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Experimental Simulation of Mass Transfer During Limestone Alteration Submitted to a Gradient of Temperature and a High CO_2 Pressure: the COTAGES Experiment

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ABSTRACT

Injection of a fluid into a geological reservoir, either for geothermal purpose but also in the context of greenhouse gas storage, implies physical, mineralogical and geochemical transformation of the rock due to an obvious disequilibrium between the reservoir and the injected fluids. The disequilibrium is not only chemical due to the undersaturation of the injected solution with respect to the solid phases, but can be also of thermal origin because of the gradient of temperature between an injected cold fluid and a hotter reservoir. In this context, chemical reactions such as dissolution and precipitation of the minerals can occur playing a role on the porosity and permeability of the rock and thus on the fluid injectivity.

In order to follow the possible mass transfer due to chemical reactions induced by a thermal gradient, we performed experimental simulations with the COTAGES autoclave. Experiments are carried out on an oolitic limestone from the Paris Basin (France), which is a good analogue of the Dogger formations used for geothermal exploitation and possible CO_2 storage in France.

The variations of pressure during experiment as well as the evidence of dissolution and precipitation of calcites show that an important mass transfer occurs. The results of experiments will be discussed in terms of global mass budget, mineralogical transformations and implications on the petrophysical changes of the reservoir rock in the vicinity of the injection well.

1. INTRODUCTION

The geological sequestration of CO_2 is known as one of the more realistic solutions to limit the atmospheric emissions of greenhouse gases.

The geological storage is made of two phases: a first phase corresponding to the injection of the CO_2 fluid, and a second, post-injection, phase. During the injection phase which can last several years, CO_2 is injected in the reservoir rock via injection wells (Fig. 1). When injection ceased, the wells are sealed with cement: the wells are then abandoned and the post-injection phase begins. However, the wells are undoubtedly the weak point of the whole CO_2 storage because they are the main discontinuity that binds the reservoir and the atmosphere, being possibly responsible for the leakage of the storage.

In this paper, we want to quantify the influence of the thermal gradient linked to the injection of a cold fluid in a hotter reservoir. The reservoir rock used for this study is an oolitic limestone from the Paris Basin (Lavoux, France),

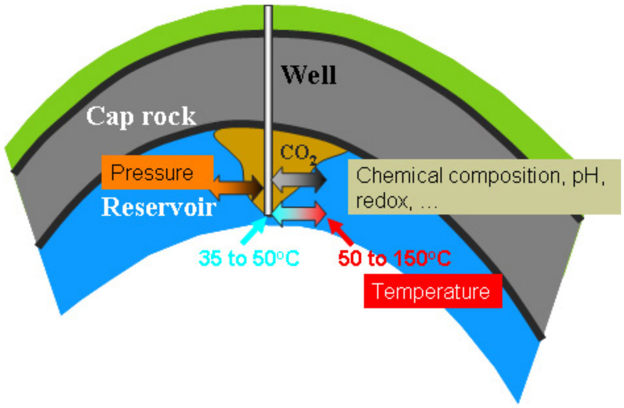

Figure 1: Sketch diagram of an injection well.

which is a good analogue of the Dogger formations used for geothermal exploitation and possible CO_2 storage. In order to follow the possible mass transfer due to chemical reactions induced by a thermal gradient, we developed a new experimental apparatus, the COTAGES autoclave, which allows carrying out experimental simulations with supercritical CO_2.

2. EXPERIMENTAL PROTOCOL

The COTAGES autoclave is a horizontal cylindrical stainless steel reactor of 72 cm length and 2.1 cm in diameter for a total volume of about 250 cm^3 (Fig. 2). Fragments (1 to 4 mm) of oolitic limestone (Lavoux, France) or grain of quartz (blank experiment) fill the autoclave together with demineralized water or a pre-equilibrated saline (4g/l NaCl) aqueous solution. The zone 3 of the autoclave is heated to reach 100°C in the middle of the zone. The zones 2 and 3 are not heated and a natural gradient of temperature occurs as a function of the thermal conductivity of the materials (steel, limestone and aqueous solution). The temperature in the middle of the zone 2 is around 54°C and reaches around 34°C in the zone 2 (Fig. 3). An initial pressure of 100 bar is reached by CO_2 injection with a pneumatic pump or N_2.

