PS Insights on Porosity and Pore-Size Distribution Using Multiple Analytical Tools: Implications for Reservoir Characterization in Geologic Storage of CO₂*

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Abstract

The geologic description and quantification of the physical properties that define a viable reservoir are fundamental for assessing the feasibility of a reservoir to receive and store injected CO_2 in the deep subsurface. Two petrophysical properties, porosity and permeability, constrain the reservoir in terms of its storage potential and injectivity. The analytical tools that are useful for measuring these properties vary and are optimally employed at various scales.

We analyzed 52 rock samples from the Cambrian-Ordovician Knox Supergroup spanning a significant area of the midwestern United States. These samples represent a wide range in both the scale and magnitude of the porosity present in this prospective storage reservoir. The samples were analyzed for total porosity and pore size distribution, using petrographic image analysis, helium porosimetry, gas adsorption, mercury porosimetry, and (ultra) small-angle neutron scattering. These analytical techniques were collectively used to understand the relationship between porosity, permeability, and pore size distribution they offer a unique opportunity to study a wide range of pore sizes and to understand the validity of employing these techniques collaboratively.

Results from nitrogen and carbon dioxide adsorption and from mercury injection capillary pressure are important in that they provide insights on small pore size that otherwise cannot be resolved by standard low-pressure helium porosimetry or by image analysis software. Additionally, results from analyses of these carbonate reservoir rocks suggest that microporosity does not have a considerable impact on permeability, but larger pores control this key petrophysical parameter for constraining fluid flow through the pore system

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ABSTRACT

The successful implementation of geologic carbon sequestration depends on the careful evaluation of the petrophysical characteristics of the storage reservoir. Two primarly petrophysical properties, porosity and permeability, constrain the reservoir in terms of storage potential and injectivity. These two key parameters may vary significantly in scale within a reservoir. Likewise, the analytical tools that are useful for measuring these properties also vary and only assess pores of a given scale.

In this investigation, a total of 52 rock samples that consist of carbonates having a high degree of dolomitization were obtained from the Cambrian-Ordovician Knox Supergroup from different depth intervals; these samples span a significant area of the midwestern United States. The samples were analyzed for total porosity and pore-size distribution using a variety of techniques including petrographic image analysis, helium porosimetry, gas adsorption, mercury porosimetry, and (ultra)-small-angle neutron scattering. Capillary entrapment, or "residual saturation," is that portion of the injected $\rm CO_2$ that remains trapped in micropores after the pressure elevated by the injection process returns to ambient reservoir pressure. Results from low-pressure nitrogen and carbon dioxide adsorption and from mercury injection capillary pressure are important in that they provide insights on small pore-size that otherwise cannot be resolved by standard helium porosimetry or by image analysis software. Results from these analyses suggest that micro-, meso-, and macroporosity ($\sim 0-35$ nm as suggested by gas adsorption and $\sim 0.0025-100~\mu m$ as suggested by mercury porosimetry) are the main controlling factors of capillary entrapment and permeability, respectively.

1 INTRODUCTION AND PURPOSE

- Deep and widespread saline aquifers, such as those that occur in the Knox Supergroup in the midwestern region of the United States, offer suitable targets for CO₂ sequestration.
- The purpose of this paper is to evaluate the porosity of a suite of samples and porosity's relationship to pore size.
- This work aligns with one of the primary goals of the Midwest Regional Carbon Sequestration Partnership —characterize and quantify the amount of resources (pore space) in saline aquifers for the geologic storage of carbon dioxide.

2 SAMPLES AND METHODOLOGY

• Studies of and comparison among techniques, such as image analysis from thin section, mercury injection capillary pressure tests (MICP), gas adsorption, and neutron scattering will help us understand the role and relative contribution to geologic storage of CO₂ provided by macro-, meso-, and microporosity (Fig. 1).

