

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. In case of

1 gas leakage in the chamber during the experiment, this pump maintains the experimental
2 pressure (7.8 MPa). The piston pump needs a CO₂ initial pressure of 1 MPa in order to inject
3 CO₂ into the Hastelloy steel chamber (3 dm³), thereby, the pressure between the piston pump
4 and the second CO₂ cylinder has to be decreased by a pressure manometer from 4.5 to 1 MPa.
5 The inside of the chamber is coated with polytetrafluoroethylene (PTFE) to protect the
6 material against corrosion. At the bottom of the chamber, a calorimeter controls the internal
7 temperature. The calorimeter and the pump are linked to the chamber with pressure and
8 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, from ambient conditions to
15 supercritical condition); b) a pressurized stabilization (24 h, no CO₂ flow inside the chamber)
16 and c) CO₂ pressure release (3 h, from supercritical conditions to ambient conditions). In
17 general, the presence of non-dissolved SC CO₂ in the brine was not in contact with the rock.
18 This occupied the top of the test chamber. Sample+brine+CO₂ were up to supercritical
19 conditions for 24 hours. Sample+brine+CO₂ were 6 hours in conditions below 38°C and 7.8
20 MPa.

21 The CO₂ injection was performed using a constrained hyperbaric chamber-reactor where the
22 dry CO₂ was pumped at pressures and temperatures of 7.8 MPa and 38°C, respectively. The
23 times of filling and emptying the chamber with supercritical CO₂ were the same (3 h),
24 following the chamber’s manufacturer recommendations. This is the time required to reach
25 the target pressure and temperature values, from the initial ambient conditions. The same time
26 was used to get back to the ambient conditions at the end of the experimental test. The applied
27 software, HEL 5.1, allows the remote control of the system (experimental conditions) through
28 the development of specific macros (pressure, temperature, time) in real time. All the
29 experimental runs were carried out in the laboratories of the Geological Survey of Spain
30 (IGME) in Tres Cantos, Madrid.

1 **3.2 Methodology of study**

2 The aim of the study was to quantify the possible textural and porosity changes due to
3 experimental CO₂ injection. We began with a detailed petrographic study using optical
4 microscopy (OpM) to identify the major mineral and textural features. The characterization
5 was performed in neighbouring areas of the blocks by OpM (30 μm thin sections) and
6 scanning electron microscopy (SEM, rock samples). Although the thin sections and SEM
7 samples do not exactly correspond to the same sample surface, they are located very close (a
8 few mm) in the original source-sample. The aim of the detailed OpM study and quantification
9 of mineralogical and textural variability was to verify that any changes observed in the
10 experiments were due to the effects of CO₂ effect and not to possible original heterogeneity.
11 Furthermore, chemical analysis of the brine and whole rock before and after SC CO₂ injection
12 were performed, as well as microscopic studies of the residue that remained in the reactor
13 chamber after the experiment.

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

1 ProgRes digital camera for pore network study by OIA. SEM studies were performed using a
2 Hitachi TM3000 microscope with X-ray microanalysis equipment.

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

8

9 **4 Results**

10 **4.1 Mineralogical and petrographic characterization and OIA pore-network** 11 **quantification**

12 **4.1.1 Samples before SC CO₂ injection**

13 The studied rock is a medium to very coarse-grained sandstone (grain size from 90-1600 µm,
14 with a mode of 250 µm) with areas of fine to medium grain sizes, showing unoriented and
15 slightly to highly variable porous structure. The pores, that are 80-500 µm (up to 1400 µm) in
16 size, constitute up to 8 to 15% of the rock volume, although there are special areas with
17 porosity up to 20%. The grains are from moderately to poorly sorted. There are zones with a
18 slight anisotropy defined by the presence of matrix rich bands. The grain skeleton (Fig. 4a, c
19 and e) consists of quartz (> 95%), very minor potassium feldspars (orthoclase) and a small
20 amount of micas (muscovite and chlorite). Accessory minerals (a total of 1-5%) are opaque
21 minerals, such as iron oxides and hydroxides (hematite and limonite), in the form of
22 aggregates of 40-100 µm in size, dispersed in the matrix or as cement. Other accessory
23 minerals are brown and green tourmalines and zircon. The rock is composed mainly by grain
24 skeleton supported with a small proportion of matrix (< 5%) composed mostly by quartz and
25 minor phyllosilicates of the mica and clay groups (muscovite and/or illite and/or kaolinite)
26 and opaque minerals. Locally, cement is present as a film coating iron oxides and syntaxial
27 quartz. According to the Folk (1974) and Pettijohn et al. (1987) classification, it is a quartz-
28 arenite (> 95% of quartz). Some areas have higher matrix concentration (>15%) classified as
29 fine-medium grained quartz-greywacke. The quartz grains are mostly monocrystalline with
30 important size variability. The grains have angular to subangular shapes, from high to low

