

Qualitative and quantitative changes in detrital reservoir rocks caused by CO₂-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) CO₂ and brine. The effects of experimental injection of CO₂-rich brine 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 CO₂-rich brine was exposed to sandstones in a reactor chamber under realistic conditions of deep saline formations ($P \approx 7.8$ MPa, $T \approx 38$ °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 CO₂-rich 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. Complementary 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 petrographic study of contiguous sandstone samples (more external area of sample blocks) before and after CO₂-rich brine injection indicates an evolution of the pore network (porosity increase ≈ 2 %). Probably, this pore changes measured could be due to intergranular quartz matrix detachment and partial removal from the rock sample, considering them as the

1 early features produced by the CO₂-rich brine. Nevertheless, the whole rock and brine
2 chemical analyses after interaction with CO₂-rich brine do not present important changes in
3 the mineralogical and chemical configuration of the rock with respect to initial conditions,
4 ruling out relevant precipitation or dissolution at these early stages to rock-block scale. These
5 results, simulating the CO₂ injection near the injection well during the first phases (24 h)
6 indicate that, in this environment where CO₂ enrich the brine, the mixture principally
7 generates local mineralogical/textural re-adjustments on the external area of the samples
8 studied.

9 The application of OpM, SEM and Optical image analysis have allowed an exhaustive
10 characterization of the sandstones studied. The procedure followed, the porosity
11 characterization and the chemical analysis allowed a preliminary approximation of the CO₂-
12 brine-rock interactions and could be applied to similar experimental injection tests.

13

14 **Key Word:** CO₂ storage, Utrillas sandstones, applied petrology, pore changes.

15

16 **1 Introduction and objectives**

17 The capture and geological sequestration of CO₂ is one of the technological options currently
18 contemplated to reduce emissions of greenhouse gases into the atmosphere. Deep geological
19 storage in porous rock formations is considered the most appropriate strategy for CO₂
20 sequestration (Bachu, 2000; Izgec et al., 2008; Benson and Cole, 2008; Gaus, 2010) and
21 injectivity is a key technical and economic issue for carbon capture and storage (CCS)
22 projects (Bacci et al., 2011). The viability of the CO₂ injection depends mainly on the porosity
23 and permeability of reservoir rocks. CO₂ interaction with the host rock, such as dissolution or
24 precipitation of minerals is also important (e.g. Ross et al., 1982; Sayegh et al.; 1990 and
25 Saeedi et al., 2011), as well as mineral trapping (Kaszuba et al., 2003; Rosenbauer et al.,
26 2005; Liu et al., 2013). Dissolution of supercritical (SC) CO₂ into brine will control the rate of
27 dissolution and precipitation of minerals constituting the porous rock. Volume changes of the
28 solid phase will modify the pore structure, affecting both porosity and permeability of the
29 porous media (André et al., 2007).

30 CO₂-water-rock interaction experiments represent a useful method to understand and explore
31 the mechanisms and processes of geological storage (Ketzer et al., 2009) and to design safe

1 underground CO₂ storage operations. Bertier et al. (2006) built an experimental setup to
2 evaluate the effect of CO₂-water-rock interactions in three sandstone aquifers concluding that
3 “CO₂-water-rock interactions might significantly influence geological sequestration of CO₂”.
4 Most of the experimental and theoretical studies are designed to simulate the injection of CO₂,
5 mixed with brine, into rocks at P-T conditions of deep storage environments. The result of
6 many of these experiments was an increase in the porosity/permeability of the reservoir rock
7 caused by partial dissolution of the carbonate components (mainly calcite) (Perkins and
8 Gunter, 1995; Svec and Grigg, 2001; Rochelle et al., 2004; Egermann et al., 2005; Izgec et al.,
9 2005; Gunter et al., 2004, Luquot and Gouze, 2009 and Desbois et al., 2011). However, other
10 set of experiments has shown porosity decreases due to the initial dissolution of carbonates
11 followed by secondary precipitation/mineralisation (Kaszuba et al., 2003; Cailly et al., 2005;
12 Kaszuba et al., 2005; Mito et al., 2008; Sterpenich et al., 2009; Luquot and Gouze, 2009).
13 André et al. (2007) presented numerical modelling of chemical fluid-rock interactions at the
14 SC-CO₂-liquid interface during CO₂ injection into a carbonate reservoir (Paris Basin, France).
15 In this case, two CO₂ injection scenarios were evaluated: CO₂-saturated water injection and
16 pure supercritical CO₂ injection. In these two scenarios, different geochemical processes
17 occurred as the distance from the injection well increased (in the first scenario there was a
18 porosity increase of up to 90%; while, in the second scenario porosity increased about 6% in
19 most of the reservoir and it decreased in the vicinity of the injection point). Besides, different
20 regions were identified depending on the saturation ranges of liquid and gas phases,
21 associated geochemical conditions and porosity variations during the injection and according
22 to the distance from the injection well (Fig. 1a).