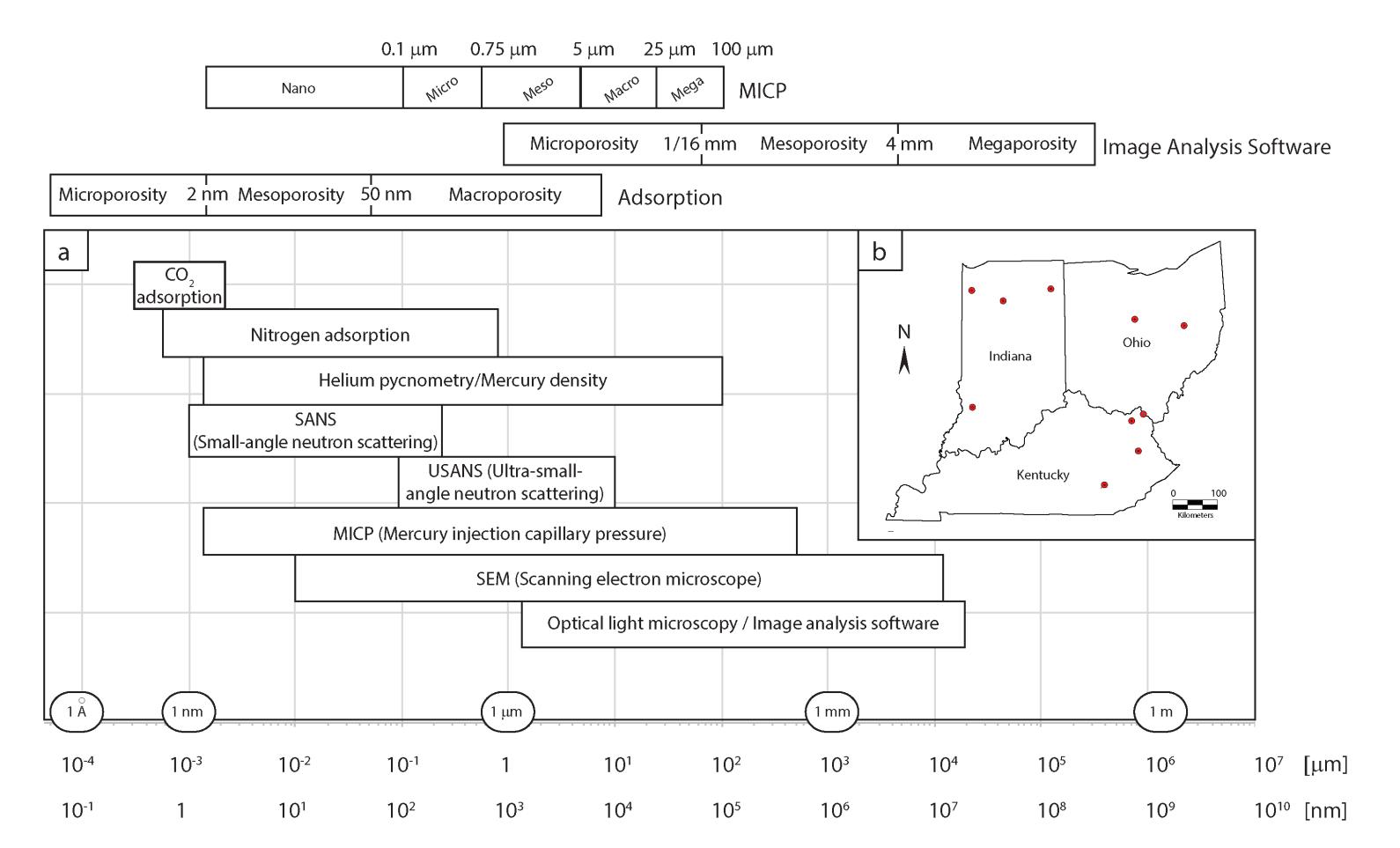


Figure 1. Current methods and the range in pore size that they can analyze. The pore-size characterization scheme used throughout this poster follows that of the International Union of Pure and Applied Chemistry (Orr, 1977) and that of Gregg and Sing (1982) (Figure 1 and Table 1).

Micropores < 2
Mesopores 2-50
Macropores > 50

Table 1. Classification of pores according to their width (Gregg and Sing, 1982).



Figure 2. Sample used for IAS, standard P&P analysis, and SANS/USANS experiments (in addition to N_2 adsorption, and MICP).

2. a Image Analysis Software and Standard Porosity & Permeability Analysis

- Porosity & permeability analysis for 34 samples (Fig. 2).
- Porosity was quantified using image analysis software (IAS) (52 samples, Fig. 3).
- Images from a scanning electron microscope (SEM) were collected (Gasaway, pers. comm.) (Fig. 4).