1 sphericity and with sizes ranging from 90 to 1400 μm . Moreover very rounded grains of
2 polycrystalline quartz (fairly minor amount) appear sometimes with a Fe oxide coating. They
3 are of significant size (900-1900 μm). Grains with internal crystals of $> 30 \mu\text{m}$ size are the
4 most common. On the other hand, there are some polycrystalline quartz grains with elongated
5 shapes and large dimensions up to 2800 μm . Sometimes the internal crystalline units of the
6 polycrystalline quartz grains show preferred orientations (meta-quartzite origin). The internal
7 units can be of sizes $< 30 \mu\text{m}$ (chert) or up to 180-240 μm . The orthoclase feldspars are very
8 scarce, have rounded edges with sizes up to 1400 μm and show a significant degree of
9 alteration to iron oxides, phyllosilicates (illite and/or kaolinite) and chlorite.

10 The porous system reaches estimated visual proportions of 8 to 15%. Adapting Choquette and
11 Pray (1970) and Lucia (1999) porosity nomenclatures for carbonates, various pore types were
12 identified. “Vuggy” pore type, corresponding to highly spherical and rounded pores with sizes
13 around 50-90 μm are common. “Intercrystalline” type pores were also observed. These are
14 irregularly shaped around skeletal grains with very rounded edges, possibly a product of
15 matrix solution. They present elongated shapes and sizes ranging from 140-220 μm up to 300
16 μm . There are also incipient “cavernous” type pores, with elongated shapes, of sizes of ca. 80-
17 170, even 550 μm . In addition, there are “fracture” type pores. The sizes of these pores
18 generally reach 80-200 μm but there are some larger elongated caverns (ca. 1400 μm).
19 “Protected” porosity below some quartz grains (500 μm) was also observed. The
20 mineralogical and pore network distribution has been corroborated by SEM observation (Figs.
21 5a, c, and e).

22 The pore network quantification by OIA (Table 1) was carried out in three thin sections with
23 images acquired with a magnification of 10x. The porosity percentage estimated by this
24 method ranges from 6.49 to 18.18% with an average of $11.41 \pm 0.14\%$. The maximum and
25 minimum area of pore was $172100 \mu\text{m}^2$ and $9.2 \mu\text{m}^2$, respectively. The average pore area size
26 was $168 \mu\text{m}^2$. Curves of relative and absolute distribution of number of pores versus pore area
27 ranges and diagrams of weighted area related to pore area classes are presented in Figs. 6a and
28 c for the samples before SC CO₂ injection.

29 **4.1.2 Samples after SC CO₂ injection**

30 The studied rock is a medium to very coarse grained, poorly-sorted sandstone (particle size
31 from 300 μm to 1800 μm). It is slightly to highly porous with a porosity of 12 to 18% of the
32 rock volume and with pore size up to 2.5 mm. The grains vary from high to low spherical and

1 from subrounded to rounded shapes and it is noteworthy that the quartz grains have a high
2 degree of fracturing. The rock has scarce anisotropy, primarily defined by a band of higher
3 matrix concentration and opaque minerals (Fe oxides). The skeleton (Fig. 4b, d and f) consists
4 mostly of quartz grains (> 95%), scarce potassium feldspars (orthoclase) and small amounts
5 of mica (muscovite). Quartz grains show high degree of fracturing and are primarily
6 monocrystalline with high or low sphericity and rounded edges. Their sizes vary from 300 to
7 1800 μm . Sometimes they are of low sphericity with rounded edges or subangular shapes,
8 with sizes ranging from 240 to 1000 μm , even up to 2.4 mm. On the other hand,
9 polycrystalline quartz is present with internal crystal units < 30 μm , with elongated shapes,
10 rounded edges and grain sizes between 700-1400 μm . Other polycrystalline quartz grains are
11 rounded with sizes up to 1000-2400 μm with internal structural units > 30 μm . Orthoclase
12 feldspars are very rounded and quite spherical, with sizes up to 2.4 mm. They sometimes
13 show alteration containing Fe oxides and phyllosilicates (possibly illite and /or kaolinite).
14 Accessory minerals are opaque minerals (iron oxides associated to iron hydroxides). These
15 opaque minerals appear in the form of large grains surrounding the skeleton grains or as
16 smaller crystals scattered in the sandy-clay matrix or oriented at the edges of matrix rich
17 bands. Other accessory minerals are tourmaline and zircon. The matrix (< 15%) is composed
18 mainly by quartz and a small amount of phyllosilicates (possibly illite and/ or kaolinite and/or
19 smectite) and iron oxides. Opaque minerals are Fe oxides and hydroxides (hematite and
20 limonite) that are often associated with phyllosilicates (kaolinite and/or illite and/or smectite)
21 and mica (possibly muscovite). Based on the modal content of quartz, feldspars, lithoclasts
22 and matrix content the rock is classified as quartz-arenite and some areas with higher matrix
23 content (ca. 15%) as medium grained quartz-wacke (Folk 1974; Pettijohn et al.1987).

