A Comparison of Measurement Techniques for Porosity and Pore Size Distribution in Mudrocks: A Case Study of Haynesville, Niobrara, Monterey and Eastern European Silurian Formations

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1. Abstract

Porosity and pore size distribution (PSD) are required to calculate reservoir quality and volume. Numerous inconsistencies have been reported in measurements of these properties in mudrocks. We investigate these inconsistencies by evaluating the effects of fine grains, small pores, high clay content, swelling clay minerals and pores hosted in organic content. Using mudrocks from the Haynesville, Eastern European Silurian, Niobrara and Monterey formations, we measured porosity and pore or throat size distribution using subcritical nitrogen (N2) gas adsorption at 77.3 K, mercury intrusion (MI), water immersion (WI), and helium porosimetry based on Gas Research Institute standard methodology (GRI). We used Scanning Electron Microscope (SEM) images to understand the pore structure at a microscopic scale. We find that differences in the porosity and PSD measurement techniques can be explained with thermal maturity, texture and mineralogy, specifically clay content and type and total organic matter (TOC) variations. We separated the samples from each formation into groups based on their clay and TOC contents and further investigated the effects of geochemical and mineralogical variations on porosity and PSD. We find that porosity and PSD measurement techniques can provide complementary information within each group provided the comparison is made between methods appropriate
for that group. Our intent is to provide a better understanding of the inconsistencies in porosity measurements when different techniques are used.

2. Introduction

Thanks to new technologies such as hydraulic fracturing and horizontal drilling in the last decade, unconventional reservoirs gained oil and gas industry’s attention as valuable resources for energy production. Passey et al. (2010) define “unconventional reservoirs” as a wide range of hydrocarbon-bearing rocks that are not economically producible without stimulation techniques. Although the term unconventional reservoir lacks adequate lithologic definition, in this paper, we refer to tight oil, or gas-producing reservoirs which may or may not be organic rich and are often called “shales”. In today’s terminology, shale reservoirs are either siliciclastic or carbonate mudrocks. They need not necessarily contain clay minerals. Although alternate terms have been used for shale reservoirs such as unconventional, self-resourcing rocks, organic-rich rocks and mudstones, the term shale has endured. In this work we use the term mudrock to refer to these reservoirs.

Mudrocks are fine-grained rocks containing silt-size particles with 50% of the grain diameters less than 62.5 µm (Folk, 1974, Friedman 2003, and Javadpour, 2005). Like other sedimentary rocks, they are composed of a wide range of minerals such as clay, quartz, feldspar, carbonates, and heavy minerals such as pyrite (Passey et al., 2010). Besides mineral components, mudrocks may contain organic matter as a significant component of the rock (Bohacs et al., 2013).

Porosity and pore size distribution are used for reservoir evaluation (Ambrose et al., 2010), permeability prediction (Nelson, 2009), and elastic property calculations (Kuila and Prasad, 2011). A major challenge in estimating transport and storage capacity of mudrocks is the poor
understanding of their pore properties including size, distribution and pore hosting components (Nelson, 2009; Chalmers et al., 2012; Loucks et al., 2012; Kuila et al., 2014a; Kuila et al., 2014b). Lack of accessibility of the displacement fluid to the pore system is the main deterrent to reliable and accurate laboratory measurements. Limited accessibility can be due to extremely low permeability, complicated mineral surface-fluid interactions, or insufficient equilibration time.

It is important to not only quantify pore space with visual techniques such as Scanning Electron Microscopy (SEM) (for example, Ambrose et al., 2010; Curtis et al., 2010; Lemmens et al., 2010; Bernard et al., 2012; Curtis et al., 2012; Alcantar-Lopez and Chipera, 2013; Zargari et al., 2013) or CT-Scanning (Coshell et al., 1994; Wildenschild and Sheppard, 2012; Milliken et al., 2013) but also with non-visual techniques. Some examples of non-visual techniques are nitrogen gas adsorption (N2) (Echeverria et al., 1999; Chalmers et al., 2012; Kuila et al., 2012), mercury intrusion (MI) (Howard, 1991), water immersion porosimetry (WI) (Howard, 1991; Kuila et al., 2014a) and nuclear magnetic resonance (NMR) (Sondergeld et al., 2010a; Jiang et al., 2013; Rylander et al., 2013; Rivera et al., 2014; Saidian et al., 2015). Porosity and pore size distribution are commonly measured with techniques such as mercury intrusion and helium expansion. These approaches yield consistent values for conventional rocks (Hossain et al., 2011). For mudrocks, however, the methods to measure porosity and PSD need careful selection. Large variations in their pore sizes and shapes can result in up to 50% inconsistency in porosity values (Howard, 1991; Katsube and Scromeda, 1991; Katsube et al., 1992; Dorsch and Katsube, 1996; Sondergeld et al., 2010b). Discrepancies in results arise because the techniques are based on specific physical phenomena and use different displacement fluids. Since accessibility to the pore space depends on the fluid, each technique yields different
results. These differences can be exploited considering the fact that each technique measures a different portion of the pore space. A combination of methods can help fully characterize complex pore spaces. Furthermore, within each technique, repeatability can be compromised due to different pretreatment methods such as grinding and sieving, laboratory conditions such as relative humidity and temperature, and millimeter scale heterogeneity which hinders the ability to produce sample aliquots for multiple measurements (Passey et al., 2010; Kuila, 2013). Differences in porosity values measured by different laboratories or under different pretreatment conditions are well documented (Passey et al, 2010, Sondergeld et al., 2010b, Comisky et al., 2011). A methodical comparison of porosity values in mud rocks determined by various techniques that examines the compositional, textural and geochemical reasons for data variations is lacking.

The main objective of our work is to understand various pore sensing techniques on the basis of textural, mineralogical and geochemical differences. We present porosity obtained from helium expansion, mercury intrusion, water immersion and nitrogen adsorption. We also present pore-size distribution data obtained from mercury intrusion and nitrogen adsorption. We investigate the controlling factors on the results of each experimental method and evaluate data variations together with textural, mineralogical and geochemical differences. Further, we compare porosity values measured with various techniques with the pore size distributions measured with three different techniques. Finally, we provide recommendations for a new approach for pore size distribution comparison in mudrocks.

In this study we use the pore size classification suggested by Rouquerol et al. (1994). In this classification micro, meso and macro pores have <2 nm, 2-50 nm and >50 nm pore width. All
the pore or throat size distribution spectra are plotted using the diameter or width of the pores and these terminologies are used interchangeably.

3. Materials

Below we briefly describe the dominant mineralogy, thermal maturity, organic matter type, and organic matter content for the samples used for this study. The details of each sample set have been published by Rivera, 2014 and Godinez; 2014 (Monterey), Kuila, 2013 (Haynesville, Niobrara, and Silurian).

