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### Citation for published version:

Busch, A, Schweinar, K, Kampman, N, Coorn, A, Pipich, V, Feoktystov, A, Leu, L, Amann-Hildenbrand, A & Bertier, P 2017, Determining the porosity of mudrocks using methodological pluralism. in EH Rutter, J Mecklenburgh & KG Taylor (eds), *Geomechanics and Petrophysical Properties of Mudrocks*. vol. 454, Geological Society Special Publications, vol. 454, Geological Society Publishing House, pp. 15-38. <https://doi.org/10.1144/SP454.1>

### Digital Object Identifier (DOI):

[10.1144/SP454.1](https://doi.org/10.1144/SP454.1)

### Link:

[Link to publication record in Heriot-Watt Research Portal](#)

### Document Version:

Peer reviewed version

### Published In:

Geomechanics and Petrophysical Properties of Mudrocks

### Publisher Rights Statement:

Geomechanical and Petrophysical Properties of Mudrocks. Geological Society, London, Special Publications, 454, <https://doi.org/10.1144/SP454.1>  
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# Determining the porosity of mudrocks using methodological pluralism

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*Keywords: Opalinus Clay, Small Angle Neutron Scattering, N<sub>2</sub> low pressure sorption, Mercury Porosimetry, Helium Pycnometry, Porosity*

## Abstract

Porosity of shales is an important parameter that impacts rock strength for seal or wellbore integrity, gas-in-place calculations for unconventional resources or the diffusional solute and gas transport in these microporous materials. From a well section obtained from the Mont Terri underground laboratory in St. Ursanne, Switzerland we determined porosity, pore size distribution and specific surface areas on a set of 13 Opalinus Clay samples. The porosity methods employed are Helium pycnometry, water and mercury injection porosimetry, liquid saturation and immersion, low pressure N<sub>2</sub> sorption as well as small/very small angle neutron scattering. These were used in addition to mineralogical and geochemical methods for sample analysis that comprise X-ray diffraction, X-ray fluorescence, total organic carbon content and cation exchange capacity. We find large variations in total porosity, ranging from ~23% for the neutron scattering method to ~10% for mercury injection porosimetry. These differences can partly be related to differences in pore accessibility while no or negligible inaccessible porosity was found. Pore volume distributions between neutron scattering and low pressure sorption compare very well but differ significantly from those obtained from mercury porosimetry which is realistic since the latter provides information on pore throats only and the two former methods on pore throats and pore bodies. Finally we find that specific surface areas determined using low pressure sorption and neutron scattering match well.

## 1 Introduction

Porosity, along with permeability, is the most important parameter for characterizing reservoir quality. For high permeability rocks like sandstones, there is usually a good correlation between these two parameters (Nelson, 1994). Similar relations are found for porosity and rock mechanical parameters, specifically rock strength, used in reservoir geomechanics (Chang et al., 2006; Hangx et al., 2015). Different methods are used for determining the porosity of reservoir rocks, of which helium pycnometry or mercury porosimetry are the most common. For highly porous and permeable rocks of reservoir-quality these porosity measurements can be considered reliable.

Porosity determined on shales, however, are much less straightforward for many reasons. First of all the lack of experience, as drilling campaigns for conventional petroleum reservoirs do not core shales on a regular basis. The exploitation of shales as unconventional reservoirs for oil and gas has only recently become commercially attractive. In the past a lot of work was therefore done on shale cuttings only. In addition, cored shale samples are not always stored in a way that avoids dehydration or mechanical disintegration (Ewy, 2015). This usually results in dehydration cracks or cracks resulting from stress unloading, which makes it difficult to impossible to prepare representative samples. Also little is known about the pore network and porosity changes resulting from shale dehydration, especially for those containing significant amounts of smectite or illite/smectite (I/S) mixed layers. Consequently the most reliable shale samples are those that are freshly cored or stored in a way that retains mechanical integrity and natural humidity.

Shale porosity is an important control on effective diffusion coefficients, driving the speed of mineral reactions (Kampman et al., 2016), the dispersion of gases in natural tight gas reservoirs (Krooss et al., 1988), leakage of injected carbon dioxide from storage sites (Busch et al., 2008; Busch and Amann-Hildenbrand, 2013) or diffusive migration of gas from nuclear waste disposal sites (Marschall et al., 2005). Porosity also plays a key role in shale gas production. It is assumed that 15 to 80 % of the gas is stored as a free gas phase in

the pore space (for Barnett, Ohio, Antrim, New Albany and Lewis shale gas plays) as opposed to the sorbed phase. Interestingly this seems to be independent of total porosity, water saturation, total organic carbon content (TOC), formation depth and temperature (Hill and Nelson, 2000). The accuracy of porosity prediction has therefore a strong impact on reservoir gas-in-place assessments. Porosity is also used as a predictor for shale strength, with the unconfined compressive strength decreasing with an increase in porosity (Dewhurst et al., 2015; Horsrud, 2001). An underestimation of porosity would therefore overestimate strength, potentially leading in seal or wellbore containment issues.

Most of the porosity in shales and mudrocks is associated with small pore throat sizes, ranging from less than 0.5 nm up to about 100 nm in diameter (Nelson, 2009). While water porosimetry and Helium pycnometry can nearly cover the entire pore size range, mercury injection porosimetry (MIP) has certain limitations. MIP has a lower pore radius limit of ~2 nm, whereas it is well known that micropores of <2 nm in size significantly contribute to porosity of shales (Sing et al., 1985). Since MIP is determining pore throats and not pore bodies, any porosity shielded behind this threshold will not be detected. The current standard for shale porosity determination in the oil and gas industry is the method proposed by the American Petroleum Institute (API) or the Gas Research Institute (GRI) which is a combination of immersion in e.g. mercury following Archimedes principle to determine sample bulk density/volume and saturating the sample with a another fluid for determining grain density/volume (Kuila et al., 2014).

In this paper several methods for the determination of the porosity of shales will be outlined and discussed. Different methods often yield different porosity values, which is due to the different accessibility of fluids to the pore network, different sample sizes and shapes or different initial water saturations (dry or moisture-equilibrated or “as-received”, Bustin et al., 2008). Nonetheless, porosity is used as an absolute, intrinsic parameter. In this work porosity, pore size distribution, and specific surface area values obtained from 6 different methods on a total of 13 Opalinus Clay samples recovered from the shaly facies at the Mont Terri underground laboratory (St. Ursanne, Switzerland) are compared and discussed.