23 Other investigations focus on the CO₂ injection into potential reservoir rock formations under
24 dry conditions (Kaszuba et al., 2003; Vickerd et al., 2006 and Berrezueta et al., 2013). The
25 injection environment is mainly envisaged as injecting CO₂ mixed with brine into sandstones.
26 However, in near-well conditions, the supercritical CO₂ laterally displaces the brine and
27 occupies the pore space of the rocks, in either dry or near-dry conditions (André et al., 2007;
28 Burton et al., 2008; Luquot and Gouze, 2009; Gaus, 2010). Therefore, dry CO₂ interaction
29 with the storage rock is a realistic scenario that takes place during the initial injection stages.
30 Some theoretical studies (Gaus et al., 2008 and Gaus, 2010) and experimental results
31 (Sterpenich et al., 2009) on dry CO₂-rock interactions indicate the absence of reactions and
32 consequently negligible textural-mineralogical changes. This is explained by the lack of H₂O
33 in the system that prevents dissolution/precipitation and any kind of chemical reactions.

1 However, experimental studies on dry-CO₂ injection into undersaturated sandstones with high
2 clay matrix content (Berrezueta et al., 2013) concluded in an increase of rock porosity,
3 causing a textural change. This was explained by detachment and partial removal of the
4 intergranular clay matrix from the sandstone samples due to supercritical CO₂ input/release
5 dragging and changes in electrical-polarity forces.

6 Our research is focussed on experimental injection of supercritical CO₂ into the selected rocks
7 (sandstones saturated by and covered with brine), similarly to previous works e.g. **Tarkowski**
8 **and Wdowin (2011)**, **Fischer et al. (2013)**, Wdowin et al., (2014a, b) and Tarkowski et al.,
9 (2015). We chose the Utrillas sandstones for the present study due to their importance as
10 potential CO₂ reservoirs in Spain. The lithological characteristics of the Utrillas sandstones
11 and the structural features of the area offer favourable conditions for the study of CO₂ storage
12 (García Lobón et al. 2010 and Martínez et al., 2013).

13 The selected P-T conditions and run-times of our experiments aim to reproduce the reservoir
14 rock dry-wet environment, adjacent to a theoretical injection borehole, (Fig. 1a and b),
15 specifically, at the interface between the supercritical CO₂ bubble and the aqueous solution.
16 This interface acts as an exchange zone where CO₂ diffuses constantly (e.g. Zone 4 defined by
17 André et al., 2007). The experimental P-T conditions were selected to guarantee that the CO₂
18 was over its supercritical point (Holloway 1997; Bachu 2000; Lake 1989; Span and Wagner
19 1996).

20 Furthermore, the textural-mineralogical and petrophysical changes in the rock samples are
21 studied before and after the experimental injection of supercritical CO₂ for a short period of
22 time (24 hours). Special care was put into the development of a **simplified** model to explain
23 the observed changes. Optical image analysis (OIA) techniques were used to monitor these
24 changes.

25

26 **2 Samples: geological setting**

27 The studied samples belong to the unit commonly known as Utrillas sandstones and locally
28 defined as Voznuevo Formation (Evers, 1967) of Upper Albian-Lower Cenomanian age
29 (Lower-Upper Cretaceous transition). The sampling took place in North Spain, at the
30 boundary between the Alpine Cantabrian Mountains and the Cenozoic Duero Basin (Fig. 2a).
31 The Utrillas sandstones belong to a 1100 m thick Cretaceous sequence and crop out near

1 Boñar village in North León province. This Cretaceous sequence lays unconformably on the
2 Paleozoic basement of the Variscan Cantabrian Zone. On top of the Cretaceous sequence, a
3 succession of almost 2500 m thick Cenozoic materials was deposited in the Duero Basin (Fig.
4 2d). The Cretaceous sequence has been divided into three parts (Manjón Rubio et al., 1982a):
5 1) a lower detrital part, which corresponds to the Utrillas sandstones, of continental origin;
6 2) an intermediate or transitional part of Turonian-Santonian age; and 3) an upper carbonate
7 part with limestones and marls of Santonian-Campanian age and marine origin (Fig. 2c). This
8 Cretaceous sequence was deposited in a post-rift stage, at the end of the Cretaceous
9 extensional phase that affected North Spain and produced the opening of the Bay of Biscay
10 (e.g. Gallastegui, 2000).

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

21 The fluvial environment, in which the Utrillas sandstones were formed, represents the
22 proximal part of the Upper Cretaceous North-Iberian paleomargin. Towards the north, this
23 fluvial facies changed into deltaic facies, then talus facies and, finally, deep basin turbiditic
24 facies (Olive Davó et al., 1989). This paleomargin was deformed during the collision between
25 Iberia and Eurasia in Cenozoic times. This compressional event produced the uplift of the
26 Cantabrian Mountains in North Spain and the development of the Duero foreland basin in the
27 frontal part of the range (Alonso et al., 1996). The structure of the sampling area is relatively
28 simple and is characterized by a great monocline (Fig. 2d), the formation of which has been
29 related with a south-directed basement thrust inclined to the north (Alonso et al., 1996). In
30 detail the structure is more complex because the inclined limb of the monocline is disrupted
31 by an important fault, known as the Sabero Fault (Sabero-Gordón line of Rupke, 1965), that
32 produces the duplication of the Cretaceous sequence (Figs. 2b and d).

