Characterization of tight gas reservoir pore structure using USANS/SANS and gas adsorption analysis

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Abstract

Small-angle and ultra-small-angle neutron scattering (SANS and USANS) measurements were performed on samples from the Triassic Montney tight gas reservoir in Western Canada in order to determine the applicability of these techniques for characterizing the full pore size spectrum and to gain insight into the nature of the pore structure and its control on permeability. The subject tight gas reservoir consists of a finely laminated siltstone sequence; extensive cementation and moderate clay content are the primary causes of low permeability. SANS/USANS experiments run at ambient pressure and temperature conditions on lithologically-diverse sub-samples of three core plugs demonstrated that a broad pore size distribution could be interpreted from the data. Two interpretation methods were used to evaluate total porosity, pore size distribution and surface area and the results were compared to independent estimates derived from helium porosimetry (connected porosity) and low-pressure N2 and CO2 adsorption (accessible surface area and pore size distribution). The pore structure of the three samples as interpreted from SANS/USANS is fairly uniform, with small differences in the small-pore range (<2000 Å), possibly related to differences in degree of cementation, and mineralogy, in particular clay content. Total porosity interpreted from USANS/SANS is similar to (but systematically higher than) helium porosities measured on the whole core plug. Both methods were used to estimate the percentage of open porosity expressed here as a ratio of connected porosity, as established from helium adsorption, to the total porosity, as estimated from SANS/USANS techniques. Open porosity appears to control permeability (determined using pressure and pulse-decay techniques), with the highest permeability sample also having the highest percentage of open porosity. Surface area, as calculated from low-pressure N2 and CO2 adsorption, is significantly less than surface area estimates from SANS/USANS, which is due in part to limited accessibility of the gases to all pores. The similarity between N2 and CO2-accessible surface area suggests an absence of microporosity in these samples, which is in agreement with SANS analysis. A core gamma ray profile run on the same core from which the core plug samples were taken correlates to profile permeability measurements run on the slabbed core. This correlation is related to clay content, which possibly controls the percentage of open porosity. Continued study of these effects will prove useful in log-core calibration efforts for tight gas.

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1. Introduction

The pore structure of unconventional gas reservoirs (tight gas, shale gas and coalbed methane) is difficult to characterize because of the ultra-fine (nanopore) structure, often associated with (but not restricted to) organic matter content, and generally broad pore size distribution (PSD). Understanding the nature of the pore structure (PSD and open versus closed porosity) is a primary objective leading to a better understanding of gas storage and transport mechanisms and their controls. This, in turn, has direct implications for gas producibility. A hybrid of techniques is typically required to investigate the full pore size spectrum (Fig. 1), including a combination of fluid invasion and radiation methods [1]. Conventional methods for pore structure characterization of unconventional gas reservoirs are limited. Mercury intrusion (MICP) in particular cannot access the finest porosity (<3 nm) in unconventional gas reservoirs (UGRs) and there is also the
possibility of damaging the pore structure because of the immense pressures required for mercury to access the finest porosity. Low-pressure adsorption (N₂ and CO₂) have been used for many years for characterizing the matrix pore structure of coals [2–4] and more recently gas shales [1,5–8]. These techniques must be combined with MICP to investigate the entire pore size spectrum of UGRs because of the variable access of the probe molecules (N₂ and CO₂) at measurement temperatures and pressures [Fig. 1]. The integration of these techniques is not straightforward, as discussed by Gan et al. [2] Further, adsorption methods are low pressure techniques and cannot be used to investigate the pore structure at realistic pressure–temperature conditions of the reservoirs.

Very recently, small-angle and ultra-small-angle neutron scattering (SANS/USANS) techniques have been utilized to investigate the pore structure of coals [9–12]. The combination of SANS and USANS techniques is advantageous due to: (1) the wide spectrum of pore sizes that can be investigated; (2) the ability to distinguish closed versus open porosity [13,14]; (3) the ability to investigate pore structure at realistic (reservoir) P–T conditions and changes in pore structure at variable P–T conditions; and (4) the non-destructive nature of the analyses (act of measurement does not alter the rock microstructure). In a SANS experiment (Fig. 2), a neutron beam is directed at a sample, and the neutrons are elastically scattered due to their interaction with nuclei of atoms in the sample – the scattering vector is related to a characteristic length scale (pore size) in the sample. Pore structure investigation is therefore not limited to the size of the molecular probe used in the experiment.

In this work, we investigate the utility of the SANS/USANS technique for quantifying the pore structure of three samples from the Montney tight gas reservoir at ambient temperature and pressure. The results of these experiments, interpreted for pore size distribution, surface area and total porosity, are then compared to more conventional methods such as nitrogen and carbon dioxide adsorption (surface area and pore size distribution) and helium porosity (connected porosity). The percentage of open porosity is inferred from the ratio of porosity accessible to helium to total porosity established from SANS/USANS, and compared to permeability estimates using pressure- and pulse-decay methods. Although the controls of mineralogy on the pore structure and permeability for the three samples analyzed are inferred, a more detailed study of these effects will be discussed in a future article.

2. Experimental methods

The focus of this study is detailed characterization of three core plugs sampled from different lithologies (finely laminated siltstone and thicker siltstone beds) contained within a 17.5 m Montney tight gas core for which a comprehensive suite of data were collected and previously described and interpreted [15]. The use of profile and pulse-decay permeability measurements for flow unit analysis was also discussed in that work. The focus of this study is on the comparison of N₂ and CO₂ adsorption, helium porosimetry and USANS/SANS results and on the applicability of USANS/ SANS techniques in tight gas reservoirs, but our findings will be related to permeability measurements and rock composition.

