Qualitative and quantitative changes in detrital reservoir rocks caused by CO_2-brine-rock interactions during first injection phases (Utrillas sandstones, Northern Spain)

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Abstract

The aim of this article is to describe and interpret qualitative and quantitative changes at rock matrix scale of Lower-Upper Cretaceous sandstones exposed to supercritical (SC) CO_2 and brine. The effects of experimental injection of SC CO_2 during the first injection phases were studied at rock matrix scale, in a potential deep sedimentary reservoir in Northern Spain (Utrillas unit, at the base of the Cenozoic Duero Basin).

Experimental wet CO_2 injection was performed in a reactor chamber under realistic conditions of deep saline formations (P ≈ 7.8 MPa, T ≈ 38 °C and 24 h exposure time). After the experiment, exposed and non-exposed equivalent sample sets were compared with the aim of assessing possible changes due to the effect of the CO_2-brine exposure. Optical microscopy (OpM) and scanning electron microscopy (SEM) aided by optical image analysis (OIA) were used to compare the rock samples and get qualitative and quantitative information about mineralogy, texture and porous network distribution. Chemical analyses were performed to refine the mineralogical information and to obtain whole rock geochemical data. Brine composition was also analysed before and after the experiment.

The results indicate an evolution of the pore network (porosity increase ≈ 2%). Intergranular quartz matrix detachment and partial removal from the rock sample (due to CO_2 input/release dragging) are the main processes that may explain the porosity increase. Primary mineralogy (≈ 95% quartz) and rock texture (heterogeneous sand with interconnected framework of

micro-channels) are important factors that seem to enhance textural/mineralogical changes in this heterogeneous system. The whole rock and brine chemical analyses after interaction with SC CO_2-brine do not present important changes in the mineralogical, porosity and chemical configuration of the rock with respect to initial conditions, ruling out relevant precipitation or dissolution at these early stages.

These results, simulating the CO_2 injection near the injection well during the first phases (24 h) indicate that, in this environment where CO_2 displaces the brine, the mixture principally generates local mineralogical/textural re-adjustments due to physical detachment of quartz grains.

Consequences deriving from these changes are variable. Possible porosity and permeability increases could facilitate further CO_2 injection but textural re-adjustment could also affect the rock physically. However, it is not clear yet what effect the quartz (solid suspension) could provoke in more distant areas of the rock. Quartz could be transported in the fluid flow path and probably accumulated at pore throats.

Key Word: CO_2 storage, Utrillas sandstones, applied petrology, pore changes.

1 Introduction and objectives

The capture and geological sequestration of CO_2 is one of the technological options currently contemplated to reduce emissions of greenhouse gases into the atmosphere. Deep geological storage in porous rock formations is considered the most appropriate strategy for CO_2 sequestration (Bachu, 2000; Izgec et al., 2008; Benson and Cole, 2008; Gaus, 2010) and injectivity is a key technical and economic issue for carbon capture and storage (CCS) projects (Bacci et al., 2011). The viability of the CO_2 injection depends mainly on the porosity and permeability of reservoir rocks. CO_2 interaction with the host rock, such as dissolution or precipitation of minerals is also important (e.g. Ross et al., 1982; Sayegh et al.; 1990 and Saeedi et al., 2011), as well as mineral trapping (Kaszuba et al., 2003; Rosenbauer et al., 2005; Liu et al., 2013). Dissolution of supercritical (SC) CO_2 into brine will control the rate of dissolution and precipitation of minerals constituting the porous rock. Volume changes of the solid phase will modify the pore structure, affecting both porosity and permeability of the porous media (André et al., 2007).

CO_2-water-rock interaction experiments represent a useful method to understand and explore the mechanisms and processes of geological storage (Ketzer et al., 2009) and to design safe underground CO_2 storage operations. Bertier et al. (2006) built an experimental setup to evaluate the effect of CO_2-water-rock interactions in three sandstone aquifers concluding that "CO_2-water-rock interactions might significantly influence geological sequestration of CO_2". Most of the experimental and theoretical studies are designed to simulate the injection of CO_2, mixed with brine, into rocks at P-T conditions of deep storage environments. The result of many of these experiments was an increase in the porosity/permeability of the reservoir rock caused by partial dissolution of the carbonate components (mainly calcite) (Perkins and Gunter, 1995; Svec and Grigg, 2001; Rochelle et al., 2004; Egermann et al., 2005; Izgec et al., 2005; Gunter et al., 2004, Luquot and Gouze, 2009 and Desbois et al., 2011). However, other set of experiments has shown porosity decreases due to the initial dissolution of carbonates followed by secondary precipitation/mineralisation (Kaszuba et al., 2003; Cailly et al., 2005; Kaszuba et al., 2005; Mito et al., 2008; Sterpenich et al., 2009; Luquot and Gouze, 2009). André et al. (2007) presented numerical modelling of chemical fluid-rock interactions at the SC-CO_2-liquid interface during CO_2 injection into a carbonate reservoir (Paris Basin, France). In this case, two CO_2 injection scenarios were evaluated: CO_2-saturated water injection and pure supercritical CO_2 injection. In these two scenarios, different geochemical processes occurred as the distance from the injection well increased (in the first scenario there was a porosity increase of up to 90%; while, in the second scenario porosity increased about 6% in most of the reservoir and it decreased in the vicinity of the injection point). Besides, different regions were identified depending on the saturation ranges of liquid and gas phases, associated geochemical conditions and porosity variations during the injection and according to the distance from the injection well (Fig. 1a).

Other investigations focus on the CO_2 injection into potential reservoir rock formations under dry conditions (Kaszuba et al., 2003; Vickerd et al., 2006 and Berrezueta et al., 2013). The injection environment is mainly envisaged as injecting CO_2 mixed with brine into sandstones. However, in near-well conditions, the supercritical CO_2 laterally displaces the brine and occupies the pore space of the rocks, in either dry or near-dry conditions (André et al., 2007; Burton et al., 2008; Luquot and Gouze, 2009; Gaus, 2010). Therefore, dry CO_2 interaction with the storage rock is a realistic scenario that takes place during the initial injection stages. Some theoretical studies (Gaus et al., 2008 and Gaus, 2010) and experimental results (Stepernich et al., 2009) on dry CO_2-rock interactions indicate the absence of reactions and

consequently negligible textural-mineralogical changes. This is explained by the lack of H_2O in the system that prevents dissolution/precipitation and any kind of chemical reactions. However, experimental studies on dry-CO_2 injection into undersaturated sandstones with high clay matrix content (Berrezueta et al., 2013) concluded in an increase of rock porosity, causing a textural change. This was explained by detachment and partial removal of the intergranular clay matrix from the sandstone samples due to supercritical CO_2 input/release dragging and changes in electrical-polarity forces.

Our research is focussed on experimental injection of supercritical CO_2 into the selected rocks (sandstones saturated by and covered with brine), similarly to previous works e.g. Tarkowski and Wdowin (2011), Fischer et al. (2013), Wdowin et al., (2014a, b) and Tarkowski et al., (2015). We chose the Utrillas sandstones for the present study due to their importance as potential CO_2 reservoirs in Spain. The lithological characteristics of the Utrillas sandstones and the structural features of the area offer favourable conditions for the study of CO_2 storage (García Lobón et al. 2010 and Martínez et al., 2013).

The selected P-T conditions and run-times of our experiments aim to reproduce the reservoir rock dry-wet environment, adjacent to a theoretical injection borehole, (Fig. 1a and b), specifically, at the interface between the supercritical CO_2 bubble and the aqueous solution. This interface acts as an exchange zone where CO_2 diffuses constantly (e.g. Zone 4 defined by André et al., 2007). The experimental P-T conditions were selected to guarantee that the CO_2 was over its supercritical point (Holloway 1997; Bachu 2000; Lake 1989; Span and Wagner 1996).

Furthermore, the textural-mineralogical and petrophysical changes in the rock samples are studied before and after the experimental injection of supercritical CO_2 for a short period of time (24 hours). Special care was put into the development of a model to explain the observed changes. Optical image analysis (OIA) techniques were used to monitor these changes.

2 Samples: geological setting

The studied samples belong to the unit commonly known as Utrillas sandstones and locally defined as Voznuevo Formation (Evers, 1967) of Upper Albian-Lower Cenomanian age (Lower-Upper Cretaceous transition). The sampling took place in North Spain, at the boundary between the Alpine Cantabrian Mountains and the Cenozoic Duero Basin (Fig. 2a).

The Utrillas sandstones belong to a 1100 m thick Cretaceous sequence and crop out near Boñar village in North León province. This Cretaceous sequence lays unconformably on the Paleozoic basement of the Variscan Cantabrian Zone. On top of the Cretaceous sequence, a succession of almost 2500 m thick Cenozoic materials was deposited in the Duero Basin (Fig. 2d). The Cretaceous sequence has been divided into three parts (Manjón Rubio et al., 1982a): 1) a lower detritical part, which corresponds to the Utrillas sandstones, of continental origin; 2) an intermediate or transitional part of Turonian-Santonian age; and 3) an upper carbonate part with limestones and marls of Santonian-Campanian age and marine origin (Fig. 2c). This Cretaceous sequence was deposited in a post-rift stage, at the end of the Cretaceous extensional phase that affected North Spain and produced the opening of the Bay of Biscay (e.g. Gallastegui, 2000).