## 2 Samples and Methods

### 2.1 Study site

All samples used in this study were taken from the Opalinus Clay formation at the Mont Terri underground rock laboratory, St. Ursanne, Switzerland (<http://www.mont-terri.ch/>). This laboratory is situated about 300 m below surface and is used as a study site for the disposal of high-level radioactive waste. The Opalinus Clay was deposited in the Aalenian (Dogger- $\alpha$ , ca. 174 Ma) in a shallow marine setting of an epicontinental sea at water depths of around 10-30m (Corkum, 2007; Elie and Mazurek, 2008; Nussbaum et al., 2011). It overlies the deposits of the Lias- $\zeta$  and is followed by the Dogger- $\beta$  which consists of oolitic, iron-bearing rocks, indicative of sea-level regression. Opalinus Clay consists of a monotonous sequence of dark grey, silty, micaceous clays and sandy shales that can be differentiated in three different facies (Bossart and Thury, 2008):

- Shaly facies: argillaceous and marly shales with micas and nodular, bioturbated layers of marls or with mm-thick layers of sandstone (lower part of formation)
- Sandy facies: marly shales with layers of sandstones and bioturbated limestones, or with lenses of grey, sandy limestones and mm-thick layers of white sandstones with pyrite (in the middle and upper part of the formation)
- Carbonate-rich sandy facies: calcareous sandstones intercalated with bioturbated limestone beds, the latter showing a high detrital quartz content (in the middle part of the formation)

In this study an approximately four meter long core section (BHG-D1\_section 4.6-8.6 m) from the shaly facies was used and provided by the National Cooperative for the Disposal of Radioactive Waste (NAGRA) and the Swiss Federal Office for Topography (SWISSTOPO). Based on CT scans the most homogeneous sections which were most promising for obtaining good plug quality were selected. From this section nine disks of about 1 cm thickness were cut for mineralogical, geochemical and petrophysical sample characterisation (referred to as CCP01-09). Plugs were drilled adjacent to these disks and were used for further petrophysical analysis (CCP10-15). Plugs and residual material were

carefully re-sealed in aluminium and PE-foil before further sample preparation. In order to achieve plane-parallel surfaces plugs were ground carefully in the dry state. Other techniques proved to be less successful. The plugs used in the experiments were 37.5 to 37.9 mm in diameter and 6.15 to 22.90 mm in length. The water and gas permeability and capillary threshold pressures of nitrogen and carbon dioxide of these plugs have been reported earlier (Amann-Hildenbrand et al., 2015). For laboratory measurements not requiring plug scale samples, chips from the 9 disks used for sample characterisation or trimmings from the plugs were used.

## **2.2 Mineralogical and geochemical characterisation**

### **2.2.1 X-ray diffraction**

X-ray diffraction (XRD) measurements were performed to determine mineralogy (Table 1). An internal standard ( $\text{TiO}_2$ , 10wt.% or  $\text{Al}_2\text{O}_3$ , 20wt.%) was added before milling manually crushed sample material in a McCrone micronizing mill. All reported mineral compositions relate to the crystalline content of the analysed samples. Quantitative phase analysis was performed on diffraction patterns from random powder specimens, which were prepared by means of a side filling method to minimise preferential orientation. The measurements were performed on a Bruker D8 diffractometer using  $\text{CuK}\alpha$ -radiation produced at 40 kV and 40 mA. The rotating sample holder was illuminated through a variable divergence slit. The diffracted beam was measured with an energy dispersive detector. Counting time was 3 seconds per step of  $0.02^\circ 2\theta$ . Diffractograms were recorded from  $2^\circ$  to  $92^\circ 2\theta$ . Quantitative phase analysis was performed by Rietveld refinement using the BGMN-Profex software (Doebelin and Kleeberg, 2015) with customised clay mineral structure models (Ufer et al., 2008). The precision of these measurements, from repetitions on the same sample, is better than 1 m% for phases of which the content is above 2%. Accuracy cannot be determined because of the lack of pure (clay) mineral standards, but is estimated to be better than 10% (relative).

### 2.2.2 X-ray Fluorescence

Major elemental compositions were determined by energy dispersive X-ray fluorescence spectrometry (XRF, Table 1) with a Spectro XLab2000 spectrometer, equipped with a Pd-tube and Co, Ti and Al as secondary targets. The spectrometer was operated at acceleration voltages between 15 and 53 kV and currents between 1.5 and 12.0 mA. Major elements were analysed on fused discs (diluted 1:10 with a Li-tetraborate/Li-metaborate mixture, FXX65, Fluxana, Kleve, Germany). Data computation was performed using a fundamental parameter procedure. Loss on ignition was determined by heating the powdered sample to 1000°C for 120min. Samples were dried at 105°C for over 24 h prior to determination of loss on ignition. Precisions and accuracy, as determined from repeated measurements on standards, are better than 0.5 m%.

### 2.2.3 Cation Exchange Capacity

Cation exchange capacities (CEC) were analysed by means of the copper(II)-triethylenetetraamine,  $[\text{Cu}(\text{Trien})]^{2+}$ , method (Table 1). A 0.02 M solution of copper(II)-triethylenetetraamine was prepared by mixing 0.1 mol triethylenetetraamine (Trien) and 0.1 mol copper(II)-sulfate pentahydrate in 100 mL deionised water and diluting appropriately. 200 mg of sample were added to 20 mL of exchange solution. The suspensions were dispersed in an overhead shaker for more than 1 h. The supernatant solutions were separated using syringe filters and analysed for their copper(II)-triethylenetetraamine concentration by spectrophotometry (Lambda 11, Perkin Elmer). The adsorption of the supernatant was measured at a wavelength of 576 nm and converted to concentration using a 7 point calibration series (0 – 0.02 M). The measured CEC values were corrected for differences between labs and methods by means of a calibration series consisting of 7 standard clays (kindly provided by Dr. S. Kaufhold, BGR, Germany) with CEC values ranging from 30 to 2000 meq/kg. After this correction the accuracy of the measurements is better than 10 %. Precision was verified by repeated analyses of the same sample and is better than 2 %.

### 2.2.4 Total Organic Carbon content

TOC data were measured with a LECO RC-412 Multiphase Carbon/Hydrogen/Moisture Determinator (Table 1). This instrument operates in a non-isothermal mode with



continuous recording of the CO<sub>2</sub> release during oxidation, which permits individual determination of inorganic and organic carbon in a single analytical run and does not require removal of carbonates by acid treatment for TOC measurement. The technique is based on the different decomposition of the phases during heating.

## 2.3 Petrophysical properties

A number of different methods were used to determine pore structure parameters. These methods are characterised by different pore accessibilities which are summarized in Figure 1 along with the IUPAC pore size classifications (International Union of Pure and Applied Chemistry, Sing et al., 1985), classifications for grain sizes for sand, silt and clay (Folk, 1980) and different transport modes related to Knudsen numbers in porous media (Karniadakis et al., 2005; Ziarani and Aguilera, 2012). The Knudsen number is the mean free path length (MFP) of a molecule to the pore diameter. Reservoir conditions for Knudsen numbers are based on temperature and pressure at a depth of about 2000 m (20 MPa and 70°C). The calculation of the MFP is described elsewhere (Shieh and Chunh, 1999). According to Figure 1 viscous flow following Darcy's Law is considered to occur at  $Kn < 0.01$ , corresponding to pore diameters of  $> 800$  nm. Slip flow takes place at  $0.01 < Kn < 0.1$  (80-800 nm) and transition/Knudsen flow at  $Kn > 0.1$  ( $< 80$  nm).

### 2.3.1 Focused Ion Beam Scanning Electron Microscopy (FIB SEM)

FIB SEM imaging was used to construct a realistic 3D pore structure for one of the Opalinus Clay samples (CCP14, Figure 2). All samples were carbon coated and imaged with a FEI Helios 600 Nanolab Dual Beam instrument and the semi-automated Slice and View software was used to stack the images. Further data processing was performed using FEI Avizo software. 499 frames were collected with nominal 10 nm step sizes at 0° tilt, i.e. the Ga<sup>+</sup> ion beam was at 38° to the sample surface during milling. SEM images were made at 1 kV, 60 μs dwell time with the in-lens backscatter detector at 38° tilt, with the viewing angle perpendicular to the milled surface. The horizontal full width was 10.3 μm and the vertical full width was 8.9 μm. The pore space was segmented with a watershed-based algorithm and a pore was defined as disconnected volume. This resulted in a porosity for the CCP14 sample of 4.48%.

