**Influence of Soxhlet-extractable bitumen and oil on porosity in thermally
maturing organic-rich shales**

Lin Wei ^{1,*}, Maria Mastalerz ², Arndt Schimmelmann ¹, Yanyan Chen ¹

¹ *Department of Geological Sciences, Indiana University, Bloomington, IN 47405-1405,
USA*

² *Indiana Geological Survey, Indiana University, Bloomington, IN 47405-2208, USA*

(*correspondence: linwei@indiana.edu)

Abstract

Porosity in shales is important for storage of shale gas in reservoirs. As organic-rich shale thermally matures and enters the oil window, generated bitumen and oil can fill pore spaces, block pore connectivity, and reduce porosity. Low-pressure N₂ and CO₂ adsorption techniques were used to quantify mesoporosity (pore size 2-50 nm, accessible to N₂ and CO₂) and microporosity (pore size <2 nm, accessible to CO₂ only) in New Albany Shale samples of Devonian and Mississippian age from Indiana and Illinois ranging from marginally mature (vitrinite reflectance R_o=0.55%) to post-mature (R_o=1.41%). After measuring their original porosity, the shale samples were Soxhlet-extracted in refluxing dichloromethane (DCM, boiling temperature 39.6 °C) to remove soluble oil/bitumen, vacuum-dried, and then re-measured for meso and microporosities. Subsequently, the same samples were Soxhlet-extracted in toluene (boiling temperature 111 °C, with enhanced solubility of oil/bitumen), vacuum-dried, and again characterized porosimetrically.

The maturation sequence of the original, non-extracted shales expresses a higher mesoporosity in lower maturity samples (vitrinite reflectance R_o 0.55%, and 0.65%), and an intermittent decrease in mesoporosity in samples of post-mature stage (R_o 1.15%) in two size fractions (4-mesh and 60-mesh). The intermittent decrease in mesoporosity is consistent with partial filling of pore spaces with bitumen and oil secondary cracking reclaims some of the lost open pore space from liquid phases. Organic matter (OM) transformation is thus a pivotal cause for the observed evolution of mesoporosity in original, non-extracted shales. Micropore volumes

display a varying trend throughout thermal maturation, and are significantly by total organic carbon content. Compared to 4-mesh sample fractions, a reduction in grain size of 60-mesh fractions for gas adsorption porosimetry prominently enhances mesopore volumes, whereas the effects on micropore volumes are variable. These findings may be associated with the fact that for smaller particles it is easier to attain equilibrium during gas adsorption porosimetry.

Solvent extraction of soluble bitumen and oil from the shale samples generally opens additional pore space for N₂ and CO₂ adsorption, although the specific effects on mesoporosity and microporosity depend on maturity, total organic carbon (TOC) content, type of solvent, and grain size of the Soxhlet-extracted shales. The mesopore volume increases more in extracted samples with higher maturity, whereas the strongest gain in micropore volume is observed at elevated TOC content and highest maturity.

Comparative porosities of original and Soxhlet-extracted shale samples constrain the evolution of porosity along maturation, as well as the effect of partial oil/bitumen filling and blocking of pores. This study also employs FTIR analyses of DCM and toluene Soxhlet extracts to differentiate low-temperature DCM-extractable, mostly aliphatic OM from higher-temperature toluene-soluble OM containing condensed cross-linked polyaromatic structures.

Keywords: shale, porosity, maturity, adsorption, extraction, KBr-FTIR

1. Introduction

Porosity plays a significant role in evaluating shale reservoir quality and the hydrocarbon potential (Hunt, 1995; Ertas et al., 2006; Loucks et al., 2009; Curtis et al., 2012; Jarvie, 2012; Romero-Sarmiento et al., 2013). Gas adsorption capacity in shales hinges on the volume of pores (Chalmers and Bustin, 2007; Bustin et al., 2008; Ross and Bustin, 2009; Curtis et al., 2011a), whereas pore size distribution and pore connectivity influence shale permeability (Bustin et al., 2008; Ross and Bustin, 2009; Clarkson et al., 2013). Knowledge of porosity characteristics, gas adsorption volumes, and shale heterogeneity aids in the prediction of shale gas contents of reservoirs, reduces the shale gas exploration risk, and mitigates production uncertainties (Pollastro et al., 2007; Bustin et al., 2008; Ross and Bustin, 2009).

In contrast to conventional reservoirs, shales have complex porosity systems featuring interparticle and intraparticle pore components (Loucks et al., 2009, 2012). Significant contributions of intraparticle porosity derive from macerals in organic-rich shales (Chalmers and Bustin, 2008; Jarvie et al., 2011). The existence of abundant nanopores in organic-rich shales has been suggested by various techniques, including low-pressure gas adsorption (e.g., Ross and Bustin, 2009; Clarkson et al., 2013; Mastalerz et al., 2013) and low-angle scattering (e.g., Melnichenko et al., 2009; Mastalerz et al., 2012; Clarkson et al., 2013). Argon ion-milling and subsequent scanning electron microscopy (SEM) of Barnett Shale imaged the presence of nanopores in close association with organic matter (OM) (Loucks et al., 2009; Slatt O'Brien, 2011). Nanopores are generated during burial and maturation of OM (Jarvie et al., 2007; Bernard et al., 2012) and are generally isolated in organic flakes (Jarvie et

2007). Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) image analysis were able to provide an appreciation of complexity of pore networks in Marcellus Shale (Chalmers et al., 2012) and that macropores and mesopores are interconnected (Curtis et al., 2011a). Furthermore, recent petrologic evidence suggests that the thermochemical conversion of kerogen to oil, bitumen, and gas creates an OM-hosted nanopore network (Loucks et al., 2009; Modica and Lapierre, 2012). It is now generally accepted that the pore network in the organic component of OM-rich shales plays an important role for the storage of hydrocarbons (Loucks et al., 2009; Wang and Reed, 2009; Passey et al., 2010; Curtis et al., 2011b; Mastalerz et al., 2013).