Profile permeability data were collected on the slibbed 17.5 m core using a PDPK-400® (CoreLab) probe permeameter at approximately 2.5 cm (1 in.) intervals. The PDPK-400 measures the rate of pressure-decay through a probe tip sealed against the core surface by an O-ring. Details of the probe permeameter measurement procedures and theory are provided in Jones [16]. The permeability range of the device is 0.001 mD to 20 Darcies. Prior to analysis, the slibbed core face was lightly sandblasted to remove surface roughness and debris, and to improve probe tip seal. During analysis, sections of the core exhibiting evidence of microfractures

![Fig. 1. Methods used to estimate porosity and pore size distributions in unconventional gas reservoirs. Modified from Bustin et al. [1].](image1)

![Fig. 2. Diagram of a neutron scattering experiment. Source: Melnichenko et al. [10].](image2)
were avoided. A total of 593 data points were collected, with measurements performed approximately parallel to bedding. Of interest to this study are the measurements taken at the locations of core plug samples 4, 5 and 24 (see Fig. 3 below).

Following the probe permeability measurements, the three core plug samples (2.5 cm (1 in.) diameter core plugs) were retrieved from the slabbed core – the plugs were cut at the same location as the probe measurements, with the probe permeability measurement point (marked on the core at time of measurement) at the approximate center of the core plug end. Sub-samples of core plugs S4, S5 and S24 were taken for low-pressure adsorption, XRD/microprobe and SANS/USANS analysis based upon a contrast in probe permeability and macroscopic appearance (lithology contrast). For these core plug samples, additional core plug material was removed and crushed to mm size particles (fine chips, not sieved) and to −4 mesh size (sieved samples) for N2 and CO2 adsorption analysis. An additional 1.2 mm thick disc (2.54 cm diameter) was cut from the core plug for SANS and USANS analysis (described below).

Samples prepared for adsorption analysis were first outgassed overnight. N2 adsorption/desorption isotherms were collected at 77 K using a Micromeritics TriStar II 3020® (fine chips). N2 adsorption/desorption and CO2 adsorption data (273 K) were collected for the −4 mesh (sieved samples) on a Micromeritics ASAP 2020® apparatus. The N2 data collected on crushed samples was interpreted using multi-point Brunauer–Emmett–Teller (BET) and Langmuir analysis for surface area and Barrett–Joyner–Halenda (BJH) analysis for pore size distributions – these methods are comprehensively discussed in Gregg and Sing [17]. BET surface areas were also measured for the entire core plug using a Micromeritics ASAP 2020® apparatus and compared to crushed sub-sample analysis. CO2 adsorption data were interpreted using the BET and Langmuir models, as well as the Dubinin–Astakhov (D–A) and Dubinin–Radushkevich (D–R) models. Additional data collected on core plug sub-samples included XRD (obtained from discs used for SANS/USANS experiments) for bulk rock mineralogy, thin sections for petrographic analysis and electron microprobe analysis.

Porosity and permeability were also measured on the core plugs at overburden pressures representative of the reservoir. Porosity measurements were carried out with a CoreLab CMS-300® using helium, while air permeability measurements (at overburden pressures) were performed with a pulse-decay permeameter (PDK-200®) using a mean gas pressure of 6890 kPa (1000 psi). Core plugs 4, 5 and 24 were subject to 14466 kPa (2098 psi) lab hydrostatic or 25468 kPa (3694 psi) reservoir confining pressure. Net overburden stress for the reservoir was estimated from lithostatic gradient and initial reservoir pressure. An additional five additional overburden pressure measurements were also performed: 6667 kPa (967 psi), 10584 kPa (1535 psi), 18417 kPa (2671 psi), 22333 kPa (3239 psi) and 26249 kPa (3807 psi) – all of these pressures represent the applied lab hydrostatic.

Following the permeability analysis, the core plugs were sent to the University of Calgary Rock Preparation lab, where petrographic thin sections were cut from the three core plug samples. The sections were cut 30 μm thick, and double polished using diamond plates. No mineral staining was done, in the interest of preserving the polished surface for future electron microprobe and SEM analysis. Petrographic analysis was completed using a Nikon Eclipse E600 POL microscope fitted with a Leica DFC 295 camera and accompanying software.

X-ray diffraction (XRD) analysis was performed on sub-samples of core plugs 4, 5 and 24 with a normal focus Cobalt X-ray tube used in a Siemens Diffractometer D8 at 40 mA and 40 kV and mineralogy was quantified by Rietveld analyses [18] using the
software Topaz. Microprobe analysis was performed on the same three samples for a more accurate mineralogical characterization. This work was done on the JEOL JXA 8200 electron microprobe located at the University of Calgary Geochemical lab.

SANS experiments were conducted on 1.2 mm thick discs cut from the three core plugs at ORNL on the General Purpose SANS instrument [19] with a neutron wavelength of \( \lambda = 12 \) Å and \( \lambda = 4.8 \) Å (\( \Delta \lambda/\lambda \sim 0.13 \)). Sample-detector distances were chosen to cover an overall range of scattering vectors (\( Q \)) \( 0.0016 < Q < 0.7 \) Å\(^{-1} \), where \( Q = 4\pi\lambda^{-1} \sin \theta \), in which \( 2\theta \) is the scattering angle. Data were corrected for instrumental background as well as detector efficiency and put on absolute scale (cross section \( I(Q) \) in units of cm\(^{-1} \)) by means of pre-calibrated secondary standards. USANS experiments were performed at NIST, using the BT5 perfect crystal SANS instrument (\( \lambda = 2.4 \) Å, Q-range \( 5 \times 10^{-2} < Q < 0.00266 \) Å\(^{-1} \)) (Barker et al. [20]). Application of these instruments allowed a broad range of pore sizes to be probed by neutrons, from approximately 5000–12 Å. Characteristic pore size (\( R \)) may be estimated based on the Bragg law \( \lambda = 2D \sin \theta \), where for disordered systems \( D \) is the characteristic length scale of the structural in homogeneities (e.g. linear pore size in a matrix). This law provides an approximate relationship between the scattering vector \( Q \) and \( R: R \approx \frac{\pi D}{Q} \). Detailed simulations show that for polydisperse porous media a more appropriate relationship is \( R \approx 2.5Q/R \) (Radlinski et al. [21]), which was used in this work to relate Q-values with \( R \).