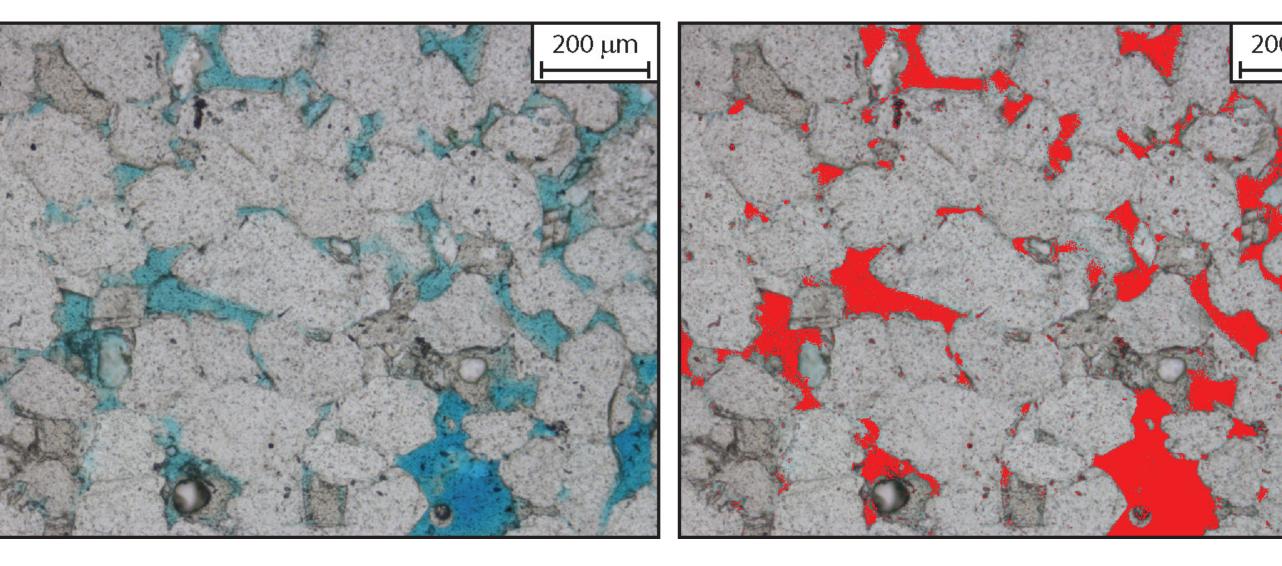
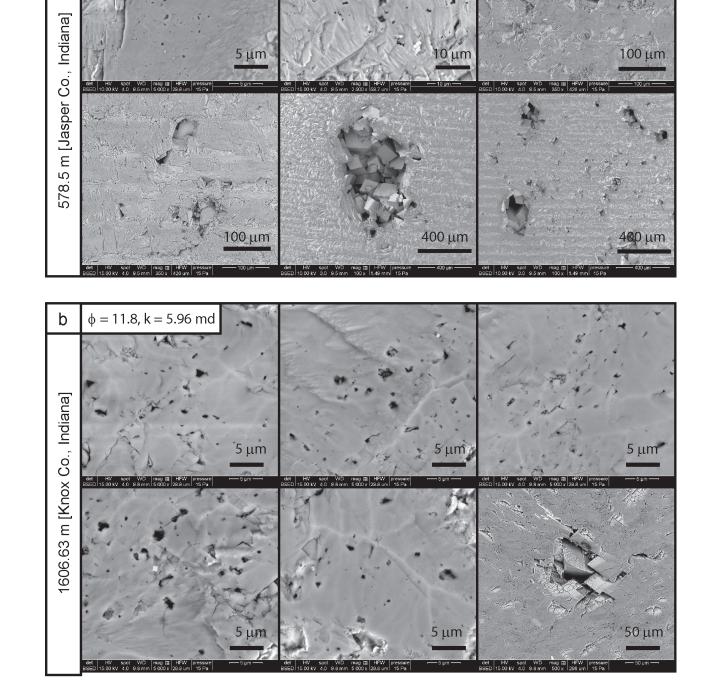


Figure 3. Example of porosity identification (in red) using image analysis software.

Figure 4. SEM images (Gasaway, pers. comm.) showing pore size ranging from less than 1 micron up to 1 mm.



2. b Mercury Injection Capillary Pressure

- Mercury porosimetry is a well-known method to determine pore-throat-size distribution, consisting of injecting mercury under low to high pressure into the rock sample.
- This method results in a log-normal saturation curve (mercury injection curve, Fig. 5a) that can be interpreted as analogous to a grain-size analysis in sedimentary rocks, where each injection pressure can be transformed to a pore size (Washburn, 1921, Fig. 5b).

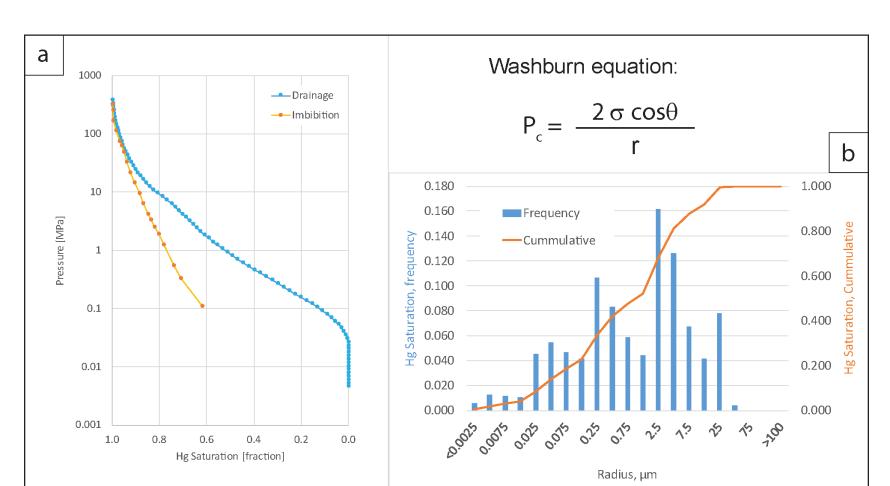
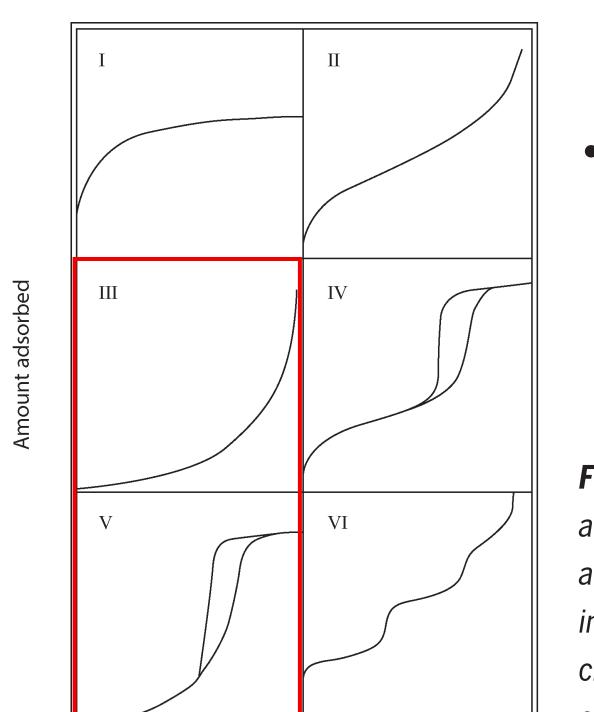