1 The Utrillas sandstone was sampled in three places of the complex inclined limb of the
2 monocline, in the area of Devesa of Boñar, performing a thorough study of the structure of
3 these target rocks and their seals (Figs. 2b, d and e). The sampling areas “Devesa 1” and
4 “Devesa 2” are located south of the Sabero Fault, in an outcrop of Cretaceous succession
5 dipping 80° towards the south. The sampling area “Devesa 3” is located north of the Sabero
6 Fault in an outcrop dipping 45° also southwards (Figs. 2b and d). For this study, we chose the
7 more consolidated sandstones (3 samples), located in “Devesa 1”, to guarantee the
8 effectiveness of the analysis. The unconsolidated sandstones of Devesa 2 and 3 were
9 discarded for the study. The samples were divided into adjoining and numbered sets of
10 blocks. Each couple of adjoining blocks was used for the experimental test and for the studies
11 before and after CO₂ injection.

12

13 **3 Methodology and experimental procedure**

14 **3.1 Experimental setup and procedure**

15 The experimental setup employed in this experiment (Fig. 1b) is based on similar systems
16 described by Luquot and Gouze (2009), Tarkowski and Wdowin (2011), Luquot et al. (2012),
17 Berrezueta et al. (2013) and Wdowin et al. (2014a, b). However, some modifications were
18 made due to the distinct characteristics of the target rock system. Sample material (rock type
19 and representative sample size), geological environment (pressure, temperature and salinity)
20 and technical equipment (materials for camera, software, pumps, etc.) were all considered for
21 the final arrangement of the experimental device and run conditions. The experiment consists
22 of the exposure of sandstones to CO₂-rich brine in a reactor with pressure and temperature
23 control. P/T conditions (7.8 MPa and 38° C, respectively) were selected to surpass the CO₂
24 supercritical point (Lake 1989; Span and Wagner 1996) and to simulate basic conditions of
25 injection and storage of CO₂ (Holloway 1997; Bachu 2000). These conditions are
26 representative of a depth of approx. 800 m. The selected exposure time (24 h) is meant to
27 model the first stage of injection. The brine used in the experiments is natural brine from a
28 borehole from a saline aquifer.

29 The system (Fig. 1b) has two CO₂ cylinders (standard industrial CO₂ at 4.5 MPa) that are
30 linked to the other elements of the system by steel connectors (diameter: 5 mm). The second
31 CO₂ cylinder is connected to a piston pump that operates with a flow of 0.01 g/s. When the

1 required pressure (7.8 MPa) decreases (due to possible leaks), this pump will inject CO₂ to
2 keep the pressure within the desired values. The piston pump needs a CO₂ initial pressure of 1
3 MPa in order to inject CO₂ into the Hastelloy steel chamber (3 dm³), thereby, the pressure
4 between the piston pump and the second CO₂ cylinder has to be decreased by a pressure
5 manometer from 4.5 to 1 MPa. The inside of the chamber is coated with
6 polytetrafluoroethylene (PTFE) to protect the material against corrosion. At the bottom of the
7 chamber, a calorimeter controls the internal temperature. The calorimeter and the pump are
8 linked to the chamber with pressure and temperature sensors and are connected to a computer.

9 The experiments began with the saturation of rock samples (6 cubes of 27 cm³ of sandstone
10 sample) with natural brine by 3 cycles during 72 h. 0.3 dm³ of this brine was extracted and
11 analysed before CO₂-rich brine exposition occurs. Then, the rock samples (6 cubes of 27 cm³
12 of sandstone sample) were introduced into the chamber and fully immersed in the rest of brine
13 (0.3 dm³) and at the end of the experiments analyzed and noted “after CO₂-rich brine”. The
14 experimental runs comprised: a) a pressurized CO₂ injection (3 h); b) a pressurized
15 stabilization (24 h, no CO₂ flow inside the chamber) and c) CO₂ pressure release (3 h). The
16 CO₂ injection was performed using a constrained hyperbaric chamber-reactor where the dry
17 CO₂ was pumped at pressures and temperatures of 7.8 MPa and 38°C, respectively. The times
18 of filling and emptying the chamber with supercritical CO₂ were the same (3 h), following the
19 chamber’s manufacturer recommendations. This is the time required to reach the target
20 pressure and temperature values, from the initial ambient conditions. The same time was used
21 to get back to the ambient conditions at the end of the experimental test. The applied software,
22 HEL 5.1, allows the remote control of the system (experimental conditions) through the
23 development of specific macros (pressure, temperature, time) in real time. All the
24 experimental runs were carried out in the laboratories of the Geological Survey of Spain
25 (IGME) in Tres Cantos, Madrid.

