Pore network quantification of sandstones under experimental CO₂ injection using image analysis

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Article info

Article history:
Received 16 June 2014
Received in revised form 9 January 2015
Accepted 9 January 2015
Available online 12 January 2015

Keywords:
Image analysis
Porosity
Pore network
Petrography
Rock texture
CO₂-injection.

Abstract

Automated-image identification and quantification of minerals, pores and textures together with petrographic analysis can be applied to improve pore system characterization in sedimentary rocks. Our case study is focused on the application of these techniques to study the evolution of rock pore network subjected to super critical CO₂-injection. We have proposed a Digital Image Analysis (DIA) protocol that guarantees measurement reproducibility and reliability. This can be summarized in the following stages: (i) detailed description of mineralogy and texture (before and after CO₂-injection) by optical and scanning electron microscopy (SEM) techniques using thin sections; (ii) adjustment and calibration of DIA tools; (iii) data acquisition protocol based on image capture with different polarization conditions (synchronized movement of polarizers); (iv) study and quantification by DIA that allow (a) identification and isolation of pixels that belong to the same category: minerals vs. pores in each sample and (b) measurement of changes in pore network, after the samples have been exposed to new conditions (in our case: SC-CO₂-injection). Finally, interpretation of the petrography and the measured data by an automated approach were done.

In our applied study, the DIA results highlight the changes observed by SEM and microscopic techniques, which consisted in a porosity increase when CO₂ treatment occurs. Other additional changes were minor: variations in the roughness and roundness of pore edges, and pore aspect ratio, shown in the bigger pore population. Additionally, statistic tests of pore parameters measured were applied to verify that the differences observed between samples before and after CO₂-injection were significant.

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1. Introduction

Automated identification and quantification of mineral phases, textures and porosity are important tools for petrographic characterization of rock samples. Despite the conventional qualitative mineralogy-texture studies performed by optical and SEM microscopy techniques, a more detailed understanding of the rock properties (mineral/pore areas, perimeters, etc.) is desirable in some geological studies. This requires a quantitative petrography procedure which is the object of this contribution. Quantitative assessment of petrography is an essential part of geosciences works as it provides a key to the successful interpretation of rock texture and mineralogy (Higgins, 2006).

Image analysis represents an important advance over traditional techniques (point counting) to automate the characterization of objects in digital-images (Berrezueta and Castroviejo, 2007; Castroviejo et al., 2002; Ehrlich et al., 1984; Grove and Jerram, 2011; Pirard et al., 1999; Russ, 1992). Measurements made from 2D sections, which form the basis of this work, record the porosity as resolvable from an optical image of the sample (total optical porosity).

Nevertheless, application of image analysis in automated identification of mineral phases in images taken from a petrographic microscope has limitations (Fabbri, 1984; Laneau et al., 1994; Petruk, 1989; Pfeiderer et al., 1992; Starkey and Samantaray, 1993). The main problem is that in plane-polarized light (PP) many minerals are colorless, whilst in cross-polarized light (XP) the interference color depends on a variety of factors in addition to mineral type (Fueten and Mason, 2001). However, these circumstances are partially overcome, using a rotating polarizers stage specifically designed as an addition to standard optical-microscope, allowing the thin section to remain fixed while the polarizers are rotated (Fuenten, 1997; Thompson et al., 2001). A simplified method of rotating polarizer stage was applied by Tarquini and Favalli (2010) for petrographic analysis. They used images of
thin sections acquired under 4 directions of polarization (each 22.5°) together with an image without polarization. This approach enhanced the use of standard image processing techniques on thin sections for the segmentation, measurement and mineral identification.

According to Shapiro and Stockman (2001) and Martínez-Martínez et al. (2007), image segmentation is the process of partitioning a digital-image into multiple segments (sets of pixels) and involves identification and isolation of pixels that belong to a same category. Mineral grains identification by DIA is usually achieved by segmentation based on edges (Goodchild and Fueten, 1998; Heilbrunner, 2000; Lumbreras and Serrat, 1996; Starkey and Samantary, 1993), regions (Faugeras and Hebert, 1983; Medioni and Parvin, 1986) or combination of both (Pavlidis and Liow 1990; Zhou et al., 2004).

Nowadays some image processing tools are based on methods originated from the fields of pattern recognition and artificial intelligence. The accuracy of the automatic image segmentation methods has been severely compromised by the presence of shared edges of grains, despite the large number of distinct strategies like: (a) seed region growing (Choudhury et al., 2006), (b) Level Sets (Lu et al., 2009), partial differential equations (Lu and Ning, 2010), cellular automata (Gorsevski et al., 2012) and image foresting transform (Mingireanov Filho et al., 2013).

The identification and classification of porous system based on image analysis of thin sections represent a simple task compared to the difficulties for identification of anisotropic minerals (e.g. color changes or birefringence properties). The described method is based on distinguishing the pore-network from the mineral-network attending their mineralogical and petrographic characteristics, paying particular attention to the possibility that in some cases pore and mineral can show similar appearances. The segmentation of the porous system is 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 are dependent on their intensity value). In this way we can quantify the evolution of small changes in the configuration of pore network.

In this present paper, the application of DIA (Digital Image Analysis) is focused on quantifying changes in the pore system of sandstones before and after being exposed to supercritical CO₂ (SC-CO₂). Deep geological storage into rock porous formations is considered the most appropriate strategy for CO₂ sequestration (Benson and Cole, 2008; Gauss, 2010; Iżeg et al., 2008) and injectivity is a technical key and economic issue for Carbon Capture Sequestration projects (Bacci et al., 2011). The viability of the CO₂-injection depends mainly on the porosity and permeability of storage rocks. Our research (Berrezueta et al., 2013) consisted of experimental injections of SC-CO₂ into rocks which are representative of potential storage reservoirs in Spain. The main result obtained was that physical and/or chemical changes due to CO₂ injection induce textural readjustments resulting in an increase of the micro porosity of the storage rocks. These studies allowed a mineralogical interpretation of variations in the pore system and the development of a conceptual model for the evolution of the textures. This work was therefore aimed at the mineralogical and petrographic study of the rocks before and after CO₂ injection and special care was put into the development of a model to explain the changes observed. DIA techniques were used to monitor the changes, although we had not established the full procedure in detail.