For both SANS and USANS experiments, the samples were confined inside a thin-wall quartz cell. All experiments were conducted at room temperature (\( T = 23 \) °C) and at ambient pressure. The neutron beam size used was about 3 cm\(^2\) in area and the total acquisition time was of the order of 60 min for SANS (total acquisition time at three sample-detector distances) and approximately 7 h for USANS.

3. Results

3.1. Core descriptions

Detailed geological core logging was completed on the 17.5 m core, with the intention of identifying any macroscopic geological variations with depth. The lithology and gamma ray profile are presented in Fig. 3 – core plug samples that are the focus of this study (S4, S5 and S24) are indicated. The dominant lithology of the core is parallel laminated coarse to fine siltstones, with very few physical or biogenic sedimentary structures. Sedimentary structures are present only in the coarse siltstone beds, and include: ripple laminations in addition to occasional horizontal trace fossils. Thickness and frequency of siltstone bedding are variable throughout the length of the core, with bed thickness generally increasing towards the bottom of the core. The frequency of fine versus coarse layers of siltstone beds/laminations allows for the division of the core into two facies. Facies A occurs at the base of the core and is characterized by thickly bedded coarse siltstones interbedded with thick, dark fine siltstone units. The distance between coarse siltstone interbeds ranges from 5 cm to 275 cm, averaging 75 cm. Two of the core plug samples used for analysis (S4 and S5) are located in Facies A. Facies B comprises the upper portion of the core, and is characterized by finely-laminated coarse and fine siltstones, with coarse beds occurring on the mm scale and separated by 0.5–10 cm (average 2.5 cm). One core plug sample used for analysis (S24) is located in Facies B.

3.2. Petrographic analysis

Petrographic analysis was performed on thin sections cut from core plug samples S4, S5, and S24 in addition to thin sections cut from other samples of the core. General mineralogy and textural features are presented in Fig. 4; we have included photomicrographs from sample locations throughout the core to illustrate variability. Thin section descriptions of the samples of interest in this study are provided in Table 1a,b. Framework grains are primarily quartz and orthoclase, with variable amounts of carbonate grains (dolomite and calcite). The matrix consists of clays and organic matter, with minor amounts of pyrite, anhydrite, and micas.

3.3. Compositional analysis using XRD and microprobe

As compositional analysis is necessary for quantitative interpretation of SANS/USANS measurements, both XRD and electron microprobe analysis were performed on samples S4, S5 and S24. These analyses were also used to help define mineralogic controls on permeability variations.

The results from the XRD analysis are presented in Table 2 and Fig. 6. S4, S5 and S24 have a similar mineralogical composition, with some differences in individual mineral percentages. S4 contains the highest percentage of quartz (over 40%), whereas S5 and S24 contain around 30%. Dolomite content increases with depth, with S4 and S5 being close in value and S24 containing greater amounts. Orthoclase content is nearly identical for S4 and S5 (18.4% and 18.6%, respectively), whereas S24 has less orthoclase (12.6%). All three samples are albite-poor. Calcite is absent in samples S4 and S5 but not in S24, which contains 8.5%. Both muscovite and its alteration product chlorite are more plentiful in S5 and present in approximately equal volumes in S4 and S24. Illicite content is surprisingly low in all three samples, although with the Rietveld analysis method [18], illite and muscovite are difficult to distinguish and, consequently, some of the volume attributed to muscovite is likely illite. Pyrite is present in nearly equal proportions in all three samples. The electron microprobe was used to create chemical maps of 7 locations (each 5 mm\(^2\)) on samples S4, S5, and S24. Three locations were chosen on both S4 and S5 to best represent grain size and textural heterogeneities. Only one location was taken on S24, due to the fact that the section is very homogeneous. Each area was scanned 8 times, and returned relative abundance maps of Si, Mg, Ca, Fe, K, Na, and Al. Backscatter electron images were collected for S4 and S5. Additional work was done on the microprobe to examine textural relationships between various grains, and determine the identity of any unknown minerals. These were photographed and some were presented in Fig. 4.

Many interesting textural observations can be made from the element maps produced by the microprobe. These are demonstrated in Fig. 5, which displays the Si, Mg, and K maps for one location on each sample. One of the most striking features is that the mineral composition of the samples remains largely constant across coarser laminations. The only exceptions to this are clay minerals, which are in much higher abundance in the finer regions; these minerals appear as the fibrous, dark to medium blue matter on Mg, and K maps (Fig. 5). Overall, the samples are all moderate to moderately well sorted, with S4 being the most sorted and S24 the least.

3.4. Permeability and porosity determination

Two independent estimates of permeability were available for core plug samples S4, S5 and S24: probe permeability measured on one end of the core plug, and pulse-decay permeability measured on the entire core plug. For the latter, measurements were performed under confined conditions, which more accurately reproduces in situ stress conditions (see Clarkson et al. [15]). S4 has the highest permeability of the three samples, but the difference depends upon the stress applied (Table 3, Fig. 7). Note
that the profile permeability measurement on one end of the core plug was taken under ambient conditions and samples a smaller volume than pulse-decay measurements, causing the discrepancies between the measurement methods.