The Utrillas sandstones, in the study area, are composed of detrital, poorly consolidated or unconsolidated whitish materials ranging from sandstone to conglomerate, with a maximum size of pebbles of 6 cm. The succession is fining upwards with dominating conglomerates at the base and progressively increasing sandstone ratio. The pebbles and grains are mainly of quartzite origin and of subrounded to subangular form, with a sandy and kaolinitic matrix. Argillaceous levels, paleochannels and cross-stratification are frequent and lignites appear locally. This succession was formed in a fluvial braided environment and with a source area composed of acid, mainly granitic and metamorphic, rocks. The transformation from feldspar to kaolin occurred after the deposition and was the result of meteorization processes (Manjón Rubio et al., 1982a).

The fluvial environment, in which the Utrillas sandstones were formed, represents the proximal part of the Upper Cretaceous North-Iberian paleomargin. Towards the north, this fluvial facies changed into deltaic facies, then talus facies and, finally, deep basin turbiditic facies (Olive Davó et al., 1989). This paleomargin was deformed during the collision between Iberia and Eurasia in Cenozoic times. This compressional event produced the uplift of the Cantabrian Mountains in North Spain and the development of the Duero foreland basin in the frontal part or the range (Alonso et al., 1996). The structure of the sampling area is relatively simple and is characterized by a great monoclinal (Fig. 2d), the formation of which has been related with a south-directed basement thrust inclined to the north (Alonso et al., 1996). In detail the structure is more complex because the inclined limb of the monocline is disrupted

by an important fault, known as the Sabero Fault (Sabero-Gordón line of Rupke, 1965), that produces the duplication of the Cretaceous sequence (Figs. 2b and d).

The Utrillas sandstone was sampled in three places of the complex inclined limb of the monocline, in the area of Devesa of Boñar, performing a thorough study of the structure of these target rocks and their seals (Figs. 2b, d and e). The sampling areas "Devesa 1" and "Devesa 2" are located south of the Sabero Fault, in an outcrop of Cretaceous succession dipping 80º towards the south. The sampling area "Devesa 3" is located north of the Sabero Fault in an outcrop dipping 45º also southwards (Figs. 2b and d). For this study, we chose the more consolidated sandstones (3 samples), located in "Devesa 1", to guarantee the effectiveness of the analysis. The unconsolidated sandstones of Devesa 2 and 3 were discarded for the study. The samples were divided into adjoining and numbered sets of blocks. Each couple of adjoining blocks was used for the experimental test and for the studies before and after CO_2 injection.

3 Methodology and experimental procedure

3.1 Experimental setup and procedure

The experimental setup employed in this experiment (Fig. 1b) is based on similar systems described by Luquot and Gouze (2009), Tarkowski and Wdowin (2011), Luquot et al. (2012), Berrezueta et al. (2013) and Wdowin et al. (2014a, b). However, some modifications were made due to the distinct characteristics of the target rock system. Sample material (rock type and representative sample size), geological environment (pressure, temperature and salinity) and technical equipment (materials for camera, software, pumps, etc.) were all considered for the final arrangement of the experimental device and run conditions. The experiment consists of the exposure of sandstones to SC CO_2 in a reactor with pressure and temperature control. P/T conditions (7.8 MPa and 38° C, respectively) were selected to surpass the CO_2 supercritical point (Lake 1989; Span and Wagner 1996) and to simulate basic conditions of injection and storage of CO_2 (Holloway 1997; Bachu 2000). These conditions are representative of a depth of approx. 800 m. The selected exposure time (24 h) is meant to model the first stage of injection.

The system (Fig. 1b) has two CO_2 cylinders (standard commercial CO_2 at 4.5 MPa) that are linked to the other elements of the system by steel connectors (diameter: 5 mm). The second

CO_2 cylinder is connected to a piston pump that operates with a flow of 0.01 g/s. When the required pressure (7.8 MPa) decreases (due to possible leaks), this pump will inject CO_2 to keep the pressure within the desired values. The piston pump needs a CO_2 initial pressure of 1 MPa in order to inject CO_2 into the Hastelloy steel chamber (3 dm^3), thereby, the pressure between the piston pump and the second CO_2 cylinder has to be decreased by a pressure manometer from 4.5 to 1 MPa. The inside of the chamber is coated with polytetrafluoroethylene (PTFE) to protect the material against corrosion. At the bottom of the chamber, a calorimeter controls the internal temperature. The calorimeter and the pump are linked to the chamber with pressure and temperature sensors and are connected to a computer.

The experiments began with the saturation of rock samples (6 cubes of 27 cm^3 of each sandstone sample) with natural brine. 0.6 dm^3 brine was chemically stabilized with the samples for the saturation. 0.3 dm^3 of this brine was extracted and analysed before SC CO_2 injection. Then, the rock samples were introduced into the chamber together with the rest of brine. The experimental runs comprised: a) a pressurized CO_2 injection (3 h); b) a pressurized stabilization (24 h, no CO_2 flow inside the chamber) and c) CO_2 pressure release (3 h). The CO_2 injection was performed using a constrained hyperbaric chamber-reactor where the dry CO_2 was pumped at pressures and temperatures of 7.8 MPa and 38°C, respectively. The times of filling and emptying the chamber with supercritical CO_2 were the same (3 h). This is the time required to reach the target pressure and temperature values, from the initial ambient conditions. The same time was used to get back to the ambient conditions at the end of the experimental test. The applied software, HEL 5.1, allows the remote control of the system (experimental conditions) through the development of specific macros (pressure, temperature, time) in real time. All the experimental runs were carried out in the laboratories of the Geological Survey of Spain (IGME) in Tres Cantos, Madrid.

3.2 Methodology of study

The aim of the study was to quantify the possible textural and porosity changes due to experimental CO_2 injection. We began with a detailed petrographic study using optical microscopy (OpM) to identify the major mineral and textural features. The characterization was performed in neighbouring areas of the blocks by OpM (30 μm thin sections) and scanning electron microscopy (SEM, rock samples). Although the thin sections and SEM samples do not exactly correspond to the same sample surface, they are located very close (a few mm) in the original source-sample. The aim of the detailed OpM study and quantification

of mineralogical and textural variability was to verify that any changes observed in the experiments were due to the effects of CO_2 effect and not to possible original heterogeneity. Furthermore, chemical analysis of the brine and whole rock before and after SC CO_2 injection were performed, as well as microscopic studies of the residue that remained in the reactor chamber after the experiment.

Simultaneously, a detailed study of the configuration of porous system was conducted by combining observation by scanning electron microscopy with backscattered electrons (SEM) and optical image analysis (OIA). This method allows the study of pore size distribution and other porosity parameters (shape, specific surface of pore, etc.). Later, the same procedure was followed for the study of the SC CO_2 exposed rocks. The OIA technique makes it possible to identify, characterize and quantify mineral elements in images captured digitally (Fig. 3) before and after SC CO_2-brine exposure. The general procedure for the automated image analysis was developed adapting the procedures and algorithms described by Berrezueta et al. (2015), in order to quantify the textural and porosity changes (area, roughness of minerals/pore boundaries, fractal dimension, roundness of minerals/pores and porosity) provoked by experimental CO_2 injection. Assessment of pore-network distribution by optical transmitted light studies of thin sections requires distinction between mineral and pore networks according to their optical characteristics. The segmentation of the porous system was made by regions, applying the "thresholding" segmentation method (based on threshold values to turn a raw image into a binary one, the pixels being partitioned according to their intensity value). In this way, we can quantify the evolution of small changes in the configuration of pore network. This work was carried out in the Oviedo IGME laboratory using a Leica DM 6000 polarization microscope and an Image Pro Plus-7.0 software and ProgRes digital camera for pore network study by OIA. SEM studies were performed using a Hitachi TM3000 microscope with X-ray microanalysis equipment.

Additionally, rock samples were analysed by X-ray fluorescence (XRF) and X-ray diffraction (XRD), and brine composition was determined by several methods (ion chromatography, ICP, pH, conductivity measurements). The studies were developed in the facilities of IGME laboratory-Tres Cantos and Oviedo University Laboratory.