Three types of experiments are performed. The first experiment (exp-Qz-CO_2) is carried out with grains of quartz supposed as chemically inert. It corresponds to a blank allowing to follow the evolution of pressure and temperature due to the gradient of temperature but not dependent on the chemical reactions. A second type of experiments (exp-Lx-N_2) are performed with the oolitic limestone but N_2 replaces CO_2 in order to have a blank allowing to follow the effect of the gradient of temperature on the limestone/water system but without the effect of CO_2. The last type of experiments (exp-Lx-CO_2) are

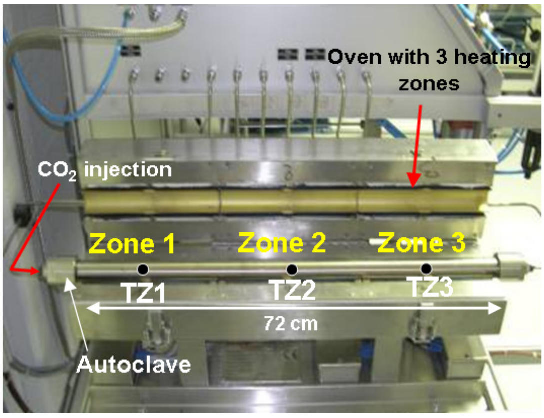

Figure 2: The COTAGES autoclave with three heating zones.

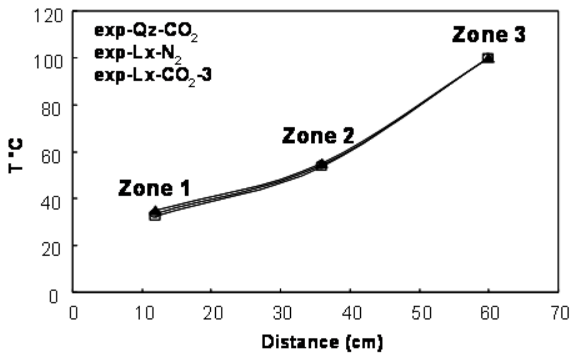

Figure 3: Gradient of temperature as a function of the distance into the COTAGES autoclave for 3 representative experiences. The temperatures are measured in the middle of the heating zones.

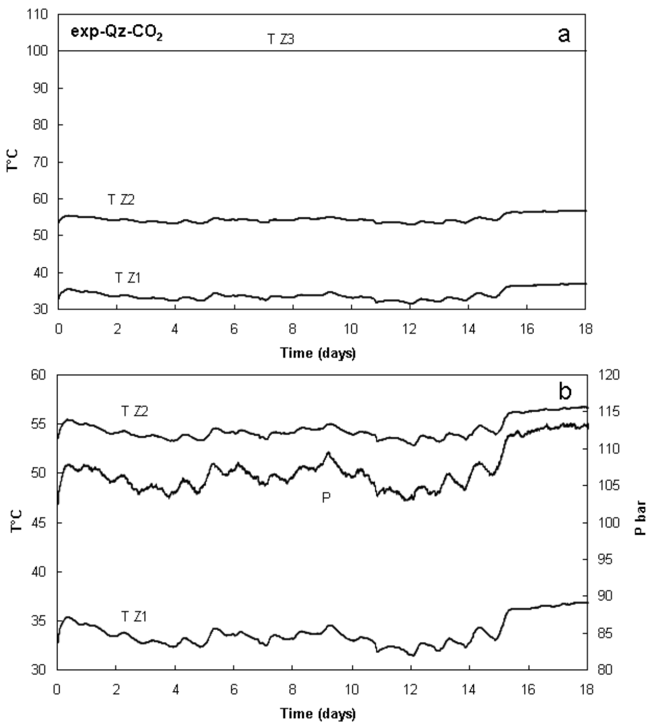

Figure 4: Experiment exp-Qz-CO_2. a: evolution of the temperature recoded in the middle of the 3 zones during experiment. b: Evolution of the total pressure to be compared with the temperatures of the non regulated zones (Z1 and Z2).

performed on the oolitic limestone with a high pressure of CO_2 and should allow to follow the behavior of an aquifer carbonate reservoir submitted to a CO_2 injection inducing a gradient of temperature.