Figure 5. (a) Example of typical curves of drainage (injection of Hg) and imbibition (extrusion of Hg) and (b) the use of the Washburn equation allows the construction of a pore-size distribution histogram. This sample is from Morrow County, Ohio (depth of

2. c Gas Adsorption



• 34 samples were analyzed using a Micromeritics ASAP 2020, a gas adsorption/desorption analyzer. From these samples, 28 were analyzed using nitrogen as the intruding gas and six using carbon dioxide.

Figure 6. Types of physisorption isotherms (modified from Sing et al., 1985). Type I isotherm is characteristic of gas adsorbed by microporous solids (Table 1). Type II isotherm describes adsorption of gases by nonporous solids. Type III and V isotherms are not common and are indicative of weak interaction between adsorbent (gas) and adsorbate (solid) in a nonporous or macroporous solid (type III) and in a mesoporous or microporous solid (type V). Type IV isotherm is characteristic of mesoporous solid. The steplike isotherm (type VI) which, although rare in occurrence, is characteristic of nonporous solids with uniform surfaces of the adsorbent material (Gregg and Sing, 1982; Sing et al., 1985).

2. d Neutron Scattering (SANS/USANS)

- Small-angle neutron scattering and ultra-small-angle neutron scattering experiments were carried out at the Oak Ridge National Laboratory and at the National Institute of Standards Technologies, respectively (Fig. 7).
- The residual scattering at zero average contrast conditions can be used to quantify the volume fraction of effective porosity (Melnichenko et al., 2012, Fig. 8).

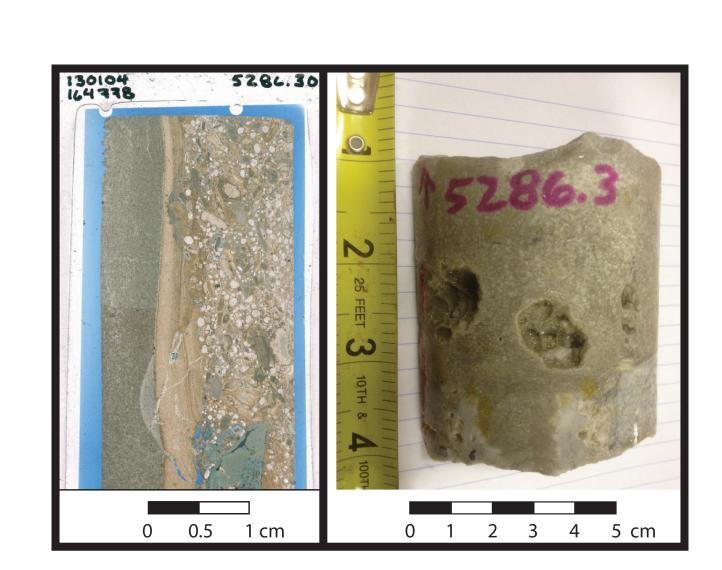


Figure 7. Photographs of the sample used in SANS/USANS experiments (in addition to IAS, N2 adsorption, and MICP).