In the following sections, data acquisition methods and automated identification of porosity will be described and explained in detail. The application of the method proposed has permitted us to quantify the porosity changes occurred when rocks interact with CO₂ at supercritical conditions.

2. Materials and methods

2.1. Samples selection

Sampling of sedimentary rocks suitable for CO₂-injection was carried out in order to study the quantification of its pores. Two contiguous blocks were collected from the homogeneous sample and two from the heterogeneous one. One of each distinct sandstone blocks was subjected to experimental tests upon which CO₂ was injected to supercritical conditions and kept within the sample during ≈ 1000 h at P–T conditions of 75 bars and 35 °C (see Berrezueta et al. (2013) for details). The four block samples (two before and two after the experimental injections) were studied by optical and SEM microscopy to qualitatively monitor the textural and mineral changes by thin sections (30 μm thick) made in the contiguous part of the blocks.

The quantification of porosity changes in the untreated and CO₂-treated was initially attempted by point counting. This method did not show significant changes, probably due to the error of the technique. Furthermore, Hg-porosimetry technique was used to quantify the pore volume. This technique did not show changes in the pore volume, between the pre-CO₂ injected and post-CO₂ injected samples. Thus, pore network changes identified by optical and SEM microscopy were attempted to be quantified by DIA establishing a systematic protocol.

The performance of DIA process was evaluated comparing the errors between DIA and point counting techniques. The sources of error could be (a) errors as a result of systematic observations of a thin section (counting error): result of counting observations being an estimate of the true area and not the true fraction, (b) The user introduced variability (operator error): result of misidentification, inconsistent identification, mistakes. (c) The error encountered when using a 2D slice to estimate volume percentage in the hand sample (specimen error), in our study this error was equivalent for DIA and point counting techniques as we used the same samples. The errors due to systematic observations (counting errors) and the interoperator variability (operator error) in point counting and DIA have been sourced from the literature (Chayes and Fairbairn, 1951; Demirmen, 1971; Galehouse (1971); Griffiths and Rosenfeld, 1954; Grove and Jerram, 2011). For point counting, Grove and Jerram (2011) calculated counting errors to 95.4% confidence level (2σ) counting five hundred points for each thin section (10 operators, 14 thin sections, and measuring porosity area) produced counting errors of 2.55%. Chayes and Fairbairn (1951) using 5 operators, 10 thin sections and measuring quartz area calculated a counting error of 2.6%. Grove and Jerram (2011), taking into account the DIA pore area analysis on thin sections (10 operators, 14 thin sections, and measuring porosity area), calculated counting errors of 0.039 (area %). In the case of operator error (1σ) for point counting Chayes and Fairbairn (1951), using 5 operators, 10 thin sections and measuring quartz area calculated an operator error of 2.5% of area. Griffiths and Rosenfeld (1954) using 5 operators, 3 thin sections and measuring quartz area calculated an operator error of 1.2%. Demirmen (1972) (using 8 operators, 5 thin sections and measuring limestone constituent’s area), calculated an operator error of 1.2%. Operator error in DIA calculated for (Grove and Jerram, 2011), 10 operators, 14 thin sections, and measuring porosity area proposed an error of 1.2% of area. In our case, the total errors considered for point counting technique was 4.20% and 1.24% for the DIA technique.

2.2. Techniques

Optical transmitted light studies of thin sections applied to pore-network distribution require distinctions between mineral and pore networks according to their optical characteristics. The
minerals can be divided into transparent and opaque. To distinguish them, the optical characteristic used is the color (shown in PP), opaque minerals do not transmit light in thin sections whereas pores behave as transparent crystals and are colorless under PP.

The transparent minerals can be isotropic or anisotropic. We distinguish them under crossed-polarizers. Anisotropic minerals show birefringence, i.e. the polarized light is split into two rays with different velocities, when they emerge their combination produces interference colors (Fig. 1). The pores optically behave as isotropic under XP and show no birefringence. The basal sections (perpendicular to the optic axis) of some anisotropic mineral are isotropic, and they can be easily identified from the pores using PP images. Furthermore, pore spaces do not show any variation of light properties independently of their position or orientation of the pore.

Taking into account the optical properties of the pores/minerals DIA-techniques were applied to quantify the porosity changes (area, roughness, pore boundaries, etc.), resulting from experimental CO2-injection. The imaging system used is based on a Red, Green and Blue (RGB) color model (i.e. in a RGB image of 24 bits, gray levels (GL) which in an 8-bit image ranges from 0 to 255 for each R, G and B channels/bands). The use of RGB images in the pore identification allows the optimization of multichannel classification approach (Launeau et al., 1994), to facilitate the pore network identification by the user and to allow further identifications on colored minerals, through the acquired images.

A motorized and computer controlled microscope (Leica DM-6000) with a digital camera (ProgRes 5) was used. A routine was implemented (Image-Pro Plus) for microscope-camera control and for image acquisition. ProgRes C5 was a digital microscope camera (5.0 Megapixel CCD-Color-2/3", A/D conversion (max.) 3x8 Bit RGB, digital interface IEEE1394a firewire, optical interface C-Mount 0.63 × ). Leica-DM-6000 is an automated research microscope for material science. It has a fully automated upright microscope system (transmitted light, 12 V–100 W, halogen lamp, polarized light, constant color intensity control, stage and focus motorized). Image-Pro Plus–7.0 is software which includes the latest tools for scientific and industrial image analysis and image processing (captures, process, measure, share, visualize and compare). Image-Pro plus also supports ProgRes C5 cameras and Leica Microscopes.