24 The identified porosity is more abundant than in the samples before CO₂ injection. The
25 estimated visual percentage ranges from 12 to 18%. Adapting Choquette and Pray (1970) and
26 Lucía (1999) nomenclatures, there are various pore types present in the rock. Intercrystalline
27 pores between quartz grains with variable sizes (90-240 μm) were observed. The presence of
28 pores that are arranged in micro-fractures within quartz grains is also common. Cavern type
29 pores appear frequently, with irregular shapes and sizes varying from 700 to 1700 μm , up to
30 2900 μm . Sometimes they are interconnected by micro-channels. Caverns are generally larger
31 than in the sample before CO₂ injection. Sometimes, matrix rich bands show elongated
32 channel pores following the anisotropy with a maximum dimension of 4.8 mm. The SEM
33 studies (Figs. 5 b, d, and f) showed again intergranular spaces constituted by cavern pores

1 interconnected by micro-channels and pore spaces sometimes filled with minerals.
2 Furthermore, the high degree of fracturing leads to fracture type pore development.

3 The pore network quantification by OIA was developed, as previously described, on digital
4 images acquired using objective lens of 10x. The estimated porosity percentage ranges from
5 7.06 to 22.05% (Table 1), with an average of $13.42 \pm 0.17\%$. The maximum area of pore was
6 $250,000 \mu\text{m}^2$ and the minimum was $9 \mu\text{m}^2$. The average pore area size was $278 \mu\text{m}^2$. Curves
7 of relative and absolute distribution of number of pores versus pore area ranges and diagrams
8 of weighted area related to pore area classes are presented in Figs. 6b and d for the samples
9 after SC CO₂ injection.

10 **4.2 Chemical analysis**

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

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

30

1 5 Discussion

2 In the studied Utrillas sandstones, OpM and SEM techniques allowed us to detect qualitative
3 changes in the pore network in the samples before and after SC CO₂ injection. Compared to
4 the pre-experiment samples, we can point out that, in general, after the experiment larger
5 pores are more common (700-1800 μm) and cavern type pores and channels dominate (Figs. 4
6 a-b and 5 a-b). There is also an increase of grain fracturing (Figs. 4c and d; Figs. 5c and d).
7 Moreover, the edges of quartz grains before the experiment contain angular pits (Fig. 5e),
8 while pits in quartz after the experiment are less numerous and distinctly rounded and
9 enlarged (Fig. 5f).

10 Quantification of these changes was systematically carried out applying OIA (Fig. 3). This
11 study reveals an increase of porosity (Δn) of 0.57-1.58-3.87% with an average of 2.01%
12 (Table 1), which value is higher than the uncertainty of the OIA technique (±5%)
13 (Demirmen, 1972; Grove and Jerram, 2011). The lower error of this method as compared to
14 others is one of the advantages of the OIA technique (e.g. error of point counting is around
15 2.5%; Chayes and Faibain, 1951; Grove and Jerram, 2011).

16 The OIA technique also allowed us a complete characterization of the pore network through
17 curves of relative and absolute distribution of the number of pores versus pore area ranges
18 (Fig. 6) and diagrams of weighted area related to pore area classes for samples before and
19 after SC CO₂ injection. The pore area ranges measured by OIA are between 9 μm² and
20 250,000 μm². The distribution of data shows that ≈ 99% of pores correspond to pores smaller
21 than 1250 μm² (Fig. 6a). In the CO₂ injected sample (Fig. 6b) these small pores represent ≈
22 98% of all the pores. The diagrams of the weighted area related to pore area classes before
23 (Fig. 6c) and after SC CO₂ injection (Fig. 6d) show that the contribution of the first class of
24 pore area is ca. 35% of the total porosity for pre-experiment samples and ca. 25% of the total
25 porosity for samples after the experiment. The approximate contributions of cumulative
26 weighted pore area for the main percentiles for the sample before SC CO₂ injection are: <
27 1,250 μm² (25%), 7,500 μm² (50%), and 38,750 μm² (75%). On the other hand, the sample
28 after injection shows contributions of 25% of pore area of 1,250 μm², 50% of 8,750 μm², and
29 75% of 65,000 μm². In general, in the original samples there are more pores of smaller and
30 intermediate pore area classes than in the ones after the injection. Besides, the maximum sizes
31 of pore area are larger in the injected samples, similarly, Tarkowski and Wdowin (2011)
32 described an increase in the mean pore diameters in their studies.