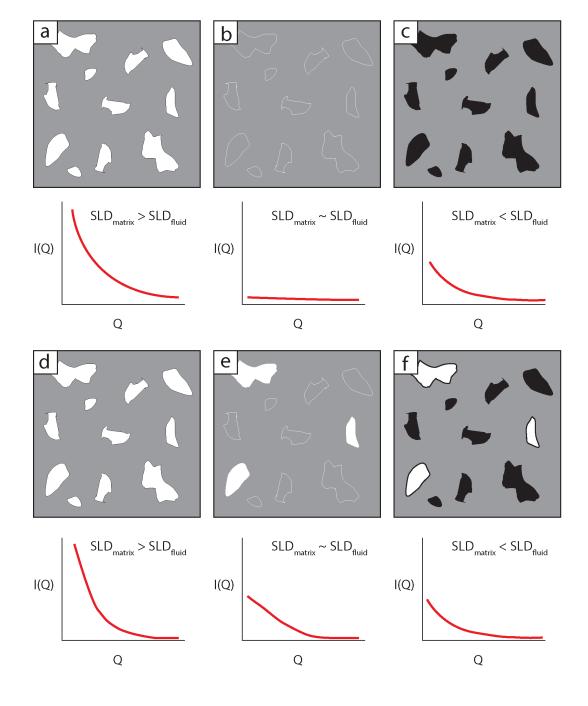


Figure 8. Qualitative presentation of contrast-matching experiments with fluid saturated porous systems. (a-c) All pores are accessible to injected fluid; (d-f) pores are partially accessible to injected fluid.



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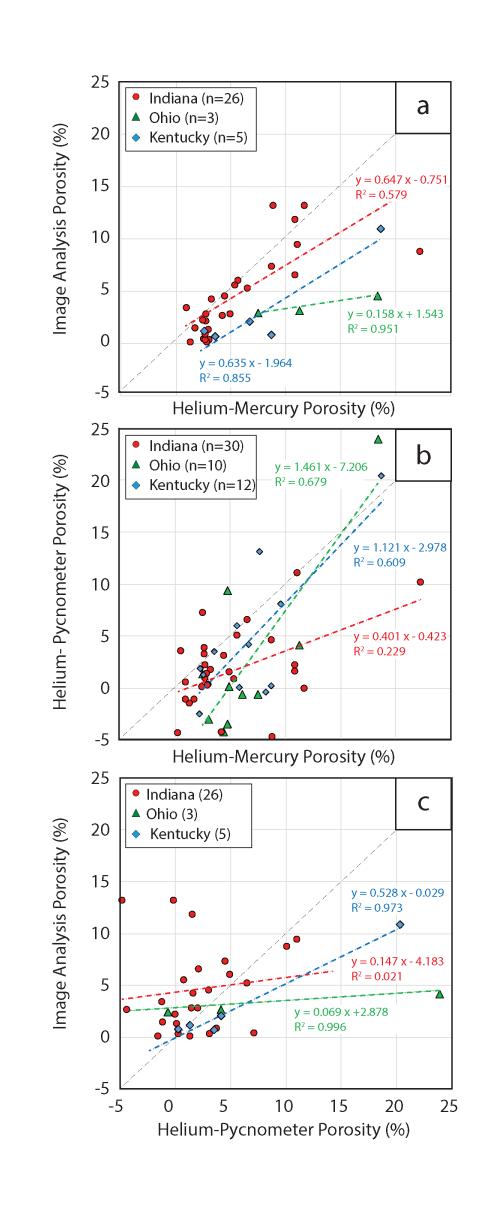
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3 RESULTS

3. a Porosity Measurements

- Values of porosity from 52 samples using:
 - 1. *IAS*;
 - 2. Core analysis by a commercial lab;
 - 3. Pycnometry (IGS laboratory).
- In general, these methods exhibit good correlation (Fig. 9). However, samples having low porosity (as indicated by core analysis) tend to result in negative porosity measured in our lab (Fig. 9b and 9c).

Figure 9. Scatter plots and linear regressions comparing porosity from three methods: a. porosity from image analysis vs. helium-mercury porosity (core analysis); b. porosity from helium-pycnometer vs. porosity from helium-mercury; and c. porosity from image analysis vs. porosity from helium-pycnometer.



3. c Gas Adsorption (Micromeritics ASAP 2020)

• In all the samples, the adsorptions isotherms follow a Type III and V curve (Figs. 6 and 13).

(<2 nm; <0.002 microns) (Fig. 14).

• All samples display a relative low amount of N_2 adsorbed at low relative pressure and a tendency to increase logarithmically with increasing pressure (Fig. 13).