4 Results

4.1 Mineralogical and petrographic characterization and OIA pore-network quantification

4.1.1 Samples before SC CO_2 injection

The studied rock is a medium to very coarse-grained sandstone (grain size from 90-1600 μm, with a mode of 250 μm) with areas of fine to medium grain sizes, showing unoriented and slightly to highly variable porous structure. The pores, that are 80-500 μm (up to 1400 μm) in size, constitute up to 8 to 15% of the rock volume, although there are special areas with porosity up to 20%. The grains are from moderately to poorly sorted. There are zones with a slight anisotropy defined by the presence of matrix rich bands. The grain skeleton (Fig. 4a, c and e) consists of quartz (> 95%), very minor potassium feldspars (orthoclase) and a small amount of micas (muscovite and chlorite). Accessory minerals (a total of 1-5%) are opaque minerals, such as iron oxides and hydroxides (hematite and limonite), in the form of aggregates of 40-100 μm in size, dispersed in the matrix or as cement. Other accessory minerals are brown and green tourmalines and zircon. The rock is composed mainly by grain skeleton supported with a small proportion of matrix (< 5%) composed mostly by quartz and minor phyllosilicates of the mica and clay groups (muscovite and/or illite and/or kaolinite) and opaque minerals. Locally, cement is present as a film coating iron oxides and sintaxial quartz. According to the Folk (1974) and Pettijohn et al. (1987) classification, it is a quartz-arenite (> 95% of quartz). Some areas have higher matrix concentration (>15%) classified as fine-medium grained quartz-greywacke. The quartz grains are mostly monocrystalline with important size variability. The grains have angular to subangular shapes, from high to low sphericity and with sizes ranging from 90 to 1400 μm. Moreover very rounded grains of polycrystalline quartz (fairly minor amount) appear sometimes with a Fe oxide coating. They are of significant size (900-1900 μm). Grains with internal crystals of > 30 μm size are the most common. On the other hand, there are some polycrystalline quartz grains with elongated shapes and large dimensions up to 2800 μm. Sometimes the internal crystalline units of the polycrystalline quartz grains show preferred orientations (meta-quartzite origin). The internal units can be of sizes < 30 μm (chert) or up to 180-240 μm. The orthoclase feldspars are very scarce, have rounded edges with sizes up to 1400 μm and show a significant degree of alteration to iron oxides, phyllosilicates (illite and/or kaolinite) and chlorite.

The porous system reaches estimated visual proportions of 8 to 15%. Adapting Choquette and Pray (1970) and Lucia (1999) porosity nomenclatures for carbonates, various pore types were identified. “Vuggy” pore type, corresponding to highly spherical and rounded pores with sizes around 50-90 μm are common. “Intercrystalline” type pores were also observed. These are irregularly shaped around skeletal grains with very rounded edges, possibly a product of matrix solution. They present elongated shapes and sizes ranging from 140-220 μm up to 300 μm. There are also incipient “cavernous” type pores, with elongated shapes, of sizes of ca. 80-170, even 550 μm. In addition, there are “fracture” type pores. The sizes of these pores generally reach 80-200 μm but there are some larger elongated caverns (ca. 1400 μm). “Protected” porosity below some quartz grains (500 μm) was also observed. The mineralogical and pore network distribution has been corroborated by SEM observation (Figs. 5a, c, and e).

The pore network quantification by OIA (Table 1) was carried out in three thin sections with images acquired with a magnification of 10x. The porosity percentage estimated by this method ranges from 6.49 to 18.18% with an average of 11.41 ± 0.14%. The maximum and minimum area of pore was 172100 μm^2 and t 9.2 μm^2, respectively. The average pore area size was 168 μm^2. Curves of relative and absolute distribution of number of pores versus pore area ranges and diagrams of weighted area related to pore area classes are presented in Figs. 6a and c for the samples before SC CO_2 injection.

4.1.2 Samples after SC CO_2 injection

The studied rock is a medium to very coarse grained, poorly-sorted sandstone (particle size from 300 μm to 1800 μm). It is slightly to highly porous with a porosity of 12 to 18% of the rock volume and with pore size up to 2.5 mm. The grains vary from high to low spherical and from subrounded to rounded shapes and it is noteworthy that the quartz grains have a high degree of fracturing. The rock has scarce anisotropy, primarily defined by a band of higher matrix concentration and opaque minerals (Fe oxides). The skeleton (Fig. 4b, d and f) consists mostly of quartz grains (> 95%), scarce potassium feldspars (orthoclase) and small amounts of mica (muscovite). Quartz grains show high degree of fracturing and are primarily monocrystalline with high or low sphericity and rounded edges. Their sizes vary from 300 to 1800 μm. Sometimes they are of low sphericity with rounded edges or subangular shapes, with sizes ranging from 240 to 1000 μm, even up to 2.4 mm. On the other hand, polycrystalline quartz is present with internal crystal units < 30 μm, with elongated shapes,

rounded edges and grain sizes between 700-1400 μm. Other polycrystalline quartz grains are rounded with sizes up to 1000-2400 μm with internal structural units > 30 μm. Orthoclase feldspars are very rounded and quite spherical, with sizes up to 2.4 mm. They sometimes show alteration containing Fe oxides and phyllosilicates (possibly illite and /or kaolinite). Accessory minerals are opaque minerals (iron oxides associated to iron hydroxides). These opaque minerals appear in the form of large grains surrounding the skeleton grains or as smaller crystals scattered in the sandy-clay matrix or oriented at the edges of matrix rich bands. Other accessory minerals are tourmaline and zircon. The matrix (< 15%) is composed mainly by quartz and a small amount of phyllosilicates (possibly illite and/ or kaolinite and/or smectite) and iron oxides. Opaque minerals are Fe oxides and hydroxides (hematite and limonite) that are often associated with phyllosilicates (kaolinite and/or illite and/or smectite) and mica (possibly muscovite). Based on the modal content of quartz, feldspars, lithoclasts and matrix content the rock is classified as quartz-arenite and some areas with higher matrix content (ca. 15%) as medium grained quartz-wacke (Folk 1974; Pettijohn et al.1987).

The identified porosity is more abundant than in the samples before CO_2 injection. The estimated visual percentage ranges from 12 to 18%. Adapting Choquette and Pray (1970) and Lucía (1999) nomenclatures, there are various pore types present in the rock. Intercrystalline pores between quartz grains with variable sizes (90-240 μm) were observed. The presence of pores that are arranged in micro-fractures within quartz grains is also common. Cavern type pores appear frequently, with irregular shapes and sizes varying from 700 to 1700 μm, up to 2900 μm. Sometimes they are interconnected by micro-channels. Caverns are generally larger than in the sample before CO_2 injection. Sometimes, matrix rich bands show elongated channel pores following the anisotropy with a maximum dimension of 4.8 mm. The SEM studies (Figs. 5 b, d, and f) showed again intergranular spaces constituted by cavern pores interconnected by micro-channels and pore spaces sometimes filled with minerals. Furthermore, the high degree of fracturing leads to fracture type pore development.

The pore network quantification by OIA was developed, as previously described, on digital images acquired using objective lens of 10x. The estimated porosity percentage ranges from 7.06 to 22.05% (Table 1), with an average of 13.42 ± 0.17%. The maximum area of pore was 250,000 μm^2 and the minimum was 9 μm^2. The average pore area size was 278 μm^2. Curves of relative and absolute distribution of number of pores versus pore area ranges and diagrams

of weighted area related to pore area classes are presented in Figs. 6b and d for the samples after SC CO_2 injection.

4.2 Chemical analysis

The composition of the brine was analyzed before and after the 24h testing and the results are shown in Table 2. The data of brine composition before and after experimental CO_2 injection show that there were some changes in the chemistry (higher that the total uncertainty of the technique: ≈ 10%): a decrease (ca. 30%) of the Ca^{2+}, Mg^{2+} and SO_4^{2-} contents and an increase on the HCO_3^- and NO_3^- contents. Other chemical parameters also decreased as a result of the CO_2 injection: the pH changed from 7.2 to 5.27 and the conductivity also decreased around 12%.

Total rock analyses were performed on blocks with and without experimental CO_2-brine exposure. The values and uncertainties are presented in Table 3. There were changes in the following contents: increase of MgO (30%), Na_2O (20%) and CaO (ca. 200%). We considered as significant a change over the uncertainties given by the laboratory for each element, which uncertainty values range from 6.8 to 19.9% depending on the element. Two samples were analysed by XRD, one previous to brine exposure and to SC CO_2 injection and the other after the SC CO_2-brine experiment. These analyses only detected quartz, the other phases being present in quantities below the detection limit of this technique. Furthermore, the residue that remained in the chamber of the reactor after the experiment was studied (Fig. 7). This residue consisted mainly of quartz in two different fractions: a fine fraction with sizes around 20μm and another fraction with rounded quartz grains sometimes reaching 1mm in size.

5 Discussion

In the studied Utrillas sandstones, OpM and SEM techniques allowed us to detect qualitative changes in the pore network in the samples before and after SC CO_2 injection. Compared to the pre-experiment samples, we can point out that, in general, after the experiment larger pores are more common (700-1800 μm) and cavern type pores and channels dominate (Figs. 4 a-b and 5 a-b). There is also an increase of grain fracturing (Figs. 4c and d; Figs. 5c and d). Moreover, the edges of quartz grains before the experiment contain angular pits (Fig. 5e),

while pits in quartz after the experiment are less numerous and distinctly rounded and enlarged (Fig. 5f).