3.1 Haynesville Formation

34 samples were taken from Upper Jurassic Haynesville Formation (Kuila, 2013). The samples were clay-rich (up to 73 wt% mainly illite with <5% to 9% expandable smectite layers) with moderate amounts of quartzo-feldspathic (average of 26 wt%) and a variable amount of calcite (between 1 to 35 wt%). A moderate amount of dolomite (up to 44 wt%) was observed in 2 samples (Figure 1a). In the Haynesville sample set the TOC varied between 0.5-6.3 wt%; the kerogen was in the gas window based on average T_max of 424 °C and HI which varied from 19 to 57 with an average of 36. RockEval S2 data between 350-400 °C showed a moderate amount of bitumen. Figure 2a and b show the SEM images for two Haynesville samples. Figure 2a shows silt-sized quartz, calcite and plagioclase particles surrounded by a mixture of illite and clay-sized quartz. Organic matter is dispersed between clay-sized particles. Figure 2b represents a dolomite rich sample with intergranular spaces filled with a mixture of quartz and clay minerals as well as organic matter.

3.2 Silurian Formation
The fourth sample set consisted of 22 samples taken from the Silurian play in Eastern Europe (Kuila, 2013). The samples contained up to 52 wt% quartz and up to 57 wt% clay which is mostly illite (Figure 1b). The kerogen was thermally mature in the gas window and TOC ranged between 1-6 wt %. No pyrogram peaks were observed in the Rock Eval results up to 550 °C which confirmed the absence of any pyrolyzable kerogen or bitumen in these samples. The HI varied from 0 to 9 with an average of 3. Figure 3a and b show SEM images of two Silurian samples. Silt-size particles such as quartz, pyrite, and dolomite are surrounded by a matrix of illite and chlorite and organic matter is dispersed between clay particles.

3.3 Niobrara Formation

22 marl and chalk samples came from a well in the Berthoud Field, Larimer County, CO, USA (Kuila, 2013), specifically from the Fort Hays limestone and the overlying Smoky Hill members of the Niobrara formation. They were calcite-rich rocks with moderate amounts of clay (up to 35 wt% with an average of 16.5 wt%), quartz (average of 11 wt%) and pyrite (Figure 1c). Type II kerogen was thermally mature and was in the oil window based on average $T_{\text{max}}$ of 436 °C and HI which varied from 119 to 386 with an average of 306. TOC varied from 0.1 to 5.3 wt% and RockEval programs between 450-500 °C showed an abundance of bitumen in these samples. SEM images for two samples are shown in Figure 4a and 4b. Figure 4a shows relatively more homogeneous intercrystalline pore distribution which is filled with organic matter. Figure 4b shows larger intercrystalline pores filled with organic matter. Note that the larger intercrystalline pores are within the peloid structures.

3.4 Monterey Formation
A combination of 12 sidewall and conventional core samples were taken from an oil producing well drilled at the western flank of the southern San Joaquin Basin in California. The samples were predominantly quartz phase porcellanites containing moderate amounts of clay (up to 24 wt% with an average of 8 wt%) and pyrite (up to 7 wt% with an average of 3 wt%). A smaller sample set (3 samples) were calcite-rich (Figure 1d). TOC varied from 0.85-4.95 wt% and RockEval S2 data showed an abundance of bitumen (Rivera, 2014). Kerogen was Type II with thermal maturity in the oil window based on average $T_{\text{max}}$ of 438 $^\circ$C and the hydrogen index (HI) varying from 184 to 473 with an average of 374. SEM images of Monterey samples (Figure 5) show moderate carbonate and dominant quartz grains with the presence of organic matter filling up the intergranular and intercrystalline pores.

4. Methods

Several methods have been used to measure porosity and pore or throat size distribution. In this section, we describe the pretreatments, displacement fluids, and methods as well as the associated challenges for each measurement. In the results and discussion part we will investigate how these challenges and limitations affect the porosity measurement for different sample sets.

4.1 Helium Expansion using the Gas Research Institute (GRI) Method and Helium Injection Under Confining Stress

The porosity was measured by a commercial laboratory using the Gas Research Institute (GRI) helium porosimetry technique. Due to sample limitations only Silurian and the Haynesville samples were used for these measurements. The porosity was also measured using helium injection under confining stress for the Monterey samples. In the GRI technique, bulk rock volume is measured by mercury immersion using Archimedes’ principle and crushed rock grain
volume is measured by Boyle’s Law (Luffel and Guidry, 1992; Luffel et al., 1992; GRI-95/0496). We measured the porosity of cleaned and dried cylindrical Monterey samples with a CMS300\textsuperscript{TM} helium injection porosimeter.

Helium expansion, using either crushed or intact samples, measures pores that are connected and accessible by helium gas. In nanodarcy permeability rocks, temperature fluctuations can compromise pressure equilibration and decrease the measurement accuracy. On the other hand, using crushed samples allows the gas to access isolated pores that might be inaccessible otherwise. Sondergeld et al. (2010b) and Passey et al. (2010) reported very high disparities in the porosity and permeability values measured by different laboratories using same samples. Kuila et al. (2014a) provided a thorough discussion of the GRI technique and investigated the effect of pretreatment and laboratory conditions on the final grain density and porosity results. For example, the Dean-Stark extraction pretreatment with a hot solvent can create porosity in thermally mature samples, such as the Niobrara and Monterey, by dissolving bitumen and lead to porosity overestimation. Luffel and Guidry (1992) suggested 30 minutes as the equilibration time for shales as opposed to 1 minute for conventional rocks.

4.2 Water Immersion (WI)

The original protocol for WI porosity measurements was recommended by the American Petroleum Institute (API RP40). In this study, we used the adapted protocol for mudrocks developed by Kuila et al. (2014a). In this adapted protocol, approximately 5 grams of rock chips are first dried and weighed in air. They are then saturated and weighed again in water. This protocol of using intact samples and measuring grain density at low humidity increases the repeatability of the experiment (Kuila et al., 2013).
Immersion porosity measurements assess the pores available to the saturating fluid (water or oil). Thus, the fluid type, the pore surface wettability, and the saturation method affect the porosity values. Also presence of expandable clays such as smectite would affect the accuracy of this technique.

4.3 Mercury Intrusion (MI)

In MI porosimetry, small intact rock chips are heated up to 200 °C for 12 hours and degassed for 30 minutes at 50 µmHg to remove water and volatile hydrocarbons. Mercury is then injected in the sample at uniform pressure steps from 0.14 to 420 MPa. Pressure is considered equilibrated when the injection rate falls below 0.001 µl/g/s. The Washburn model (Washburn, 1921) is used to convert the pressure data to pore throat size distribution. A conformance correction, for example, the Bailey method from Comisky et al. (2011) must be applied to high pressure measurements to account for mineral compressibility. The porosity is calculated by measuring the bulk volume of the sample submerged in the mercury and the pore volume measured by the volume of intruded mercury.