An image processing and analysis sequence comprises of the following general steps (González and Woods, 1992; Pirard et al., 1999): Updating DIA tools, Image acquisition, segmentation, feature extraction and classification.

The following factors were considered to evaluate and adjust DIA tools (Pirard et al., 1999): noise, spatial and temporal drifts, color calibration, gain, white color fine tune and geometric calibration. Image acquisition has to be done in optimal conditions (camera stabilization, microscope light source stabilization, number of images on average). Once the DIA-equipment calibration was done, the image acquisition would be focused to highlight the optical properties of the pore network, for its automated identification. Following the idea of Tarquini and Favalli (2010), of simplifying the rotating polarizers stage proposed by Fueten (1997), we proposed the acquisition of multiple images (6 in crossed-polarizers and 1 in plane polarizers) of the same petrographic scene (considering scene as field of interest). Manual synchronized-change in the polarizers orientation would be every 10° (polarizers must always have 90° between them), which in turn, lead to resolve the pore network characterization of our sample. This approach generates a distinct answer in the minerals (birefringence). Meanwhile, pores would show constant GL values (i.e. gray values that are in an 8-bit image range from 0 to 255). The identification of a phase as a pore would require keeping the characteristics for the classification as a pore in all the images studied under cross-polarized light. In order to prevent a mineral in extinct state being considered a pore caused by similarity in GL range, PP images would then be taken.
Systematic automated quantification of pore-system has been based on the determination of segmentation ranges (maximum and minimum GL for R, G and B bands) which allows the identification and isolation of pixels that belong to a pore category. These supervised preset values were established by the sampling of 100 scenes (10 x 10 pixels) of known pore zones. These windows were considered for each of 7 different RGB images of the same mineral scene. Final pore segmentation ranges could be obtained for each RGB band of the selected scenes as average values of all the images. In XP, the gray values of the pores would remain constant (close to 10 for RGB bands). Likely, in PP pores would always have GL close to 235 for RGB bands.

Calculated segmentation ranges are saved in a macrofile (a set of instructions that is represented in an abbreviated format – Visual Basic) for implementing the ranges on the images and finding the identification and measurement of a pore system. The following step is to apply these segmentation ranges to all mineral images acquired for the study. The final pore classification results from intersection of the 7 pore partial segmentations (from 6 RGB images in PX and 1 in PP). Although the systematic is considered reproducible, it would be possible to use an interactive supervision to detect errors in the process (i.e. to avoid problems in the focus during image acquisition).

Given a classified image containing a set of pores, specific features could be used to measure them such as, area, roughness, roundness and pore aspect. The evolution of these parameters allows us to quantify changes or evolution of these features i.e. when CO₂ was injected.

The DIA results (before and after SC-CO₂-injection) were statistically tested. In general, in these sandstones, the pore area showed a lognormal distribution and other features (aspect ratio, roundness, roughness) showed normal distributions. We have converted the original area data to a normal distribution using a log transformation. We also applied Student’s t-distribution and Mann-Whitney U test using commercial software packages (SYSTAT®-11.0 for Windows (2004) and MINITAB®-15.0 for Windows (2006), to determine if there were significant changes in the pore area and shapes of pores (aspect ratio, roundness, roughness), between the pre- and post-CO₂ injection samples.

Further to this, we have used the null hypothesis of no changes in porosity. The p-value is the probability that there are no differences between samples (null hypothesis). If we set an α-value (significance level) at, for example, 0.1, then the null hypothesis would be rejected if the p-value is lower than this α-value (at 0.1) but at the risk of being wrong in 10% of the cases (Davis, 1986).

2.3. DIA procedure

Our main task was to provide quantitative petrographic data using two-dimensional images of thin sections to measure morphological parameters of pores and grain spaces. We propose a reproducible procedure to generate semi-automatic data acquisition, as well as to improve the classical petrographic studies dealing with the pore-network in sandstones.

2.3.1. Updating of DIA tools

According to Berrezueta and Castroviejo (2007), Olaya (2011) and Pirard (2004), DIA, as other techniques, is subject to errors.

<table>
<thead>
<tr>
<th>Table 1</th>
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<tr>
<td>Configuration (setting up) of the optical microscope and digital camera to ensure the reproducibility of the measurements to be performed on sandstones. The configuration parameters are stored in the DIA-software that controls the digital camera and the microscope. Modified from Berrezueta and Castroviejo (2007).</td>
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<tr>
<th>Element</th>
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<th>Complementary information</th>
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<td>Objectives that allow the optimal</td>
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<td>Lens: 1 x</td>
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<td>(pore) vs. field of</td>
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<td>Over-saturation of</td>
<td>Appropriate lighting to avoid</td>
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<td>transmitted light</td>
<td>saturation of images</td>
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<td>100 ms is the min period</td>
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<td>Electronic Noise</td>
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<td>2560 x 1920 VGA pixels</td>
<td>Geometrical calibration²</td>
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| Gray level (GL) | Min: 0 |
| Max: 255 |
and the total error is accumulated at each individual step of sampling and analysis. The updating of DIA tools including a digital camera and an optical microscope was necessary and had been done before the image-analysis planning in this study. A rigorous protocol for acquiring mineral images based on ad hoc experimentation was established in order to warrant the reproducibility of results (Table 1).