Quantification of these changes was systematically carried out applying OIA (Fig. 3). This study reveals an increase of porosity (Δn) of 0.57-1.58-3.87% with an average of 2.01% (Table 1), which value is higher than the uncertainty of the OIA technique (≈ 1.25%) (Demirmen, 1972; Grove and Jerram, 2011). The lower error of this method as compared to others is one of the advantages of the OIA technique (e.g. error of point counting is around 2.5%; Chayes and Faibain, 1951; Grove and Jerram, 2011).

The OIA technique also allowed us a complete characterization of the pore network through curves of relative and absolute distribution of the number of pores versus pore area ranges (Fig. 6) and diagrams of weighted area related to pore area classes for samples before and after SC CO_2 injection. The pore area ranges measured by OIA are between 9 μm^2 and 250,000 μm^2. The distribution of data shows that ≈ 99% of pores correspond to pores smaller than 1250 μm^2 (Fig. 6a). In the CO_2 injected sample (Fig. 6b) these small pores represent ≈ 98% of all the pores. The diagrams of the weighted area related to pore area classes before (Fig. 6c) and after SC CO_2 injection (Fig. 6d) show that the contribution of the first class of pore area is ca. 35% of the total porosity for pre-experiment samples and ca. 25% of the total porosity for samples after the experiment. The approximate contributions of cumulative weighted pore area for the main percentiles for the sample before SC CO_2 injection are: < 1,250 μm^2 (25%), 7,500 μm^2 (50%), and 38,750 μm^2 (75%). On the other hand, the sample after injection shows contributions of 25% of pore area of 1,250 μm^2, 50% of 8,750 μm^2, and 75% of 65,000 μm^2. In general, in the original samples there are more pores of smaller and intermediate pore area classes than in the ones after the injection. Besides, the maximum sizes of pore area are larger in the injected samples, similarly, Tarkowski and Wdowin (2011) described an increase in the mean pore diameters in their studies.

The brine chemistry study showed that Na^+, K^+, Cl^- and SiO_2 values did not suffer any relevant changes after the injection. On the other hand, the Ca^{2+}, Mg^{2+} and SO_4^{2-} content decreased by approx. 30% (Table 2), probably all as a result of local mineral precipitation of Mg, Ca and Na minerals, evidenced by an increase of these oxides in the chemistry of the rock after the experiment (Table 3). The brine chemistry data, in relative terms is similar to those found in the literature (Kaszuba et al., 2005), but different to the analysis completed by Tarkowski and Wdowin 2011; Luquot et al., 2012; Yu et al., 2012 and Wdowin et al., 2014a,

b. This is probably due to the initial composition of our samples, conditioned by the chemically resistant quartz (95% wt.) and the short period of our experimentation (24 h). We can say that preliminarily CO_2-brine contact with the rock initiated some mineral precipitation though not to a relevant scale. It also caused brine pH reduction (changing from 7.2 to 5.2), similarly to other cases (Kaszuba et al., 2005; Tarkowski and Wdowin, 2011). The pH reduction is due to the increase of carbonic acid and NO_3^- content of the brine after the experiment (Table 2). The higher amount of carbonic acid originates from the CO_2 dissolution in the brine, while that of the NO_3^- may be due to reactions with organic material present in the rock sample. The overall data of the total rock composition of before and after SC CO_2-brine exposure do not show precipitation/dissolution of mineral phases. We can conclude that that the reactions between minerals and fluids were not significant (Gunter et al., 1997 and Hitchon, 1996) and the changes in the porosity configuration (Table 1) are due to physical processes.

The observed and measured changes in the studied samples are due to the SC CO_2-brine exposure and can be of importance in the vicinity of the injection well (Fig. 1a) where the interaction of the CO_2 and the rock takes place initially in wet conditions (Kharaka et al. 2006; Gaus, 2010; André et al., 2007). Any modification in mineralogy and porosity (Figs. 4, 5 and Table 1) changing the rock texture could affect the injection well and its closest environment and hence the injection efficiency (Wdowin et al., 2014a). Our experimental investigation indicates that the main effects observed after the experiment are relevant to the pore network characteristics and quantification, while changes regarding chemical characteristics of the brine and total rock are minor. The initial heterogeneity of the rock could condition the comparison of physical and chemical parameters between the before and after CO_2 injection tests samples, as described by Tarkowski and Wdowin (2011) and Wdowin et al. (2014b). In our study we tried to minimize this effect studying rock surfaces few millimetres separation and employing expert criteria in petrography.

All these considerations allow us to build a conceptual model for the experimental SC CO_2 injection (Figs. 8a to d). The CO_2 input and release affected the quartz matrix and quartz skeletal grains in different ways that finally lead to detachment and partial re-adjustment of the quartz volume (except in the area with firmly fixed quartz grains or areas without CO_2-brine access). These effects resulted in a partial loss of the quartz (both grains and matrix), present as residue after the experiment (Fig. 7). Our conceptual model consists of four stages.

- Stage 1 (Fig. 8a): Initial mineralogical and textural conditions of the rock saturated with brine. Quartz constitutes 95% of the rock sample and brine partially fills intergranular spaces.

- Stage 2 (Fig. 8b): pressurized SC CO_2 injection: initial CO_2 input would mix with brine and percolate through the rock pore system generating a mechanical dragging force probably opening/widening some of the inter quartz-particle cracks.

- Stage 3 (Fig. 8c): pressurized CO_2-brine stabilization: this stage extends through most of the experimental run (24 h). During this time, SC CO_2 continues to diffuse into the pore structure causing accommodation inside (small fractures) and between quartz grains, producing instability in the rock cohesion.

- Stage 4 (Fig. 8d): CO_2-brine pressure release and expansion: Intra-quartz particle CO_2 expansion during pressure release would promote further internal quartz breakdown and generation of free micro-quartz grains (Figs 4b, d and f; Figs. 5b, d and f). This pressure release and gas and brine expansion generated outward dragging forces that probably favoured partial loss of quartz grains that were collected in the chamber when the experiment was finished. This would allow us to explain the porosity increase in the rock.

This model explains how the indirect mineralogical-compositional changes, (identified by OpM, SEM Figs. 4 and 5), may be related to possible de-cohesion of the quartz matrix possibly caused by CO_2-brine pressure (Fauria and Rempel, 2011; Berrezueta et al., 2013). If the system is open, the de-cohesion causes part of the mineral phases of the matrix to leave the system generating a mineralogical-compositional change. The nature of this change is physical and not chemical. The possible de-cohesion of the matrix, by the action of CO_2, leads logically to an increase in the porosity. Therefore, the observed increase in porosity is most probably caused by this de-cohesion and matrix loss, in our experiments.

6 Conclusions

Quantitative assessment of petrography and mineralogy by OIA can be an important tool for geosciences, providing numerical values as a key to the successful interpretation of the rock texture and mineralogy.

The proposed methodology, consisting of mineralogical and petrographic studies by OpM, SEM and OIA techniques on sandstones subjected to SC CO_2-brine exposure (7.8 MPa, 38º

C, during 24 h), proved to be highly effective for the identification and measurement of changes in the pore network. For this study, the Utrillas sandstones were selected due to their potential as CO_2 reservoir in Spain. However, the same methodology could be applicable for future studies considering other rock types, different CO_2 storage conditions or longer periods of exposure time.

The influence of the original rock composition and texture is very important and leads to different effects of the SC CO_2-brine exposure. The study of potential changes at rock matrix scale depends on the facies variations of any sedimentary formation, when evaluating a possible CO_2 reservoir. The facies studied in this work is characterized by 95% quartz content and heterogeneous rock texture, where micro-channels in the quartz matrix areas favour the SC CO_2-brine injection resulting in the development of bigger cavities and pore channels. The main pore evolution measured by OIA was an increase of porosity (2.10 %) and a readjustment of pore network distribution regarding pore size classes.

The chemical analysis of whole rock and brine, before and after SC CO_2-brine injection, point out the prevalence of physical processes with regard to chemical processes (dissolution/precipitation) during the early injection phases. The chemical-compositional evolution of the analysed elements did not evidence significant mineralogical processes. Supercritical CO_2 causes brine pH to decrease as a consequence of carbonic acid increase, validating published models about the effect of supercritical CO_2 on brine.

The results of this experiment show that the changes occurred due to physical process allowing a rough approximation of the CO_2-brine-rock interactions. Furthermore, these changes may have an important impact on the behaviour of reservoir rocks during first injection phases of SC CO_2: i) changes in the rock system that lead to the porosity evolution could facilitate further CO_2 injection, ii) mobilization of solid material (quartz) should be considered during experiments and/or future modelling of the reservoir.