• Six samples were injected with CO₂ for analyzing microporosity

An inverse relationship exists between permeability, porosity, and

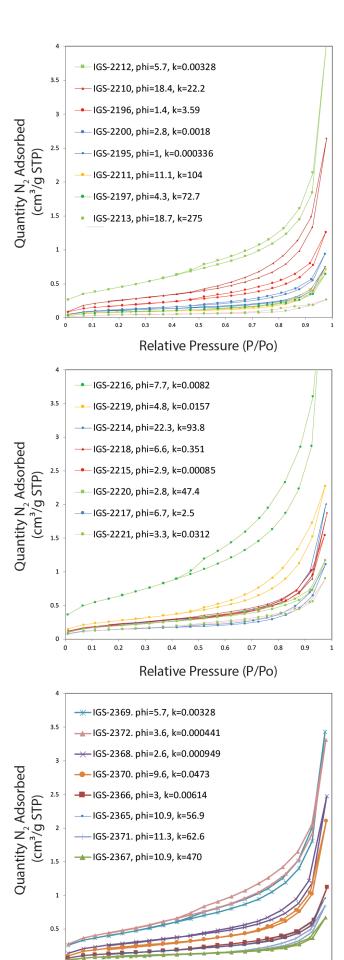
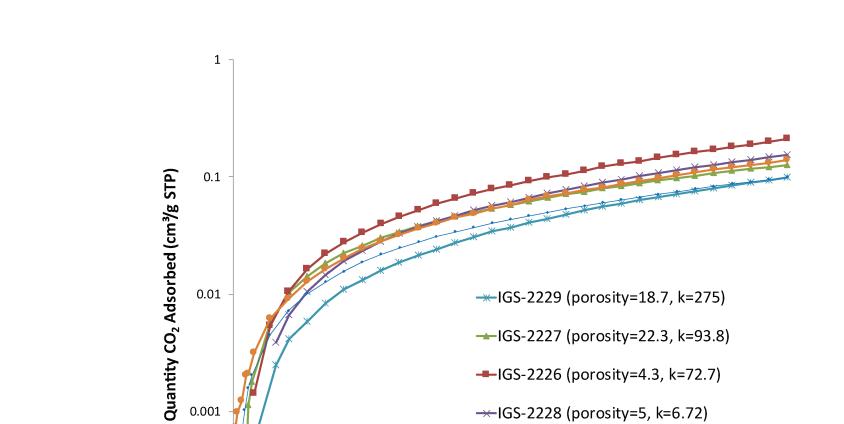


Figure 13. Graphs of nitrogen adsorption

(lower curve) and

desorption (upper

curve) isotherms.



the micropore volume (Fig. 15).

Figure 14. Line graph of low-pressure CO₂ adsorption isotherms for six samples under study. Note that there not a clear relationship between amount of CO₂ adsorbed

-IGS-2225 (porosity=6.6, 0.351)

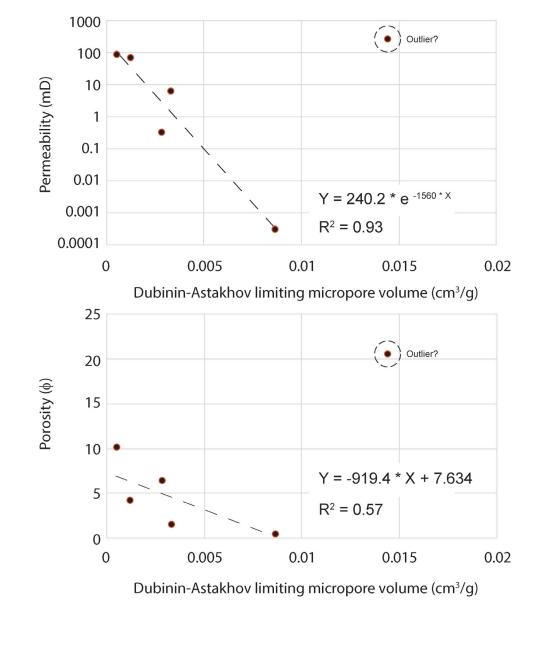
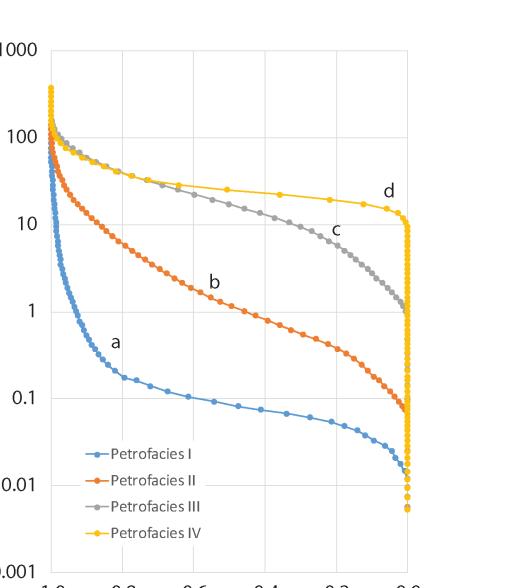
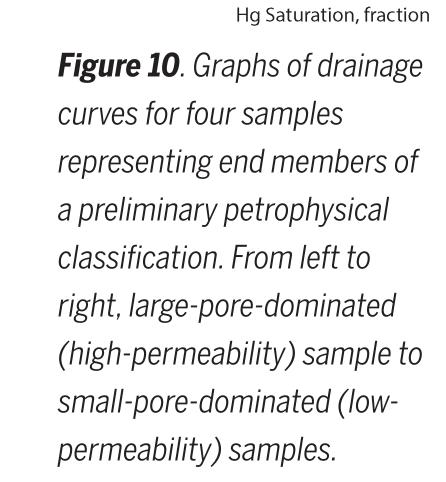