2.3.2. Image acquisition

RGB color-model image was acquired using the software bundled with the digital-camera/optical-microscope. To transform the information from the sensor into a digital-image, each cell-content was converted into a pixel value (intensity) ranging from black (0) to white (255). When the microscopy and the digital-camera were ready, all the necessary parameters were adjusted using a macro (instructions developed in the DIA-software using VisualBasic-6.0 language in Image-Pro Plus software). At which point, we could start the semi-automated digital-image acquisition in a macro by Image-Pro Plus program.

Fig. 2. Algorithm of semi-automatic acquisition of mineral images written in a macro by Image-Pro Plus program.

The procedure was as follows:

a) Region of the interest selection to study by manual focusing under cross-polarized light. We have studied the entire surface area of 4 thin sections one for each sample. The homogenous sample images were acquired using objective lenses 10 × (NA 0.225). 22 Scenes were studied for pre-CO2 sample and 25 from post- CO2 one. The heterogeneous sample images were acquired using objective lenses 4 × (NA 0.09). 13 Scenes were studied for the pre-CO2 sample and 24 from the post-CO2 one. Choosing objectives was made taking into account the correct visualization of big pores. The 4 × and 10 × objectives were considered adequate to detect them.

b) Establish the initial cross-polarizer light conditions in the optical microscope: 0°–0° (orientation of the lower polarizer with respect to the X-axis and orientation of the upper polarizer with respect to the Y-axis).

c) Time averaging: images from the same scene in a t-interval of 100 ms, were considered as a primary average image (IxpC1 = Σ(images 1 to 8)/8). This operation would further reduce the electronic noise generated by the camera.

d) The system repeated this operation (time averaging) 8 times with intervals of 2 s, obtaining the images IxpC1 to IxpC8 in 16 s. From these images an average image was generated according to IxpP1 = Σ(IxpC1 + ... + IxpC8)/8. This operation reduced the GL periodic oscillations of the pixels detected in the system.

e) Each average image was mathematically corrected by using black standard (dark reference image – BRI) and white standard (white reference image – WRI). The result was the corrected average image IxpP1 = 255 x ((image IxpP1 – BRI)/(WRI – BRI)). Adapted formula of the one proposed by Pirard et al. (1999) and applied in Berrezueta and Castroviejo (2007). This operation reduced the problems of different microscope illumination and camera noise.

f) Synchronized movement of polarizers +10° (both at the same time, keeping the 90° among them). This preceded the execution of steps c, d and e, and took around 4 s. This operation is performed 5 times in total producing 6 images and the resulting images were saved in tif format (corrected average image IxpPC2 to IxpPC6).

g) Acquisition of an image under plane polarized light with microscope and camera configured to initial conditions, repeating the steps c, d and e, and creating images IppC1 (primary average image) and IppP1 (average image). Only the resulting image was saved (corrected average image IppPC1).

h) Selecting a new region of interest with manual focus and manual or automated X–Y displacements. We repeated the sequence until all regions of interest had been studied.

Although the DIA-technique allowed filtering to improve the quality of the original RGB-images (e.g. as low pass or median filters were able to remove the noise of the images), in this study we only used images without any filtering because the improvement was not up to expectations.

2.3.3. Image segmentation

According to Shapiro and Stockman (2001), image segmentation is the process of partitioning a digital-image into multiple segments (sets of pixels). The segmentation involves identification and isolation of pixels that belong to the same category of interest with similar gray level values ranges (Martínez-Martínez et al., 2007). In this paper, our main goal was to separate the pore spaces from the mineral phases of a thin section.

Gray level values of pores were calculated by using a supervised training step. This was conducted by sampling windows (10 × 10 pixels). The windows were placed on a region that could be definitely considered as a pore. Although pores displayed in optical microscopy should be uncolored (black in crossed polarizers and white in parallel ones*), a range of RGB values commonly appeared.

In Fig.3, the segmentation of the pores was produced taking the RGB-levels of the pore ranges: Red [0–16] (where mean x: 8; standard deviation σ: 2.60; normal distribution, significance level of γ: 99.9%); Green [10–18] (where x: 9; σ: 2.76; normal distribution, γ: 99.9%) and Blue [0–20] (where x: 10; σ: 3.04; normal distribution, γ: 99.9%) for the cross-polarized light images. The segmentation produced in the plane-polarized light image was taken within the following ranges: Red [220–255] (where x: 238; σ: 5.32; normal distribution, γ: 99.9%), Green [225–255] (where x: 240; σ: 4.56; normal distribution, γ: 99.9%) and Blue [215–255] (where x: 235; σ: 6.08; normal distribution, γ: 99.9%). These ranges are normally used for the segmentation of pores in thin sections of sandstones. With the use of RGB images (3 combined GL images)
and 7 distinct positions of image acquisition (6 PX and 1 PL), the significance level of the final pore segmentation is of $\gamma$: 97.9%.

These ranges of pore system identification were applied to six images under cross-polarized light (a–f in Fig. 3) and an image in plane-polarized light (image n in Fig. 3). This resulted in 7 segmented images (binary images where pore=1, other=0; binary
The classification of a pixel as a pore occurred if the same pixel (exact same x and y location) was considered a pore in all partial images (GL-ranges within prescribed limits), final segmented image resulted from the intersection of partial images. We will take this final raster image (image p, Fig. 3) to measure all variables of interest (area, shape, etc.).

Image-Pro Plus software managed to generate a pore contour (pore outlined, image q, Fig. 3) on the final segmented image which was used for measurement of the pore network parameters. Occasionally, we verified the segmentation during a supervised quality control to avoid errors, by, superimposing the original pore (RGB image) with the classified pores (pore outlined) (Fig. 4).