Profile permeability measurements are compared with core gamma ray measurements in Fig. 8. Also shown in this figure are the profile permeability (black stars) and pulse-decay permeability (red circles) measurements (at 4.9 MPa (710 psi) net overburden (NOB) pressure) for S4, S5 and S24. As discussed in Clarkson et al. [15], the profile permeability measurements show cyclicity above 2209 m, and an increasing trend above 2200 m. In some portions of the core, the gamma ray signature appears to track permeability, particularly for the trend above 2200 m; a ‘cleaning upward’ trend (decreasing API) in gamma ray (GR) signature appears to track the increase in permeability. S4 and S5 were collected in this portion of the core, with S4 having a higher permeability and lower API. The primary controls on GR API are chlorite/illite/muscovite (illite/muscovite are difficult to distinguish using XRD) and potassium-feldspar content – the presence of the clay minerals (illite + chlorite) is expected to lower the permeability in the samples due to blocking of pore throats [22]. Therefore, the lower estimated clay content is consistent with the higher.
The quartz is sub-rounded to sub-angular and shows pressure solution features (shared boundaries, overgrowths, and embayments). These diagenetic features in quartz appear to be more prominent in the layers of coarser silt. In some locations, dust rims can be seen. The dolomite occurs as a space-filling species, as well as in euhedral rhombs. Clays are present as coatings and alteration products of framework grains, particularly the feldspar.

This thin section is overthick, and therefore it is difficult to distinguish grain boundaries. However, pressure dissolution features are still visible in the quartz. These include shared grain boundaries, overgrowths, and embayments. Texturally, this sample is moderately sorted – there are some larger (>20 µm) quartz, dolomite and anhydrite grains dispersed throughout. The dolomite occurs as a space-filling species, as well as in euhedral rhombs. Clays are present as coatings and alteration products of framework grains, particularly the feldspar.

Texturally the sample is moderately to well sorted, with occasional larger (>20 µm) quartz, dolomite or anhydrite grains. Pyrite is noticeably more dominant than other, coarser samples. In addition, large masses of OM are present. Diagenetic features (such as shared boundaries, overgrowths, and embayments) are seen in the quartz grains. The dolomite occurs as a space-filling species, as well as in euhedral rhombs. Clays are present as coatings and alteration products of framework grains, particularly the feldspar.

3.5. N2 and CO2 adsorption

N2 adsorption isotherms (Fig. 9) are Type IV according to the Brunauer, Demming, Deming and Teller classification [23], which are common for mesoporous (pore diameters between 2 and 50 nm) solids [17]. The hysteresis loop (difference between N2 adsorption/desorption isotherms) shape in Fig. 9 for S4 and S5 was previously [15] interpreted to be indicative of slit-shaped pores, which is consistent with what has been observed in other tight gas reservoirs [24]. We note, however, that this interpretation of pore shape is not consistent with the scattering patterns observed from SANS/USANS (see Section 4).

The various sample types (chip samples, – 4 mesh and 1” core plugs) yielded comparable N2 BET surface areas (Table 5), which suggests relative sample homogeneity. Sample 5 adsorbs the most N2 gas and has the greatest surface area (2.32–3.05 m²/g), followed by sample 4 (2.08–2.59 m²/g) and sample 24 (0.62–1.54 m²/g). Two of the sample surface areas are quite large compared to conventional reservoirs, which generally have surface areas ~1 m²/g [25]. We interpret these relatively large surface areas to be due to a combination of clay content, organic matter and very fine grain size.

CO2 adsorption is commonly used to estimate micropore surface areas and pore volumes in coal and shale – the fact that the CO2 surface areas (Table 6) are comparable, if not smaller than the N2 surface areas, suggests that there is very limited microporosity in these samples, possibly due to the low organic matter content. D-A micropore volumes ranging from 0.001756 (sample 4) to 0.005115 (sample 5) cm³/g are indeed much smaller than in shales with higher organic matter content [7].

The pore size distributions, as interpreted by BJH Theory, and using the desorption branch of the isotherm (Figs. 10a and 11a), indicate that S4 and S5 have a bimodal distribution with the larger peak at ~800 Å. S24 appears devoid of pore volume at pore sizes less than ~500 Å and has a peak at around 1000 Å. Clarkson et al. [15] noted that the larger PSD peak is reasonably consistent with the dominant pore throat size obtained from mercury intrusion data – the dominant pore throat size is useful for flow unit identification. The PSD peak (Fig. 10) at 40 Å is believed to be an artifact caused by the Tensile Strength Effect associated with the desorption branch of the isotherm [26]. The PSDs interpreted from the adsorption branch (Fig. 10b) do not have this peak. Further, the bimodal distribution of S4 and S5 is less obvious using the adsorption branch, and the peaks are shifted to larger pore sizes.

3.6. Analysis of the raw USANS data (effect of multiple scattering)

Fig. 12 shows raw USANS data (slit geometry, before applying desmearing routine) from S4 (blue circles) compared with the rocking curve (scattering with no sample in the instrument) of the USANS BT-5 instrument. As may be seen in Fig. 12, shapes of the two curves are markedly different for small values of the scattering vector (Q < 3 × 10⁻³ Å⁻¹): the intensity with the sample in is by a factor of ~6 lower and the shape is more flattened compared to the primary beam. These effects are rather unexpected, considering the relatively high values of neutron transmission of all shale samples (Tₑ ~ 0.93) which compensates for the reduction of the primary beam intensity caused by incoherent scattering, absorption, and possible coherent wide-angle diffraction [20]. Therefore, the significant decrease of the beam intensity shown
in Fig. 12 is most likely related to the multiple small-angle scattering [27–30]. It has been established theoretically and confirmed experimentally that the effect of multiple scattering is proportional to the product $I(Q) \cdot d \cdot \lambda^2$, where $I(Q)$ is the differential cross section of scattering, $d$ is sample thickness and $\lambda$ is the neutron de Broglie wavelength. Therefore, multiple scattering is accentuated for thicker samples (~5–10 mm thick and above) and long wavelengths ($\lambda \sim$ 10–14 Å). We speculate that one of the possible reasons for this strong multiple scattering from rather transparent ($T_I \sim 0.93$) and thin (~1.2 mm) samples observed at relatively short wavelength of $\lambda = 2.4 \text{ Å}$ might be caused by the reduction of neutron mean free path due to the presence of large number of macropores and/or micrometer size mineral inclusions with scattering length density significantly different from the average rock matrix value. We plan to study this effect in more detail by measuring USANS as a function of sample thickness, which should allow us to estimate the average size of the pores or inclusions using Sabine–Bertram theory [27]. The effect of multiple scattering diminishes for decreasing values of $I(Q)$ (and, therefore, increasing values of $Q$). It follows from our data presented in Fig. 12 (and also from other data presented below) that this effect may be neglected for $Q$-values larger than about $1 \times 10^{-4} \text{ Å}^{-1}$, where both USANS and SANS intensities vary linearly with the same slope on the log-log scale.
three samples measured at ambient conditions. The scattering data
3.7. USANS/SANS scattering profiles and power law fitting