In spite of recent progress, the development of porosity with increasing maturity of organic-rich shales remains controversial. Original immature kerogen owes its internal porosity to the structure of partially preserved biological tissues. Thermal cracking and the loss of hydrocarbons along maturation may add new pores or enlarge pre-existing ones, but research has failed to provide unambiguous and quantitative measures. For example, Milliken et al. (2013) demonstrated that variations in total organic carbon (TOC) content exert stronger control on organic-hosted pore systems than thermal maturity between vitrinite reflectance (R_o) values 1.0 and 2.1%. SEM visualization of comparatively sized and shaped pores in low and high-maturity Jurassic Kimmeridge Clay Formation shales from the North Sea prompted Fishman et al. (2012) to claim that pores were not related to OM transformation. In contrast, Mastalerz et al. (2013) investigated porosity in a suite of Devonian and Mississippian

New Albany Shale samples collected from core material archived at the Indiana Geological Survey and the Illinois State Geological Survey with different maturities and concluded that OM transformation and migration are major causes for observed differences in porosity.

Maturation of kerogen generates liquid hydrocarbons that can occupy and/or obstruct, and thus mask open pore space. An improved understanding of the pore hydrocarbon filling in shales constrains the inventory of pre-hydrocarbon and the formation of new evolving hydrocarbon related porosity. For example, Bernard et al. (2012) documented the chemical evolution from immature ($T_{\max}$ 420 °C) to post-mature ($T_{\max}$ >500 °C) Mississippian Barnett Shale (Fort Worth Basin, Texas, USA) and suggested that nanoporous pyrobitumen was formed as a result of secondary cracking at the post-mature stage. At an early mature stage, the removal of solvent-extractable hydrocarbons can modify OM porosity, as recently documented on high-volatile bituminous coals (Furmann et al., 2013). Similarly, other studies strongly suggested that hydrocarbon generation, cracking, and the formation of solid bitumen can influence the porosity of shales (Jarvie et al., 2007; Loucks et al., 2009; Mastalerz et al., 2013). Weatherford Laboratories routinely conduct porosity measurements following Gas Research Institute (GRI) procedures for core analyses and use the standard Dean-Stark toluene extraction process prior to porosimetry (Lasswell, 2011), but few published data have compared pre- and post-extraction porosity with maturity (Valenza et al., 2013). Further evidence is needed to clarify the impact of generated hydrocarbon products on porosity at different stages of maturation.

In a recent study of porosity in the New Albany Shale across a range of maturity, Mastalerz et al. (2013) suggested that hydrocarbon-related phenomena influenced total porosity and modified pore size distributions in response to increasing maturity. The present study is a continuation of that work, aiming to elucidate the influence of solvent-extractable OM on mesopores and micropores in shales.

2. Materials and Methods

2.1. Low-pressure gas adsorption measurements

This study utilized four samples (MM4, NA2, IL-5 and IL-1) of the New Albany Shale from Indiana and Illinois with maturities corresponding to R_o values of 0.55, 0.65, 1.15, and 1.41% (Table 1), thus covering a range from marginally mature (MM4) to post-mature (IL-1). The OM content expressed as TOC concentration ranges from 4.3 to 13.0 wt. % (Table 1). The porosities of the original, unextracted 4-mesh (<4.76 mm diameter) samples have been characterized in our previous study (Mastalerz et al., 2013).

This study used 2-g aliquots of two different size fractions from each shale that were individually folded into filter paper like ‘tea bags’ in preparation for Soxhlet-extractions with organic solvents. The <4.76 mm grain size samples are referred to as 4-mesh fractions, whereas the <0.250 mm size grain size samples are called 60-mesh fractions. We use subscript numbers after sample acronyms to distinguish between 4 and 60-mesh fractions and additionally mark original samples before extraction (e.g., MM4_{4orig} and MM4_{60orig}). The TOC values of two shale

fractions are comparable. Each sample was first characterized porosimetrically before being Soxhlet-extracted with refluxing dichloromethane (DCM, CH_2Cl_2) at 39.6°C for 72 hours. After vacuum-drying and non-destructive gas adsorption porosimetry measurements, a second Soxhlet-extraction of the same samples used refluxing toluene (C_7H_8) at 111°C for 96 hours, followed by vacuum-drying for two days and repeated porosimetry. DCM's lower boiling point limits the solubility of larger hydrocarbon molecules and bitumen, while the higher boiling point and aromatic character of toluene enhance dissolution of bitumen and moderately cross-linked bituminous OM. Solvent-extracted samples are characterized by additional subscript letters D for dichloromethane and T for toluene (e.g., $\text{MM4}_{4\text{D}}$ and $\text{MM4}_{60\text{T}}$, respectively). Subscript T implies that the sample had been extracted sequentially with DCM and toluene. The toxicity and flammability of both solvents mandate the use of chemical fume hoods.