26 **3.2 Methodology of study**

27 The aim of the study was to quantify the possible textural and porosity changes due to
28 experimental CO₂ injection. We began with a detailed petrographic study using optical
29 microscopy (OpM) to identify the major mineral and textural features. The characterization
30 was performed in neighbouring areas of the blocks by OpM (30 µm thin sections) and
31 scanning electron microscopy (SEM, rock samples). Although the thin sections and SEM
32 samples do not exactly correspond to the same sample surface, they are located very close (a

1 few mm) in the original source-sample. The aim of the detailed OpM study and quantification
2 of mineralogical and textural variability was to verify that any changes observed in the
3 experiments were due to the effects of CO₂ effect and not to possible original heterogeneity.
4 Furthermore, chemical analysis of the brine and whole rock before and after SC CO₂ injection
5 were performed, as well as microscopic studies of the residue that remained in the reactor
6 chamber after the experiment.

7 Simultaneously, a detailed study of the configuration of porous system was conducted by
8 combining observation by scanning electron microscopy with backscattered electrons (SEM)
9 and optical image analysis (OIA). This method allows the study of pore size distribution and
10 other porosity parameters (shape, specific surface of pore, etc.). Later, the same procedure
11 was followed for the study of the SC CO₂ exposed rocks. The OIA technique makes it
12 possible to identify, characterize and quantify mineral elements in images captured digitally
13 (Fig. 3) before and after SC CO₂-brine exposure. The general procedure for the automated
14 image analysis was developed adapting the procedures and algorithms described by
15 Berrezueta et al. (2015), in order to quantify the textural and porosity changes (area,
16 roughness of minerals/pore boundaries, fractal dimension, roundness of minerals/pores and
17 porosity) provoked by experimental CO₂ injection. Assessment of pore-network distribution
18 by optical transmitted light studies of thin sections requires distinction between mineral and
19 pore networks according to their optical characteristics. The segmentation of the porous
20 system was made by regions, applying the “thresholding” segmentation method (based on
21 threshold values to turn a raw image into a binary one, the pixels being partitioned according
22 to their intensity value). In this way, we can quantify the evolution of small changes in the
23 configuration of pore network. This work was carried out in the Oviedo IGME laboratory
24 using a Leica DM 6000 polarization microscope and an Image Pro Plus-7.0 software and
25 ProgRes digital camera for pore network study by OIA. SEM studies were performed using a
26 Hitachi TM3000 microscope with X-ray microanalysis equipment.

27 Additionally, rock samples were analysed by X-ray fluorescence (XRF) and X-ray diffraction
28 (XRD), and brine composition was determined by several methods (ion chromatography,
29 ICP-OES, pH, conductivity measurements). The studies were developed in the facilities of
30 IGME laboratory-Tres Cantos and Oviedo University. **Laboratory and elements analysed**
31 **were limited/conditioned to techniques available.**

32

1 4 Results

2 4.1 Mineralogical and petrographic characterization and OIA pore-network 3 quantification

4 4.1.1 Samples before SC CO₂ injection

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

1 The porous system reaches estimated visual proportions of 8 to 15%. Adapting Choquette and
2 Pray (1970) and Lucia (1999) porosity nomenclatures for carbonates, various pore types were
3 identified. “Vuggy” pore type, corresponding to highly spherical and rounded pores with sizes
4 around 50-90 μm are common. “Intercrystalline” type pores were also observed. These are
5 irregularly shaped around skeletal grains with very rounded edges, possibly a product of
6 matrix solution. They present elongated shapes and sizes ranging from 140-220 μm up to 300
7 μm . There are also incipient “cavernous” type pores, with elongated shapes, of sizes of ca. 80-
8 170, even 550 μm . In addition, there are “fracture” type pores. The sizes of these pores
9 generally reach 80-200 μm but there are some larger elongated caverns (ca. 1400 μm).
10 “Protected” porosity below some quartz grains (500 μm) was also observed. The
11 mineralogical and pore network distribution has been corroborated by SEM observation (Figs.
12 5a, c, and e).

13 The pore network quantification by OIA (Table 1) was carried out in three thin sections with
14 images acquired with a magnification of 10x. The porosity percentage estimated by this
15 method ranges from 6.49 to 18.18% with an average of $11.41 \pm 0.14\%$. The maximum and
16 minimum area of pore was 172100 μm^2 and 9.2 μm^2 , respectively. The average pore area size
17 was 168 μm^2 . Curves of relative and absolute distribution of number of pores versus pore area
18 ranges and diagrams of weighted area related to pore area classes are presented in Figs. 6a and
19 c for the samples before SC CO₂ injection.

