rates

\[ Q = 0.2 \text{ mL.h}^{-1} \]

\[ Q = 1 \text{ mL.h}^{-1} \]

CO₂-rich gypsum equilibrated brine injection at various flow rates

The gypsum precipitation into the porous clay layer clogged the porosity and in some point “push” the clay particles and close the fracture.

How and where precipitation occurs in a porous medium?
How the precipitation affects the dissolved pattern and the permeability?
Role of mobile and immobile zones.
How and where precipitation occurs in a porous medium? How the precipitation affects the dissolved pattern and the permeability? Role of mobile and immobile zones.

In olivine porous sample (injection of CO$_2$-rich brine)

Concomitant Fe oxidation and CO$_2$ reduction

Luquot et al., Chem. Geol. 2012

Andreani et al., ES&T. 2009
How and where precipitation occurs in a porous medium?
How the precipitation affects the dissolved pattern and the permeability?
Role of mobile and immobile zones

In olivine porous sample (injection of CO$_2$-rich brine)

In zeolite and chlorite rich sandstone (injection of CO$_2$-rich brine)

Andreani et al., ES&T. 2009
Luquot et al., Chem. Geol. 2012
How and where precipitation occurs in a porous medium? How the precipitation affects the dissolved pattern and the permeability? Role of mobile and immobile zones.

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In zeolite and chlorite rich sandstone (injection of CO$_2$-rich brine)

Andreani et al., ES&T. 2009
Luquot et al., Chem. Geol. 2012
Conclusions

Importance of the localization of the precipitation:

- in case of undissolved clusters: permeability decrease due to the non-dissolved cluster which remains in the fracture vicinity at low flow rate,

- at high flow rate the precipitation never occurred indicating the transport control on the precipitation processes,

- the transport control is also observed in olivine sample, where different various chemical reaction occurs depending on the local transport conditions (advection vs. diffusion, mobile vs. immobile zone),

- in rich zeolite and chlorite sandstone, we also observed the role of the local transport condition coupled with the mineral heterogeneity. We observed local redox reaction or coupled dissolution precipitation processes.

- The localization of the different chemical reactions depending on the mineral heterogeneity and transport control zones has various implication on permeability changes still difficult to predict.
CONCLUSIONS

Dissolution localization

Clogging mechanism

Role of undissolved grains on the localization

Precipitation localization
Conclusions

• Most of the processes of dissolution and precipitation are controlled by local heterogeneity (structure, flow, mineralogy)
  ✓ Wormhole formation is controlled by the pore size diameter, local connectivity and tortuosity (role of the micro-porosity)
  ✓ Role of the non-dissolved grains on the localization of the dissolution (homogenization)
  ✓ Precipitation is more important in immobile (diffusive controlled) zones.

• Local processes affect macroscopic parameters
  ✓ Particle dragging, which locally clogs some pores induces, permeability decrease
  ✓ Relationship as $k-\phi$, $S_r-\phi$ always depend on the rock structure and not only on the reactivity and the transport boundary conditions (Pe and Da numbers)
  ✓ The local precipitation can influence the pattern of the permeability change.

Heletz study (experimental and numerical): role of local hydrodynamic and mineralogical heterogeneity on reactive processes

Joaquim Soler seminary (beginning of June)
Precipitation localization

Clogging mechanism

Role of undissolved grains on the localization

Precipitation localization