2.3.4. Feature extraction
Once we had defined our objects (pores), we selected the most appropriate pore features for assessing size and shape of the pores. All definitions of geometrical properties and equations were
adopted from Image-Pro® Plus User's Guide (7.0) for Windows (2009). The main parameters considered were: the area, aspect ratio, roughness, and roundness. Furthermore, a graphical description of the most important geometrical featured is illustrated in Fig. 5.

The area is measured as the sum of pixels having intensity values within the selected ranges. The aspect ratio reported the ratio between the major and the minor diameter of the ellipse equivalent to the object (i.e. ellipse with the same area, first and second degree moments). Aspect ratio was always \( \geq 1 \).

Roughness of grain pore boundaries also called surface texture of the particle was evaluated using the fractal dimension of the object's outline. Based on Image-Pro® Plus User's Guide (7.0) for Windows (2009), Fractal dimension was defined as “the slope of the linear part of the function that relates the log of the outline length to the log of the stride length, where the length is how long a ruler we attempt to lay along the perimeter of the object”. Fractal dimension concept had been used by earth scientist (Akbulut, 2002; Vallejo, 1997) to better analyze the roughness of particles (rock fragments, pore network, sand grains). Their results confirmed the significance of the roughness effect on fractal dimension.

Roundness is a measure of how circular an object is (in general, the actual perimeter divided by the expected perimeter of a circular object with the same area). We have calculated the roundness (\( R_o \)) with the following formula (adapted from Kuo et al. (1998))

\[
R_o = \frac{P^2}{4\pi A}
\]

where \( P \) is the perimeter of the particle outlined and \( A \) is the area particle outlined. A circular object will have roundness close to 1, while more irregular objects would have higher values than 1.

### 3. Results

The samples for this study were collected from different sedimentary basins within Spain that represent suitable CO\(_2\)-storage formations (see Berrezueta et al. (2013) for details). Two Triassic Sandstones the South-East and the North-East of Spain were selected: homogeneous sandstone of the Linares–Manuel Formation (HoS) and heterogeneous sandstone of the Tiermes Formation (HeS) respectively. Both formations have significant porosities (HoS 17% Hg porosimetry and 15% modal point counting; HeS 27% Hg-porosimetry or 18% modal point counting) and are partially sealed by impermeable cap rocks. In both cases the geological formations are unaffected by faults and fractures related to recent seismic activity.

#### 3.1. Standard petrographic study

The mineralogy of both sandstones samples is similar: quartz, K-feldspar, phyllosilicates (e.g. sericite and other clays), carbonate and less abundant biotite, muscovite, plagioclase, apatite, zircon and Fe-oxides. The phyllosilicates form the rock matrix while the carbonates constitute the cement. In some sample domains sericitic clays and Fe-rich (hematite) particles form a mixture of clay-matrix iron-oxides. The clay/matrix/carbonate cement ratio can be variable within a single sample. The main difference between the two rock formations is the texture. The Tiermes Sandstone (HeS) is heterogeneous and has high porosity and permeability produced by an interconnected framework of micro-channels. In contrast, Manuel Sandstone (HoS) is more homogeneous and shows better sorting. Its porosity is more regularly distributed and does not show micro-channel structures (see Berrezueta et al. (2011) and Robles (2011) for details).

#### 3.1.1. Rock samples before the SC–CO\(_2\)-injection

Sample HoS is constituted by quartz (\( \approx 40\% \)), feldspars (\( \approx 13\% \)) and carbonates (cement \( \approx 15\% \)) as the main mineral phases (determined by modal point counting). Minor phases represent \( \approx 5\% \) of the modal content and consist of muscovite, chlorite, zircon, tourmaline and oxide-minerals (probably a mixture of hematite and limonite). Rock fragments represent about 7% of the total rock. All these phase components (mineral phases and rock fragments) are surrounded by clay matrix and carbonate cement, the clay forms about 5% of the rock (Fig. 6). The rock texture is well sorted having homogeneous mineral grain distribution. The porosity is regularly distributed and represents \( \approx 15\% \) of the total rock content.

Sample HeS is constituted by quartz (\( \approx 33\% \)), feldspars (\( \approx 21\% \)) and carbonates (cement \( \approx 14\% \)) as the main mineral phases (determined by modal point counting). Rock fragments represent \( \approx 5\% \) of the modal content and minor mineral phases are less than 1% of the total rock (muscovite, chlorite, zircon, tourmaline, hematite and limonite). Clay-matrix is irregularly distributed within the samples and accounts for \( \approx 7\% \) of the total rock. The texture is moderately sorted and different grain sizes occur throughout the sample. Porosity (\( \approx 18\% \)) is mainly developed as micro-channels partially filled with a mixture of clay matrix and oxide minerals (left images of Fig. 7).

![Fig. 6. Mineral and textural changes observed in the homogeneous sandstones collected (HoS).](image-url)

(a) Optical microscope images acquired using objective lenses 10 ×: (a) before CO\(_2\) injection sample and (b) after CO\(_2\) injection sample. Qtz (quartz), Dol (dolomite), and Kfs (K feldspar).
3.1.2. Rock samples after the SC–CO₂-injection

The effect of injecting SC–CO₂ into these rocks under dry conditions was well documented by the optical and electronic microscopy techniques (Berrezueta et al. 2013). Because of the dry nature of the experiments, no chemical reactions were expected and the possible CO₂ effects on the rock were expected to be minor. Nevertheless, the results showed changes in the mineral contents and texture caused by percolation of the CO₂, removing the matrix clay from its sites and the leaching out of the rocks. This led to porosity and permeability changes, mainly increases and decreases in the modal proportions of clay minerals and other minor textural changes. The original rock texture exerted an important control for the effects of CO₂-injection where the porosity formed micro-channel structures (HeS sample, right images of Fig. 7), intense clay leaching took place in those domains; where the porosity was more homogenous (HoS sample, Fig. 6), the clay leaching occurred over all the rock sample but the intensity of clay leaching was less severe. Due to the absence of water, the carbonate cement was stable and no changes within this mineral phase occurred. In general the clay removal produced smaller holes in homogeneous samples (min. diameter ≈ 30 μm) when compared with the heterogeneous one (min. diameter ≈ 80 μm).