Low-pressure gas adsorption measurements with nitrogen (N_2) and carbon dioxide (CO_2) were conducted on a Micromeritics ASAP-2020 gas adsorption porosimeter. Shale sample aliquots were analyzed with N_2 to obtain information about mesopores (2–50 nm in diameter), whereas CO_2 was used to characterize micropores (<2 nm in diameter) that are more accessible for CO_2 than for N_2 . The classification of pore sizes follows the system of the International Union of Pure and Applied Chemistry (Orr, 1977). Samples were automatically degassed at $\sim 110^\circ\text{C}$ under vacuum for about 14 hours to remove adsorbed moisture and volatile matter prior to adsorption analyses with either N_2 or CO_2 . Nitrogen gas adsorption was quantified

after exposure to N₂ at a pressure up to 97.3 kPa (730 mm Hg) at the temperature of liquid nitrogen -196 °C (~77 K). CO₂ adsorption occurred at a pressure of up to 104.5 kPa (784 mm Hg) at 0 °C (~273 K). The equilibration interval (i.e., the time during which the pressure must remain stable within a narrow range) was 30 seconds and the pressure tolerance was set at ±0.666 kPa (i.e., ±5 mm Hg). Low-pressure adsorption isotherms were used to calculate surface areas, pore volumes, and pore distributions based on multiple adsorption theories, i.e., Langmuir, Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH), Dubinin-Radushkevich (D-R), and Dubinin-Astakhov (D-A), among others. Mesopore size distribution was determined by the BJH method, whereas micropore size distribution was determined by the Density Functional Theory (DFT) method (Webb and Orr, 1997). A detailed description of theories and techniques can be found in Gregg and Sing (1982).

2.2. Potassium bromide (KBr)—FTIR analysis

A few drops of extracted bitumen and oil from DCM and toluene Soxhlet extractions were diluted with the respective pure solvents DCM or toluene, followed by mixing with 300 mg of KBr in an agate mortar. Pure DCM and toluene were mixed separately with KBr for comparative FTIR measurements. The preparation of KBr pellets relied on our standardized procedure (i.e., grinding time, pressure, and pellet weight) to enhance reproducibility (Chen et al., 2012). Pellets for KBr-FTIR characterization were analyzed on a *Nicolet 6700* spectrometer equipped with a DTGS detector, collecting 400 scans per sample at a resolution of 4 cm⁻¹. The FTIR signals of oil and bitumen in spectra of solvent-containing extracts were separated

from those of the solvents via subtraction of the spectra of pure solvents.

3. Results

3.1. Mesopores

Significant differences in the quantities of adsorbed N₂ among the studied samples translate into differences in surface areas and mesopore volumes.

Low-pressure N₂ adsorption isotherms for original, non-extracted 4-mesh fractions indicate that early mature sample NA2_{4orig} (R_o 0.65%) and post-mature sample IL-1_{4orig} (R_o 1.41%) adsorb more N₂ than the other two samples (Fig. 1A), and therefore NA2_{4orig} and IL-1_{4orig} have relatively larger BET surface areas (Fig. 1A).

The equivalent relationship holds for BJH mesopore volumes (Fig. 2B) where marginally mature sample MM4_{4orig} (R_o 0.55%) and late mature sample IL-5_{4orig} (R_o 1.15%) express lowest mesopore volumes.

Soxhlet extraction of the same 4-mesh fractions with DCM did not cause noticeable changes in the quantities of adsorbed N₂ for marginally mature sample MM4_{4D} (Fig. 3A) or late mature sample IL-5_{4D} (Fig. 3C), but resulted in large increases in adsorbed N₂ in early mature sample NA2_{4D} (Fig. 3B) and post-mature sample IL-1_{4D} (Fig. 3D). These observations relate to 82% and 26% increases in BET surface areas and mesopore volumes, respectively, in early mature NA2_{4D}, as well as respective 161% and 22% increases in post-mature IL-1_{4D} (Table 2).

Subsequent Soxhlet extraction with toluene at the elevated temperature of 111 °C (i) further increased the quantity of adsorbed N₂ in all 4-mesh samples (Fig. 3A-D), (ii) increased the surface areas in early mature NA2_{4T} and post-mature IL-1_{4T} (Fig. 2A),

and (iii) greatly increased the mesopore volume in sample NA2_{4T} (Fig. 2B). Similar to DCM extraction, Soxhlet extraction with toluene did not result in notable increases in surface areas or mesopore volumes for marginally mature sample MM4_{4T}. However, toluene extraction of sample IL-5_{4T} caused an 820% increase in mesopore surface area and a 223% increase in mesopore volume, which are the largest increases among all four samples (Table 2).

In contrast to the original, non-extracted 4-mesh fractions, low-pressure N₂ adsorption isotherms of MM4_{60orig} and NA2_{60orig} indicate increased adsorption of N₂ relative to the two higher-maturity samples IL-5_{60orig} and IL-1_{60orig} (Fig. 1D). Consequently, the largest BET surface area in non-extracted 60-mesh samples occurs in marginally mature sample MM4_{60orig} and the smallest BET surface area is found in post-mature sample IL-1_{60orig} (Fig. 4A).