Both temperature and pressure are recorded for the complete duration of the experiments. Aqueous solutions and solids are collected to be analyzed after experiments. A detailed study of the grain size (granulometry) of the solid phase before and after experiments is made.

3. RESULTS AND DISCUSSION

3.1 exp-Qz-CO_2

The first experiment acts as a blank performed with inert grains of quartz. Fig. 5 shows the evolution of the total pressure and temperature of the 3 zones as a function of time. The temperature of regulated zone (zone 3) remains constant during the 18 days of the experiment. The non regulated zones (1 and 2) shows variations of the temperatures linked to the room temperature and especially to the night/day cycles. The total pressure moves between 101 and 113 bar with an average value of 107 bar and is correlated to the variations of temperatures of zones 1 and 2.

The granulometric study (Fig. 6) shows that the size of the grains does not drastically vary during experiment whatever the location in the gradient of temperature. The weak differences recorded close to the extremities can be linked to the operations of filling and emptying of the autoclave.

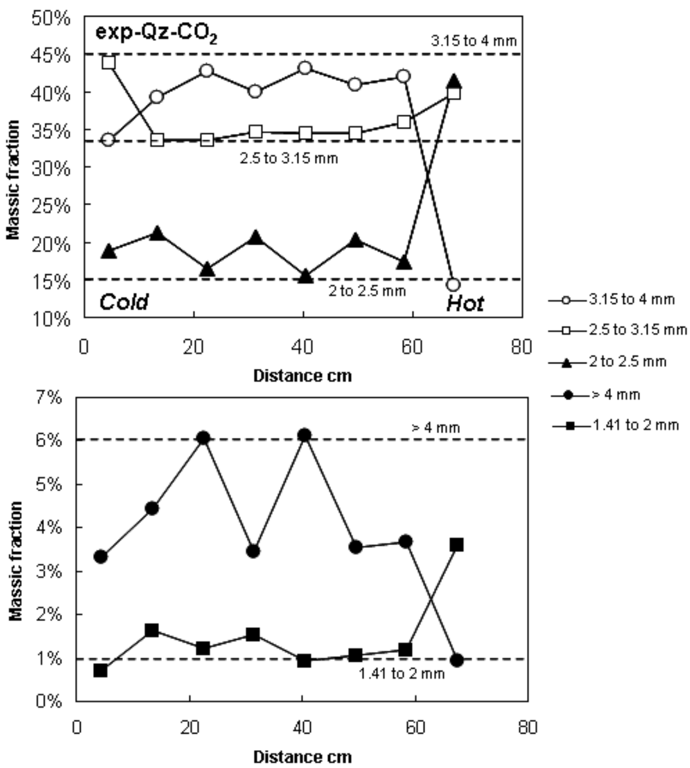

Figure 5: Evolution of the granulometric fraction of the quartz (exp-Qz-CO_2) as a function of the location in the autoclave. The temperature increases with the distance in the autoclave (cold zone at 0 and hot zone at 72 cm). Dashed lines correspond to the fresh grains, before experiment.