Figure 3 shows pore alignment relative to bedding for pores smaller than 25 voxels, resulting in a pore diameter cut-off at about 40 nm. The majority of pores is oriented parallel to bedding (horizontal in Figure 3) with the exception of distinct pore families aligned at angles of 35 and 125°. The sphericity  $\psi$  of the pores is plotted as a function of equivalent pore diameter in Figure 4 and describes how spherical or round a pore is: A perfect sphere has a sphericity of 1 and any small deviation from a perfect sphere results in a value <1:

$$\psi = \frac{\pi^{1/3}(6V_p)^{2/3}}{A_p} \quad (1)$$

Where  $V_p$  [m<sup>3</sup>] is the pore volume and  $A_p$  [m<sup>2</sup>] is the pore surface area. Although sphericity values vary significantly for small pore sizes, they generally decrease with increasing pore radius (Figure 4).

### 2.3.2 Water Content Porosity

Plugs were weighted and vacuum-dried at 105°C to constant weight. Aliquots were taken for mercury injection porosimetry (MIP, s. below) and some fragments for the determination of the water-filled pore space after water saturation. The water content porosity was determined from the mass loss after drying. The skeleton density was taken from He-pycnometry measurements (s. below) and a value of 1 g.cm<sup>-3</sup> was used for the density of water. This value might only be an approximation valid for meso- and macropores (>2 nm). It was shown that confinement in small pores can change water properties such as density (Bocquet and Charlaix, 2010), e.g. 0.92 g/cm<sup>3</sup> as measured for water confined in carbon micropores under ambient conditions (Alcaniz-Mongue, 2001). The pore size at which this transition occurs is strongly dependent on the solid surface chemistry and the pore geometry (Evans, 1990).

The molecular diameter of water is ~2.9Å (Webster et al., 1998) which would in theory be the lower limit of pore sizes that can be accessed. It was shown in experimental studies performed on coal that due to clustering of water the lower limit of pore accessibility is ~4Å. Coal and carbon materials are probably less water wet than quartz and clay minerals

in shales (Iglauer et al., 2015), which strongly impacts pore accessibility. In this study, we use the kinetic diameter value of 2.9Å as the lower limit for water accessibility.

### 2.3.3 Mercury Intrusion Porosimetry (MIP)

For the MIP measurements a Micromeritics AutoPore IV 9500 porosimeter was used, yielding information about porosity, density, pore size distribution and critical capillary pressures. The maximum mercury pressure  $P_{max}$  applied was 413MPa. Using a Hg/air interfacial tension  $\gamma$  of 480 mN/m and a contact angle  $\theta$  of 140°, the smallest pore diameter that is accessed is therefore  $\sim 3.6E-9$  m (3.6nm), based on the Young-Laplace equation expressed for cylindrical pores:

$$r = \frac{2\gamma \cdot \cos(\theta)}{P_{max}} \quad (2)$$

The pore throat diameter does not directly provide a value for the smallest pore body radius. The pore body diameter can be much larger, depending on pore aspect ratio (pore throat/pore body, Busch and Amann-Hildenbrand, 2013). In slit-shaped pores this aspect ratio can be close to one, whereas in a spherical pore it is <1. For the measurements, sample cuttings of  $\sim 7-10$  mm diameter were used. Prior to testing, the samples were dried in a vacuum oven at 105°C until weight constancy.

During the initial low-pressure phase of the experiment, a significant amount of “injected” mercury is often recorded, followed (in low-permeable media) by a non-intrusion zone. This is interpreted as the filling of sample surface irregularities (rugosity) and preparation artefacts (fissures). For an accurate quantification of porosity and critical capillary pressures, this initial volume has to be subtracted from the entire intrusion volume (surface roughness correction). This, however, involves a certain degree of subjectivity. In this study we have assumed fractional intrusion rates below  $0.1/\log_{10}(p[\text{MPa}])$  to result from these surface irregularities. After this intrusion, a “real” entry into the sample is expected to occur. The pore entry pressure ( $P_{entry}$ ) correlates to the pressure at which mercury first enters the largest pores of the porous material. In this study on Opalinus Clay, the recorded capillary entry pressures correspond to equivalent pore radii of approximately 2-3  $\mu\text{m}$ .

With increasing Hg-pressure successively more pores are filled, until, at a critical pressure, a continuous filament of mercury extends through the sample (Dullien, 1992). As demonstrated by electrical resistance measurements (Katz and Thompson, 1986, 1987), electrical continuity is established at the inflection point (percolation threshold pressure,  $p_p$ ) of the cumulative intrusion curve, or the pressure at which the first derivative of the intrusion curve (pore radius distribution) has its maximum. This point represents the most prominent equivalent pore radius of the sample. The critical pressure required to form such a continuous, non-wetting phase-filled pore network is somewhat lower than  $p_p$  and is defined as the displacement pressure ( $p_d$ ), which is routinely used for the estimation of capillary sealing efficiency of rocks (Schowalter, 1979). However, different terminologies and methods are used in the literature. Dewhurst et al. (2002) use the term threshold pressure for the pressure corresponding to “the large gradient increase on the first derivative”. Others define the displacement pressure,  $p_d$  by the “tangent-method”, where a tangent is fitted to the inflection point of the cumulative intrusion curve and extrapolated to the logarithmic pressure axis (Schlömer and Krooss, 1997).

Results are shown in Figure 5 for the 13 different Opalinus Clay samples where pore radius (1.8 to ~3000 nm) is plotted against normalized incremental intrusion volume. This mode of visualization allows the identification of the most prominent pore radii. All curves show a similar behaviour while the difference in the most prominent pore radii are quite high with values ranging between 3.5 and 5 nm.

#### **2.3.4 Low Pressure N<sub>2</sub> Sorption**

For specific surface area, micropore volume and pore radius distribution, low-pressure N<sub>2</sub> gas adsorption isotherms were recorded at 77.3 K, by means of the static-volumetric method, using a Micromeritics Gemini VII 2390t device. Adsorption/desorption was measured at 71 relative pressure steps between 0.001 and 0.995. Both, the multipoint BET- (Brunauer et al., 1938) and the Barret-Joyner-Halenda (BJH) methods (Barrett et al., 1951) were applied to calculate specific surface areas (SSA). The BET SSA was calculated for comparison with published data on the Opalinus Clay (Pearson et al., 2003); BJH SSA is assumed to be closer to SSA values calculated from neutron scattering tests (see below). For

the former a cross-sectional area of the nitrogen molecule of  $0.162 \text{ nm}^2$  was used. Differential mesopore volume distributions were calculated from the adsorption branch of the isotherms using the BJH theory, using the Harkins-Jura thickness equation with Faas correction (for  $P/P_0 > 0.35$  or 2 up to  $\sim 180 \text{ nm}$  pore radius range). Gurvich total pore volume was determined from adsorption at a relative pressure of 0.995, corresponding to pore diameters below  $350 \text{ nm}$ . A detailed discussion on the method as well as pitfalls can be found in Bertier et al. (2016). The  $\text{N}_2$  isotherms for the different Opalinus Clay samples are shown in Figure 6 demonstrating a nearly identical  $\text{N}_2$  sorption behaviour. Specific surface area (SSA) as well as porosities determined from the pore volumes using grain density from He-pycnometry are listed in Table 3.