In general, DCM extraction of the 60-mesh fraction causes little change in the quantity of adsorbed N₂ (Fig. 3E-H) except in case of the late mature sample IL-5_{60D} (Fig. 3G). In contrast, extraction with toluene increases the volumes of adsorbed N₂ for all samples, with the smallest increase observed in the marginally mature sample MM4_{60T} (Fig. 3E). Similar to the 4-mesh fraction, extraction with toluene increases the surface area in all 60-mesh samples, with the largest increase in late mature sample IL-5_{60T} and post mature sample IL-1_{60T} (Fig. 4A). Toluene extraction strongly increases measured surface areas. However, unlike the 4-mesh fractions, extractions of the 60-mesh fractions with either solvent fail to increase mesopore volumes (Fig. 4B). Mesopore surface areas increase with maturity after toluene extractions of

60-mesh samples in the sequence $MM4_{60T} < NA2_{60T} < IL-5_{60T} < IL-1_{60T}$ (Fig. 4A), whereas parallel extractions of the respective 4-mesh samples yield no clear trend and sample $IL-5_{4T}$ expresses a lower mesopore surface area than the less mature $NA2_{4T}$ (Fig. 2A).

A comparison of mesopore size distributions of samples before and after extractions is presented in Fig. 5. The marginally mature sample MM4 shows almost no change in pore size distribution after solvent extractions for either size fraction (Fig. 5A, B) and exhibits relatively stable surface areas and mesopore volumes (Fig. 4). In turn, toluene-extracted sample $NA2_{4T}$ documents the generation of pores with 7.5-87 nm diameters in its 4-mesh fraction (Fig. 5C). The toluene-extracted late mature sample $IL-5_{4T}$ features opened pores most notably in the 16.6-90.3 nm size fraction (Fig. 5E), whereas toluene extraction of the 60-mesh fraction yielded no rearrangement of the mesopore size distribution ($IL-5_{60T}$; Fig. 5F). In post-mature sample IL-1, only the 60-mesh fraction and only mesopore sizes above 16.6 nm are notably affected after extractions with both solvents (Fig. 5H).

3.2. Micropores

Micropore characteristics were quantified by CO_2 adsorption and low-pressure CO_2 isotherms for the original, non-extracted samples for 4-mesh and 60-mesh fractions (Fig. 6A, B). Late mature samples of $IL-5_{orig}$ feature lowest and those of post-mature $IL-1_{orig}$ highest CO_2 adsorption values, whereas marginally mature samples $MM4_{orig}$ and mature $NA2_{orig}$ express intermediate, similar CO_2 adsorption.

DCM extraction caused an increase in CO_2 adsorption for all samples (Fig. 7)

regardless of size fraction. However, the increase declines in the order IL-1_D (post-mature) > MM4_D (marginally mature) > NA2_D (early mature) > IL-5_D (late mature) (Fig. 8A, B). Toluene extraction of the 4-mesh fractions caused further increases in the amount of adsorbed CO₂ (Fig. 7A-D), except in the case of marginally mature MM4_{4T} for which the CO₂ isotherm is almost identical to that of MM4_{4D} (Fig. 7A). Toluene extraction of the 60-mesh fractions did not change, or slightly increased the amounts of adsorbed CO₂ for samples relative to respective DCM-extracted 60-mesh fractions (Fig. 7E-H).

Micropore surface areas (Fig. 9A, B) and D-R micropore monolayer capacities (Fig. 9C, D) were calculated from low-pressure CO₂ isotherms for all samples and increased after DCM extractions. Subsequent extractions with toluene caused little change, especially for 60-mesh fractions (Fig. 9B, D).

The DFT distribution of pore sizes within the micropore range (Fig. 10) indicates that DCM and toluene extractions of 4-mesh fractions increased pore volumes predominantly within the 0.5-0.7 nm and 0.8-0.9 nm pore size ranges. The smallest original micropore volume in late mature sample IL-5_{4orig} (Fig. 10E) increased only marginally during extractions, unlike other samples. In contrast to distinct increases in volumes of several micropore ranges in the 4-mesh fractions, both solvent extractions did not result in notable changes in 60-mesh fractions, except in marginally mature sample MM4_{60T} featuring an increase in micropore volume for the 0.55 to 0.85 nm pore size range (Fig. 10B).

3.3. Soluble OM extracts

FTIR analysis provides data about the distribution and abundances of chemical functional groups. Figure 11 illustrates the distribution of functional groups in KBr FTIR spectra of organic matter extracted by DCM and toluene. Each spectrum represents combined extracted OM from four studied samples. Of particular interest to this study are the aliphatic stretching region ($2800\text{--}3000\text{ cm}^{-1}$), aromatic stretching region ($3000\text{--}3100\text{ cm}^{-1}$) and the aromatic out-of-plane vibration region ($700\text{--}900\text{ cm}^{-1}$). The aliphatic stretching region is used to calculate a CH_2/CH_3 ratio that provides information about the chain length and the degree of branching of aliphatic compounds (Ganz and Kalkreuth, 1987; Guo and Bustin, 1998; Walker and Mastalerz, 2004). The CH_2/CH_3 ratio is higher for the primary DCM Soxhlet extract ($\text{CH}_2/\text{CH}_3=2.2$) than for the secondary, sequential extract in toluene ($\text{CH}_2/\text{CH}_3=1.5$). This indicates that the extract in DCM contains more long-chain and unbranched aliphatics, whereas the extract in toluene is rich in short-chain and highly branched aliphatics that may in part be present as side chains attached to larger, partially aromatic molecules. The aromatic carbon peak at $\sim 1600\text{ cm}^{-1}$ and aromatic out-of-plane bands between 750 cm^{-1} and 860 cm^{-1} are discernible only in the toluene extract.