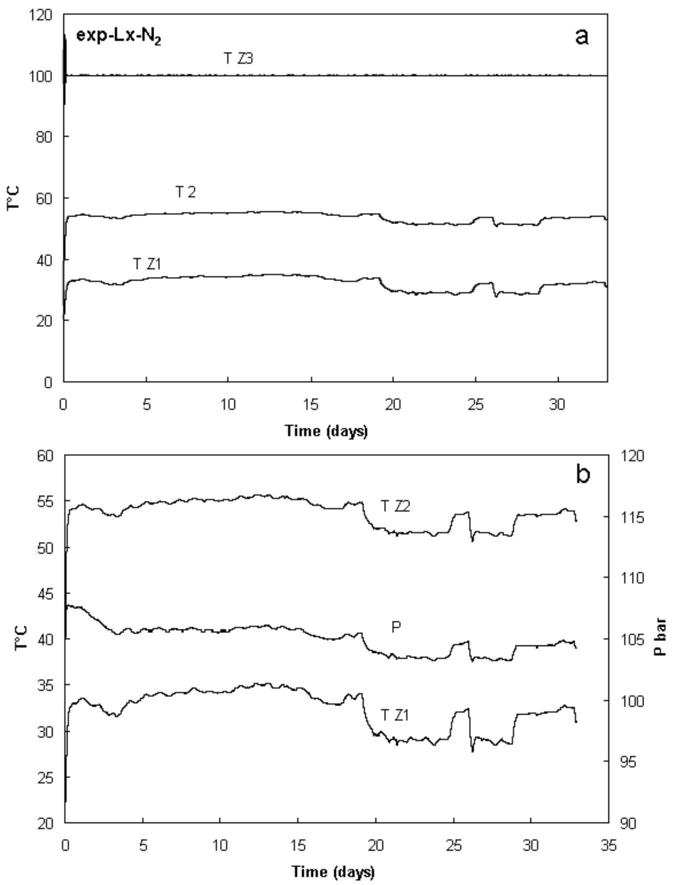

Figure 6: Experiment exp-Lx-N_2. a: evolution of the temperature recoded in the middle of the 3 zones during experiment. b: Evolution of the total pressure to be compared with the temperatures of the non regulated zones (Z1 and Z2).

3.2 exp-Lx-N_2

This experiment is devoted to understand the system limestone/aqueous solution submitted to a gradient of temperature under pressure but without the effect of CO_2. Fig. 7 shows the evolution of the total pressure and of the temperature of the 3 zones during the experiment. The temperature of the hottest zone remains constant during the complete duration of the experiment whereas the temperature of the non regulated zones (1 and 2) varies with time due to variations of the room temperature. The total pressure varies between 103 and 108 bar with an average value of 105 bar. The average value of the temperature of the cold zone (zone 1) is 32°C and reaches 54°C in the zone 2.

The study of the grain sizes (Fig. 7) shows that, in average, the hottest zone has a tendency to be enriched in the fraction 3.15 to 4 mm together with a decrease in the fractions 1.4 to 2.5 mm. This could be explained by a re-equilibration between the zones: the CO_2 is more soluble in the cold zone implying more acidic conditions and thus calcite dissolution. Calcium ions can migrate to the hottest zone by diffusion or thanks to fluid movements and can precipitate and thus change the grain size of the hottest zone. However, the simple observation of the grains shows that this mass transfer remains limited.

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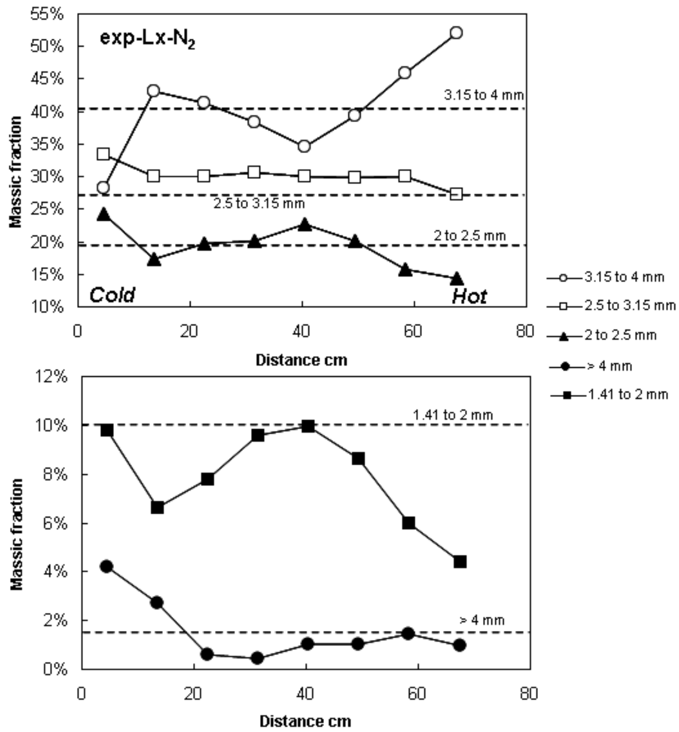