Acknowledgements

The authors would like to thank the funding provided through the ALGECO2-IRMC Project (Instituto Geológico y Minero de España: 2294-2013), CO2-Pore Project (Plan Nacional de España: 2009-10934, FEDER-UE), Minería XXI Project (CYTED: 310RT0402) and DIA-CO2 Projects I and II (CIUDEN: ALM/09/032 and ALM/12/028). Thanks are due to Roberto

Martínez, Félix Mateos, Luís González-Menéndez, Isabel Suárez and Ricardo Molinero for providing help in OIA techniques, SEM analysis, data acquisition, and statistical treatment for rock sample collection and to Timea Kovacs for her suggestions.

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Table 1. Total porosity of Utrillas sandstones (3 samples), before and after SC CO_2-brine exposure, measured by Optical Image Analysis (OIA). Average % is the average porosity of the 3 samples. *Uncertainly (1.25%) given by Oviedo- IGME Laboratory. Difference % is calculated as the variation in porosity % before and after CO_2-brine injection. Total Average % is the average of the differences between Porosity % before and after CO_2-brine injection.

	Before SC CO_2-brine		**After SC CO_2-brine**		**Porosity variation**		**Interpretation**
	Porosity %	Average %*	Porosity %	Average %*	Difference %	Total Average %	
Sample 1	18.18		22.05		3.87		
Sample 2	9.55	11.41±0.14	11.13	13.42±0.17	1.58	**2.01**	**Increase**
Sample 3	6.49		7.06		0.57		

Table 2. Chemical composition of natural brine before and after the experiment. *Uncertainty (10%) given by Madrid-IGME Laboratory (Water Analysis).

	Rock before CO_2 and brine (mg/L) *	Rock after CO_2 and brine (mg/L) *	Interpretation
Na^+	2378 ± 237.80	2351 ± 235.10	No change
K^+	139 ± 13.90	114 ± 11.40	No change
Ca^{2+}	570 ± 57.00	440 ± 44.00	Decrease: 30% (Δ = 130 mg/L)
Mg^{2+}	268 ± 26.80	200 ± 20.00	Decrease: 34% (Δ = 68 mg/L)
Cl^-	5200 ± 520	4640 ± 464.00	No change
SO_4^{2-}	624 ± 62.40	464 ± 46.40	Decrease: 34% (Δ = 160 mg/L)
HCO_3^-	14 ± 1.40	36 ± 3.60	Increase: 157% (Δ = 22 mg/L)
NO_3^-	1.1 ± 0.11	10 ± 0.10	Increase: 809% (Δ = 8.9 mg/L)
SiO_2	9.3 ± 0.93	8.3 ± 0.83	No change
pH	7.2 (pH. Unit.)	5.27 (pH. Unit.)	Decrease: 36% (Δ = 1.93)
Conductivity	15350 (μS/cm)	13650 (μS/cm)	Decrease: 20% (Δ = 1700 μS/cm)

Table 3. Chemical composition of whole rock (Utrillas sandstone) before and after the experiment. Uncertainty given by IGME Laboratory (XRF Analysis).

	Uncertainty (%)	Rock before CO_2 and brine (%)	Rock after CO_2 and brine (%)	Interpretation
SiO_2	8.20	97.15 ± 2.5260	96.81 ± 2.5430	No change
Al_2O_3	11.57	0.98 ± 0.1135	1.12 ± 0.1300	No change
Fe_2O_3	9.55	0.30 ± 0.0290	0.28 ± 0.0270	No change
MnO	9.31	0	0	No change
MgO	7.96	0.03 ± 0.0025	0.04 ± 0.0030	Increase: 33% (Δ = 0.01 mg/L)
CaO	6.80	0.04 ± 0.0030	0.12 ± 0.0080	Increase:200%(Δ = 0.08 mg/L)
Na_2O	8.20	0.05 ± 0.0040	0.06 ± 0.0050	Increase: 20% (Δ = 0.01 mg/L)
K_2O	19.94	0.08 ± 0.0160	0.08 ± 0.0160	No change
TiO_2	8.37	0.03 ± 0.0025	0.03 ± 0.0025	No change
P_2O_5	10.95	0.01 ± 0.0010	0.01 ± 0.0010	No change
LOI	12.00	0.48 ± 0.0540	0.64 ± 0.0770	Increase: 33% (Δ = 0.16 mg/L)
TOTAL		99.16	99.20	

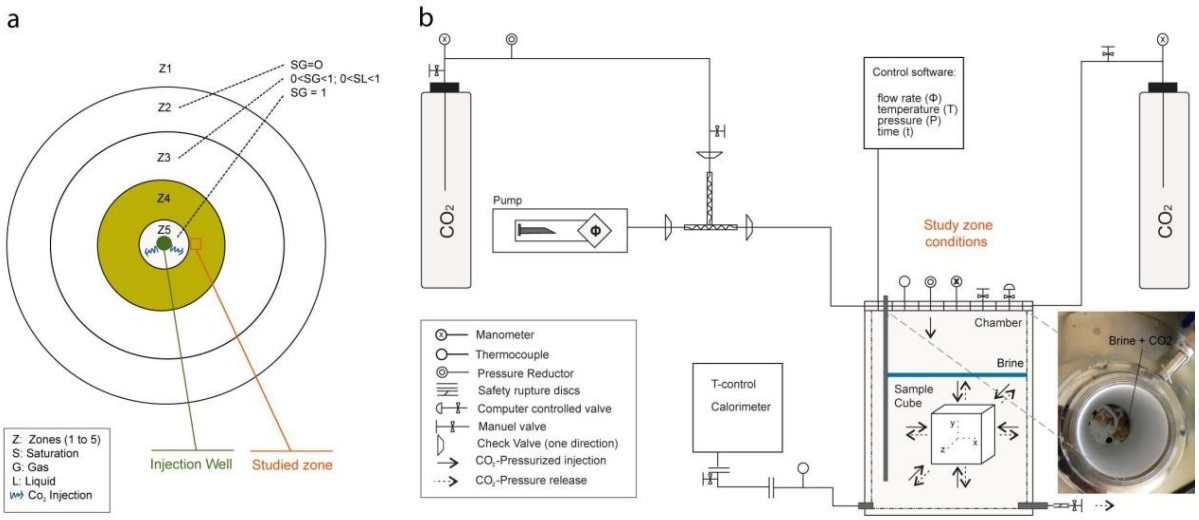

Figure 1. (a) Conceptual diagram of the reactive zones (Z1, Z2, Z3, Z4 and Z5) around the injection well acording to André et al., 2007 and Gaus et al., 2008. Zone 1: Zone not affected by CO_2 injection; Zone 2: Acicified zone with dissolution and precipition of minerals. Zone 3: Dissolution and precipitation of minerals (e.g. calcite and dolomite) and highly buffered pH. Zone 4: Highly saline water and salt precipitation (e.g. NaCl and Ma_2SO_4). Zone 5: Dehydratation reactions in open systems. (b) Layout of the experimental setup. Reactor system used for the pressurized CO_2 injection (modified from Berrezueta et al., 2013).