Traditional techniques were preliminary applied to quantify the porosity changes previously observed in SEM and optical microscopy. Using the Hg-porosimetry method, we obtained porosity values of ≈ 15% for the homogeneous sample (pre- and post-CO₂-injection) and ≈ 27% values for the heterogeneous sandstone (pre- and post-CO₂-injection). Using modal point counting the values obtained were ≈ 15% for the homogeneous sample (pre- and post-CO₂-injection) and ≈ 18% for the heterogeneous one (pre- and post-CO₂-injection). In both cases pore changes were not considered significant.

The purpose of this work was to quantify the porosity changes through a DIA automated procedure that allowed the quantification of distinct pore network changes, observed by using optical microscopy and SEM.

3.2. Automated petrography study

The main objective of this section is to determine the possible evolution of the rock porous system by DIA technique and see whether there have been significant changes in the porosity of the samples after interaction with SC–CO₂. Due to the distinct

Table 2

<table>
<thead>
<tr>
<th></th>
<th>HoS pre-CO₂</th>
<th>HoS post-CO₂</th>
<th>HeS pre-CO₂</th>
<th>HeS post-CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore area (pixels)</td>
<td>13657837</td>
<td>15909724</td>
<td>12142772</td>
<td>24961636</td>
</tr>
<tr>
<td>Mineral area (pixels)</td>
<td>108134400</td>
<td>122880000</td>
<td>63897600</td>
<td>117964800</td>
</tr>
<tr>
<td>Total porosity (%)</td>
<td>12.63</td>
<td>12.94</td>
<td>19.00</td>
<td>21.16</td>
</tr>
<tr>
<td>Porosity variation (% Δn)</td>
<td>0.3</td>
<td>2.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7. Mineral and textural changes observed in the sandstones collected (heterogeneous sample HeS) by (a) optical microscope images acquired using objective lenses 4 × and (b) SEM images. Before CO₂ injection (left images) and after CO₂ injection samples (right images). Qtz (quartz), Dol (dolomite), Cal (calcite), and Kfs (K feldspar).
mineralogical characteristics of the samples studied, two distinct magnifications were used (10 × objective lenses for homogeneous sandstones and 4 × objective lenses for the heterogeneous samples). Therefore independent analysis and interpretation has to be done. According to this, for homogeneous sandstones pores studied were greater than > 4 μm² and for the heterogeneous sandstone pores studied were greater than > 24 μm².

Analyzing the percentage of pore area measured by DIA (Table 2) in the homogeneous pre-CO₂ sample we found a total porosity of 12.63 ± 1.24% and for the post-CO₂ injection sample a total porosity of 12.94 ± 1.24% is found. The change is then calculated as 0.3%, but this is within the limit of error and we cannot infer that there is an increase of porosity. Similarly in the homogeneous pre-CO₂ sample the total pore area found is 19.00 ± 1.24% and 21.16 ± 1.24% for the post-CO₂ sample. The measured increase is 2.16%. In this case the change in porosity is higher than the total error of the technique.

The curves of relative/absolute distribution of the number of pores versus pore area ranges in Fig. 8a and c, allow to identify for homogeneous samples, the pore area ranges measured by DIA are between 4 μm² (pore diameter ϕ ≈ 2.3 μm) and ca. 82,400 μm² (ϕ ≈ 324 μm). The distribution of data shows that ≈ 95% of pores correspond to pores smaller than 824 μm² (ϕ ≈ 30 μm) for the pre-CO₂ injection (Fig. 8a). In the CO₂ injected sample (Fig. 8c), these small pores represent 94% of all the pores. The diagrams of the weighted area related to pore are classes for the pre- (Fig. 8b) and post-CO₂ (Fig. 8d) show that the contribution of the first class of pore area is ca. 10% of the total porosity. In both samples the approximate contributions of cumulated weighted pore area for the main percentiles for the pre-CO₂ injected sample are 15,000 μm² (25%), 34,000 μm² (50%), and 51,000 μm² (75%). On the other hand the injected sample show contributions of 25% for 18,000 μm², 50% of 38,000 μm², and 75% of 54,000 μm².

In the heterogeneous sample (Fig. 9a and c), pore area ranges measured by DIA are between 24 μm² (ϕ ≈ 5.6 μm) and ca. 486,720 μm² (ϕ ≈ 787 μm). The distribution data shows that 96.3% of the pores correspond to pores with areas smaller than 4860 μm² (ϕ ≈ 80 μm). This population reaches 95.9% when the sample is CO₂-injected. The diagrams of the weighted area related to pore are classes for the pre- (Fig. 9b) and post-CO₂ (Fig. 9d) show that the contribution of the first class of pore areas is ca. 10%
of the total porosity. In both cases, the contribution of this class to the total porosity is ca. 2%. The approximate contributions of cumulative weighted pore area for the main percentiles for the pre-CO2 injected sample are 127,000 $\mu$m$^2$ (25%), 248,000 $\mu$m$^2$ (50%), and 345,000 $\mu$m$^2$ (75%). On the other hand the injected sample show contributions of 25% for 128,000 $\mu$m$^2$, 50% of 250,000 $\mu$m$^2$, and 75% of 346,000 $\mu$m$^2$.