20 **4.1.2 Samples after SC CO₂ injection**

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

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

15 The identified porosity is more abundant than in the samples before CO_2 injection. The
16 estimated visual percentage ranges from 12 to 18%. Adapting Choquette and Pray (1970) and
17 Lucía (1999) nomenclatures, there are various pore types present in the rock. Intercrystalline
18 pores between quartz grains with variable sizes (90-240 μm) were observed. The presence of
19 pores that are arranged in micro-fractures within quartz grains is also common. Cavern type
20 pores appear frequently, with irregular shapes and sizes varying from 700 to 1700 μm , up to
21 2900 μm . Sometimes they are interconnected by micro-channels. Caverns are generally larger
22 than in the sample before CO_2 injection. Sometimes, matrix rich bands show elongated
23 channel pores following the anisotropy with a maximum dimension of 4.8 mm. The SEM
24 studies (Figs. 5 b, d, and f) showed again intergranular spaces constituted by cavern pores
25 interconnected by micro-channels and pore spaces sometimes filled with minerals.
26 Furthermore, the high degree of fracturing leads to fracture type pore development.

27 The pore network quantification by OIA was developed, as previously described, on digital
28 images acquired using objective lens of 10x. The estimated porosity percentage ranges from
29 7.06 to 22.05% (Table 1), with an average of $13.42 \pm 0.17\%$. The maximum area of pore was
30 $250,000 \mu\text{m}^2$ and the minimum was $9 \mu\text{m}^2$. The average pore area size was $278 \mu\text{m}^2$. Curves
31 of relative and absolute distribution of number of pores versus pore area ranges and diagrams

1 of weighted area related to pore area classes are presented in Figs. 6b and d for the samples
2 after SC CO₂ injection.

3 **4.2 Chemical analysis**

4 The **chemical** composition of the brine was analyzed before and after the 24h testing and the
5 results are shown in Table 2. The data of brine composition before and after experimental
6 CO₂ injection show that there were some changes in the chemistry (higher than the total
7 uncertainty of the technique ≈ 10%): a decrease (ca. 30%) of the Ca²⁺, Mg²⁺ and SO₄²⁻
8 contents and an increase on the HCO₃⁻ and NO₃⁻ contents. Other chemical parameters also
9 decreased as a result of the CO₂ injection: the pH changed from 7.2 to 5.27 and the
10 conductivity also decreased around 12%.

11 Total rock analyses were performed on blocks with and without experimental CO₂-brine
12 exposure. The values and uncertainties are presented in Table 3. There were changes in the
13 following contents: increase of MgO (30%), Na₂O (20%) and CaO (ca. 200%). We
14 considered as significant a change over the uncertainties given by the laboratory for each
15 element, which uncertainty values range from 6.8 to 19.9% depending on the element. Two
16 samples were analysed by XRD, one previous to brine exposure and to SC CO₂ injection and
17 the other after the SC CO₂-brine experiment. These analyses only detected quartz, the other
18 phases being present in quantities below the detection limit of this technique. Furthermore,
19 the residue that remained in the chamber of the reactor after the experiment was studied (Fig.
20 7). This residue consisted mainly of quartz in two different fractions: a fine fraction with sizes
21 around 20µm and another fraction with rounded quartz grains sometimes reaching 1mm in
22 size.

23

24 **5 Discussion**

25 In the studied Utrillas sandstones, OpM and SEM techniques allowed us to detect qualitative
26 changes in the pore network in the samples before and after SC CO₂ injection. Compared to
27 the pre-experiment samples, we can point out that, in general, after the experiment larger
28 pores are more common (700-1800 µm) and cavern type pores and channels dominate (Figs. 4
29 a-b and 5 a-b). There is also an increase of grain fracturing (Figs. 4c and d; Figs. 5c and d).
30 Moreover, the edges of quartz grains before the experiment contain angular pits (Fig. 5e),

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

3 Quantification of these changes was systematically carried out applying OIA (Fig. 3). This
4 study reveals an increase of porosity (Δn) of 0.57-1.58-3.87% with an average of 2.01%
5 (Table 1), which value is higher than the uncertainty of the OIA technique (25%)
6 (Demirmen, 1972; Grove and Jerram, 2011). The lower error of this method as compared to
7 others is one of the advantages of the OIA technique (e.g. error of point counting is around
8 2.5%; Chayes and Faibain, 1951; Grove and Jerram, 2011).

9 The OIA technique also allowed us a complete characterization of the pore network through
10 curves of relative and absolute distribution of the number of pores versus pore area ranges
11 (Fig. 6) and diagrams of weighted area related to pore area classes for samples before and
12 after SC CO₂ injection. The pore area ranges measured by OIA are between 9 μm^2 and
13 250,000 μm^2 . The distribution of data shows that $\approx 99\%$ of pores correspond to pores smaller
14 than 1250 μm^2 (Fig. 6a). In the CO₂ injected sample (Fig. 6b) these small pores represent \approx
15 98% of all the pores. The diagrams of the weighted area related to pore area classes before
16 (Fig. 6c) and after SC CO₂ injection (Fig. 6d) show that the contribution of the first class of
17 pore area is ca. 35% of the total porosity for pre-experiment samples and ca. 25% of the total
18 porosity for samples after the experiment. The approximate contributions of cumulative
19 weighted pore area for the main percentiles for the sample before SC CO₂ injection are: <
20 1,250 μm^2 (25%), 7,500 μm^2 (50%), and 38,750 μm^2 (75%). On the other hand, the sample
21 after injection shows contributions of 25% of pore area of 1,250 μm^2 , 50% of 8,750 μm^2 , and
22 75% of 65,000 μm^2 . In general, in the original samples there are more pores of smaller and
23 intermediate pore area classes than in the ones after the injection. Besides, the maximum sizes
24 of pore area are larger in the injected samples, **similarly, Tarkowski and Wdowin (2011)**
25 **described an increase in the mean pore diameters in their studies.**