1 The brine chemistry study showed that Na^+ , K^+ , Cl^- and SiO_2 values did not suffer any
2 relevant changes after the injection. On the other hand, the Ca^{2+} , Mg^{2+} and SO_4^{2-} content
3 decreased by approx. 30% (Table 2), probably all as a result of local mineral precipitation of
4 Mg, Ca and Na minerals (e.g. gypsum.), evidenced by an increase of these oxides in the
5 chemistry of the rock after the experiment (Table 3).

6 The brine chemistry data, in relative terms is similar to those found in the literature (Kaszuba
7 et al., 2005), but different to the analysis completed by Tarkowski and Wdowin (2011);
8 Luquot et al., (2012); Yu et al., (2012) and Wdowin et al., (2014a, b). According to them,
9 dissolution of clay and feldspar of the matrix could take place due CO_2 -rich brine. In this
10 case, K^+ , Na^+ , Si^+ could be releases but they do not show relevant variation in the brine
11 analysis after CO_2 .

12 This is probably due to the initial composition of our samples, conditioned by the chemically
13 resistant quartz (95% wt.), the short period of our experimentation (24 h) and that interaction
14 between CO_2 -rich brine is limited to external area of the block sandstones studied. We can say
15 that preliminarily CO_2 -brine contact with the rock initiated some mineral precipitation though
16 not to a relevant scale. It also caused brine pH reduction (changing from 7.2 to 5.2), similarly
17 to other cases (Kaszuba et al., 2005; Tarkowski and Wdowin, 2011). **The measured pH (5.2)**
18 **is not representative of the solution pH during the experiment, as it was measured after the**
19 **experiment during depressurization (Table 2).** The pH reduction is due to the increase of
20 carbonic acid and NO_3^- content of the brine after the experiment (Table 2). The higher
21 amount of carbonic acid originates from the CO_2 dissolution in the brine, and could allow
22 carbonation and formation of CaCO_3 and MgCO_3 due to the depressurization process
23 followed, while that of the NO_3^- may be due to reactions with organic material present in the
24 rock sample. The overall data of the total rock composition of before and after SC CO_2 -brine
25 exposure do not show important precipitation/dissolution of mineral phases. We can conclude
26 that the reactions between minerals and fluids were not significant (Gunter et al., 1997 and
27 Hitchon, 1996) and the changes in the porosity configuration measured (Table 1), are limited
28 to external areas of the sandstone blocks exposed to CO_2 -rich brine and probably due to local
29 chemical changes; and may represent the early physical display of the chemical influence of
30 the CO_2 -rich brine on the rock.

31 The observed and measured changes in the studied samples are due to the CO_2 -rich brine
32 exposure and can be of importance in the vicinity of the injection well (Fig. 1a) where the

1 interaction of the CO₂ and the rock takes place initially in wet conditions (Kharaka et al.
2 2006; Gaus, 2010; André et al., 2007). Any modification in mineralogy and porosity (Figs. 4,
3 5 and Table 1) changing the rock texture could affect the injection well and its closest
4 environment and hence the injection efficiency (Wdowin et al., 2014a). Our experimental
5 investigation indicates that the main effects observed after the experiment are relevant to the
6 pore network characteristics and quantification, while changes regarding chemical
7 characteristics of the brine and total rock are minor. The initial heterogeneity of the rock
8 could condition the comparison of physical and chemical parameters between the before and
9 after CO₂ injection tests samples, as described by Tarkowski and Wdowin (2011) and
10 Wdowin et al. (2014b). In our study we tried to minimize this effect studying rock surfaces
11 few millimetres separation and employing expert criteria in petrography.

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

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

19 Stage 2 (Fig. 8b): pressurized SC CO₂ injection: initial CO₂ input would enrich the brine with
20 CO₂ (at subcritical CO₂ conditions), in which the samples are immersed. This CO₂-rich brine
21 will interact with the rock and the brine that is inside the pore network. **We assume that the
22 acidified brine interacts with the brine that is filling the pores. The low compressibility
23 coefficient of a fluid in the case of an increase of pressure and temperature (as in this
24 experiment) does not favour displacements of the fluid.**

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

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

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

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

12

13 **6 Conclusions**

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

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

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

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

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

12

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21

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