Figure 7: Evolution of the granulometric fraction of the quartz (exp-Lx-N_2) as a function of the location in the autoclave. The temperature increases with the distance in the autoclave (cold zone at 0 and hot zone at 72 cm). Dashed lines correspond to the fresh grains, before experiment.

3.3 exp-Lx-CO_2

The experiment carried out with CO_2 under a gradient of temperature shows a specific behavior with important variations of the total pressure.

Fig. 8 shows the variations of temperature and pressure during experiment exp-Lx-CO_2. The temperatures of the regulated zone remain relatively constant during the 30 days of the experiment (with the exception of the two power shortages). The temperatures of the non regulated zones (1 and 2) have cyclic variations due to the fluctuations of the room temperature. The variations of the total pressure, if partly related to the variations of temperature, should have been dependent to chemical reactions occurring in the reactor. Indeed, after several hours of pressure increase due to temperature, the pressure drastically decreases (up to 30 bar less). These variations of pressure in the global system might de linked to chemical reactions occurring between the limestone and the aqueous phase in the zones affected by different temperatures. If we consider a higher CO_2 solubility in the cold zone, it follows a more acidic solution leading to carbonate dissolution and thus to an increase of the CO_2 fugacity and consequently of the total pressure of the system. The calcium content of the cold zone is greater than that of the hotter zone which leads to diffusion phenomenon and to an increase of the Ca content in the system with a precipitation of calcite in the hot zone. This is observed in the autoclave with the formation of a plug of several centimeters in the hot zone linked to a massive precipitation of calcite (Fig. 9)

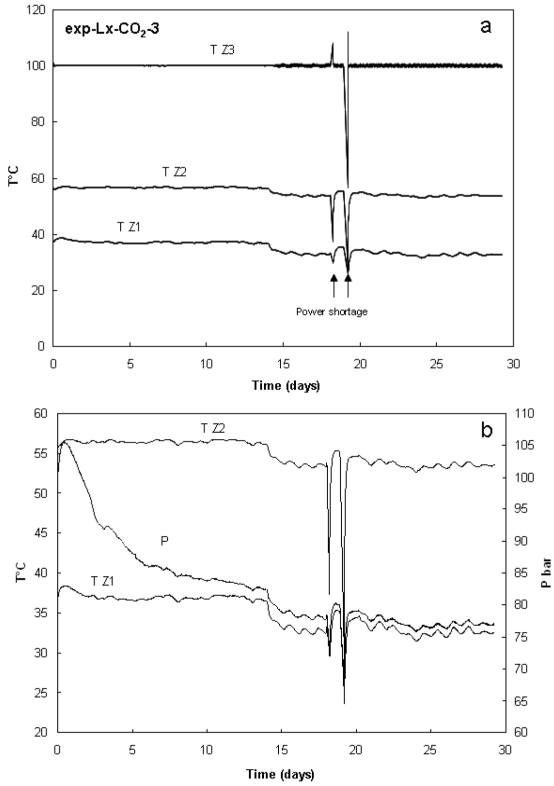

Figure 8: Experiment exp-Lx-CO_2. a: evolution of the temperature recoded in the middle of the 3 zones during experiment. b: Evolution of the total pressure to be compared with the temperatures of the non regulated zones (Z1 and Z2).