4. Discussion

Three distinct processes result in the formation of different thermal products within shale during maturation (Jarvie et al., 2007): (1) the decomposition of kerogen to bitumen and gas; (2) the decomposition of bitumen to oil; (3) the decomposition of

oil and bitumen to pyrobitumen and gas. Solid bitumen is assigned a position on a continuum between immature and post-mature stages (Curiale, 1986). Pyrobitumen is generated at higher maturity and contains only a minor amount of solvent-extractable matter (Jacob, 1989).

4.1. Implications for the evolution of porosity during maturation

The occupancy and blockage of pore spaces in shales by bitumen and oil may significantly affect customary porosity measurements based on adsorption of gases N_2 and CO_2 . Presumably it also limits the penetration of metallic mercury (Hg) used in conventional mercury capillary injection analyses. N_2 and Hg have limited solubility in liquid and solid hydrocarbon phases, whereas CO_2 and gaseous hydrocarbons have a stronger affinity to oil and bitumen (Svrcek and Mehrotra, 1982) and can dissolve into oil and bitumen-filled pores, especially under pressure and at low temperatures. It follows that traditional N_2 and Hg-based measures of porosity may be biased and have limited relevance for quantifying the ability of shale to store hydrocarbon gas if a significant portion of pores is affected by the presence of oil and bitumen. Sorption of gas onto shale is sensitive to pressure and temperature. Little published information could be found about the solubility of these gases in bitumen at conditions similar to those of our porosimetric analyses. However, we can estimate the amounts of methane, carbon dioxide, and nitrogen that can be dissolved in oil/bitumen in shales under source rock reservoir conditions with a hydrostatic pressure of 2 MPa and a temperature of 23.9 °C based on (i) the concentrations of extractable oil and bitumen in our shales (Table 3), (ii) Tharanivasan et al.'s (2006) measurements of CO_2

solubility in heavy oil under reservoir conditions (~3.25 wt. %; Tharanivasan et al., 2006), and (iii) comparative data on the solubility of N₂ in bitumen (~0.21 wt.%; Svrcek and Mehrotra, 1982). This suggests that CO₂ is ~15 times more soluble in fluid hydrocarbon phases than N₂. Adsorption isotherm data based on CO₂ are therefore far more affected by dissolution in hydrocarbons and less susceptible to blocking of hydrocarbon-filled pores than adsorption isotherm data using N₂. Because of the large differences in N₂ and CO₂ solubilities in liquid hydrocarbons that are occupying some of the pore space in organic-rich shales within the oil window, traditional N₂ and CO₂-based porosity measurements underestimate the mesopore space (due to low N₂ solubility) and overestimate the micropore space in shale where CO₂ dissolving into fluid hydrocarbons mimicks CO₂ adsorption along open pore surfaces. The apparent bias does not decrease until the onset of secondary cracking when fluid hydrocarbon phases transform to gas and pyrobitumen.

Our mesoporosity data for original, non-extracted shales qualitatively agree with recent studies (e.g., Furmann et al., 2013; Milliken et al., 2013; Valenza et al., 2013) and can be interpreted in terms of the evolution of OM-based porosity as a function of partial transformation of OM into hydrocarbons along maturation. Valenza et al. (2013) observed increased surface areas of shales after solvent extraction, especially noticeable within a R_o range of 1.00-1.5%, and attributed the effect to the opening of formerly bitumen-clogged pores. A similar increase in porosity is observed in our study. Our results demonstrate that pore filling along maturation modifies sample porosity from marginally mature MM4 (R_o=0.55%) to post-mature IL-1 (R_o=1.41%).

However, maturity is not the only controlling factor. Our samples encompass a wide range of OM contents (TOC 4.3 to 13.0 wt. %) that can influence the abundance of micropores and the measured porosity. Additional influential factors could be, for example, burial depth and depth-related pressure and temperature that are known to influence mesoporosity of coal in the Illinois Basin (Mastalerz et al., 2008), as well as the content of clay minerals that are known to contribute micropores in shales (Javadpour, 2009; Loucks et al., 2009; Mastalerz et al., 2013; Kuila and Prasad, 2013).

Soxhlet extraction of crushed shale with organic solvents removes soluble OM from pores that can be accessed by solvent. Closed pores will neither be affected by solvent extraction, nor are they recognized by traditional porosimetry. Higher maturity of shale tends to increase the molecular weight of hydrocarbon molecules in oil and bitumen via cross-linking and limits not only their solubility but also lowers their diffusion coefficient (Tharanivasan et al., 2006). Access of an organic solvent to poorly soluble, partially cross-linked bitumen and pyrobitumen in pores causes swelling of hydrocarbons and a decline of open porosity (Ertas et al., 2006). Therefore, it is mandatory to dry the solvent from shale after Soxhlet extraction and reverse the swelling prior to porosimetric measurements. In case of toluene extraction, we found it necessary to dry the Soxhlet-extracted shale in the vacuum of a freeze-dryer at room temperature for two days until the dry weight became constant. Careful gravimetric recording of the dry weight of shale samples after final drying and before extraction is not only important for quantification of Soxhlet-extracted soluble OM, but also to

ascertain quantitative evaporation of the solvent.