26 The brine chemistry study showed that Na⁺, K⁺, Cl⁻ and SiO₂ values did not suffer any
27 relevant changes after the injection. On the other hand, the Ca²⁺, Mg²⁺ and SO₄²⁻ content
28 decreased by approx. 30% (Table 2), probably all as a result of local mineral precipitation of
29 Mg, Ca and Na minerals (e.g. gypsum.), evidenced by an increase of these oxides in the
30 chemistry of the rock after the experiment (Table 3).

31 The brine chemistry data, in relative terms is similar to those found in the literature (Kaszuba
32 et al., 2005), but different to the analysis completed by **Tarkowski and Wdowin (2011)**;

1 Luquot et al., (2012); Yu et al., (2012) and Wdowin et al., (2014a, b). According to them,
2 dissolution of clay and feldspar of the matrix could take place due CO₂-rich brine. In this
3 case, K⁺ Na⁺, Si⁺ could be releases but they do not show relevant variation in the brine
4 analysis after CO₂.

5 This is probably due to the initial composition of our samples, conditioned by the chemically
6 resistant quartz (95% wt.), the short period of our experimentation (24 h) and that interaction
7 between CO₂-rich brine is limited to external area of the block sandstones studied. We can say
8 that preliminarily CO₂-brine contact with the rock initiated some mineral precipitation though
9 not to a relevant scale. It also caused brine pH reduction (changing from 7.2 to 5.2), similarly
10 to other cases (Kaszuba et al., 2005; Tarkowski and Wdowin, 2011). The pH reduction is due
11 to the increase of carbonic acid and NO₃⁻ content of the brine after the experiment (Table 2).
12 The higher amount of carbonic acid originates from the CO₂ dissolution in the brine, and
13 could allow carbonation and formation of CaCO₃ and MgCO₃ due to the depressurization
14 process followed, while that of the NO₃⁻ may be due to reactions with organic material present
15 in the rock sample. The overall data of the total rock composition of before and after SC CO₂-
16 brine exposure do not show important precipitation/dissolution of mineral phases. We can
17 conclude that the reactions between minerals and fluids were not significant (Gunter et al.,
18 1997 and Hitchon, 1996) and the changes in the porosity configuration measured (Table 1),
19 are limited to external areas of the sandstone blocks exposed to CO₂-rich brine and probably
20 due to local chemical changes; and may represent the early physical display of the chemical
21 influence of the CO₂-rich brine on the rock.

22 The observed and measured changes in the studied samples are due to the CO₂-rich brine
23 exposure and can be of importance in the vicinity of the injection well (Fig. 1a) where the
24 interaction of the CO₂ and the rock takes place initially in wet conditions (Kharaka et al.
25 2006; Gaus, 2010; André et al., 2007). Any modification in mineralogy and porosity (Figs. 4,
26 5 and Table 1) changing the rock texture could affect the injection well and its closest
27 environment and hence the injection efficiency (Wdowin et al., 2014a). Our experimental
28 investigation indicates that the main effects observed after the experiment are relevant to the
29 pore network characteristics and quantification, while changes regarding chemical
30 characteristics of the brine and total rock are minor. The initial heterogeneity of the rock
31 could condition the comparison of physical and chemical parameters between the before and
32 after CO₂ injection tests samples, as described by Tarkowski and Wdowin (2011) and

1 Wdowin et al. (2014b). In our study we tried to minimize this effect studying rock surfaces
2 few millimetres separation and employing expert criteria in petrography.

3 The porosity changes observed could be understood by the following simplified conceptual
4 model (Figs. 8a to d). The CO₂-rich brine interaction with saturated samples produces a
5 change in the external surface of the sandstone blocks. These effects resulted in a partial loss
6 of the quartz (both skeletal grains and matrix), present as residue after the experiment (Fig. 7).
7 Our conceptual model consists of four stages.

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

10 • Stage 2 (Fig. 8b): pressurized SC CO₂ injection: initial CO₂ input would enrich the brine
11 with CO₂ (at subcritical CO₂ conditions), in which the samples are immersed. This CO₂-rich
12 brine will interact with the rock and the brine that is inside the pore network.