### 2.3.5 Helium Pycnometry

Cylindrical plug samples with dimensions of  $\sim 37.5 \text{ mm}$  in diameter and  $6\text{-}23 \text{ mm}$  in length were drilled. These plugs were dried in a vacuum oven at  $105^\circ\text{C}$  until constant weight was established. Subsequently, samples were mounted into a sample cell connected to a reference volume. Both cell volumes were calibrated using stainless steel volume standards. He-pycnometry measurements were performed in an oven at  $\sim 41^\circ\text{C}$  and Helium pressures up to  $0.6 \text{ MPa}$  were applied in different pressure steps. This yields skeletal volumes from which matrix densities can be derived using the sample dry mass. By calculating the bulk sample density (from the dry mass and geometric sample volume), the porosity can directly be calculated. In this method, any changes in the pore structure due to drying has been neglected but is mentioned here as a potential source of error. Helium is considered to have the best accessibility to pore space among all fluid invasion methods used in this study which is due to its low kinetic diameter of  $0.6 \text{ \AA}$ .

### 2.3.6 Liquid saturation and immersion technique (LSI)

Liquid saturation and immersion techniques (LSI) are standard techniques for measuring bulk-, grain density and porosity. Porosity is determined by saturating a sample with a liquid with known density, and calculating the pore volume from the weight difference between the fully saturated and dehydrated states. The total volume of the sample is determined using Archimedes' principle (Kuila et al., 2014). Here, we determined the total

sample volume by immersing the vacuum-oven dried sample in mercury, which enables the use of samples with irregular shape like cuttings or chips. Subsequently the grain volume of each sample is determined by immersing a 100% chloroform-saturated sample in chloroform. Chloroform saturation is achieved by placing the samples in a pressure vessel and applying a vacuum down to  $\sim 60$  Pa, followed by the filling of the vessel with chloroform. After sample saturation for  $\sim 30$  min a pressure of 3 MPa is applied for  $\sim 45$  min for full sample saturation by dissolution of trapped air. Grain density is calculated from sample weight and grain volume. This, in principle, is the preferred method by the American Society for Testing and Materials (ASTM, 2011) and the American Petroleum Institute (1998). The fluid used for pore saturation can however be different and may vary from tetrachloromethane or water, to light hydrocarbons. An overview is given by Kuila et al. (2014). The kinetic diameter of chloroform is  $\sim 4.6$  Å (Webster et al., 1998) which is considered as the lower limit for pore accessibility.

### **2.3.7 Small and Very Small Angle Neutron scattering**

Total sample porosity, specific surface area and pore size distribution were analysed using small angle (SANS) and very small angle (VSANS) neutron scattering techniques. Experiments were carried out using the instrument KWS-1 (SANS) and KWS-3 (VSANS) operated by the Jülich Center for Neutron Science (JCNS) at Heinz-Meier-Leibnitz Zentrum (MLZ) in Garching, Germany. Opalinus Clay samples were cut parallel to bedding, fixed on quartz glass carriers and polished to a thickness of about 200  $\mu\text{m}$  for measurements. Exact sample thicknesses, required for absolute pore volume calculations, were determined using the average of micrometre calliper measurements at various sample positions. Samples were dried at room temperature and at 105°C in a vacuum oven overnight. Measurements were performed under ambient pressure and temperature conditions. For dry measurements, a second glass slide was placed on the sample and the sandwich was sealed to avoid rehydration. The same samples were measured hydrated at lab humidity and dry to determine the effect of adsorbed water, assumed to impact micro and mesopores. The illuminated sample area was constrained by a rectangular cadmium mask with 10 mm side length.

In (V)SANS, a collimated neutron beam is elastically scattered by the sample (Guinier and Fournet, 1955; Radlinski, 2006). Position-sensitive detectors measure the scattering intensity  $I(Q)$  as a function of the scattering angle, which is defined as the angular deviation from the incident beam. The scattering vector  $Q$  ( $\text{\AA}^{-1}$ ), is related to the scattering angle  $\theta$  by  $Q = (4\pi/\lambda)\sin(\theta/2)$ , where  $\lambda$  is the wavelength of the neutron beam. Thus, the size range of features accessible with neutron scattering depends on the neutron wavelength  $\lambda$  and the collected range of the scattering angle  $\theta$ .

Data at KWS-1 were collected at a wavelength of  $\lambda$  of 6  $\text{\AA}$  with a wavelength distribution of the velocity selector  $\Delta\lambda/\lambda=0.10$  (full width at half-maximum). Measurements were performed at sample-to-detector distances of 19.7 m, 7.7 m and 1.2 m, covering a wide  $Q$ -range of 0.002 – 0.35  $\text{\AA}^{-1}$ . The detector was a  $^6\text{Li}$  glass scintillation detector with an active area of 60×60  $\text{cm}^2$ . Data at KWS-3 were collected at  $\lambda = 12.8$   $\text{\AA}$ ,  $\Delta\lambda/\lambda = 0.2$ , and a sample-to-detector distance of 9.5 m, covering a  $Q$ -range from 0.0024 to 0.00016  $\text{\AA}^{-1}$ . As for KWS-1 a  $^6\text{Li}$  scintillation detector was used but with a detector diameter of 9 cm. Hence, pore radii for the combined SANS and VSANS measurements range between  $r \approx 2.5/Q = 7$   $\text{\AA}$  and 1.5  $\mu\text{m}$ . Instrument data analysis and background subtraction was carried out using the QtiKWS software provided by JCNS. During background subtraction the lower pore sizes were cut off at  $Q=0.2$   $\text{\AA}^{-1}$  or  $r\sim 12.5$   $\text{\AA}$ , to remove analytical artefacts arising from ordered stacking of clay minerals and errors from background values due to possible incoherent scattering on hydrogen atoms that become significant at high  $Q$  or small pore size values.

The processing and evaluation of the data sets has been done using the PRINSAS software (Hinde, 2004). PRINSAS is a Windows-based software, which was designed to display, process and interpret data obtained from small-angle scattering of X-rays or neutrons. Various input parameters and boundary conditions have been tested for their sensitivity and certain calculations have been carried out manually to overcome numerical problems encountered when using the software. SSA and PSD have been calculated for the entire sample set. In a first step, SANS data can be entered in PRINSAS and be displayed as  $I(Q)$  versus  $Q$  curves. Within the Porod limit, the curve is expected to be linear (on a log-log scale). Deviations from this linearity towards higher  $Q$ -values are related to a constant

background, e.g. produced by incoherent background scattering on hydrogen atoms or by pores smaller than the cut-off range which, in this study, is 12.5 Å for the radius (Bahadur et al., 2015). A built-in routine can automatically determine the background by calculating the deviation of the last defined data point (set Q-range) from the regression of the linear part of the curve. Background corrected SANS data can then be merged with VSANS data. VSANS data can be calibrated by matching to the corresponding SANS scattering curves (Hinde, 2004).