Not only pore volume, but also pore surface area and pore size are important factors controlling the gas storage potential and sorption capacity of shales (Furmann et al., 2013; Yang et al., 2014). Higher surface area and smaller pore size enhance adsorption of gas molecules, and thus increase the gas adsorption potential in shales (Gregg and Sing, 1982). Comparisons of porosity parameters before and after solvent extractions of shales constrain the effects of hydrocarbon pore filling. Shales' responses to extractions by solvents with different boiling points and abilities to dissolve OM offer insight about the pore-filling materials. This study specifically differentiates low-temperature DCM-extractable OM from higher-temperature toluene-soluble OM. FTIR spectra of Soxhlet extracts confirm the presence of condensed polyaromatic structures in toluene extracts (Fig. 11). These lines of experimental evidence from solvent extractions of shales can jointly constrain and explain the evolution of pore filling with increasing maturity.

Our results demonstrate that mesoporosity and microporosity differ with regard to their responses to increasing maturity. Marginally mature sample MM4_{orig} has not yet generated significant amounts of oil. Consequently MM4 yielded little oil and bitumen during extraction with DCM and did not witness a significantly increased nitrogen adsorption volume or BET surface area in mesopores (Fig. 3A, E). The secondary extraction with higher-boiling toluene yielded a smaller extract compared to the first extract with DCM, implying that oil/bitumen remains highly soluble and has not yet intensively cross-linked and reduced its solubility at $R_o=0.55\%$. MM4's

elevated TOC content is likely responsible for the observation that solvent extraction caused the strongest increase in microporosity (in absolute terms) among all shale samples, as indicated by CO₂ adsorption data (Fig. 9A-F).

Analyses of Devonian Woodford Shale samples from Oklahoma in the oil window ($R_o \leq 0.90\%$) with focused ion beam milling (FIBM) and SEM suggested that organic porosity did not contribute to total porosity in shale (Curtis et al., 2011a). However, imaging sub-10 nm size pores in OM by SEM is challenging (Walters, 2013) due to low density of carbon and artifacts from Au or Pt coatings. Our sample NA2_{orig} with somewhat lower maturity ($R_o = 0.65\%$) increased its BET surface area after extractions (NA2_{4T} and NA2_{60T}) and thus indicated that some meso- and microporosity had been occupied by oil or extractable bitumen. Our observation suggests that this original shale harbors oil/bitumen-filled pores that would be undetectable with traditional SEM because electron microscopy does not see sufficient contrast between oil and other OM. In contrast to lower-maturity sample MM4_{orig} ($R_o = 0.55\%$), the extraction of oil/bitumen from NA2_{orig} with toluene yielded more material from pores compared to DCM extraction (Fig. 3B, F), possibly due to the higher Soxhlet extraction temperature and efficiency when using toluene. In addition, as found previously for kerogen, bitumen becomes more aromatic (less aliphatic) and thus less soluble in DCM with increasing maturity. KBr-FTIR spectra of DCM and toluene Soxhlet extracts illustrate chemical differences between both extracts (Fig. 11). Toluene extracts exhibit elevated aromaticity (i.e., aromatic stretching region, aromatic out-of-plane region, and increased aliphatic chain length

expressed as CH_2/CH_3 ratio), indicating that hot aromatic toluene is a better solvent than cooler DCM for extracting cross-linked bitumen. The gains in BET surface area in shales due to secondary toluene extraction increase with maturity (Table 5, bottom row) in agreement with Feng et al.'s (2013) observation that the average aliphatic chain length in bitumen shortens with increasing maturity when bitumen is thermally decomposing.

Positive relationships are expected between OM content and total porosity, or between OM content and micropore or mesopore volumes (Chalmers and Bustin, 2007; Ross and Bustin, 2009; Milliken et al., 2013). The relationship between micropore surface area and TOC may explain the greatly enhanced micropore surface area and monolayer capacity of TOC-rich sample MM4 (Fig. 9A-D). High TOC in MM4 did not cause, however, enhanced mesoporosity compared to lower-TOC samples. The absence of a strong relationship between mesopore volume and TOC may be due to differences in maturity.

We interpret the lowest observed meso- and microporosities in late mature sample IL-5_{orig} ($R_o=1.15\%$; Figs. 2A, 4A; Fig. 9A, B) to be a result of pores being partially or entirely occupied/blocked by oil and bitumen. Shale IL-5_{orig} has the lowest meso and micro-porosity values among all four samples because its higher maturity provided liquid hydrocarbons to occupy pore space. Secondary toluene extraction significantly increased mesoporosity in IL-5_T and allows us to conclude that mesopores in IL-5_{orig} are occupied by bitumen with limited solubility in DCM. In contrast to observed differences in extraction efficiencies between toluene and DCM

for bitumen-filled mesopores, toluene could not extract significant amounts of additional aromatic bitumen than DCM from micropores, as indicated by limited to no increase in micropore surface area after toluene extraction (Fig. 9A, B). One possible reason is that micropores are too small or marginally connected to allow efficient penetration of solvents and diffusive removal of solutes.

4.2. Effect of shale particle size on measured pore parameters

For non-extracted shales, crushing and sieving from 4-mesh to 60-mesh has a limited effect on shales' microporosity, which is confirmed by the observation that the evolutionary trends in microporosity of both size fractions with increasing thermal maturity are generally similar for samples before extractions (Fig. 9A-F). In contrast, grinding and dry-sieving of shale samples from 4-mesh to 60-mesh resulted in significantly higher mesopore volumes and mesopore surface areas (Figs. 2A, B; 4A, B) in agreement with the concept of facilitated access of gas to mesopores after grinding. A contributing factor may be incomplete equilibration of the interior of larger shale particles (e.g., 4-mesh fraction) during gas adsorption porosimetry (Chen et al., in review; Clarkson and Bustin, 1999), whereas 60-mesh particles can more readily attain adsorption equilibrium with N₂ and provide more reliable mesopore data.