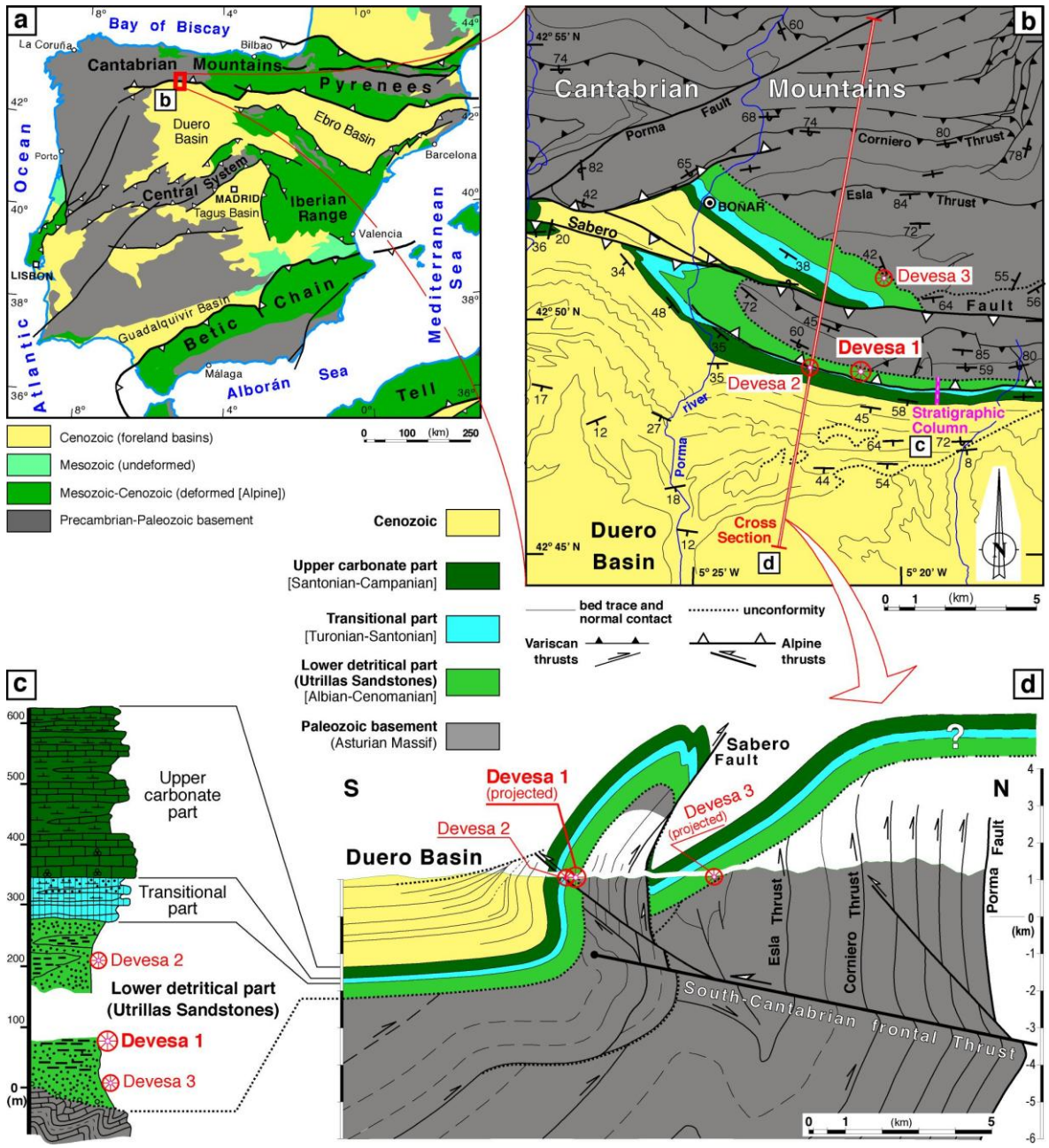

Figure 2. a) Location of the studied area in North Spain; modified from Quintana et al. (submitted) b) Geological map and location of the sampling areas modified from Lobato et al. (1985), Manjón Rubio et al. (1982b) and Alonso et al. (1996). c) Stratigraphic column of the Cretaceous succession of the studied area. Location in "b". Manjón Rubio et al. (1982b). d) Geological cross-section along the sampling areas: boundary between the Cantabrian Mountains and the Duero Basin. The geometry of the South Cantabrian frontal thrust and of the Cenozoic materials of the Duero Basin taken from Alonso et al. (1996). Location in "b".

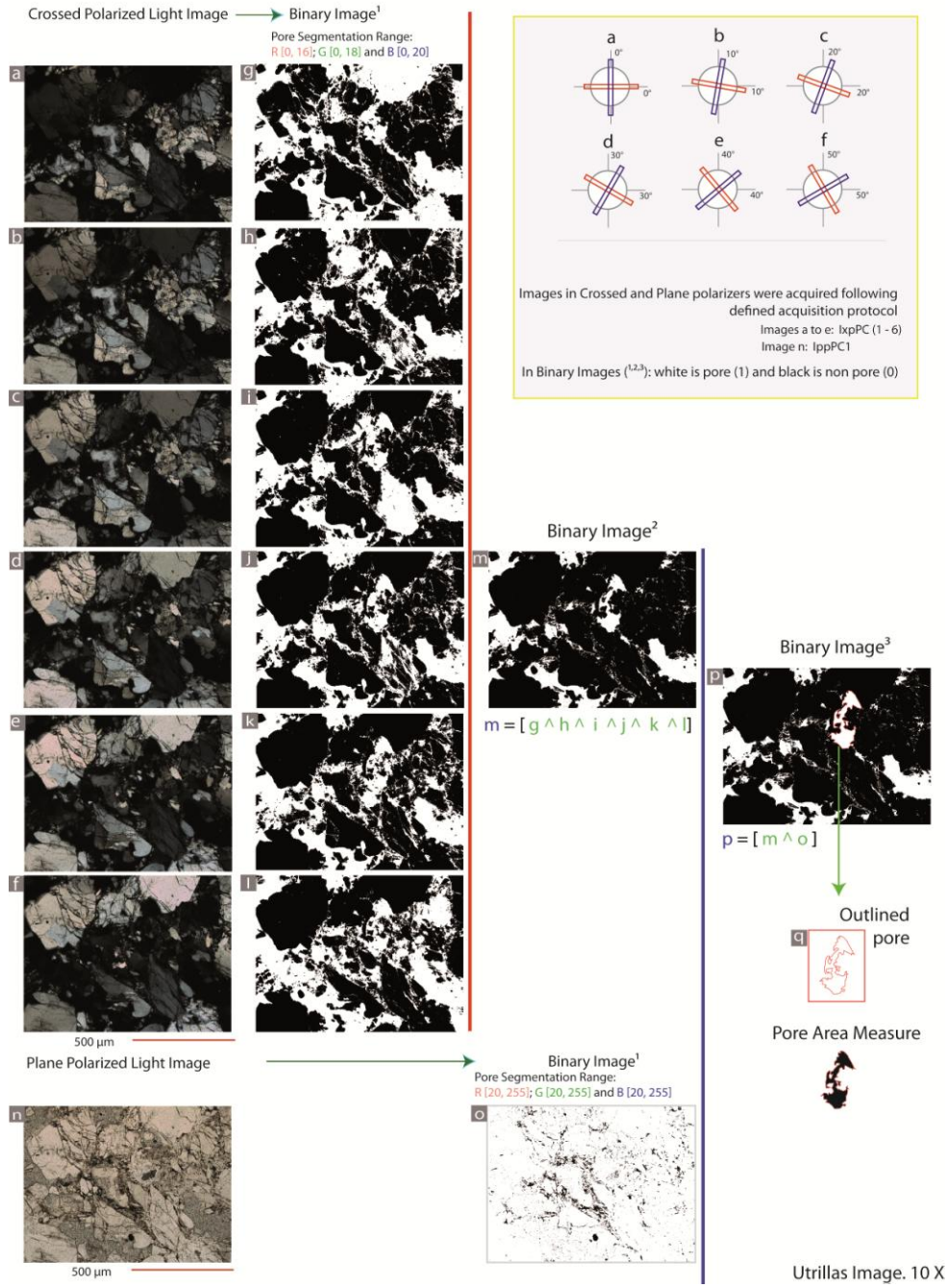

Figure 3. Schematic representation of the sequence of pore segmentation and pore area quantification performed on digital images (modified from Berrezueta el al., 2015) of the studied Utrillas sandstone. a to f) Images under cross polarized light conditions. g to l) Binary images[1] obtained using pore segmentation ranges: R(0-16); G(0-18) and B(0-20). m) Binary image[2] obtained by the interception of binary images[1] (g to l). n) Image under plane polarized light conditions. o) Binary image[1] obtained using pore segmentation ranges: R(20-255); G(20-255) and B(20-255). p) Binary image[3] obtained by the interception of binary images m and o. q) Pore outlined image.