We used MI to measure porosity and pore throat size distributions for all sample sets. The MI technique measures pore and bulk volume as well as pore-throat size distribution. Since MI can only measure the volume of pores with throat-diameter larger than 3.6 nm (at 420 MPa), a significant portion of the pore space in fine-grained rocks is neglected.

4.4 Nitrogen Adsorption (N2)

This technique has traditionally been used to measure total specific surface areas (TSSA) in conventional reservoir rocks. Due to practical limitations N2 technique can only assess the volume of pores with a diameter of less than 200 nm (Gregg and Sing, 1983). 1-3 grams of
samples are crushed, sieved through a 40 mesh (420 µm) sieve, and then degassed under vacuum at 200 °C until the outgassing rate is less than 0.005 Torr/min over a 15 minute interval. Nitrogen is injected into the analysis chamber and adsorption of nitrogen to the degassed sample starts. The adsorption takes place under constant temperature of liquid nitrogen. Pressure and adsorbed quantity of nitrogen are recorded as isotherms and used to calculate pore size distribution. We used the Barrett, Joyner and Halenda (BJH) inversion (Barrett et al., 1951) as recommended by Kuila (2013) for mudrocks. This inversion method calculates the PSD assuming non-connecting cylindrical pores. The total pore volume is calculated by measuring the amount of nitrogen adsorbed in the sample. The Harkins and Jura (1944) thickness curve is utilized for both BJH inversion and micropore (pores smaller than 1.7 nm) volume calculation with t-plot analysis. The total pore volume is calculated by combining the micropore volume and the total volume measured from 1.7 nm to 200 nm. We used this technique to measure pore size distribution and pore volume in all samples.

5. Results

We analyzed samples with representation from major lithology types (Figure 1): predominantly carbonate (Niobrara); predominantly quartz (Monterey); predominantly clay (Haynesville); and a mineral mixture (Silurian). Each sample set has varying amounts of clay and TOC contents. This richness of data allowed us to analyze and explain porosity mismatch between the methods for mineralogy, pore size distribution, and measurement condition effects.

5.1 Haynesville Formation

Porosity values are measured by N2, WI, GRI and MI techniques (Figure 6). The following observations can be made from this figure:
• MI underestimates the porosity when compared with N2 and WI (Figure 6a and 6b).
• WI and N2 porosities are comparable within 2 p.u. difference (Figure 6c).
• GRI and N2 are comparable within 2 p.u. difference (Figure 6d).
• Except some low content samples that show higher GRI porosity, the WI and GRI porosity show similar porosities within 2 p.u. difference (Figure 6e). Note that in Figure 6 N2 and WI and GRI experiments are not performed for all samples.
• The presence of clays does not affect the porosity measurements and porosity value increases with clay content.

The PSD was measured using the N2 technique (Figure 7). As shown in this figure the PSD spectra varies significantly for different samples. Figure 7a and 7b show the PSD colorcoded by clay and TOC content, respectively. Samples with high clay (low TOC) show large amplitudes at the small mesopore range (< 10nm). Samples with low clay (high TOC) show large amplitudes at the big mesopores (10-50 nm) and macropore range (>50 nm). MI throat size distribution was also measured for a subset of Haynesville samples (Figure 8). The MI spectra suggests that there are pores with throats smaller then 3.6 nm which are not assessed by this technique.

5.2 Silurian Formation

We measured the porosity of the Silurian samples using WI, MI and N2 techniques (Figure 9). The following observations can be made:

• MI, N2 and WI measurements show an increase in porosity with increase in TOC (Figure 9a to 9c).
• MI highly underestimates the porosity compared to WI and N2 techniques (Figure 9a and 9b).
• WI and N2 porosities are comparable within 2 p.u. difference (Figure 9c).

• GRI generally underestimates the porosity compared to WI and N2 in these samples (Figure 9d and 9e).

We measured PSD using N2 (Figure 10) and MI (Figure 11) techniques for all Silurian samples. The N2 PSD spectra are color coded by both clay (Figure 10a) and TOC (Figure 10b) contents.

We make the following observations:

• Significant variation in amplitude in the small mesopore range (<10 nm) is observed.

• The big mesopore (10-50 nm) and macropore range (>50 nm) show similar spectra with small variations in amplitude.

• TOC and clay content do not show a clear effect on the PSD spectra.

• The MI PSD results (Figure 11) suggest that there are pores that are not accessible using the MI technique.

• Clay content does not show a effect on the MI spectra amplitude (Figure 11a) whereas TOC and spectra amplitude show a direct correlation (Figure 11b).

5.3 Niobrara Formation

Figure 12 shows the comparison between porosity values measured using the N2, MI and WI techniques. Two distinct groups of data are observed in Figure 12a. Group 1 (data circled by a blue dashed line in Figure 12a) shows higher WI porosity compared to N2 porosity, whereas Group 2 (data circled by a red solid line in Figure 12a) shows more comparable WI and N2 porosities (within 2 p.u. difference). We make the following observations for samples with a wide distribution of pore sizes and high clay content such as the Niobrara samples:
Comparing N2 and WI samples show that N2 underestimates the porosity for some samples and WI overestimates the porosity for some samples (Figure 12a).

WI and MI porosities are comparable within 2 p.u. for low clay content (<10 wt%) samples. WI overestimates the porosity for high clay samples (>10 wt%) (Figure 12b).

N2 shows higher porosity for high clay content samples and MI shows higher porosity for low clay samples (Figure 12c).

We measured PSD for Niobrara samples using the N2 (Figure 13) and MI (Figure 14) techniques:

- The shapes of the PSD spectra (Figure 13) for low clay content samples show increasing PSD amplitude which suggests the presence of pores larger than 200 nm. The high clay content samples show a dominant pore size of 80-100 nm.
- Similar to N2-PSD data, the MI PSD data (Figure 14) show two different sets of spectra. One set shows a PSD spectrum with a dominant pore size 80-100 nm (low clay content) and the other set shows an abundance of small pores smaller than 20 nm (high clay content) (Figure 14).
- The shape of MI spectra for high clay samples indicates the presence of pores that are not accessible by mercury.

5.4 Monterey Formation

Porosity values were measured for Monterey samples using WI, MI, HE and N2 techniques (Figure 15). We make the following observations:

- WI, MI and HE porosities show comparable values within 2 p.u. difference (Figure 15a to 15c).
HE and WI show the best correlation (Figure 15b).