13 • Stage 3 (Fig. 8c): pressurized CO₂/CO₂-rich brine stabilization: this stage extends through
14 most of the experimental run (24 h). During this time, CO₂-rich brine continues interacting
15 with the rock and brine in the pores under SC CO₂ conditions.

16 Stage 4 (Fig. 8d): CO₂/CO₂-rich brine pressure and temperature decrease to ambient
17 conditions: CO₂-rich brine will continue to interact with the rock until ambient conditions are
18 reached.

19 During this phase there is a leak of quartz particles and matrix that were collected in the
20 chamber when the experiment was finished. Furthermore, internal quartz breakdown and
21 generation of free micro-quartz grains (Figs 4b, d and f; Figs. 5b, d and f) were observed by
22 OpM.

23 This model (at thin section scale of surface block rocks), explains how the changes identified
24 by OpM, SEM Figs. 4 and 5, probably were originated by the chemical influence of the CO₂-
25 rich brine on the saturated rocks. In particular the action of CO₂-rich brine could produce a
26 de-cohesion/dissolution of the matrix, leading an increase in the porosity. The chemical
27 analyses (0.27 dm³ rock blocks and 0.3 dm³ brines) did not showed up major
28 dissolution/precipitation processes at these early stages, probably also due to an effect of the
29 scale of analysis.

30

1 6 Conclusions

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

5 The proposed methodology, consisting of mineralogical and petrographic studies by OpM,
6 SEM and OIA techniques on sandstones subjected to CO₂-rich brine exposure (7.8 MPa, 38°
7 C, during 24 h), proved to be highly effective for the identification and measurement of
8 changes in the pore network. For this study, the Utrillas sandstones were selected due to their
9 potential as CO₂ reservoir in Spain. However, the same methodology could be applicable for
10 future studies considering other rock types, different CO₂ storage conditions or longer periods
11 of exposure time.

12 The influence of the original rock composition and texture is very important and leads to
13 different effects of the CO₂-rich brine exposure. The study of potential changes at rock matrix
14 scale depends on the facies variations of any sedimentary formation, when evaluating a
15 possible CO₂ reservoir. The facies studied in this work is characterized by 95% quartz content
16 and heterogeneous rock texture, where micro-channels in the quartz matrix areas favour the
17 SC CO₂-brine injection resulting in the development of bigger cavities and pore channels. The
18 main pore evolution measured by OIA was an increase of porosity (2.01 %) and a
19 readjustment of pore network distribution regarding pore size classes.

20 The chemical-compositional evolution of the analysed elements did not evidence significant
21 mineralogical processes. Supercritical CO₂ causes brine pH to decrease as a consequence of
22 carbonic acid increase. Some improvements would allow understand the chemical processes
23 occurring in the experiments: e.g. number of analyses, elements to analyze, accuracy of
24 techniques and use of PHREEQC models.

25 The results of this experiment show that the changes occurred due to chemical interaction of
26 the acidified brine allowing a rough approximation of the CO₂-brine-rock interactions.
27 Furthermore, these changes may have an important impact on the behaviour of reservoir rocks
28 during first injection phases of SC CO₂: i) changes in the rock system that lead to the porosity
29 evolution could facilitate further CO₂ injection, ii) mobilization of solid material (quartz)
30 should be considered during experiments and/or future modelling of the reservoir.

31

1 **Acknowledgements**

2 The authors would like to thank the funding provided through the ALGECO2-IRMC Project
3 (Instituto Geológico y Minero de España: 2294-2013), CO2-Pore Project (Plan Nacional de
4 España: 2009-10934, FEDER-UE), Minería XXI Project (CYTED: 310RT0402) and DIA-
5 CO2 Projects I and II (CIUDEN: ALM/09/032 and ALM/12/028). Thanks are due to Roberto
6 Martínez, Félix Mateos, Luís González-Menéndez, Isabel Suárez and Ricardo Molinero for
7 providing help in OIA techniques, SEM analysis, data acquisition, and statistical treatment for
8 rock sample collection and to Timea Kovacs for her suggestions.

9

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- 22
- 23

1 **Table 1.** Total porosity of Utrillas sandstones (3 samples), before and after SC CO₂-brine
 2 exposure, measured by Optical Image Analysis (OIA). Average % is the average porosity of
 3 the 3 samples. *Uncertainly (1.25%) given by Oviedo- IGME Laboratory. Difference % is
 4 calculated as the variation in porosity % before and after CO₂-brine injection. Total Average
 5 % is the average of the differences between Porosity % before and after CO₂-brine injection.