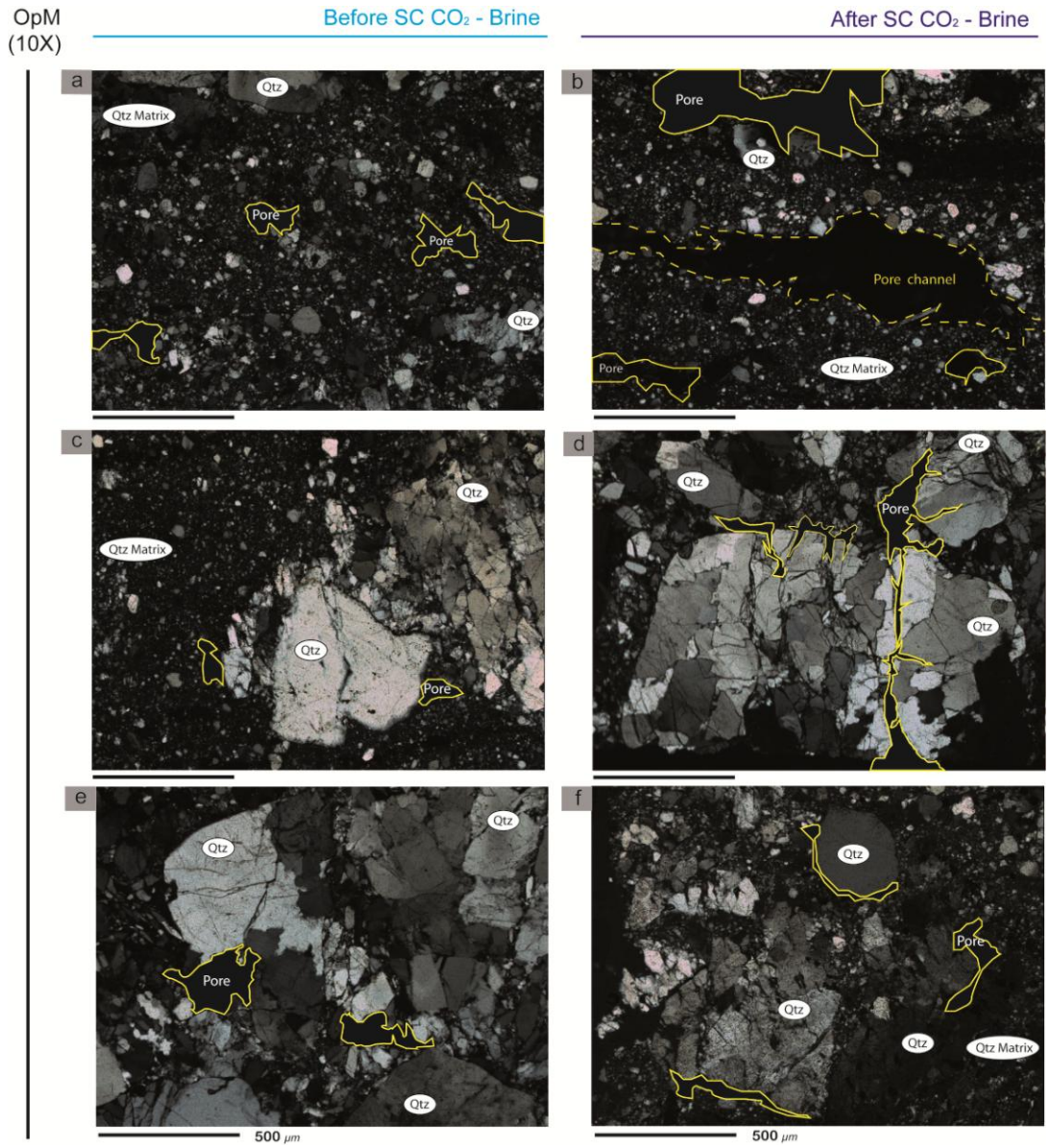

Figure 4. Textural and mineralogical characterization of the Utrillas sandstones. Optical microscopy images obtained under cross-polarized light conditions acquired using objective lens of 10x. Left images (a, c and e) correspond to samples before SC CO_2 injection; showing the main textural and mineralogical features corresponding to quartz grains and sandy matrix and intercrystalline pores within the matrix or in the vicinity of skeletal quartz grains. Right images (b, d and f) correspond to samples after SC CO_2 injection; showing no changes in the mineralogical features and a pore network characterized by the presence of channels, caverns and pores within large quartz grains.

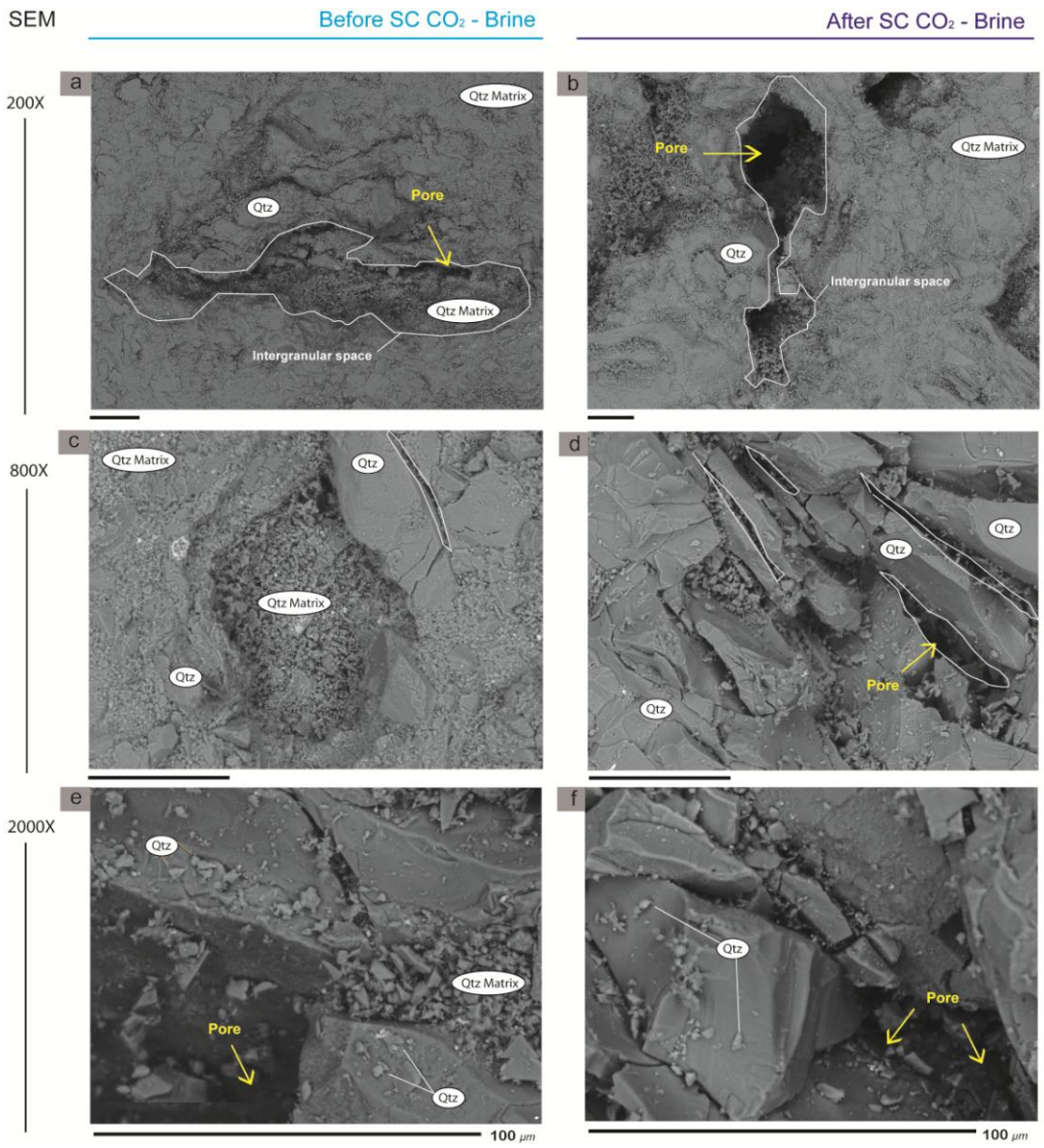

Figure 5. Secondary electron SEM micrographs of the Utrillas sandstones. Left images (a, c and e) correspond to samples before SC CO_2 injection. Right images (b, d and f) correspond to samples after SC CO_2 injection. a) Intergranular space filled with minerals; b) intergranular spaces constituted by cavern pores interconnected by micro-channels with pore spaces sometimes filled with minerals; c) intercrystalline space; d) high degree of fracturation of quartz grains; e) the edges of quartz grains in the starting material (before CO_2-brine exposure) contain angular pits; f) pits in quartz from the experiment are less numerous and distinctly rounded and enlarged.