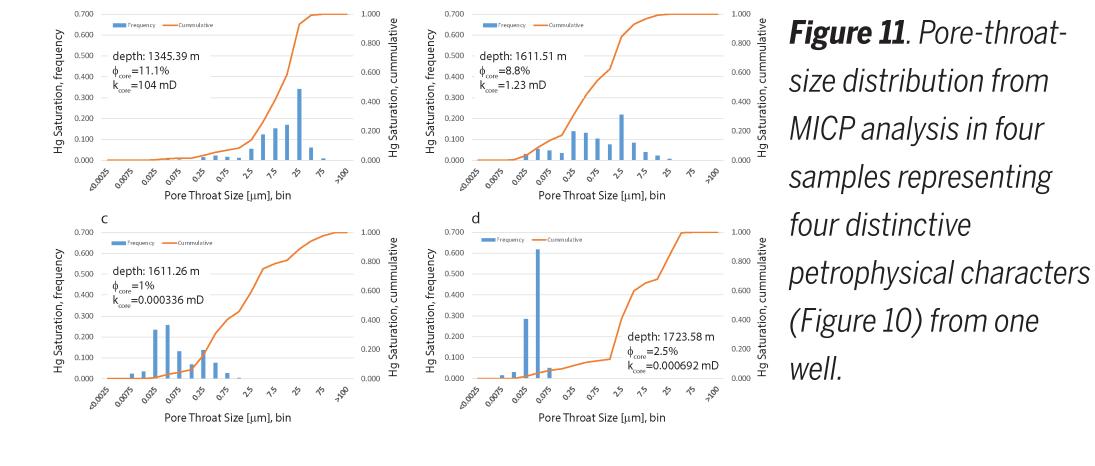
Figure 15. Scatter plots and linear regressions illustrating porosity and permeability and their relationship to micropore volume measured with adsorption of CO_2 .

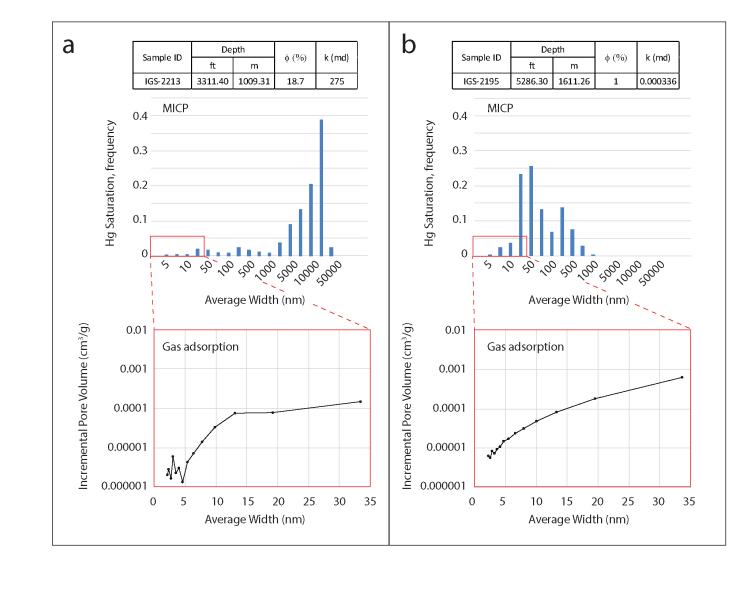
3. b Mercury Injection Capillary Pressure

- All 52 samples were analyzed using mercury porosimetry.
- Four groups with distinctive petrophysical properties (Fig. 10) were identified.
- Each one of these groups also displays a particular pore-throat-size distribution (Fig. 11).
- There is a clear distinction between larger-pore-dominated samples in higher porosity and permeability in sample IGS-2213 (ϕ =18.7; k=275 md) (Fig. 12a) and in smaller-pore-dominated sample IGS-2195 (ϕ =1; k=0.000336 md) (Fig.









and MICP pore-size distribution from sample IDs IGS-2213 and IGS-2195. These samples are contrasting in porosity and permeability and display a distinct pore-size distribution, with larger pores controlling fluid flow in high-permeability

Figure 12. Gas adsorption

3. d Neutron Scattering (SANS/USANS)

- The SANS results indicate the presence of fractal pores (2–50 nm, ~0.1 %) and micropores (<2 nm, ~5%).
- The USANS data suggest a similar fraction of fractal pores and micropores.
- The total porosity obtained using conventional core analysis is 1 percent.
- This discrepancy between the porosity values obtained by conventional core methods and SANS suggests that 80 percent of the pores are inaccessible to helium.