N2 significantly underestimates the porosity for high porosity (>5 p.u.) samples.

N2 and HE show comparable values (within 2 p.u.) for low porosity samples (<5 p.u.).

Clay content does not affect the porosity measurements.

Pore size distributions were measured for Monterey samples using N2 (Figure 16) and MI (Figure 17) techniques, colorcoded by clay content:

- The N2 pore size amplitude (Figure 16) for pores larger than 10 nm varies significantly and shows no correlation with the clay content.

- The amplitude for small mesopores (<10 nm) is small except for one high clay content sample (Figure 16).

- The MI throat size distributions (Figure 17) also show a significant variation in both amplitude and throat size.

- For these spectra clay content does not show any correlation with the shape and amplitude either.

6. Discussion

The main driver for this comparative study was to analyze the differences in each method and to exploit these differences to learn more about the samples honoring the mineralogical and geochemical properties of each sample set. Samples were chosen from different formations. Haynesville and Silurian formations are highly mature (gas window) with a very low hydrogen index (average of 36 and 3, respectively). The Niobrara and Monterey samples are less mature (oil window) with a very high hydrogen index (average of 306 and 374). We discussed the results considering the effect of thermal maturity, TOC and clay content on the porosity, pore size distribution and pore types. We worked with the strengths and drawbacks of each method as
listed in Table 2 for porosity and pore size distribution measurement. Here, we discuss our results and evaluate the benefits and applicability of each technique for organic-rich mudrocks.

As mentioned in Table 2 MI technique measures the porosity for pores with a throat diameter smaller than 3.6 nm. Underestimation of MI porosity values for Haynesville (Figure 6a and 6b) and Silurian (Figure 9a and b) is because of the high thermal maturity (low HI) and consequently the abundance of organic matter (OM)-hosted pores in these samples. OM-hosted pores are in the mesopore (2-50 nm) and small macropore size (50-200 nm) range and not accessible by MI technique. MI porosity values for low clay content (< 10 wt%) Niobrara (Figure 12b) and Monterey samples (Figure 15a and c) are comparable with other techniques. The porosity in these samples are mainly intercrystalline and accessible by mercury.

WI porosity measures the pores that are filled with distilled water. The presence of expandable clays in the samples causes overestimation of porosity. Mineralogy of Niobrara samples showed presence of expandable clays (smectite) in these samples. The clay content in other sample sets mainly consisted of Kaolinite and illite which are less expandable. The effect of expandable clays in Niobrara high clay (> 10 wt%) samples can be seen when WI is compared against N2 (Figure 12a) and MI (Figure 12b). In more thermally mature samples such as Haynesville (Figure 6c) and Silurian (Figure 9c) and low clay content samples such as Monterey (Figure 15a and 15b) the clay swelling is not significant and WI porosity is comparable with other techniques within 2 p.u. difference. As mentioned in Table 2 water might not be able to fill the hydrophobic organic hosted pores. We can not directly observe this phenomena in the porosity data presented in this study but there are some indications of the effect of hydrophobic pores on WI porosity measurement. There is higher scatter in the WI-N2 porosity comparison for Haynesville (Figure 6c) and Silurian (Figure 9c) samples compared to the HE-WI porosity comparison for Monterey.
samples (Figure 15b). Monterey samples are in the oil window and intercrystalline pores are the dominant pore types, but Haynesville and Silurian are in the gas window and OM-hosted pores form the dominant pore type which is hydrophobic.

Since the N2 technique can not assess pores with a diameter larger than 200 nm, the comparable N2 porosity for Haynesville (Figure 6c and 6d) and Silurian (Figure 9c) shows the abundance of pores within the mentioned range in these samples. High Clay (> 10 wt%) Niobrara samples also show the presence of OM-hosted pores. The N2 technique is able to measure the porosity in High Clay (> 10 wt%) Niobrara samples while the MI technique underestimates and WI overestimates the porosity. OM-hosted pores are not abundant in the low porosity (< 5 p.u.) Monterey samples. The similarity of N2 porosity with other techniques (Figure 15a to 15c), for these samples is due to the presence of intercrystalline pores with a diameter smaller than 200 nm.

GRI porosity was measured for Haynesville samples and a limited number of Silurian samples. The higher scatter in low clay (<35 wt%) Haynesville samples (Figure 6e) is due to hot solvent extraction prior to GRI measurements. Removal of soluable organic matter increases the porosity measured by the GRI technique. This effect is ruled out for Silurian samples since no soluble bitumen was observed in these samples. The underestimation of GRI for Silurian samples might be due to inacsessibility of gas to the micropores. The HE technique successfully measures porosity for the Monterey samples since no OM-hosted pores are present in these samples.

Comparison of porosity values measured by different techniques show that when the N2 and MI techniques measure comparable porosity with other techniques, the pore size distribution assessed by these techniques can be used to study the pore structure. For example the N2 pore
size distribution can be used to study the pore structure for highly mature gas window samples (Haynesville and Silurian), Clay rich oil window samples (Niobrara with clay content more than 10 wt%), and oil window tight samples (Monterey samples with porosity lower than 5 p.u.). MI pore throat size distribution spectra can not be used in gas window samples (Haynesville and Silurian), but it is an appropriate technique for studying the pore structure in oil window low clay (<10 wt%) Niobrara and high porosity Monterey (>5 p.u.) samples.

The pore size distributions in Figure 7 are divided into 5 groups based on the PSD spectra shapes (Figure 18). The correlation between the TOC and clay content for the Haynesville samples (Figure 19) shows an inverse correlation between TOC and clay content. Clay content cut offs for different groups are defined as <35 wt%, 35-50 wt%, 50-60 wt% and >60 wt%. Group 5 samples are dolomite rich samples with >30 wt% dolomite content. Group 1 samples (Figure 18a) show dominant pore size of 20 nm. These samples have high TOC and consequently an abundance of OM-hosted pores (Figure 20). Group 2 to 5 (Figure 18b to d) show an increase in the small mesopore size range (<10 nm) and decrease in the big mesopore (10-50 nm) and macropore size (>50 nm) range. Group 2 samples have slightly lower TOC and higher clay content compared to Group 1. They show an abundance of OM-hosted pores and the presence of intercrystalline pores in clay minerals (Figure 21). SEM images for Group 3 samples (Figure 22) confirm the N2 PSD results (Figure 18c) which demonstrate both intercystalline (< 10 nm) and OM-hosted pores (> 10 nm). Group 4 samples are clay rich (60-80 wt%) and show an abundance of small mesopores (<10 nm) measured by N2 PSD (Figure 18d). SEM images (Figure 23) show that intercrystalline pores in clay minerals are the dominant pores in these samples. Group 5 samples are dolomite rich (> 30 wt%) with a very low TOC content (< 1.5 wt%). The spaces
between dolomite grains are filled with a mixture of clay and quartz particles which host the intercrystalline pores in these samples (Figure 24).