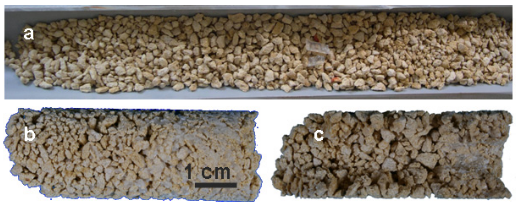

Figure 9: Fragments of oolitic limestone after experiment with CO_2 (exp-Lx-CO_2-1). a: in the cold zone, b and c: view of calcite precipitation (in white) in the hotter zone leading to a plug in the autoclave.

The study of the grain size (Fig. 10) confirms this observation with a decrease of the fraction with the biggest grains (3.15 to 4 mm) and an increase of the 1 to 2.5 mm fraction when going from the cold to the hot zone.

Grains are sampled after experiment as a function of their position into the thermal gradient. They are than impregnated with a fluorescent resin in order to better visualize the pores with confocal scanning laser microscopy (CSLM). Fig. 11 shows in yellow the connected porosity in the cold zone (Fig. 11b) and in the hot zone (Fig.11a). It is obvious that the sample from the hot zone exhibits a lower porosity than that from the cold zone. SEM observations (Fig. 12) confirm that mono-crystals of calcite massively precipitate in the hot zone and is responsible for the total filling of the intra-oolitic porosity.

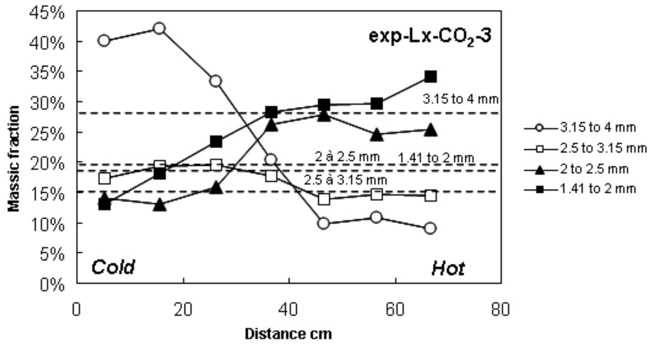

Figure 10: Evolution of the granulometric fraction of the quartz (exp-Lx-CO_2) as a function of the location in the autoclave. The temperature increases with the distance in the autoclave (cold zone at 0 and hot zone at 72 cm). Dashed lines correspond to the fresh grains, before experiment.

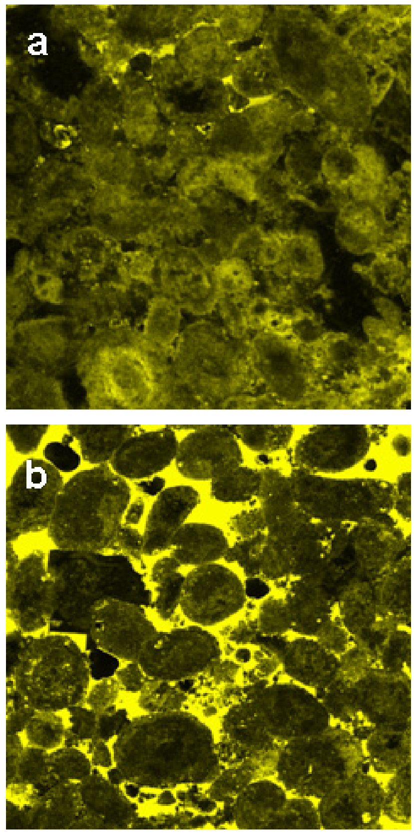

Figure 11: Cross section of fragments of oolitic limestone after experiment with CO_2 (exp-Lx-CO_2-1). Yellow zones correspond to the fluorescence of the resin used for impregnation of the samples and thus to the connected porosity a: in the hotter zone where calcite has precipitated, b: in the cold zone.