Fig. 13 shows combined USANS and SANS patterns from all
three samples measured at ambient conditions. The scattering data
look qualitatively similar to the typical scattering curves for shales
[31]. In the range of $10^{-4} < Q < 0.3$ Å$^{-1}$ the scattering intensity
can be represented on the log–log scale by a straight line with a slope
close to –3 (see Figs. 14–16), which indicates a power-law scattering characteristic of a very rough surface fractal pore-matrix
interface, with fractal dimensions of $D_S = 6-3.2 \pm 2.8$ (for S4), $D_S = 6-3.13 \pm 2.87$ (for S5), and $D_S = 6-3.28 \pm 2.72$ (for S24).
In this Q-range, the scattering is dominated by pores of linear dimensions
in the range 2.5 μm > 2.5/Q > 8 Å. As discussed in the previous section,
the observed flattening of the scattering intensity at $Q < 10^{-4}$ Å$^{-1}$ is a result of multiple scattering and thus the USANS data in this Q domain were excluded from the further analysis,
which is based on single scattering models.

In the limit of high Q-values ($Q > 0.4$ Å$^{-1}$), SANS intensity for all
samples transforms into a flat background. Scattering in this do-
main (of the order of $4 \times 10^{-2}$ cm$^{-1}$) is caused predominantly by
incoherent scattering on hydrogen atoms present in the organic
matter embedded in the rock plus possibly scattering on small scale structural in homogeneities of the rock matrix.

3.8. SANS/USANS structural analysis based on Porod Law

The composition of S4 is re-presented in Table 8 along with the scattering length density (SLD) calculation. All other samples
studied here have similar composition, with slightly different mole fractions of the components shown in column 1 of Table 7. The SLD of each mineral was calculated using the formula $SLD = (b_i/M_{Ni})d_i$, where $b_i$ and $M_{Ni}$ is a scattering length and atomic mass of the $i$-th element in the mineral, $d_i$ is the mass density of the $i$-th mineral, and $N_A$ is the Avogadro number [31,32]. As may be seen in Table 7, the major contribution in the total SLD is coming from quartz
due to the highest mole fraction of this component. The total SLDs of each sample was calculated as a sum of SLDs of all constituent minerals weighed by their mole fraction and the resulting values are tabulated in Table 8. We note from Table 2 that the composition of all samples are dominated by quartz (30–40%) and dolomite (20–30%), and therefore mineral composition variance associated with minor components (ex. illite) will not greatly impact SLD calculations.

According to Refs. [30,33,34] the specific surface area (SSA, $S_v$)
of surface fractals scales with the length scale ($r$) as:

$$ S_v = \lim_{Q \to \infty} Q^{6-D_S}I(Q) $$

$$ \pi(\Delta \rho_p)^{-1} \rho F(D_S) $$

where $\Delta \rho_p$ is the scattering length density contrast, $\rho$ is mass den-
sity, $D_S$ is the fractal dimension, and:

$$ F(D_S) = \Gamma(5-D_S) \sin(3-D_S)(\pi/2)/(3-D_S) $$

Fits of the experimentally observed intensities (with back-
ground subtracted, Figs. 14–16) to Eq. (1) gives the values of SSA shown in Table 9. For comparison, we have also included the $N_2$
BET surface areas; for all samples, the surface areas calculated from the SANS/USANS models are significantly larger than for $N_2$.  

<table>
<thead>
<tr>
<th>Sample</th>
<th>Profile permeability (md)</th>
<th>Pulse-decay permeability$^a$ (md)</th>
<th>Pulse-decay permeability$^b$ (md)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.011</td>
<td>0.0033</td>
<td>0.0024</td>
</tr>
<tr>
<td>5</td>
<td>0.0025</td>
<td>0.0012</td>
<td>0.00075</td>
</tr>
<tr>
<td>24</td>
<td>0.0076</td>
<td>0.0015</td>
<td>0.0011</td>
</tr>
</tbody>
</table>

$^a$ Measured at 4.9 MPa (710 psi) net overburden (NOB) pressure.  
$^b$ Measured at reservoir net overburden (NOB) pressure (25.5 MPa or 3700 psi).
adsorption, suggesting that there is a significant amount of pore volume that is inaccessible to \( \text{N}_2 \) under the experimental conditions.

Total volume fraction of pores (total porosity, \( \phi \)) in the samples was determined using the Porod invariant \( (Z) \), defined as \[ Z = \int_0^\infty Q^2 I(Q)dQ = 2\pi^2(\Delta \rho \cdot \chi)^2(1 - \phi) \]

The accurate evaluation of \( Z \) requires integration of the scattering intensity weighed by \( Q^2 \) from \( Q = 0 \) to \( Q = \infty \), and these limits are not usually accessible in scattering experiments. The evaluation of \( Z \) in Eq. (3) is thus usually performed by numerical integration in three \( Q \)-domains: (I) unmeasured domain between 0 and \( Q_L \) \( (Q_L = 1 \times 10^{-4} \text{ Å}^{-1} \) in this work), (II) experimentally accessible domain \( Q_L < Q < Q_0 \) \( = 0.4 \text{ Å}^{-1} \) and (III) unmeasured \( Q > 0.4 \text{ Å}^{-1} \). The contribution to the invariant from the (unmeasured) cross section in domain (I) was estimated by extrapolating the observed power law scattering to \( Q = 0 \). The contribution to the invariant from the (unmeasured) domain (III) was estimated using power law \( (I(Q) = A Q^{-n} + B) \), with appropriate values of the exponent \( n \) (Figs. 14–16).