N2 PSD for Silurian samples (Figure 10) show relatively similar amplitudes for large mesopores (10-50 nm) and macropores (>50 nm). The PSD amplitude for pores with a diameter smaller than 10 nm varies significantly. The TOC-Clay content correlation for the Silurian samples (Figure 25) shows two different trends; low clay-low TOC samples (Group 1) and high clay-high TOC samples (Group 2). In Group 1 the amplitude for pores with a diameter less than 10 nm increases as the clay content increases (Figure 26a). However in Group 2 the peak amplitude for pores smaller than 10 nm increases as the TOC increases (Figure 26b). The SEM images for a sample from Group 1 (Figure 27) show the presence of both OM-hosted pores and intercrystalline pores. However, Group 2 sample SEM images show an abundance of OM-hosted pores. The intercrystalline pores are filled with organic matter which hosts the majority of the pores (Figure 28).

Although both Haynesville and Silurian are in the gas window and show relatively similar TOC-Clay content correlations, there are key differences between the pore structure of these samples:

- The clay content varies between 30 to 60 wt% for the Silurian samples and 20-80 wt% for the Haynesville samples.
- The dominant pore type for the Silurian samples is OM-hosted and the pore structure is dictated mainly by TOC, whereas for the Haynesville samples both clay content and TOC control the pore structure.
- Silurian samples belong to a geologically older formation than the Upper Jurassic Haynesville samples which come from an over-pressured formation.
N2 PSD for the Niobrara samples are divided into two groups based on the PSD spectra shapes (Figure 29). The PSD of the Group 1 samples (Figure 29a) shows the presence of pores larger than 200 nm that were not assessed by the N2 technique. The PSD of the majority of Group 2 samples (Figure 29b) show that the dominant pore size is close to 100 nm. These groups correspond to the groups shown in Figure 12a. Group 1 samples belong to Chalky and Group 2 samples belong to the Marly formations. TOC-Clay correlation for these samples (Figure 30) demonstrates that the majority of Group 1 samples show TOC less than 2 wt% and Group 2 samples show TOC higher than 2 wt%. In Group 1 samples the pores are mainly intercrystalline and reside in the clay minerals that fill the space between calcite grains (Figure 31). Figure 31a shows how quartz, calcite and clay particles fill the space between calcite grains and form the intercrystalline pore structure. No organic matter or organic-hosted pores are present in this sample. Figure 31b shows a connected network of intercrystalline pores which are accessible to displacement fluids for porosity measurements. The pores in the Group 2 samples (Figure 32) reside in the organic matter and show smaller pores compared to Group 1. A significant amount of TOC is visible in this sample which fills the intercrystalline pores (Figure 32a). Figure 32b shows the organic-hosted porosity. As shown by the annotations in this figure the pores are smaller than 100 nm. Small pore size and possibly lack of connectivity limit the accessibility of the displacement fluids to these pores for porosity measurements.

The clay content range (20-40 wt%) and TOC-Clay content correlation for the Group 1 Niobrara samples (Figure 25) are similar to the Group 2 Haynesville samples (Figure 19). The N2 PSD measured for these samples are also similar (Figure 18b and Figure 29b). Since both groups of samples have high TOC and an abundance of OM-hosted pores, this similarity confirms that 100 nm is the signature pore diameter for these pore types.
Based on the porosity comparisons presented in Figure 15 the Monterey samples can be divided into two groups; Group 1 with low porosity samples (< 5 p.u.) and Group 2 with high porosity samples (>5 p.u.). N2 PSD data for both groups are shown in Figure 33a and b, respectively. Both groups show very low amplitudes at small mesopores range (<10 nm), except one high clay sample in Group 1. N2 PSD of Group 1 samples represents the whole pore structure whereas the Group 2 PSD spectra only represents pores smaller than 200 nm. Since the Monetery samples have very low clay content there is no correlation between the PSD spectra and clay content for either groups. The PSD spectra are mainly a function of the intercrystalline pores in the quartz phase. Group 1 samples have intercrystalline pores in the clay phase and interacrystalline pores within the quartz and calcite grains (Figure 34). The intercrystalline space is filled with organic matter which holds very low OM-hosted porosity. Group 2 samples show larger intercrystalline pores compared to Group 1 samples. The pores are developed in the space between quartz grains (Figure 35).

Although the N2 technique does not assess the whole pore space for either Group 1 Niobrara (Figure 29a) or Group 2 Monterey (Figure 33b) samples, the N2 PSD spectra shapes are different. Since MI PSD is the appropriate technique for pore structure characterization for these samples we will discuss the main reason for this difference in the following section.

Throat size distribution for Group 2 Haynesville samples (Figure 8) indicates that there are pores with throat diameter smaller than 3.6 nm that are not assessed by the MI technique. Based on N2 PSD results, Group 2 samples have the highest macropore volume amongst all groups in this sample set, so the MI technique would not be able to assess a major part of the pore space for the other groups either.
Similar to Haynesville samples, Silurian MI throat size distribution also showed that there are pores with throat diameter smaller than 3.6 nm that are not reached by the mercury. The MI spectra for Group 1 samples (Figure 36a) do not demonstrate the same clay content dependency as N2 spectra for these samples (Figure 26a). On the other hand MI spectra amplitude of Group 2 samples (Figure 36b) increases with increasing TOC, similar to N2 PSD (Figure 26b).

Throat size distributions assessed by the MI technique for Groups 1 and 2 Niobrara samples are shown in Figure 37a and 37b, respectively. For the samples in Group 1 (Figure 37a) mercury successfully accessed the pores which were not accessible by N2. On the other hand, the pore throat size spectra for Group 2 show that there are pores associated with throats smaller than 3.6 nm.

MI PSD spectra show more heterogeneity in the Monterey samples (Figure 38) compared to the Niobrara samples (Figure 37). The dominant throat size distributions for Monterey samples vary significantly from less than 20 nm for Group 1 samples (Figure 38a) to more than 200 nm for Group 2 samples (Figure 38b). Besides heterogeneity, Group 2 samples show a wider range of throat size distribution for individual samples, whereas in Group 1, Niobrara samples MI PSD shows a more uniform PSD with variable amplitudes (Figure 37a).