The Image-Pro Plus software includes an extensive list of features that apply to a wide range of applications. We were most interested in the variations of geometrical features extracted from each pore space in the different rocks studied, before and after CO2-injection. The morphological features selected were aspect ratio, roughness and roundness. Those statistical studies indicate that for the entire pore population, no significant changes are evidenced, regarding the previously stated parameters. However, the previous petrographic observations showed changes in the case of large-pores population HoS > 824 $\mu$m$^2$ and HeS > 4860 $\mu$m$^2$ ($\geq 2000$ pixels), and the higher area percentage of sample porosity (HoS ≈ 87%; HeS ≈ 90%) was located in this pore area class (Figs. 8 and 9). For the pore class, we have presented in Fig. 10, the pore area distribution (log data) for the homogeneous and heterogeneous sandstone, before and after CO2-injection.

Mann–Whitney statistical test results are HoS $p$-value = 0.0015 and HeS $p$-value = 0.0001 and area shows increase for both sandstones. Furthermore, in this figure we also see the evolution of distinct pore parameters (pore aspect, roundness and roughness) when CO2 treatments of samples are made (Table 3). For homogeneous samples, pore aspect and roundness did not change with CO2-injection but the roughness decreased, and the pores boundaries were smoothed. In heterogeneous samples with CO2-injection, the pores became more ellipsoidal, decreased because of smoothing of the pore boundaries and the frequency of a mean value is slightly lower than when CO2-injection takes place. These results agree with observations made in the previous mineralogical study.

4. Discussion

In the case of the sandstones studied, the modal point counting using SEM and optical microscopy was not able to detect the changes in porosity which could otherwise be easily observed in the samples of pre- and post-CO2 stages. The changes were more local, therefore Hg-porosimetry and modal counting point

![Image 9](image-url)

**Fig. 9.** Heterogeneous sandstone (HeS), minimum size for being considered pore is 10 pixels (> 24 $\mu$m$^2$). (a) X-axis vs left Y-axis: frequency diagrams of number of pores (log scale) related to pore area classes ($\mu$m$^2$) before CO2-injection (bars). X-axis vs right Y-axis: cumulative number of pores (%) related to pore area ($\mu$m$^2$) (points). Dash 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 ($\mu$m$^2$) before CO2-injection sample (bars). X-axis vs right Y-axis: cumulative weighted pore area (%) related to pore area classes ($\mu$m$^2$) (points). Dash lines represent percentiles 25, 50, and 75. (c) X-axis vs left Y-axis: frequency diagrams of number of pores (log scale) related to pore area ($\mu$m$^2$) after CO2-injection sample (bars). X-axis vs right Y-axis: cumulative number of pores (%) related to pore area ($\mu$m$^2$) (points). Dash line represents the contribution of the first class to pore area. (d) X-axis vs left Y-axis: frequency diagrams of weighted pore area (log scale) related to pore area ($\mu$m$^2$) after CO2-injection sample (bars). X-axis vs right Y-axis: cumulative weighted pore area (%) related to pore area classes ($\mu$m$^2$) (points). Dash lines represent percentiles 25, 50, and 75.
Table 3

N1 denotes number of pores pre-CO2. N2 is number of pores post-CO2 injection (pores considered are of size greater than 2000 pixels (HoS: > 824 μm²; HeS: > 4867 μm²)). Mean values of the distinct pore-parameters studied: aspect, roughness and roundness. Paired \(t\)-students (for log data, using N1 population) and Mann–Whitney (for log data) of different pore-parameters measured (pixels) through DIA techniques. Statistical interpretation of parameters distribution when CO2 injection.

<table>
<thead>
<tr>
<th>(\alpha = 0.1)</th>
<th>(N1)</th>
<th>Pre-CO2 inject mean</th>
<th>(N2)</th>
<th>Post-CO2 inject mean</th>
<th>(p)-Value (t)-students</th>
<th>(p)-Value Mann–Whitney</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HoS pore aspect</td>
<td>468</td>
<td>2.0500</td>
<td>698</td>
<td>2.0000</td>
<td>0.472</td>
<td>0.7464</td>
<td>No change</td>
</tr>
<tr>
<td>HoS pore roughness</td>
<td>468</td>
<td>1.1870</td>
<td>698</td>
<td>1.1800</td>
<td>0.006</td>
<td>0.0057</td>
<td>Decrease</td>
</tr>
<tr>
<td>HoS pore roundness</td>
<td>468</td>
<td>5.0200</td>
<td>698</td>
<td>4.7200</td>
<td>0.109</td>
<td>0.1642</td>
<td>No change</td>
</tr>
<tr>
<td>HeS pore aspect</td>
<td>544</td>
<td>1.9610</td>
<td>835</td>
<td>2.1590</td>
<td>0.012</td>
<td>0.0687</td>
<td>Increase</td>
</tr>
<tr>
<td>HeS pore roughness</td>
<td>544</td>
<td>1.1520</td>
<td>835</td>
<td>1.1350</td>
<td>0.006</td>
<td>0.0265</td>
<td>Decrease</td>
</tr>
<tr>
<td>HeS pore roundness</td>
<td>544</td>
<td>3.8660</td>
<td>835</td>
<td>4.2590</td>
<td>0.006</td>
<td>0.0265</td>
<td>Decrease</td>
</tr>
</tbody>
</table>

Fig. 10. Diagrams of the variations of the pore parameters: area, aspect, roughness and roundness. Left side of the figure corresponds to the homogeneous sandstone sample (HoS). Right side of the figure corresponds to heterogeneous sandstone sample (HeS). In blue are the curves for samples before CO2 injection and the red ones the after CO2 injection data. Pores considered for this study are larger than 2000 pixels (HoS: > 824 μm²; HeS: > 4867 μm²). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
methods had not been entirely helpful. Due to this, a method to systematically quantifying them was needed (DIA).

