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 are important rock properties which are required to calculate reservoir quality and volume. In mudrocks, measurement of these properties is challenging due to the presence of fine grains, small pores, high clay content, swelling clay minerals, pores hosted in organic content, and possibly, mixed wettability. In this study, we compare porosity measurements with various techniques on mudrocks from different formations, such as Monterey, Haynesville, Niobrara and Eastern European Silurian 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 microscopic scale. We analyzed our data for the effect of texture and mineralogy, specifically clay content and total organic matter (TOC) on the porosity and pore-size distribution data. We divided the samples from each formation to different groups based on the clay and TOC content and investigated the effect of geochemical and mineralogical variations on the porosity and pore size distribution measurements.

We find that the various porosity and PSD measurements provide complementary information. Selection of the most appropriate method depends on the clay content, thermal maturity, and anticipated range of pore sizes. Reliability of a porosity measurement depends on the accessibility of the pores to the displacing fluid. Our results help explain so-called inconsistencies in porosity measurements measured with different techniques. Our second assessment shows that a combination of different porosity methods yields a better assessment of the pore space topology.

2. Introduction
The main objective of our work was to understand various pore sensing techniques on the basis of textural, mineralogical and geochemical differences. Various researchers have documented inconsistencies (as high as a factor of two) between porosities measured with different techniques (Passey et al., 2010, Sondergeld et al., 2013). These differences have been explained variously as choosing inappropriate method (Saidian et al., 2014), sample preparation (Passey et al., 2010, Sondergeld et al., 2013) and using different protocols or practices for the same experiment (Sondergeld et al., 2013, Kuila et al., 2014). We investigated these methods systematically using a wide range of samples from four formations. We present here our porosity and pore-size distribution data measured with four different techniques for the four selected formations. 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. Note that we use the pore size classification suggested by Rouquerol et al. (1994) where micro, meso and macro pores have <2 nm, 2-50 nm and >50 nm pore width, respectively. Note that the pore size and the pore throat size distribution spectra are plotted using the diameter or width of the pores and both are referred to as pore throat size distributions (PSD).

3. Materials
A combination of sidewall and conventional core samples were taken from an oil producing well drilled at the western flank of the southern San Joaquin Basin from Monterey Formation in California. The marl and chalk samples came from a well in the Berthoud Field, Larimer County, CO, USA, specifically from the Fort Hays limestone and the overlying Smoky Hill members of the Niobrara formation. The Upper
Jurassic Haynesville Formation samples came from a gas producing well. The fourth sample set was taken from the Silurian gas reservoir in Eastern Europe (Kuila, 2013). Figure 1 shows the mineralogy and TOC for all sample sets.

Figure 1: Mineralogy of (a) Monterey (b) Haynesville (c) Niobrara (Chalk, Marl and Fort Hays) (d) Silurian samples measured by QXRD and color coded by TOC. See sample descriptions for more information.

4. Methods
We measured porosity with the Water Immersion (WI) method as developed by the American Petroleum Institute (API RP40) and porosity and pore size distributions with mercury intrusion (MI; for pore throat size) and nitrogen method adsorption (N2; for pore body size). In addition, we measured porosity with the Gas Research Institute (GRI) helium porosimetry technique in two sample sets (Silurian and Haynesville) and helium injection technique for the Monterey sample set.

5. Key Results for Niobrara Samples (The rest will be presented at the workshop)
The main driver for this comparative study was (1) to analyze the differences in each method and (2) to exploit these differences to learn more about the mineralogical and geochemical effects on pore topology of each sample set. This richness of data allowed us to analyze and explain porosity mismatch due to clay content and TOC, pore size distribution, and measurement conditions.

Figure 2 shows a comparison of porosity values measured using N2, MI and WI techniques. Two distinct groups of data are observed in Figure 2.a. In Group 1 (data circled by a blue dashed line in Figure 2a), WI porosity is higher compared to N2 porosity, whereas in Group 2 (data circled by a red solid line in Figure 2a), WI and N2 porosities are comparable within 2 p.u. (porosity units). The following observations can be made for samples with a wide distribution of pore sizes and high clay content such as the Niobrara
samples: (a) N2-porosity is reliable in nanoporous rocks (for example, Group 2), but it is underestimated when the pores are larger than 200 nm; (b) WI-porosity is overestimated if expandable clays are present; (c) If clay content is low and small pore sizes are absent (for example, Group 1 samples), WI- and MI-porosities are comparable; (c) Limited accessibility of mercury to micropores (for example, in the organic-hosted pores in Group 2 Figure 2

The effect of clay content and TOC on pore structure is confirmed using the N2-pore size (N2-PSD; Figure 3) and MI-throat size (MI-PSD; Figure 4) distributions. The N2-PSD of Group 1 samples (Figure 3.a) hints at the presence of pores larger than 200 nm that cannot be assessed by this technique. Most of the Group 2 samples (Figure 3.b) show a dominant pore size around 100 nm. Pore-throat size distributions assessed by MI technique for the same samples are shown in Figure 4. In samples with a wide distribution of pore sizes, such as Group 1, MI-PSD (Figure 4.a) provides complementary data on large pores to augment the small pore sizes assessed by N2-PSD. On the other hand, in the absence of large pores, such as in Group 2, MI-PSD could not capture the small pores. Based on the observations in porosity and pore size distribution comparisons for Groups 1 and 2 we can conclude that for Group 1 samples MI assesses the whole pore space whereas for Group 2 samples N2 is the suitable tool for assessing the pore size distribution.

Figure 3: 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) hints at 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.
Next, we investigate the effect of compositional (clay content and TOC) and textural variations on porosity and pore size distribution in Groups 1 and 2 of the Niobrara sample set. Figure 5 shows that TOC and clay content directly correlated when TOC is less than 2 wt%, and inversely correlated at higher TOC, although more data are required to establish a robust correlation.

To explain the pore topology and associations with minerals, we used high magnification SEM images (Figure 6 and Figure 7). Figure 6.a shows how quartz, calcite and clay particles fill the space between calcite grains and form intercrystalline pore structure in a Group 1 sample. Organic matter and organic-hosted pores are absent. Figure 6.b shows a connected network of intercrystalline pores which can be accessed by the fluids used for porosity measurements. Figure 7 shows SEM images for a Group 2 sample. Significant amount of TOC filling is visible in the intercrystalline pores (Figure 7.a). Organic-hosted pores are smaller than 100 nm. Small pore sizes and a possible lack of connectivity can limit the accessibility to these pores.

Figure 5: 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 6: Higher magnification SEM images for sample N-22 which belongs to Group 1 samples. (a) shows how 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 (TOC of 0.06 wt%). Figure 6(b) Shows a connected network of intercrystallines pores which are accessible to displacement fluids for porosity measurements.

Figure 7: Higher magnification SEM images for sample N-16 which belongs to Group 2 samples. (a) Significant amount of TOC is visible in this sample which fills the intercrystalline pores. (b) Figure 7.b shows the organic-hosted porosity. As is shown by the annotations in (b) 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.

The variations in porosity, pore size distribution, mineralogy, and geochemical properties of the samples can be explained by the geology of the Niobrara formation in the area of study. A majority of the Group 1 samples are from the Fort Hays member and the clay-rich marls of the Smokey Hill member. Group 2 samples mainly belong to the organic-rich chalks with some exceptions possibly due to diagenesis as well as heterogeneity due to fine laminations in the Smokey Hill member.