7. Conclusions

The porosity and pore size distribution were measured for four sample sets from different formations ranging from high thermal maturity (gas window Haynesville and Silurian) to low maturity (oil window Niobrara and Monterey). The clay content and TOC vary significantly within each sample set. Based on the results presented in this study the following conclusions can be drawn:
Using samples from different formations and maturities, we have shown that without a priori knowledge regarding thermal maturity, TOC, clay type and content porosity and pore size distributions in mudrocks cannot be assessed or studied using a single method. Our assessment of pore size sensitivity for each technique emphasizes the significance of combining various techniques to describe the full pore topology in organic-rich mudrocks. MI technique underestimates the porosity for thermally mature samples (Haynesville) with an abundance of OM-hosted pores. It also underestimates the porosity in less mature Niobrara samples when TOC is high and tight Monterey samples (<5 p.u.). WI provides reliable porosity when samples are thermally mature or when no expandable clays are present. N2 technique is appropriate for porosity and pore size distribution assessment for thermally mature samples (Haynesville and Silurian) or samples with an abundance of OM-hosted pores (Niobrara). It also successfully assesses the low porosity Monterey samples. The reliability of the measured porosities depends on the accessibility of the displacement fluid to the pores. Thus, pore accessibility or wettability of the solid to the probe fluid can be investigated by comparing the pore size distributions measured by different techniques. A combination of methods is required to reliably measure porosity and pore size distribution in mudrocks.

8. Acknowledgements

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9. References


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Gaucher,


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Milad Saidian is currently a petroleum engineering PhD candidate at Colorado School of Mines. He holds BS degree from Petroleum University of Technology and MS degree from Sharif University of technology. His PhD research interest is fluid properties and pore space characterization using Nuclear Magnetic Resonance for conventional and unconventional reservoir rocks focusing on porosity and pore size distribution measurement methods. His industrial work experience includes internships at BP America and Maersk Oil Houston Inc. as petrophysicist, NIOC as reservoir engineer and Maroon Oil and Gas Production Company as production field engineer.

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Figure 1: Mineralogy of (a) Haynesville, (b) Silurian, (c) Niobrara (Chalk, Marl and Fort Hays), and (d) Monterey samples measured by QXRD and colorcoded by TOC. See sample discriptions for more information. The TOC values for Monterey samples used in this study are not available.

Figure 2: SEM images for two Haynesville samples. (a) Silt-sized quartz, calcite and plagioclase particles surrounded by a mixture of illite and clay-sized quartz. Organic matter is dispersed between clay-sized particles. (b) Dolomite rich sample with intergranular spaces filled with a mixture of quartz and clay minerals as well as organic matter. The Haynesville samples are clay-rich (illite and smectite) with moderate amounts of quartz and calcite. Moderate amount of dolomite is observed in some samples. The TOC varies between 0.5-6.3 wt%; the kerogen is in the gas window based on average Tmax of 424 °C and HI varying from 19 to 57 with an average of 36. RockEval S2 data between 350-400 °C show a moderate amount of bitumen. Qz= Quartz, Cal=Calcite, Dol=Dolomite, Py=Pyrite, Pl=Plagioclase, Ilt=Illite, Chl=Chlorite, OM=Organic Matter.

Figure 3: SEM images for two Silurian samples. (a) and (b) Silt-size particles such as quartz, pyrite, and dolomite are surrounded by a matrix of illite and chlorite. Organic matter is dispersed between clay particles. The Silurian samples are quartz- and clay-rich (mostly illite and smectite). The kerogen is thermally mature in the gas window and TOC ranges between 1-6 wt %. No pyrogram peaks were observed in the Rock Eval results up to 550 °C which confirms the absence of any pyrolyzable kerogen or bitumen in these samples. The HI varies from 0 to 9 with an average of 3. Qz= Quartz, Cal=Calcite, Dol=Dolomite, Py=Pyrite, Pl=Plagioclase, Ilt=Illite, Chl=Chlorite, OM=Organic Matter, TiO₂=Titanium Dioxide.
Figure 4: SEM images for two Niobrara samples. (a) shows relatively more homogeneous intercrystalline pore distribution which is filled with organic matter. (b) shows larger intercrystalline pores filled with organic matter. Note that the larger intercrystalline pores are within the peloid structures. Niobrara samples are calcite-rich rocks with moderate amounts of clay, quartz and pyrite. Type II kerogen is thermally mature and is in oil window based on average Tmax of 436 °C and HI varying from 119 to 386 with an average of 306. TOC varies from 0.1 to 5.3 wt% and RockEval programs between 450-500 °C show abundance of bitumen in these samples. Qz= Quartz, Cal=Calcite, Dol=Dolomite, Py=Pyrite, Hem= Hematite, Pl=Plagioclase, Il=Illite, OM=Organic Matter, TiO2=Titanium Dioxide, Ms=Mascovite.

Figure 5: SEM images for two Monterey samples. (a) and (b) moderate carbonate and dominant quartz grains with presence of organic matter filling up the intergranular and intercrystalline pores. The Monetery samples are predominantly porcellanites containing moderate amounts of clay and pyrite. A smaller sample set is calcite-rich. TOC varies from 0.85-4.95 wt% and RockEval S2 data show an abundance of bitumen (Rivera, 2014). Kerogen is Type II with thermal maturity in the oil window based on average Tmax of 438 °C and hydrogen index (HI) varying from 184 to 473 with an average of 374. Qz= Quartz, Cal=Calcite, Dol=Dolomite, Py=Pyrite, Hem= Hematite, Pl=Plagioclase, Il=Illite, OM=Organic Matter.

Figure 6: Porosity comparison for Haynesville samples. The porosities are measured by (a) WI and MI, (b) N2 and MI, (c) WI and N2, (d) N2 and GRI and (e) WI and GRI. Data points are color-coded by clay content. Since all the measurements are not performed for all samples, circle and square symbols are used to differentiate different samples with similar measurements. (a) and (b) MI underestimates the porosity when compared with WI and N2. (c) WI and N2 show comparable porosity values within 2 p.u.. (d) and (d) GRI and N2 show similar porosity values.
within 2 p.u. and (e) Except some low content samples that show higher GRI porosity, the WI and GRI porosity show similar porosities within 2 p.u. difference

Figure 7: N2 PSD spectra of Haynesville samples colorcoded by (a) clay content and (b) TOC content. Samples with high clay and low TOC show high amplitudes at small mesopore range (<10nm) and samples with low clay and high TOC show high amplitudes at big mesopores (10-50 nm) and macropores range (>50 nm).

Figure 8: MI throat size distributions for Group 2 which has the highest macropore volume compared to other groups. The MI porosity was highly underestimated compared to other techniques. This implies that the throat size distributions do not assess the whole pore space.