The procedure proposed started with a specific and exhaustive mineralogical-petrographic study to set the criteria for DIA application and formulate it in appropriate terms of the research target (pores/mineral phases to quantify). To control external influences in the method, a rigorous calibration of equipment (microscope and camera) was followed through to ensure proper image acquisition was applied by Pirard et al. (1999).

The criteria for image acquisition and target object identification (pore) was based on conditions of moving synchronously both polarizers Fueten (1997) and keeping one in plane-polarized light. This procedure allowed us to work in identification using multi-images. The values used to segment each of the mineral/pore phases of interest were found through statistical sampling of the GL. These values were measured using sampling windows on pores. Finally, automated pore identification for a mineral scene was achieved automatically by including segmentation ranges for each RGB-band of 7 different images using a specially designed routine (macro).

The success of the method was dependant on properly setting down the initial conditions of images acquisition and the establishment of mineralogical criteria to define the ranges of pore segmentation applicable to the acquired images. The method can also be applied in analogous microscopic and DIA equipment-devices, since the DIA tools settings can be adapted to them.

The DIA quantification method has allowed us to define a porosity increase for the heterogeneous sandstones (2.16%). In the case of the homogeneous sandstones due to the error of the technique we cannot consider the increase of 0.3% would be significant. These values are valid for a pore population of a specific size–pore diameter– (HoS: > 2.3 μm and < 324 μm; HeS: > 5.6 μm and < 787 μm). The existence of big size pores will condition the quantification by DIA. In the case of the homogeneous sandstone, a single big pore could represent 4% of the total porosity for this sample (≈12%) that is 0.5% of porosity measured. In the case of the heterogeneous sandstone, a single big pore could represent 3% of the total porosity (≈20%), being a ± 0.6% of the porosity measured.

Therefore, a single new pore of high size would explain the porosity increases in the homogeneous sandstone when CO2 injection occurs. The presence of four big size pores would explain the porosity differences in the heterogeneous sandstone (among the pre- and post-CO2 injection).

Previous petrographic observations evidenced changes, when CO2 injection occurs, in pores of populations: HoS > 824 μm2 and HeS > 4860 μm2. For those cases, we focused a specific quantification of the distinct pore parameters as pore aspect, roundness and roughness. The measurement of pore parameters allowed quantification of the possible changes in the configuration of the pore caused by the injection of CO2 in the samples.

Some improvements would make the method more efficient, for example using a current stabilizer to limit the electronic noise or an automatic controller of synchronized polarizers to reduce the time needed to acquire images, ensuring appropriated final segmentation of pore system. Concerning the DIA measurements, it must be also noted that the model might have restrictions to quantify porosity due to analytical errors in the estimation of porosity, contribution of larger pores to the total porosity and natural heterogeneities of the samples.

Nevertheless, the present DIA model allows us to estimate individual sample porosity. The combination of distinct analytical techniques would help us to better define the presence/absence of porosity changes when SC–CO2 injection occurs.

5. Conclusions

The development of an automated procedure is a necessary tool to perform a quantitative study of the petrographic features observed in SEM and optical microscopy images. The presented DIA procedure is an efficient method for semi-automated recognition and quantification of the porous system in thin sections. In the present work, it was applied to rock samples without any pre-treatment to highlight porosity (e.g. blue-resin impregnated thin sections). The method provided us quantitative data of the pore system and geometrical features from each pore space. This expands the possibilities of advanced petrographic studies and mineralogical characterization of the porous system in 2D. This too, is an important and useful method for the study of rocks with significant amounts of micropores and heterometric rocks where fissures networks may predominate.

Quantitative assessment of petrography and mineralogy by DIA can be an important tool for geosciences, providing numerical values as a key to the successful interpretation of the rock texture and mineralogy. Semi-automatic method allows identification of mineral phases/pores and furthermore multi-functional mathematical treatments of all the images, implying the ability to address different industrial or scientific problems without having to repeat image acquisition.

Porosity measurements using DIA-techniques represent an effective, accurate and easy method of measuring porosity and can be considered as providing the most statistically robust compared to point counting. Regarding the results obtained, by applying the procedure proposed to homogeneous and heterogeneous sandstones we can conclude an increase of total porosity for the heterogeneous sandstones of 2.6% and a nonrepresentative change of 0.3% for the homogeneous ones due to error the technique.

The value for the heterogeneous sandstone is within the expected results because the increase is related to loss of clay matrix. The estimated initial clay content by optical microscopy and SEM was ca. 7%. In the case of the homogeneous sandstones the clay content was smaller (ca. 5%), therefore the expected changes would be smaller and the technique was not able to quantify them. The clay minerals are prone to be leached by the CO2-injection. These modal values for the clay matrix would represent the maximum new porosity that could have been generated in the CO2 treated sample.

Acknowledgments

The authors would like to thank the funding for this work provided through the CO2-Pore Project (Plan Nacional de España: 2009-10934, FEDER-UE), ALGECO2-IRMC Project (Instituto Geológico y Minero de España: 2294-2013), Minería XXI Project (CYTED: 310RT0402) and DIA-CO2 Projects I and II (CIUDEN: ALM/09/032 and ALM/12/028) are greatly appreciated. We also would like to thank Laura Arenas, José Luis García Lobón, Roberto Martínez and Félix Mateos for providing help in DIA techniques, data acquisition, statistical treatment and rock sample collection, and thanks to R. Lastra (NRCan-CANMET Mining) for his suggestions.

We also would like to thank Jef Caers for the editorial handling. Helpful revisions and suggestions of Mingireanov Filho, I., and an anonymous referee of Computers and Geosciences are kindly acknowledged.

Appendix 1 Mineral symbols (after Kretz (1983))

Cal. Calcite
References