For the calculation of pore features of Opalinus Clay samples it is assumed that the scattering intensity  $I(Q)$  is directly proportional to the scattering contrast:

$$I(Q) = \phi V_p (\rho_1^* - \rho_2^*)^2 P(Q) S(Q) \quad (3)$$

Here,  $\rho_1^*$  and  $\rho_2^*$  are the coherent scattering length densities (SLD) for neutrons for the two phases, shale matrix and air, respectively, and  $\phi$  and  $V_p$  are the volume fraction of the scattering phase and the volume per scatterer, respectively. The terms  $P(Q)$  and  $S(Q)$  denote the form and structure factors, for which analytical expressions exist for different geometries of scatterers, including volume and surface fractals (Radlinski, 2006). The SLD of each mineral was calculated as:

$$SLD = \frac{N_A b_i}{M_i} d_i \quad (4)$$

where  $b_i$  and  $M_i$  are scattering length and atomic mass of the  $i^{\text{th}}$  element in the mineral,  $d_i$  is the mass density of the  $i^{\text{th}}$  mineral, and  $N_A$  is Avogadro's number. Scattering length densities were calculated using the NIST SLD calculator (NIST, 2015) and following the approach explained in Jin et al. (2011). Results are provided in Table 2. Since the scattering contrast between the shale matrix and the pores is large, all scattering is attributed to shale matrix-pore features. SLD values for the Opalinus Clay studied are on average  $3.73 \times 10^{-6} \text{ \AA}^{-2}$ , for air it can be considered zero. The SLD calculation is important and relies on exact mineralogy and, depending on mineralogy, on accurate mineral stoichiometry. As will be shown later, porosity and surface area are both proportional to the inverse of  $SLD^2$ .



Pore volume distributions (*PVD*) as a function of length scale,  $r$ , porosity  $\phi$  and specific surface area were calculated using the PRINSAS software discussed above (Hinde, 2004; Radlinski, 2006). For porosity calculations a polydisperse spheres model (PDSP) is considered, i.e. all pores are assumed to be spherical. Scattering and background-subtracted scattering curves for the samples analysed are shown in Figure 7. The specific surface area, SSA, of surface fractals scales with the length scale  $r$  as (Hinde, 2004; Radlinski, 2006):

$$SSA = \frac{\lim_{Q \rightarrow \infty} [Q^{6-D_s} I(Q)]}{\pi(\Delta\rho^*)^2 \rho F(D_s)} r^{2-D_s}, \quad (5)$$

where  $\Delta\rho^*$  is the scattering length density contrast,  $\rho$  is mass density,  $D_s$  is the surface fractal dimension and

$$F(D_s) = \Gamma(5 - D_s) \sin \left[ (3 - D_s) \left( \frac{\pi}{2} \right) \right] / (3 - D_s). \quad (6)$$

Experimentally determined  $I(Q)$  curves are fitted, after background subtraction, using equation 5 to obtain the specific surface area.

## 3 Discussion

### 3.1 Porosity

The purpose of this study is to compare porosity values derived by different methods and to draw conclusions on the applicability of each method, fluid accessibility and pore network connectivity. Most methods used are more or less straightforward standard methods, such as MIP, He-pycnometry, water porosimetry or the liquid saturation and immersion (LSI) method. Although sometimes used rather uncritically and considered as a standard method, interpretation of N<sub>2</sub> low pressure sorption relies on a thorough understanding of the different interpretation approaches. A comprehensive discussion on this topic is given elsewhere (Bertier et al., 2016; Thommes, 2010). SANS is not a new method but its application to sedimentary rocks, especially coal and organic-rich shales, became popular only recently (Bahadur et al., 2014; Bahadur et al., 2015; Clarkson et al., 2012; Clarkson et al., 2013; Gu et al., 2015; Jin et al., 2013; King et al., 2015; Ruppert et al., 2013). We will not put the focus on the neutron scattering method itself, like many of these previous studies did. This study will focus on measured data and discuss their relevance for the general understanding of shale porosity and surface area.

Porosity of shales, although often used as an intrinsic rock property without distinction, can be divided into the fraction that is connected and contributes to fluid flow, the so-called effective porosity, and the ineffective porosity. The latter relates to pores that are completely inaccessible, the so-called closed porosity, e.g. interlayer spaces of clays or (ultra)-micropores in organic matter that are largely inaccessible to most fluids. It should be clear that the individual limitations, like molecule size, pressure or fluid-rock interaction of each testing method will provide a different fraction of this effective/ineffective porosity. In this contribution, no direct distinction between effective and ineffective porosity is made, as the data does not allow for this distinction without choosing an arbitrary reference. However, as has been shown in earlier studies and as will be discussed later this is in theory possible using SANS/VSANS. We will however be able to draw some conclusions on the open and closed porosity. From the fluid invasion methods used in this study the effective

porosity was determined on a set of 13 Opalinus Clay samples. These are MIP (n=13), He pycnometry (n=9), water porosity (n=13), low pressure N<sub>2</sub> sorption (n=8) and LSI (n=8). Each of these methods provides total porosity values but only MIP and N<sub>2</sub> sorption provide pore volume distributions (PVD). In addition, SANS (n=8) as the only radiation method, determines total porosity (connected plus unconnected) together with SSA and PVD. Table 3 and Figure 9 show porosity values from all methods used in comparison to literature values, obtained for the shaly facies of the Opalinus Clay (Pearson et al., 2003). Porosities from SANS, helium and water are similar, with values of  $\sim 23 \pm 3\%$ ,  $\sim 20 \pm 2\%$  and  $\sim 19 \pm 1\%$ , respectively. SANS determined either for dry or lab humidity equilibrated samples show no differences in porosity (Table 3).

Porosities determined from other methods differ substantially with  $\sim 15 \pm 0.5\%$  for the LSI method,  $\sim 13 \pm 0.2\%$  for N<sub>2</sub> sorption and  $\sim 10 \pm 0.7\%$  for MIP. The latter therefore provides less than half the porosity compared to SANS, and about half the value for water and helium, but is in line with almost identical published values determined on the shaly facies of Opalinus Clay (Pearson et al., 2003). Literature helium and water porosities of 18% and 16% respectively (Pearson et al., 2003) are slightly lower than in this study (Figure 9). Finally, FIB/BIB SEM provides porosities of about 3% on average, including this study,, owing to the pore size resolution limits of  $\sim 10$  nm. Nuclear magnetic resonance (NMR) porosities for Opalinus Clay on samples with higher quartz and lower total clay contents than in this study have been reported to be 10.2% (Dunn et al., 2002, in Sarout et al., 2014).