Figure 9: Porosity comparison for Silurian samples. The porosities are measured by (a) WI and MI, (b) N2 and MI, (c) WI and N2, (d) WI and GRI and (e) N2 and GRI, all colorcoded by TOC content. (a) to (c) MI, N2 and WI measurements show an increase in porosity with increase in TOC. (a) and (b) MI highly underestimates the porosity compared to WI and N2 techniques (c) WI and N2 porosities are comparable within 2 p.u. difference. (d) and (e) GRI generally underestimates the porosity compared to WI and N2 in these samples.

Figure 10: The pore size distribution measured by N2 technique for Silurian samples colorcoded by (a) clay content and (b) TOC content. (a) and (b) Significant variation in amplitude in small mesopore range (<10 nm) is observed. The big mesopore (10-50 nm) and macropore range (>50 nm) show similar spectra with small variations in amplitude. TOC and clay content do not show a clear effect on the PSD spectra.
Figure 11: The throat size distribution measured by MI technique for Silurian samples colorcoded by (a) clay content and (b) TOC content. The MI PSD results suggest that there are pores that are not accessible by MI technique. (a) Clay content does not show a effect on the MI spectra amplitude whereas (b) TOC and spectra amplitude show a direct correlation.

Figure 12: Porosity comparison for Niobrara samples. The porosities are measured by (a) WI and N2, (b) WI and MI, and (c) MI and N2, all colorcoded by total clay content. (a) Comparing N2 and WI samples show that N2 underestimates the porosity for some samples and WI overestimates the porosity for some samples. (b) WI and MI porosities are comparable within 2 p.u. for low clay content (<10 wt%) samples and WI overestimates the porosity for high clay samples (>10 wt%). (c) N2 shows higher porosity for high clay content samples and MI shows higher porosity for low clay samples.

Figure 13: PSD for Niobrara samples using N2 technique, colorcoded by clay content Some of the spectra (low clay content) show an increasing PSD amplitude which suggest the presence of pores larger than 200 nm. The other group of spectra (high clay content) shows a dominant pore size of 80-100 nm.

Figure 14: The PSD measured by MI technique, colorcoded by clay content. The MI PSD data show two different sets of spectra. One set shows a PSD spectrum with a dominant pore size 80-100 nm (low clay content) and the other set shows abundance of small pores smaller than 20 nm (high clay content). The shape of MI spectra for high clay samples indicates the presence of pores that are not accessible by mercury.

Figure 15: Porosity comparison for Monterey samples. The porosities are measured by (a) MI and WI, (b) HE and WI, (c) HE and MI, (d) N2 and WI, (e) N2 and MI, and (f) N2 and HE, all
colorcoded by total clay content. (a) to (c) WI, MI and HE porosities show comparable values within 2 p.u. difference. (b) HE and WI show the best correlation. (d) to (f) N2 significantly underestimates the porosity for high porosity (>5 p.u.) samples. N2 shows comparable values (within 2 p.u.) for low porosity samples (<5 p.u.). Clay content does not affect the porosity measurements.

Figure 16: Pore size distribution spectra measured for Monetery samples using N2 technique, colorcoded by clay content. The N2 pore size amplitude for pores larger than 10 nm varies significantly and shows no correlation with the clay content. The amplitude for small mesopores (<10 nm) is small except for one high clay content sample.

Figure 17: Throat size distribution spectra measured for Monetery samples using MI technique colorcoded by clay content. The MI throat size distributions also show a significant variation in both amplitude and throat size. For these spectra clay content does not show any correlation with the spectra and amplitude either.

Figure 18: N2 PSD spectra of Haynesville samples for (a) Group 1, (b) Group 2, (c) Group 3, (d) Group 4 and (e) Group 5. The samples are grouped based on the PSD spectra shape. The spectra can be divided in two parts; pores smaller than 10 nm and larger than 10 nm. From Group 1 to 4 the amplitude of small pores increases and the amplitude of large pores decreases. Group 5 samples are dolomite rich and behave differently compared to the rest of groups.

Figure 19: Correlation between TOC and clay content for Haynesville samples. The samples can be divided in five groups based on the TOC and clay content. Clay content cut offs for different groups are defined as <35 wt%, 35-50 wt%, 50-60 wt% and >60 wt%. Group 5 samples are dolomite rich samples with more than 30 wt% dolomite content.
Figure 20: SEM images of Haynesville samples in Group 1. These samples are TOC rich (> 6 wt%) and show dominant pore size of 20 nm (Figure 18a). As a result of thermal maturation lots of pores are developed within the organic matter. Qz=Quartz, Cal=Calcite, Ilt=Illite, OM=Organic Matter.

Figure 21: SEM images of Haynesville samples in Group 2. These samples have slightly lower TOC and higher clay content compared to Group 1. Although OM-hosted pores are the dominant pore types, the images demonstrate presence of intercrystalline pores in clay minerals. Qz=Quartz, Py=Pyrite, Ilt=Illite, Chl=Chlorite, OM=Organic Matter.

Figure 22: SEM images of Haynesville samples in Group 3. These samples have a combination of organic- and mineral-hosted pores. The N2 PSD results (Figure 18c) also indicates the presence both intercystalline (< 10 nm) and OM-hosted pores (> 10 nm). As a result of thermal maturation lots of pores are developed within the organic matter. Qz=Quartz, Ilt=Illite, OM=Organic Matter.

Figure 23: SEM images of Haynesville samples in Group 4. These samples are clay rich (60-80 wt%) and show abundance of small mesopores (<10 nm) measured by N2 PSD (Figure 18d). The SEM images show that intercrystalline pores in clay minerals are the dominant pores in these samples. Qz=Quartz, Ilt=Illite.

Figure 24: SEM images of Haynesville samples in Group 5. These samples are dolomite rich (> 30 wt%) which have very low TOC content (< 1.5 wt%). The space between dolomite grains are filled with a mixture of clay and quartz particles which host the intercrystalline pores in these samples. Although the organic content is minimal in this Group, organic-hosted pores are developed where OM is present. Qz=Quartz, Cal=Calcite, Dol=Dolomite, Py=Pyrite, Ilt=Illite.
Figure 25: The relationship between clay and TOC content for Silurian samples. The samples can be divided in two groups. Group 1 which has clay and TOC content lower than 48 and 1.8 wt%, respectively and Group 2 which has TOC and Clay content higher than the mentioned values. In Group 1 the TOC is relatively constant whereas in Group 2 the TOC and clay content have inverse correlation.

Figure 26: The pore size distribution measured by N2 technique for (a) Group 1 and (b) Group 2 a. Increasing in clay content for samples in Group 1 (a) results in increase in pore size distribution amplitude at 3 nm pore size range. The samples of Group 2 (b) do not follow the same trend. The highest amplitudes belong to the samples with the highest TOC content and samples with either high clay or TOC content show higher amplitude at 1.7-5 nm pore size range.