Particle size also limits the ability of organic solvents to efficiently extract soluble OM from the interior of dense shale particles. Smaller particle size offers a larger surface area and reduces the path length of solvent penetration and diffusive removal of solutes from pores in the center of particles. Smaller grain size of crushed

shale, higher-boiling point of the solvent (Tamimi and Uysal, 1990), and the aromatic structure of the solvent (i.e., toluene) improve the oil/bitumen extraction efficiency. The difficulty of DCM-extraction of hydrocarbons from the 4-mesh fraction of IL-5_{orig} is indicated by small increases in both mesopore and micropore surface areas after extraction (Figs. 2A, 9A). Possibly some pore space is rendered inaccessible by mineral blockage (Curtis et al., 2012) or via encapsulation in impermeable clay within the shale matrix (Klaver et al., 2012). Furthermore, relative to toluene-extracted 4-mesh fractions, the toluene-extracted 60-mesh fractions show decreased mesopore volumes, increased micropore volumes (Fig. 4B), and decreased mesopore sizes (Fig. 5B, D, F, H; Table 4). Similarly, DCM-extraction of soluble OM from high volatile bituminous coals with $R_o=0.69\%$ reduced the BET surface areas and mesopore volumes due to progressive opening of larger pores (Furmann et al., 2013). Perhaps the removal of oil/bitumen from mesopores in our 60-mesh shale fractions enlarged the open pore space to enter the macropore range, thus resulting in decreased mesopore volumes after extraction (Fig. 4B). A similar shift in open pore volume may be responsible for declined micropore volumes in 4-mesh shale fractions after extractions (Fig. 9E). A finer grain size of 60-mesh is not only beneficial for efficient solvent extraction of soluble OM, but also kinetically favors gas adsorption equilibration of the interior of shale particles (Chen et al., in review), and therefore is more appropriate for gas adsorption porosimetry for both unextracted and extracted shales.

5. Conclusions

Consecutive Soxhlet-extractions with dichloromethane and toluene have been applied to two grain size fractions of a suite of New Albany Shale samples spanning a range of thermal maturity in order to evaluate the influence of extractable organic matter on the evolution of porosity in shales. The following conclusions have been reached:

1. Mesopore volumes in Soxhlet-extracted shales indicate that mesoporosity in original, unextracted shales follows a non-monotonous evolutionary path with increasing thermal maturity in response to primary cracking of kerogen and secondary cracking of bitumen. The TOC content is less influential on mesopores volumes than on micropore volumes. Thermal maturity affects microporosity during the post-mature stage as secondary cracking of OM produces additional micropores. The occupation of pores by oil and bitumen during the early mature stage prior to significant generation of oil and bitumen affects mesoporosity only slightly, and this influence becomes strongest during the late mature stage.
2. Soxhlet extraction with higher-boiling point toluene more aggressively removes marginally soluble organic matter from shale than lower-boiling DCM. KBr-FTIR spectra of DCM and toluene Soxhlet extracts illustrate that the oil and bitumen in toluene extracts exhibit elevated aromaticity that may be linked to enhanced cross-linking of organic matter with reduced solubility in DCM. The average aliphatic chain length in extracted organic matter

increases during early maturation but later shortens with increasing maturity when bitumen is thermally decomposing.

3. Particle size significantly impacts gas adsorption results and surface area and mesopore characteristics in particular. Mesopore volumes increase as particle size decreases from 4-mesh to 60-mesh. Different particle size fractions of unextracted shale samples exhibit contrasting mesoporosity trends with increasing maturity. Finer grain size improves the efficiency of solvent extraction as smaller particles offer a larger surface area and reduce the distance of solvent penetration and diffusive removal of solutes from the center of particles. In addition, particles can more readily attain adsorption equilibrium with N₂ and provide more reliable mesopore data. In contrast, the respective trends for micropore volumes of the two size fractions do not exhibit large differences.

In summary, thermal maturity is an important factor controlling total porosity in organic-rich shales. However, the simultaneous effects of other factors demand that reliable predictions of adsorbed gas capacities of shales need to be based jointly on the multitude of factors, including kerogen type, lithostatic pressure, organic matter (or total organic carbon) content, mineralogy, and thermal maturity.

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Figure 1. Low-pressure N₂ adsorption isotherms of shale samples. P = actual gas pressure; P₀ = vapor pressure of the adsorbing gas. STP: standard ambient temperature and pressure (25 °C and 100 kPa). We use subscript numbers after sample acronyms to distinguish between 4 and 60-mesh fractions and additionally mark original samples before extraction (e.g., MM4_{4orig} and MM4_{60orig}). Solvent-extracted samples are characterized by additional subscript letters D for dichloromethane and T for toluene (e.g., MM4_{4D} and MM4_{60T}).

Figure 2. (A) BET surface area and (B) BJH mesopore volume of 4 mesh shale

samples before extractions and after DCM and toluene extractions.

Figure 3. Low-pressure N_2 adsorption isotherms of shale samples before extractions and after DCM and toluene solvents extractions for 4 mesh (A-D) and 60 mesh samples (E-H). P = actual gas pressure; P_o = vapor pressure of the adsorbing gas.