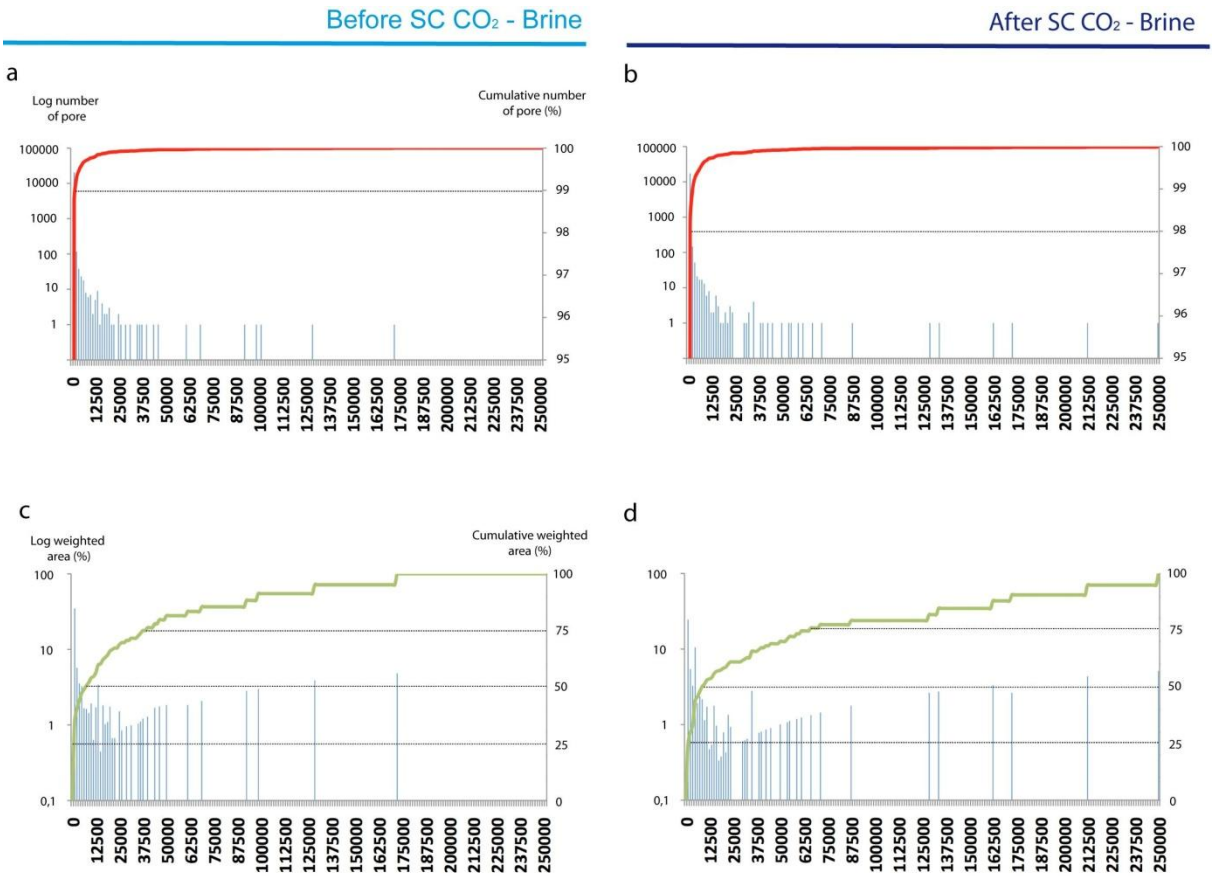

Figure 6. (a) X-axis *vs* left Y-axis: frequency diagrams of number of pores (Log scale) related to pore area classes (µm^2) before CO_2 injection (blue bars). X-axis *vs* right Y-axis: cumulative number of pores (%) related to pore area (µm^2) (red symbols). Red dashed line represents the contribution of the first class of pore area. (b) X-axis *vs* left Y-axis: frequency diagrams of weighted pore area (Log scale) related to pore area (µm^2) after CO_2 injection (blue bars). X-axis *vs* right Y-axis: cumulative weighted pore area (%) related to pore area classes (µm^2) (green symbols). Black dashed lines represent percentiles 25, 50, 75. c) X-axis *vs* left Y-axis: frequency diagrams of number of pores (Log scale) related to pore area (µm^2) before CO_2 injection (blue bars). X-axis *vs* right Y-axis: cumulative number of pores (%) related to pore area (µm^2) (red symbols). Red dashed line represents the contribution of the first class to pore area. d) x *vs* left y axis: frequency diagrams of weighted pore area (Log scale) related to pore area (µm^2) after CO_2 injection (blue bars). X-axis *vs* right Y-axis: cumulative weighted pore area (%) related to pore area classes (µm^2) (green symbols). Black dashed lines represent percentiles 25, 50, 75. Minimum pore size considered in the study is > 9 µm^2.

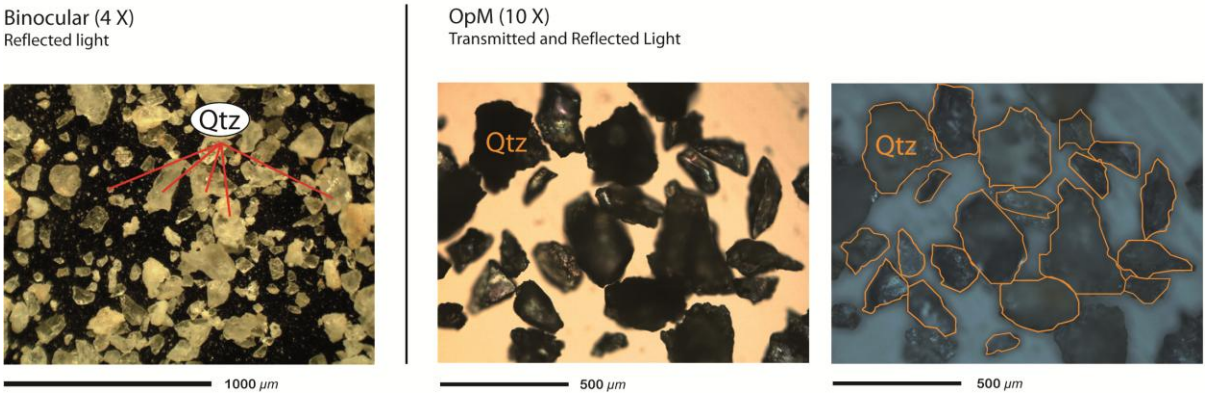

Figure 7. Photomicrographs by binocular microscope (reflected light) and by optical microscope (transmitted and reflected light) of the residue that remained in the reactor chamber after the experiment.

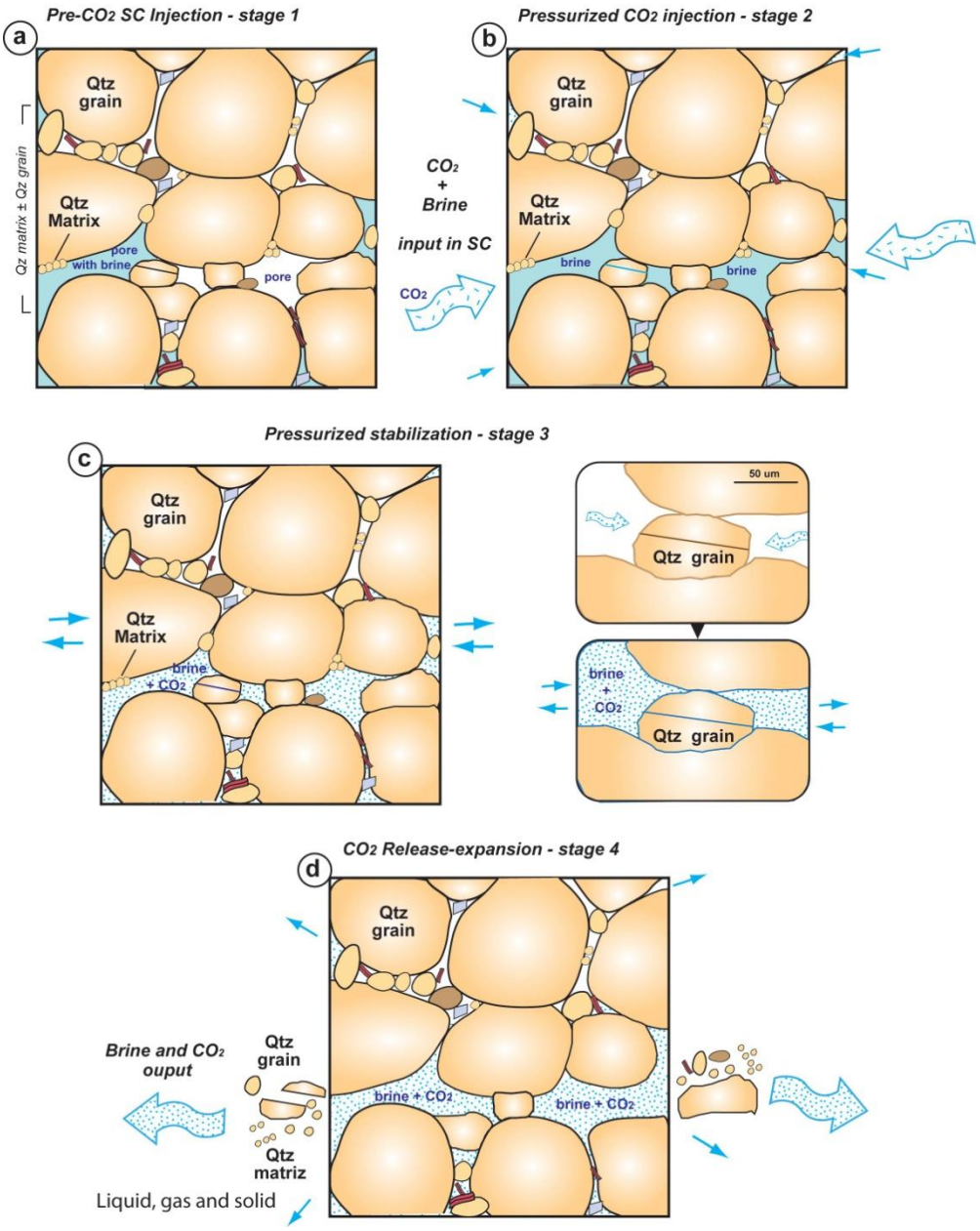

Figure 8. Scheme of the model developed from the observed mineralogical/textural changes after the SC CO_2 injection in the Utrillas sandstones. As a summary: (a) initial mineralogy and texture of the sandstones: quartz is the 95% of the rock sample and brine partially fills some intergranular spaces. b) When the pressurized SC CO_2 injection begins, the injected gas fills the pore network (pores filled with brine and empty pores). c) During supercritical experimental stage, the pressurized CO_2 and brine is accommodated inside quartz grains (small fractures) and in the contacts between quartz, producing instability in the original rock cohesion. d) When the pressure releases, at the end stage of the experiment, CO_2 and brine expands generating more instability inside the sample, provoking an outwards drag force that causes leaks and may explain the observed quartz loss in the samples after the experiment.