For comparison with the results based on fits to the polydisperse spheres model, in which only experimentally measured values of \( I(Q) \) are involved, we also present results based on Porod

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**Table 4**

Helium porosity results for samples S4, S5, and S24.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Porosity (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>7.9</td>
<td>7.1</td>
</tr>
<tr>
<td>5</td>
<td>6.3</td>
<td>5.3</td>
</tr>
<tr>
<td>24</td>
<td>5.6</td>
<td>5.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Measured at 0 MPa confining pressure.

<sup>b</sup> Measured at reservoir net overburden (NOB) pressure (25.5 MPa or 3700 psi).
invariant calculated using measured \( I(Q) \) data (without extrapolations). The results are presented in Table 10 along with the porosity data obtained using helium porosimetry at ambient conditions. As may be seen in Table 10, all samples have slightly different porosities, and different methods of extrapolation provide similar results. The integration, performed according to Eq. (3), over extrapolated range of \( Q \) on both ends of the measured \( Q \)-range gives porosity values 7–8% higher than integration limited to the experimentally measured values of the scattering vector. These porosity values also agree well with the results of helium porosimetry.

While there is good agreement between helium porosimetry data SANS-USANS derived values, total porosities determined using helium porosimetry are systematically lower than corresponding “Porod invariant” porosities listed in column 2 of Table 10. This is most likely caused by the fact that neutron scattering provides information on total porosity (both closed and open

---

**Table 5**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( N_2 ) BET surface area chip samples (^a) (m²/g)</th>
<th>( N_2 ) BET surface area – 4 mesh samples (^b) (m²/g)</th>
<th>( N_2 ) BET surface area core plug samples (^c) (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.08</td>
<td>2.11</td>
<td>2.59</td>
</tr>
<tr>
<td>5</td>
<td>3.05</td>
<td>3.22</td>
<td>2.82</td>
</tr>
<tr>
<td>24</td>
<td>0.75</td>
<td>0.62</td>
<td>1.54</td>
</tr>
</tbody>
</table>

\(^a\) Crushed samples, not sieved.
\(^b\) Crushed and sieved to – 4 mesh.
\(^c\) 1” core plug sample.

---

**Table 6**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( CO_2 ) BET surface area (^a) (m²/g)</th>
<th>( CO_2 ) Langmuir surface area (^a) (m²/g)</th>
<th>( CO_2 ) D-R micropore surface area (^a) (m²/g)</th>
<th>( CO_2 ) D-R micropore volume (^a) (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.7</td>
<td>1.86</td>
<td>1.90</td>
<td>0.0017756</td>
</tr>
<tr>
<td>5</td>
<td>1.53</td>
<td>1.64</td>
<td>1.84</td>
<td>0.005115</td>
</tr>
<tr>
<td>24</td>
<td>1.46</td>
<td>1.65</td>
<td>1.28</td>
<td>0.004053</td>
</tr>
</tbody>
</table>

\(^a\) Samples crushed and sieved to – 4 mesh.

---

![Fig. 10](image1.png)  

**Fig. 10.** BJH pore size distributions obtained from desorption branch (a) and adsorption branch (b) of \( N_2 \) isotherms for S4, S5, and S24 chip samples. Modified from Clarkson et al. [15].

![Fig. 11](image2.png)  

**Fig. 11.** BJH cumulative desorption (a) and adsorption (\( N_2 \)) pore volume plots for S4, S5, and S24 chip samples. Modified from Clarkson et al. [15].
pores), whereas the helium porosimetry method only provides the total volume of pores accessible to helium (connected porosity). There is some expected error caused by using different pore volumes (core plug for helium versus core plug sub-sample for SANS/USANS). We believe that for the same reasons the SSA values measured using nitrogen adsorption are systematically smaller than those measured using neutron scattering techniques (Table 9), but that accessibility of N\textsubscript{2} is further limited due to molecular size and temperature of adsorption measurements. For S4, total porosity as determined from SANS/USANS is nearly equal to helium porosity (connected porosity), which we interpret as an indication that almost all pores are interconnected. For the other two samples there is a significant amount of closed porosity (Table 10). The greater percentage of open porosity for S4 is the possible cause of its higher permeability relative to S5 and S24.

Fig. 12. Rocking curve of the empty beam (normalized by sample transmission, circles) compared to rocking curve with sample S4 in the beam (squares).

Fig. 13. Combined neutron scattering profiles for three shale samples. The arrows show ranges of the scattering vector covered in the SANS and USANS experiments.

3.9. SANS/USANS structural parameters based on the Polydisperse Sphere Particle (PDSP) Model

Fig. 17 shows a fit of experimental data acquired for S4 to the PDSP model, performed using PRINSAS software [36]. Similar high-quality fits were obtained for the other samples. The pore size distribution and specific surface area (SSA) of S4 as a function of the probe size obtained from the fit to the PDSP model is presented in Fig. 18. The total pore volume and the SSA of each sample were calculated by summing individual pore volumes and their surface areas as a function of pore radius, \( r \), and normalizing to the sample volume. We note that such procedure involves only the actually measured scattering intensity in the range of \( 10^{-4} < Q < 0.4 \text{ Å}^{-1} \) (no extrapolation at low and high Q limits is involved) and thus total porosity obtained for each sample should be compared with corresponding “Porod invariant” porosity values shown in column 3 of Table 10. We note that in the calculations of \( f(r) \), it is assumed that all minerals are equally likely to have pores, all of the same size.

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Fig. 14. Scattering profile for S4 with background subtracted. Solid line represents a fit to the power law model.