6

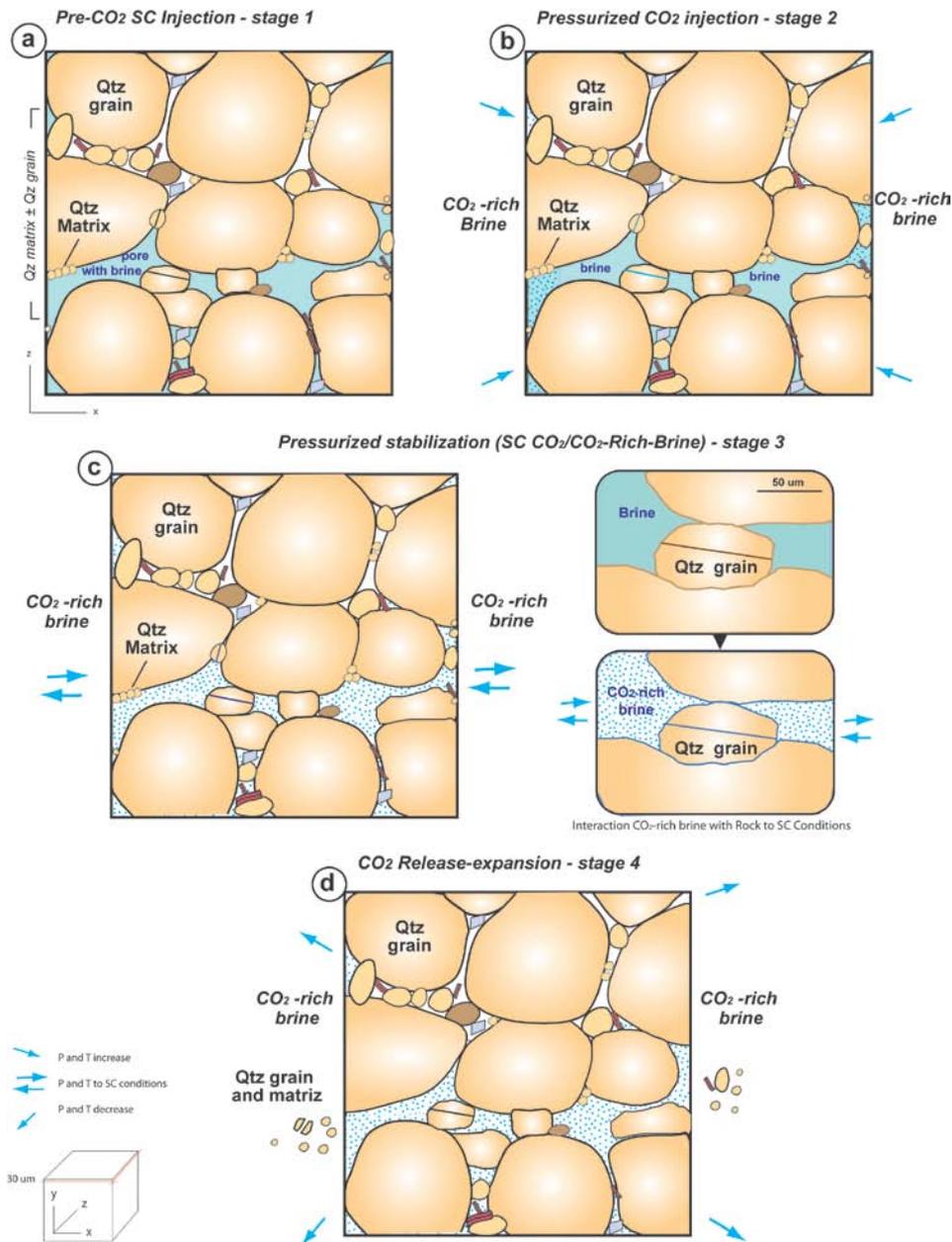
	Before CO ₂ -rich brine		After CO ₂ -rich brine		Porosity variation		Interpretation
	Porosity %	Average %*	Porosity %	Average %*	Difference %	Total Average %	
Sample 1	18.18		22.05		3.87		
Sample 2	9.55	11.41±0.14	11.13	13.42±0.17	1.58	2.01	Increase
Sample 3	6.49		7.06		0.57		

7

8 **Table 2.** Chemical composition of natural brine before and after the experiment. *Uncertainty
 9 (10%) given by Madrid-IGME Laboratory (Water Analysis).

10

	Brine before CO ₂ (mg/L) *	Brine after CO ₂ (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	5.27	Decrease: 36% (Δ = 1.93)
Conductivity	15350 (μS/cm)	13650 (μS/cm)	Decrease: 20% (Δ = 1700 μS/cm)



1
 2 **Figure 8.** Scheme of a simplified model developed from the observed mineralogical/textural
 3 changes after the SC CO₂ injection in the Utrillas sandstones. As a summary: (a) initial
 4 mineralogy and texture of the sandstones: quartz is the 95% of the rock sample and brine
 5 filling intergranular spaces. b) When the pressurized SC CO₂ injection begins, the injected gas
 6 acidified the brine (CO₂-rich brine) and it interacts with the rock and the brine that is inside
 7 the pore network. c) During supercritical experimental stage, the pressurized CO₂-rich brine
 8 and brine interact under SC conditions producing instability in the original rock cohesion
 9 probably due to local chemical changes. d) When the pressure releases, at the end stage of the
 10 experiment, may produce the leaks of quartz particles and matrix.