Figure 27: SEM images of Silurian samples in Group 1. Both OM-hosted and intercrystalline pores are present in these samples. In this group the amplitude for pores with diameter less than 10 nm increases as the clay content increases (Figure 26a). Qz=Quartz, Ilt=Illite, OM=Organic Matter.

Figure 28: SEM images of Silurian samples in Group 1. The intercrystalline pores are filled with organic matter which holds the majority of the pores. The organic hosted pores are in the mesopore range. The size of the pores and possibly lack of connectivity limits the capability of the porosity and pore size distribution measurements to assess the pores. Qz=Quartz, Ilt=Illite, OM=Organic Matter.

Figure 29: Examples of PSD measured by the N2 technique for samples from (a) Groups 1 and (b) Group 2. The PSD of the Group 1 samples (a) shows presence of pores larger than 200 nm
that were not assessed by the N2 technique. The PSD of the majority of Group 2 samples (b) shows that the dominant pore size lies around 100 nm.

Figure 30: The Niobrara samples are divided in two groups based on their TOC contents. Group 1 has low TOC content (below 2 wt%) and group 2 has high TOC content (above 2 wt%). Clay and TOC content control the porosity and pore size distribution in Niobrara samples.

Figure 31: SEM images of Silurian samples in Group 1. Quartz, calcite and clay particles fill the space between calcite grains and form the intercrystalline pore structure. No organic matter and organic-hosted pores are present in this sample. The intercrystalline pores form a connected network which is accessible to displacement fluids for porosity measurements. Qz=Quartz, Cal=Calcite, Ilt=Illite.

Figure 32: SEM images of Niobrara samples in Group 2. Significant amount of TOC is visible in this sample which fills the intercrystalline pores. The OM-hosted pores are developed in the organic matter. As it is shown by the annotations in the pores are smaller than 100 nm and possibly not connected. Both small pore size and lack of connectivity limit the accessibility of the displacement fluids to these pores for porosity measurements. Cal=Calcite, Ilt=Illite, Py=Pyrite, OM=Organic Matter.
Figure 33: Pore size distribution spectra measured for Monterey samples using N2 technique for (a) Group 1 and (b) Group 2. Since samples in Group 1 (a) show more comparable N2 porosity values when compared with HE and MI techniques we can consider the spectra in (a) a suitable representation of pore size distribution for these samples. N2 measures a highly underestimated porosity for Group 2 samples, so N2 spectra (b) does not represent the whole pore space.

Figure 34: SEM images of Monterey samples in Group 1. These samples have intercrystalline pores in clay phase and interacrystalline pores within the quartz and calcite grains which are exposed due to polishing. The intercrystalline space is filled with organic matter which holds very low OM-hosted porosity. Qz= Quartz, Cal=Calcite, Dol=Dolomite, Ilt=Illite, Py=Pyrite.

Figure 35: SEM images of Monterey samples in Group 2. These samples show larger intercrystalline pores compared to Group 1 samples. The pores are developed in the space between quartz grains. Qz= Quartz, Ilt=Illite, OM=Organic Matter.

Figure 36: The throat size distribution measured by MI technique for (a) Group 1 colorcoded by clay and (b) Group 2 colorcoded by TOC. (a) The MI spectra for Group 1 samples do not demonstrate the same clay content dependency as N2 spectra for these samples (Figure 26a). (b) On the other hand MI spectra amplitude of Group 2 samples increases with increasing TOC, similar to N2 PSD (Figure 26b).

Figure 37: Throat size distributions assessed by MI technique for samples in (a) Group 1 and (b) Group 2, colorcoded by clay content. (a) For Group 1 samples mercury successfully assessed the pores which were not accessible by N2 (Figure 29a). (b) On the other hand for samples in Group 2 mercury did not reach the small pores hosted by the organic matter, these pores were assessed by N2 (Figure 29b).
Figure 38: Throat size distribution spectra measured for Monterey samples using MI technique for (a) Group 1 and (b) Group 2. The dominant throat size distributions for Monterey samples vary significantly from less than 20 nm for Group 1 (a) and more than 200 nm for Group 2 samples (b).
Figure 1

Figure 2
Figure 7

Figure 8
Figure 9

Figure 10
Figure 11

(a) Incremental porosity (p.u.) vs. Pore Diameter (nm)

(b) Incremental porosity (p.u.) vs. Pore Diameter (nm)

Figure 12

(a) WI-N2 Niobrara

(b) WI-MI Niobrara

(c) MI-N2 Niobrara

Group 1 WI-N2 Niobrara

Group 2
Figure 15

Figure 16

Figure 17
Figure 18

Figure 19
Figure 29

Figure 30
Figure 31

Figure 32

N2 PSD Monterey Group 1

N2 PSD Monterey Group 2
Figure 36

Figure 37
Figure 38
Table 1. Summary of measurement techniques and number of samples measured.

<table>
<thead>
<tr>
<th>Method</th>
<th>Haynesville</th>
<th>Monterey</th>
<th>Niobrara</th>
<th>Silurian</th>
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<td>GRI</td>
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<td>NA</td>
<td>NA</td>
<td>9</td>
</tr>
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<td>Helium Injection (HE)</td>
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<tr>
<td>Nitrogen Adsorption (N2)</td>
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<td>22</td>
<td>19</td>
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Table 2. Summary of the disadvantages of each measurement technique and the resulting effect on porosity measurements.

<table>
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<tr>
<th>Methods</th>
<th>Disadvantage</th>
<th>Effect on Porosity Measurement</th>
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<tbody>
<tr>
<td>GRI</td>
<td>- Hot solvent extraction removes soluble bitumen</td>
<td>- Creates artificial porosity and causes overestimation</td>
</tr>
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<td></td>
<td>- Clay minerals can swell with water</td>
<td>- Causes higher grain volume and porosity underestimation</td>
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<tr>
<td>Water Immersion</td>
<td>- Water might not fill organic-hosted pores and these pores might be hydrophobic</td>
<td>- Porosity overestimation in smectite rich samples</td>
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<tr>
<td>Mercury Intrusion</td>
<td>- Does not measure pores associated with throat smaller than 3.6 nm</td>
<td>- Misses pores with throat smaller than 3.6 nm and causes porosity underestimation</td>
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<td></td>
<td>- Clay tactoid pores are missed</td>
<td>- Causes porosity underestimation in clay-rich samples</td>
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<tr>
<td>Nitrogen Adsorption</td>
<td>- Does not measure pore bodies larger than 200 nm</td>
<td>- Misses pore bodies larger than 200 nm and causes porosity underestimation</td>
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<tr>
<td></td>
<td>- Gas might get sorbed in certain minerals or organic matter</td>
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