Fig. 15. Scattering profile for S5 with background subtracted. Solid line represents a fit to the power law model.
distribution. However, as was mentioned in the previous section, the dominant contributor in the total SLD value is quartz and the calculated pore size distribution is most likely dominated by the contribution from this mineral. At this time, we are contemplating experimental methods to verify this interpretation. Although small amounts of organic matter (<1.5 wt.%) exist in the rock, our work suggests that this is not kerogen and therefore does not have a porous structure – this will be discussed in detail in a future paper.

4. Discussion

A variety of techniques, including low-pressure adsorption and SANS/USANS have been applied to tight gas samples in order to gain an understanding of pore structure in these samples and its control on permeability. The three core plug samples selected in this study were chosen because of lithologic variability and permeability variation. The pore structure and permeability of the samples exhibit differences, possibly related to variation in cementation and mineralogy, specifically clay (illite and chlorite) content.

The gamma ray signature of the core appears to track permeability in some sections of the core (Fig. 8) – the gamma ray signature is variable for this core likely due to variable chlorite/illite/muscovite and potassium-feldspar content. Clay content is often an important control on permeability in tight sand reservoirs, and we suggest that this is also the case for the core that we have studied. Samples 4 and 24 have a lower clay content (and lower GR signature), as determined from XRD and microprobe analysis, and have a greater permeability than sample 5 (Figs. 7 and 8). An increase in core permeability in the upper few meters of the core, appears to correspond with a “cleaning upward” trend on the gamma ray (Fig. 8).

Despite differences in macroscopic appearances in the 3 core plug samples analyzed as inferred from thin section and microprobe images (see Figs. 4 and 5), this information cannot be used quantitatively to infer pore structure and permeability. The reason is that the controlling pore sizes are at the sub-micron scale, with the largest pores (Fig. 10) typically <2000 Å in width (as inferred from adsorption measurements). Independent methods such as low-pressure adsorption (N₂ and CO₂) and SANS/USANS must therefore be used to investigate the pore structure in detail.

Although the hysteresis loop shape from N₂ adsorption/desorption was initially interpreted [15] to indicate slit-shaped pores, this interpretation is not consistent with scattering patterns observed

![Slope = -3.3](Image)

**Fig. 16.** Scattering profile for S24 with background subtracted. Solid line represents a fit to the power law model.

### Table 7
Mineral composition, density (d), atomic mass (M) and scattering length density (SLD) and mole fraction (w) of each component in S4.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>d (g/cm³)</th>
<th>M (g/mol)</th>
<th>SLD (10⁻¹⁸ cm⁻²)</th>
<th>w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite</td>
<td>(K,Na,Al,Mg,Fe)₃(Si₂Al₄O₁₀)(OH)₂</td>
<td>2.75</td>
<td>389.3</td>
<td>2.95</td>
<td>0.005</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₂(Si₂Al)₃O₈(OH)₃</td>
<td>2.83</td>
<td>398.7</td>
<td>3.86</td>
<td>0.027</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>2.65</td>
<td>60.1</td>
<td>4.18</td>
<td>0.744</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>KAl₃(Al,Mg)₄O₁₀(OH)₃</td>
<td>2.55</td>
<td>278.3</td>
<td>3.64</td>
<td>0.072</td>
</tr>
<tr>
<td>Albite</td>
<td>NaAlSi₃O₈</td>
<td>2.62</td>
<td>263.0</td>
<td>3.97</td>
<td>0.013</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>5.01</td>
<td>119.9</td>
<td>3.81</td>
<td>0.015</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>2.71</td>
<td>100.1</td>
<td>4.69</td>
<td>0.0006</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
<td>2.84</td>
<td>184.4</td>
<td>5.4</td>
<td>0.117</td>
</tr>
<tr>
<td>Clinohlorite</td>
<td>(Mg,Fe)₃Al₃Si₄O₈(OH)₃</td>
<td>2.65</td>
<td>595.2</td>
<td>3.21</td>
<td>0.007</td>
</tr>
</tbody>
</table>

### Table 8
Scattering length density (SLD) of studied samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SLD (10⁻¹⁸ cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4.26</td>
</tr>
<tr>
<td>5</td>
<td>4.27</td>
</tr>
<tr>
<td>24</td>
<td>4.40</td>
</tr>
</tbody>
</table>

### Table 9
Scattering length density (SLD) of studied samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SLD (10⁻¹⁸ cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4.26</td>
</tr>
<tr>
<td>5</td>
<td>4.27</td>
</tr>
<tr>
<td>24</td>
<td>4.40</td>
</tr>
</tbody>
</table>

* Based on the modified Porod law (Eq. [3]).
* Based on the PDSP model.
* Based upon N₂ BET analysis – chip samples.

### Table 10
Total porosity of the samples (S4, S5, and S24) obtained using the Porod invariant method (with different extrapolations) and analysis based on the PDSP model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ϕ (%)a</th>
<th>ϕ (%)b</th>
<th>ϕ (%)c</th>
<th>ϕ (%)d</th>
<th>% Open porositye</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>8.08</td>
<td>7.52</td>
<td>6.83</td>
<td>7.9</td>
<td>98%</td>
</tr>
<tr>
<td>5</td>
<td>8.28</td>
<td>7.55</td>
<td>6.82</td>
<td>6.3</td>
<td>76%</td>
</tr>
<tr>
<td>24</td>
<td>7.60</td>
<td>7.04</td>
<td>6.31</td>
<td>5.6</td>
<td>74%</td>
</tr>
</tbody>
</table>

* ϕ(Q) extrapolated to Q = 0 and Q = 10⁻⁴.<br>  
  * Experimentally measured Q-range 10⁻⁴ < Q < 0.4.<br>  
  * Results based on the PDSP model. The SSA is calculated using a probe size of 6.31 Å that is close to the nitrogen gas size.<br>  
  * % open porosity as determined from the ratio of helium porosity to that determined from Porod method.
from SANS/USANS. The dominant dimensionality of scattering objects is reflected in the slope of the scattering curve [32]. For the samples studied in this work, the slope of these plots (Figs. 14–16) is between $-4/3$ and $-2/3$, which indicates a polydisperse distribution of uncorrelated 3D objects (equivalent to a surface fractal). 2D objects, such as fractures (or flattened pores), would be expected to have a slope in the range of $-2$ to $-1$. We are uncertain of the cause of this discrepancy, but note that phenomena such as pore network effects may obscure the interpretation of hysteresis loops in terms of pore shape [26].