Molecular and atomic sizes of H<sub>2</sub>O and He differ significantly in diameter with 0.29 and 0.06 nm respectively. Therefore, the theoretical pore size accessibility should differ and differences in porosity could be expected. This is however not the case within the uncertainty of the measurements, indicating that the porosity below 0.29 nm is negligible for the samples tested. SANS provides higher porosities with smaller pore size range (minimum pore size of 2.5 nm). Compared to invading fluids neutrons are able to detect all pores in a microporous material, including those that are inaccessible to fluids, such as the porous inclusions within minerals. This inaccessibility might either be due to small pore throat radii that do not allow access to water/helium molecules or it might be pores that

are completely disconnected. From another perspective, certain pores might simply be inaccessible within the time scale of the measurement. Slow or activated diffusion can control the filling of the pore space at time scales much larger than planned for the measurement (Bertier et al., 2016). Even if pressure equilibrium (for helium typically within minutes) or weight equilibrium (for water within hours or days) was achieved, a higher accessibility might be possible within longer equilibration times. In neutron scattering equilibration time is irrelevant. The statistical significance of porosity measurements by SANS is largely determined by the total counting time, yet for the measurements presented here, doubling the counting time did not result in significantly different porosities. Theoretically, the difference to the SANS porosity can be explained by pores not accessible to water or helium. In principle, the ratio of connected to total porosity can be determined from (V)SANS by saturating the pore space with a contrast matching fluid. This is a mixture of H<sub>2</sub>O/D<sub>2</sub>O (heavy water) matching the rock matrix scattering length density. Only pores not invaded by heavy water will be detected, corresponding to the unconnected porosity. Using this approach, a number of SANS studies report large differences in the connected and unconnected porosity. For a weathering profile in Rose Hill shales the percentage of connected porosity varies between 0 and 73% (Jin et al., 2011), for Cretaceous shales from Alberta, Canada between 63 and 80% (Bahadur et al., 2014) and for the organic-rich Marcellus Shale in the USA from 29-53% (Gu et al., 2015). Accordingly the unconnected porosity can roughly range between 20% and 100% for organic-rich and organic lean shales, without any obvious relation with respect to organic matter. It is questionable whether such high numbers for the unconnected porosity can be justified. This would indicate that (i) a substantial part of the porosity is accessed only through very small pores (< ~1 nm), (ii) a certain fraction of the total porosity can be completely disconnected, (iii) achieving full pore saturation with heavy water is difficult, even under controlled conditions such as in a triaxial flow test where water is injected at high pressure. Evidence for complete water saturation is however lacking in the studies summarised above or (iv) a combination of these points. For a better understanding of the differences in porosity values a comparison of skeletal and bulk densities obtained from MIP, He pycnometry and water porosimetry is given in Figure 10. The bulk density determined using the weight and dimensions of a sample plug dried at 105 °C provides the lowest values

on a set of 13 samples. Yet, the scatter of this data is relatively large. In comparison bulk densities determined using MIP (after surface roughness correction) and LSI are similar, though not identical, but higher than those from the geometric calculations using a caliper. In MIP the determination of the bulk volume is based on the assumption that a certain pressure is required to fill surface roughness and irregularities such as cracks and scratches. This is not considered in the LSI method, which may result in higher bulk densities for MIP. The variance of the measured grain densities is larger than for the bulk densities, with MIP providing by far the lowest mean value of  $\sim 2.57 \text{ g.cm}^{-3}$ , which could be attributed to the accessibility limit to pores  $\leq 3.6 \text{ nm}$ . Helium pycnometry provides the highest value of  $2.71 \text{ g.cm}^{-3}$ . This value is slightly lower than the theoretical value of  $2.72 \text{ g.cm}^{-3}$  determined from combined XRD and TOC data and mineral densities given in Table 1 and Table 2. These mineral densities are approximations since the exact stoichiometry of most minerals is not known. Critical phases are chlorite for which the iron-rich end-member was chosen based on XRD patterns and earlier publications (Lerouge et al., 2014). In illite the octahedral positions were assumed to be occupied by Al, Mg and Fe and all layer charge originates from Al substituting Si in the tetrahedral layers (0.65/half unit cell), resulting in an average density of  $2.7 \text{ g.cm}^{-3}$ . Smectite content in the illite/smectite mixed layers (I/S ML) is approximated using the cation exchange capacities (CEC) in Table 1 compared to CEC values for clays summarised previously (Bergaya et al., 2006). As a result smectite contents are low with bulk values of  $\sim 3.5\%$ . The nearly identical values between a skeleton density determined from helium and the mineralogy suggest that the complete pore system of the sample is accessible to He. The mean value for skeleton density from the LSI method, determined using chloroform saturation is  $2.69 \text{ g.cm}^{-3}$ , only slightly lower compared to the He skeleton density measured on plugs or the mineralogy-based density. This indicates that the relatively low porosity obtained by the LSI method is only to a small amount related to incomplete chloroform saturation of the sample, which would result in lower skeletal density.

In summary, we can note that the bulk and skeleton densities determined from mercury differ from other methods, which in combination results in low porosities. LSI, helium pycnometry and the XRD mineralogy result in similar grain densities, with the highest value

( $2.72 \text{ g.cm}^{-3}$ ) obtained from mineralogy. Compared to the skeleton densities obtained by helium pycnometry and LSI, this implies that only  $\sim 1\%$  of the porosity is not accessible by either fluid which implies that the larger SANS porosities cannot be related to closed pore space.

It remains unclear why SANS provides higher porosities compared to He pycnometry or water porosimetry, especially when considering the lower pore size limit of 2.5 nm. Gu et al. (2015) demonstrated that total porosity and specific surface area strongly depend on sample orientation with respect to the neutron beam. For dry Marcellus shale they determined porosities 2.4 to 7.2 times higher for samples cut perpendicular to bedding compared to their parallel equivalents. This difference is even higher for SSA with factors ranging between 3.6 and 10.8. Scattering patterns for bedding parallel samples are isotropic and those for bedding-perpendicular samples anisotropic. These authors note that SANS porosity might be inaccurate, yet a comprehensive understanding of this issue still seems to be lacking and requires further studies.

The measured Opalinus Clay samples cut bedding-parallel, scatter isotropically. This either indicates isotropic pore geometries, anisotropic pores that are randomly oriented within the sample, or spheroidal pores with a specific orientation that creates an isotropic detector image. It seems unlikely that the SANS porosities presented here are underestimated since values are higher than for all other methods. The FIB SEM results (Figure 3 and Figure 4) suggest that the larger the pore the more anisotropic it is and that the majority of pores are rather well aligned in the bedding planes. In theory those pores that are not bedding-parallel (at an angle of  $35^\circ$  and  $125^\circ$  in Figure 3) could result in a slight anisotropy which, according to previous studies (Gu et al., 2015), could result in an overestimation of porosity. There are some uncertainties with this approach. Pores that are not in the bedding plane could be an artefact of the small FIB SEM volume ( $\sim 10 \times 10 \times 5 \text{ }\mu\text{m}$ ) studied here and a more statistical approach would be required to strengthen this finding. In the segmentation process, pores are defined as disconnected bodies which can contain several pores connected through throats having a diameter within the resolution of the instrument. It seems likely that such a pore cluster could have a different orientation compared to a single pore. In addition it is difficult to state that the pore size range and related pore orientation

extracted from FIB SEM is comparable to the entire pore size range of the samples. On visual inspection, the scattering pattern for (V)SANS are isotropic which would indicate that the 'out-of-bedding plane pores' in Figure 3 do not significantly contribute to anisotropy.