4 CONCLUSIONS

- Samples from the Knox Supergroup exhibit pore sizes that span several orders of magnitude. A clear relationship between porosity and permeability does not exist, but pore-size distribution seems to have a direct influence on permeability.
- The best correlations among porosity values are those obtained by image analysis and core analysis (Fig. 9a). Porosity from pycnometry produced several negative values, which makes that method unreliable (Fig. 9b-c).
- The samples tested under high-pressure injection of mercury reveal strong relationships among the capillary entry pressure curve, pore-size distribution, and permeability (Figs. 10–11). Based on this behavior of the curves, we have identified four major groups (termed "petrofacies").
- Our attempts to compare different methodologies resulted in agreement between MICP and gas adsorption in that both analyze a portion of the pore system composed of micropores (Fig. 12). This fraction of total porosity must not be ignored because it can store significant amounts of supercritical carbon dioxide in the form of capillary entrapment.
- There is not a clear correlation between averaged values of surface area, pore width, and permeability calculated from nitrogen gas adsorption (Fig. 16). However, the gas isotherms and their relative position indicating the amount of N₂ or CO₂ adsorbed are in agreement, in general, with total porosity of the samples (Fig. 13).
- A substantial difference was observed between porosity measured using standard helium porosimetry ($\phi = 1\%$) and porosity from neutron scattering $(\phi = 5\%)$. Gas adsorption methods using CO₂ also suggest the presence of effective porosity via micropores (<2 nm) (Figs. 14, 15, and 17).

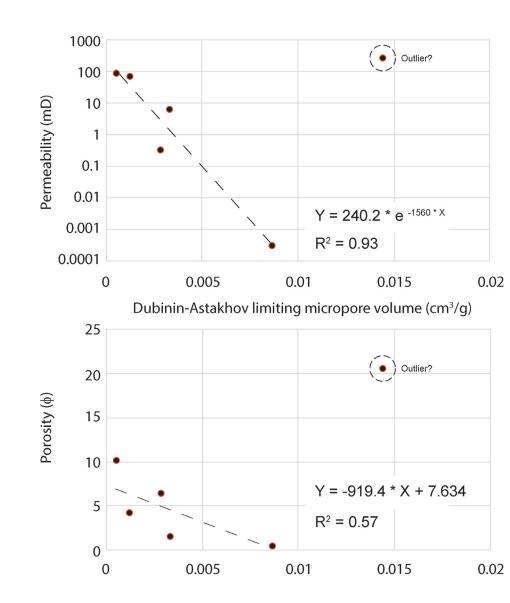


Figure 16. Scatter plots of adsorption results indicating no clear correlations between permeability and surface area.

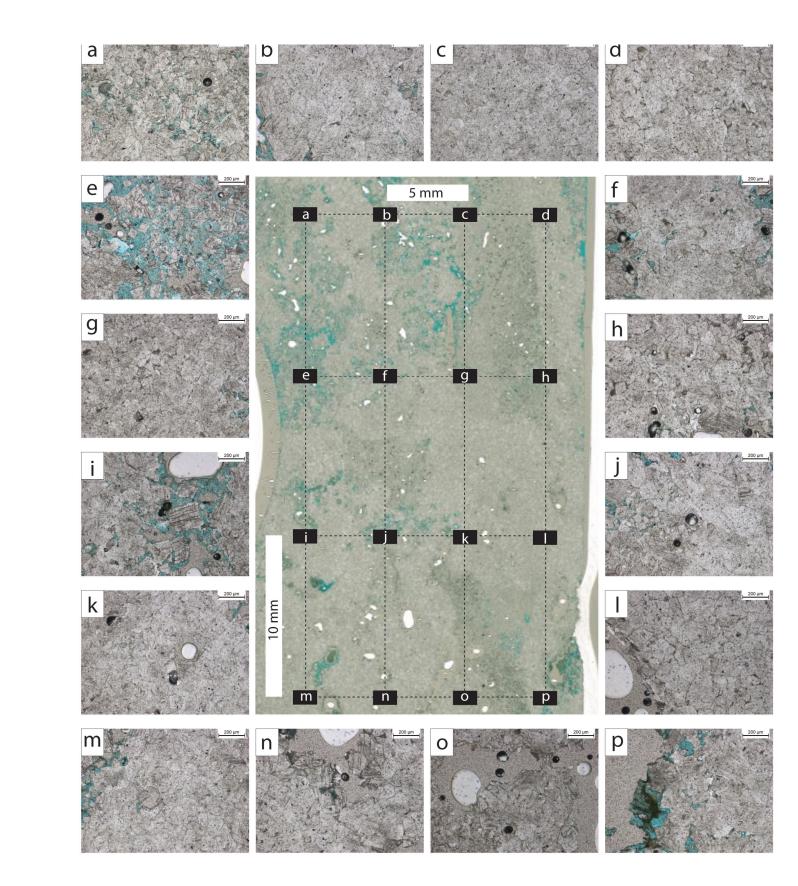


Figure 17. Photographs of porosity heterogeneity observed in a thin section of sample at depth of 886.75 m [2,909.3 ft] (Morrow County, Ohio). Depending on the quadrant, porosity measured from image analysis software (ImageJ) varies from <1% (quadrant 'c') to 31.6% (quadrant 'e'). Blue color is the epoxy impregnation and represents porosity.

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