Comparisons of USANS/SANS – derived surface areas and porosities with low-pressure adsorption and helium porosimetry allows insight to be gained into the nature of the pore structure. Low-pressure adsorption yields smaller surface areas, and helium porosimetry, smaller porosities, than SANS/USANS (Tables 9 and 10). We interpret this to mean that closed porosity (to gas) is significant in two of our samples (S5 and S24). In the future, it would be useful to investigate the impact of open porosity (using a combination of helium porosimetry and SANS/USANS data) on permeability using a statistically significant sample set – in our limited dataset, the highest permeability sample also has the greatest % of open porosity. Further, independent means of establishing open versus closed porosity for tight gas and shale samples using only SANS/USANS data should be investigated [14].

Both interpreted SANS/USANS and low-pressure adsorption data suggest that microporosity (pore diameters $<20 \text{ Å}$) is limited. The interpreted pore size distributions from SANS/USANS (Fig. 18) suggest a lack of pore volume below pore diameters $20 \text{ Å}$ (2 nm) or pore radii $<10 \text{ Å}$ (microporosity). However, within the accuracy of the SANS measurement, which is limited by the presence of incoherent scattering background in the large-$Q$ region, the number density of the smallest pores may be lower than expected by the surface fractal microstructural model. Nonetheless, surface areas determined from $N_2$ and $CO_2$ adsorption also suggest that microporosity is very small. In shales and coal reservoirs, a controlling factor on microporosity is the amount and type of organic matter [1,3,7]. At the time of writing, the organic matter content of several core samples were being measured and were not available for this study, but analysis of offset cores suggests TOC values (total organic carbon) values are $<2–3$ (wt. %) in the interval of interest. Further, estimates of TOC using log data suggest TOC values are $<2\%$ [37]. The relatively small amount of organic matter is a plausible cause for the lack of microporosity in these samples.

We note that the PSDs derived from $N_2$ adsorption/desorption (Fig. 10) are not directly comparable to the SANS/USANS results (Fig. 18a) because $N_2$–derived results represent a pore volume distribution, whereas the SANS/USANS results represent a number density of the pores versus pore size. Further, in Fig. 10, the derivative of pore volume is taken with respect to log of pore size – this plotting method was also recently used by others [38] for comparing pore size distributions of clays and shales. If the derivative is taken with respect to pore size, which is more common in the literature, the resulting PSDs (Fig. 19a) do not display a bimodal signature for any of the samples, and look qualitatively similar to the SANS/USANS PSD. Further, the absence of the PSD peak (Fig. 10) at $\sim 40 \text{ Å}$ in the SANS/USANS plots (Fig. 18a) suggests that the adsorption branch of the isotherm may be more appropriate for PSD calculations. Finally, to facilitate more direct comparison of the SANS/USANS PSDs and the isotherm PSDs, the SANS/USANS data for sample S4 were converted to a pore volume distribution (Fig. 19b). The resulting PSDs for S4 show a remarkable consistency in trends, particularly for pore radii from 40 to 1000 Å (4–100 nm), or 1.5 log cycles on the PSD plot. The same is true for the other samples (not shown).

SANS/USANS data appear to suggest that there are some pores in the micrometer size range in our samples (Fig. 18). This appears to contradict a previous conclusion that pores in the 500–1000 Å (50–100 nm) range, as established from adsorption and mercury porosimetry techniques, are controlling permeability in these samples.
5. Conclusion

In this work, we have examined the use of SANS/USANS and low-pressure adsorption methods to characterize the pore structure of a tight gas reservoir, and relate these observations to petrographic and compositional data and permeability measurements. The primary conclusions from this study are:

1. The dominant pores in the three tight gas samples analyzed are in the mesopore/macropore range, as interpreted from low-pressure adsorption data.
2. Pore size distributions from SANS/USANS and low-pressure N₂ adsorption show consistent trends over 1.5 log cycles of pore radius.
3. Both SANS/USANS and low-pressure adsorption data suggest very small amounts of microporosity, possibly due to a relatively low organic matter content.
4. SANS/USANS data appear to indicate the presence of pores in the micrometer range (i.e. macropores), but these may be isolated.
5. SANS/USANS-derived surface areas and porosities are systematically higher than those derived from low-pressure adsorption and helium porosimetry, respectively.
6. The ratio of porosity derived from helium porosimetry to total porosity derived from SANS/USANS may be useful as an indicator of the percentage of open versus closed porosity.
7. The percentage of open porosity may be an important factor controlling permeability, which in turn may be related to the clay content of the samples.
8. The core gamma-ray signature appears to track profile permeability measurements, reflecting changes in clay and potassium-feldspar content.

Several of the conclusions above are tentative because they are based upon only 3 samples analyzed using SANS/USANS and low-pressure adsorption. The current work represents a test of the usefulness of the technology for characterizing the pore structure of tight gas samples – we believe the techniques have provided useful insight into the nature of the pore structure in these samples. Future work will endeavor to expand the dataset to multiple samples from the analyzed core, plus additional samples from other cores in the study area. We will also obtain additional data, such as CT scans to investigate the macropore structure of the samples, and additional SANS/USANS data to obtain independent estimates of closed versus open porosity using techniques described in Melnichenko et al. [14].

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References