In comparison to the fluid invasion and SANS methods used in this study, electron microscopy or nano-tomography can provide qualitative and quantitative information on Opalinus Clay. In this study FIB SEM was used qualitatively, i.e. to get an impression on pore alignment and pore cluster distribution (Figure 2). A certain pore alignment exists for the different clusters and these clusters are quite randomly distributed within the  $\sim 10 \times 10 \times 5$   $\mu\text{m}$  cube. The different clusters are not connected within the resolution of this method. This is realistic since MIP demonstrates that pore connections have the most prominent radii between 3.5 and 5 nm, which is below the FIB SEM resolution. Focused Ion Beam nano tomography (FIB-nt) have been used to determine Opalinus Clay porosity on three different samples (Keller et al., 2013a; Keller et al., 2011a; Keller et al., 2011b; Keller et al., 2013b). Similar to this study they used samples from the shaly facies. They found that FIB-nt can only resolve comparatively large pores (i.e. radii  $> 10$  nm), resulting in porosity values of 2-3%. According to these authors this corresponds to  $\sim 20$ - $30\%$  of the total pore space. In their study porosity values were determined by converting pore volumes from  $\text{N}_2$  low pressure sorption to total porosity which yielded 10.4 to 11.5%.  $\text{N}_2$  sorption data was evaluated using a so called 'modeless' method which does not consider any pore geometry as has been done in the study presented here. Porosity values from this approach are somewhat lower than the  $\sim 13\%$  in our study. When comparing to He, water or SANS porosities determined for the sample set in this study ( $\sim 19$ - $23\%$ ), only 5-10% seems to be accounted for by FIB-nt for Opalinus Clay. In addition, the same authors used scanning transmission electron microscopy (STEM) and X-ray tomography (XCT), resolving 13% and 0.6% porosity respectively. These differences are due to differences in resolution and sample size. Lower pore radius limits for STEM, FIB-nt and XCT are  $\sim 2$  nm,  $\sim 5$  nm and  $\sim 2000$  nm respectively. Another microscopic study used Broad-Ion-Beam polishing in combination with Scanning Electron Microscopy (BIB SEM), reporting values for the shaly facies of the Opalinus Clay of up to  $\sim 2.4\%$  (Houben et al., 2013). These low values are due

to differences in sample resolution between the different methods, since BIB SEM is restricted to pores >50 nm.

### 3.2 Pore size distribution

Several representations of pore volume distribution (PVD) are in common use. A comprehensive summary is provided by Meyer and Klobes (1999). For comparison between the different methods (SANS, MIP, N<sub>2</sub>) we employed the differential and log differential pore volume approaches  $dV/dr$  and  $dV/dlgr$ , respectively. The former is the recommended method for PVD visualisation by IUPAC while the latter was chosen to add weighting to the larger pore radii. This is shown exemplarily for sample CCP9 in Figure 11, which is representative for all other samples. We find an almost perfect match for the dry and lab-humidity equilibrated (called “moist” in the following) SANS measurements, indicating that small amounts of water do not affect the SANS quantification of porosity. In theory differences can be expected for SLD calculations (assumed to be zero for pores) or incoherent scattering from additional hydrogen molecules present in water (Bahadur et al., 2015).

The N<sub>2</sub> PVD is similar to SANS, indicating that both methods provide comparable PVDs for the overlapping pore radius range. This finding is in a qualitative agreement with earlier findings by Clarkson et al. (2012) comparing SANS/USANS with low pressure N<sub>2</sub> sorption on North American organic-rich shales. As discussed earlier SANS does not only record the connected pore space but also the pore space inaccessible to fluids, assuming there is a measurable difference. This might especially be true for smaller mesopores and micropores. While micropores are excluded in the evaluation of the SANS and N<sub>2</sub> low pressure sorption data we find a surprisingly good agreement for pores <30 Å in diameter and small deviations for pores between 30 and 200 Å. Differences might be in the interpretation of the raw data for both methods. While SANS assumes spheres as pore geometry, the BJH concept for N<sub>2</sub> assumes cylinders.

The PVD from MIP is different from those determined with N<sub>2</sub> or SANS, with large discrepancies in the mesopore range. Pore radii for MIP are calculated based on capillary pressures (from the experiment), interfacial tension and contact angle (from literature).



Strictly speaking, these are pore throat radii and not pore body radii. N<sub>2</sub> and SANS record both, pore throat and pore body radii. Consequently the pore volume within a certain radius range can be of any radius larger than the pore throat radius and direct comparison of the MIP with the SANS/N<sub>2</sub> curves is therefore inappropriate.

### 3.3 Specific Surface Area

Along with total porosity and pore size distribution the specific surface area (SSA) can be obtained from SANS data using the PRINSAS software. The software assumes a polydisperse spheres (PDSP) model, so surfaces are directly related to the surfaces of spheres of different radii. For N<sub>2</sub> physisorption, the Brunauer-Emmet-Teller (BET, Brunauer et al., 1938) is the standard method for surface area assessment. The BET method is valid for the entire pore space (including micropores) and is based on the assumption of multilayer adsorption. There are several shortcomings with this method, especially for microporous materials, which are filled by a different mechanism than the layer adsorption underlying the BET theory (Thommes and Cychosz, 2014). In this study BET SSA is provided and compared with literature BET values for the shaly facies of Opalinus Clay in Figure 12, which shows an excellent match. Additionally, we used the Barrett-Joyner-Halenda (BJH, Barrett et al., 1951) approach, which is valid for mesopores and macropores only, see Bertier et al. (2016) for details. The BJH approach is based on the Kelvin equation and assumes a cylindrical pore geometry. The resulting PSD represents an equivalent capillary bundle which is analogous to MIP. The BJH method seems to be best comparable to the SANS method, which also excludes the micropore range but assumes a spherical pore shape instead of the cylindrical geometry. Figure 12 shows that the SSA from both methods compare very well with average values around 25-28 m<sup>2</sup>.g<sup>-1</sup>. It could be argued that SANS derived SSA values are somewhat higher because the larger pore sizes accounted for, up to 3 μm as compared to 0.35 μm for N<sub>2</sub>. However, the range in SSA values for SANS is much larger and the SSA proportion within macropores can be considered very low. Another argument for the smaller N<sub>2</sub> SSA might be the accessibility of N<sub>2</sub> to the unconnected part of the pore system. In this case, we assume the N<sub>2</sub> inaccessible surface area to be rather small. Speculations remain however vague and differences between the values could well be within the overall standard deviation of the 8 measurements performed for each method.



## 4 Conclusions

Various microscopic, fluid invasion and neutron scattering techniques were used to determine porosity on a set of 13 Opalinus Clay samples obtained from a core section of about 4 m from the Mont Terri underground laboratory in Switzerland. These measurements are supported by a mineralogical and geochemical characterisation demonstrating the homogeneity of the core section.

Averaged porosity values decrease in the order (V)SANS>He>water>LSI>N<sub>2</sub>>MIP>FIB SEM. Of these, He pycnometry and water porosimetry are similar with values around 20%. This value is reduced by half for MIP, while SANS-derived values are slightly higher (~23%). A good agreement is found between skeleton densities for LSI, He and the XRD mineralogy with 2.69, 2.70 and 2.72 g.cm<sup>-3</sup> respectively. This indicates that at most only a small fraction of the pore space, like 1%, is inaccessible to either helium or chloroform and contradicts earlier studies that identified a large fraction of closed or water-inaccessible porosity for different shales using SANS. This inaccessible fraction is sufficiently small as to potentially represent only pores on the interior of minerals (i.e. water and gas filled inclusions), suggesting near complete connection of the mineral external pore volume. For the Opalinus Clay samples tested, the porosity closest to the true value is therefore considered to be ~20% as obtained by He pycnometry and water porosimetry. The reason why LSI results in lower porosities of ~15% is related to overestimated bulk densities determined using mercury. The same holds for MIP, for which the bulk density is higher and the skeleton density lower than for the other methods (Gu et al., 2015; Jin et al., 2011).