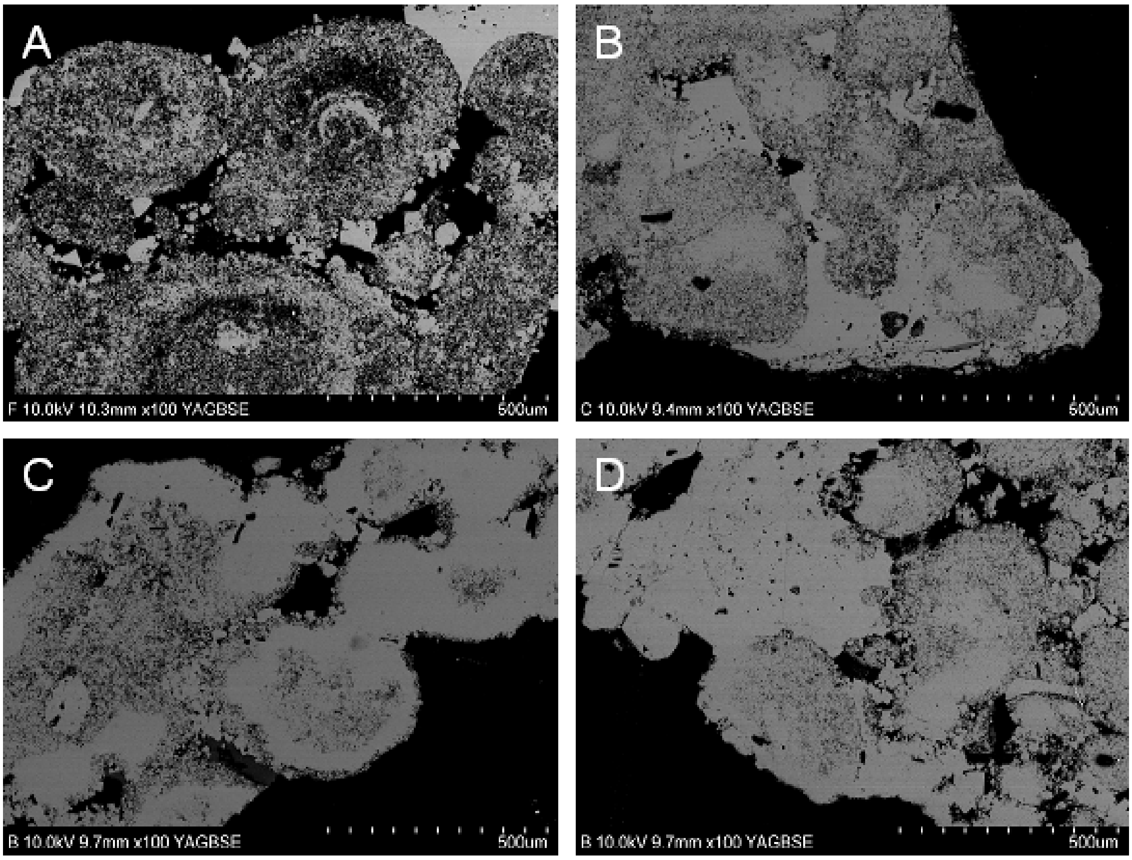

Figure 12: Cross section of fragments of oolitic limestone after experiment with CO_2 (exp-Lx-CO_2-2) observed by SEM (BSE). a: in the cold zone, b: in the hot zone, c and d : in the hot zone where calcite has massively precipitated (plug).

4. CONCLUSION

This study has shown that the effect of a gradient of temperature due to the injection of a fluid rich in CO_2 on a eservoir can be experimentally modeled by the COTAGES experiment. These first experiments performed on a carbonate reservoir show that the gradient of temperature leads to a dissolution of calcite in the cold zone and consequently to a massive precipitation in the hot zone. The calcite precipitation can drastically affect the porosity and thus the permeability of the reservoir rock. This phenomenon should be also interpreted in terms of CO_2 injectivity since permeability of the reservoir can be strongly affected by important mass transfers due to thermal gradient.