From SANS we obtain higher porosities of ~23% with minimum pore diameters of 2.5 nm. This indicates an overestimation of the total porosity. There are different uncertainties with the SANS porosity that are independent of any measurement errors. The method for calculating porosity, PSD and SSA assumes spherical pore shapes for the entire pore size range. This might be realistic for small pores, but larger pores are less spherical (Figure 4). The latter are considered to impact total porosity, but the specific surface area only to a limited extent. Another issue with the evaluation of SANS data is that samples cut parallel to

bedding scatter isotropically while samples cut perpendicular to bedding scatter anisotropically. The latter will result in an overestimation of total porosity when using the PDSP model. Further, the method integrates the pore volumes within the interior of minerals, which are not accessible by other methods.

Pore size distributions of Opalinus Clay were obtained from three different methods. N<sub>2</sub> physisorption and SANS PVDs are not significantly different for the smallest pore size range. Also for the specific surface area, these methods only provide small differences. Relatively large differences between PVD from these methods and MIP were identified and are attributed to the fact that N<sub>2</sub> and SANS provide information on pore bodies and pore throats and MIP determines pore throat diameters only. For the different Opalinus Clay samples tested these features are similar and further analysis and interpretation seems only reasonable when relying on similar datasets for a variety of different shale samples, and ideally for samples for which the permeability is known. This topic will be the focus of future efforts. Any pore scale modelling of flow in argillaceous rocks has to rely on a solid understanding of pore network features which is currently not or insufficiently available. It is important to realise that such an understanding is not gained from a single method but only from a combination of different methods that allow validation, verification and quantification of uncertainties and absolute values.

## **Acknowledgements**

This work was partially funded through the CO<sub>2</sub> Capture Project (CCP3), its members were BP, Chevron, Eni, Petrobras, Shell and Suncor. We thank NAGRA and SWISSTOPO for providing Opalinus Clay core material, Shell Global Solutions International B.V. for the allowance to publish this study and DECC who provided a CCS Innovation grant. Further, we thank Dr. Claudio del Piane and one anonymous reviewer for valuable suggestions that helped to improve the quality of this paper.

## Figure Caption

Figure 1. Illustration showing porosity methods used with their respective lower and upper representation for pore sizes (diameter). The lower boundary for  $N_2$  low pressure sorption is specific for this study (see below); in theory this boundary can be lower. For comparison and to get an impression on scales, pore and grain size classifications as well as flow regimes corresponding to different Knudsen numbers or pore sizes are included.

Figure 2. Visualisation of Opalinus Clay porosity (CCP14) using Focused Ion Beam SEM for two different viewing directions. Single pore clusters (dark spots) can be observed that are largely disconnected within the measurement resolution (about 10 nm). Horizontal scale, x and y direction, is 10.3 and 7  $\mu\text{m}$  and thickness about 5  $\mu\text{m}$  (z-direction),

Figure 3. Absolute pore orientation of  $\sim 3000$  pores in relation to bedding (E-W direction) for  $5^\circ$  intervals. Most pores are aligned parallel to bedding with the exception of pore families aligned at an angle of  $35^\circ$  and  $125^\circ$ .

Figure 4. Equivalent pore radius versus sphericity for sample CCP14. The pore radius is calculated based on pore volume and assuming spherical pore geometry. Pores represented by less than 25 voxels, resulting in a minimum equivalent pore size of  $\sim 40$  nm, are excluded. The total number of pores in this plot is  $\sim 3000$ .

Figure 5. Hg-intrusion volume for 13 Opalinus Clay samples, corrected for surface roughness. a) normalised incremental volumes and b) cumulative volumes.

Figure 6.  $N_2$  low pressure sorption isotherms for 8 Opalinus Clay samples, demonstrating similar sorption behaviour for all samples tested.

Figure 7. Log-log plot of raw (a & c) and background corrected (b & d) neutron scattering data for nine different Opalinus Clay samples equilibrated with ambient humidity (a & b) as well as seven dry samples (c & d).

Figure 8. Differential pore volume distribution  $dV/dr$  for the SANS data on 8 Opalinus Clay samples equilibrated with lab humidity. Since no additional information is gained for pores  $>1000$  Å in radius, data was discarded to better highlight the smaller pore sizes. a) shows the data on a semi-log plot according to recommendations in Meyer and Klobes (1999); b) shows the data on a power-law plot for comparison with the I-Q curves presented in Figure 7.

Figure 9. Whisker-box plot of porosity derived from the different methods and compared to literature data for the shaly facies of Opalinus Clay (Pearson et al., 2003). Upper and lower whiskers represent maximum and minimum values.

Figure 10. Bulk (a) and skeletal (b) density comparison for a selection of the fluid invasion methods used. Upper and lower whiskers represent maximum and minimum values.

*Figure 11. Differential  $dV/dr$  (left) and log differential  $dV/dlgr$  (right) pore volume for SANS,  $N_2$  and MIP on CCP9 representative for all Opalinus Clay samples. The difference in the two ways of documenting the data is that during normalisation for  $dlgr$  more focus is given on the larger pore sizes as compared to the  $dr$  normalisation. For a discussion see Meyer and Klobes (1999). Also note that the radius range for the  $dr$  normalisation (left side) is different to the  $dlgr$  normalisation (right side). No additional information is gained at pore radii larger than  $1000 \text{ \AA}$  for the  $dr$  plot.*

*Figure 12. Whisker-Box plot for SSA for the SANS and  $N_2$  BET and BJH methods. Data derived from this study is compared with literature data for the shaly facies of Opalinus Clay (Pearson et al., 2003). Upper and lower whiskers represent maximum and minimum values.*

## Table Caption

*Table 1. Mineralogy (XRD), geochemistry (XRF), Total Organic Carbon (TOC) and Cation Exchange Capacity (CEC) determined on a set of samples originating from a core section of ~4 m total length (Amann-Hildenbrand et al., 2015). Data are compared with data summary of Pearson et al. (2003) showing generally a good agreement with the measurements performed in this study.*

*Table 2. Structural formula, mineral density  $\rho$  and molar mass  $M$  used to calculate scattering length densities SLD for each individual mineral phase. \*SLD and vitrinite reflectance for organic matter taken from literature (Elie and Mazurek, 2008; Thomas et al., 2014).*

*Table 3. Summary of porosity and specific surface area (SSA) values for Opalinus Clay. For porosities we used small and very small angle neutron scattering [(V)SANS] on dry and lab humidity equilibrated samples, helium pycnometry, water porosity, liquid saturation and immersion (LSI), low pressure  $N_2$  sorption and MIP. For SSA we used (V)SANS and  $N_2$  sorption. Samples CCP1-9 relate to the geochemical/mineralogical analysis in Table 1. Samples CCP10 - 15 are from the same core section but taken in between samples CCP1-9.*



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