Figure 4. (A) BET surface area and (B) BJH mesopore volume of 60 mesh shale samples before extractions and after DCM and toluene extractions.

Figure 5. Incremental mesopore volumes of shale samples obtained by low pressure N_2 adsorption porosimetry.

Figure 6. Low-pressure CO_2 adsorption isotherms of shale samples. P = actual gas pressure; P_o = vapor pressure of the adsorbing gas. STP: standard ambient temperature and pressure (25 °C and 100 kPa).

Figure 7. Low-pressure CO_2 adsorption isotherms of shale samples before and after DCM, toluene extractions for 4 mesh (A-D) and 60 mesh (E-H). P = actual gas pressure; P_o = vapor pressure of the adsorbing gas. STP: standard ambient temperature and pressure (25°C and 100 kPa).

Figure 8. Low-pressure CO_2 adsorption isotherms of shale samples before and after extraction for 4 mesh (A and C) and 60 mesh (B and D). P = actual gas pressure; P_o = vapor pressure of the adsorbing gas. STP: standard ambient temperature and pressure (25°C and 100 kPa).

Figure 9. Micropore characteristics: Dubinin-Radushkevich (D-R) surface area (m^2/g), Dubinin-Radushkevich monolayer capacity (cm^3/g), and Dubinin-Astakhov (D-A) volume (cm^3/g) of shale samples before extractions and after DCM and toluene extractions.

Figure 10. Incremental micropore volumes of shale samples obtained by low pressure CO₂ adsorption porosimetry.

Figure 11. KBr-Fourier transform infrared (FTIR) spectrometry of combined extracted OM from four studied samples in solvents dichloromethane (DCM) and toluene. Each spectrum represents the difference between the extract in solution and the spectrum of the respective pure solvent (e.g., the extract in DCM minus the spectrum of pure DCM). Aliphatic C-H stretching exhibits peaks at $\sim 2922\text{ cm}^{-1}$ and 2860 cm^{-1} . Aromatic carbon peaks at $\sim 1600\text{ cm}^{-1}$, whereas aromatic out-of-plane vibrations appear between 750 cm^{-1} and 860 cm^{-1} .

Figure 1

Figure 2

BET surface areas of original and extracted shales **BJH volumes of original and extracted shales**

Figure 3

Figure 4

Figure 5

Figure 8

Figure 9

Figure 10

Figure 11

Table 1. Vitrinite reflectance (R_o), total organic carbon (TOC) content, maturity, bitumen content, and total porosity by helium porosimetry of shale samples. The bitumen content was determined by maceral analysis (volume %, on mineral matter free basis, mmf) (modified from Mastalerz et al., 2013).

Sample	R_o (%)	TOC (wt. %)	Depth (m)	Maturity stage	Bitumen content (vol. %, mmf)	Helium porosimetry (total pore volume cm^3/g)
MM4	0.55	13.0	764	marginally mature	2	0.0186
NA2	0.65	5.3	853	early mature	10	0.0210
IL-5	1.15	4.3	1607	late mature	45	0.0059
IL-1	1.41	6.4	78	post mature	75	0.0141

Table 2. Changes in pore parameters (in %) after sequential extractions of original shales with dichloromethane (DCM) and toluene. For example, Soxhlet extraction of the original shale sample MM4 with DCM resulted in a 20% increase in the mesopore BET surface area. All changes are relative to the original, unextracted shales.

		MM4		NA2		IL-5		IL-1	
		DCM	Toluene	DCM	Toluene	DCM	Toluene	DCM	Toluene
60 mesh fractions									
Mesopores	BET surface area (%)	20	23	12	42	52	110	27	208
Mesopores	BJH adsorption cumulative volume of pores between 2.0 nm and 50.0 nm width (%)	9	-16	-8	0	-12	-11	-29	-19
Micropores	Dubinin-Radushkevich micropore surface area (%)	29	41	33	0	24	28	15	28
4 mesh fractions									
Mesopores	BET surface area (%)	6	35	82	170	20	820	161	394
Mesopores	BJH adsorption cumulative volume of pores between 2.0 nm and 50.0 nm width (%)	1	24	26	57	-50	223	22	35
Micropores	Dubinin-Radushkevich micropore surface area (%)	225	221	111	246	57	105	15	23

Table 3. Helium porosimetry, dry weights, and dry extract weight percentages as a consequence of sequential DCM and toluene Soxhlet extractions.

	MM4	NA2	IL-5	IL-1
	4 mesh			
Helium porosimetry (cm ³ /g)	0.019	0.021	0.006	0.014
Original weight of rock (g)	2.041	2.094	2.121	2.106
Dry DCM extract (g)	0.020	0.021	0.017	0.036
Dry DCM extract (wt. % of original rock)	0.98	1.00	0.79	1.59
Dry weight of rock after DCM extraction (g)	2.019	2.073	2.104	2.073
Dry toluene extract (g)	0.021	0.022	0.027	0.034
Dry toluene extract (wt. % of original rock)	1.03	1.05	1.27	1.61
	60 mesh			
Original weight of rock (g)	1.974	1.815	1.832	1.804
Dry DCM extracted (g)	0.024	0.026	0.032	0.037
Dry DCM extracted (wt. % of original rock)	1.22	1.44	1.73	2.02
Dry weight of rock after DCM extraction (g)	1.949	1.789	1.801	1.768
Dry weight of rock after toluene extraction (g)	0.025	0.030	0.036	0.039
Dry toluene extraction (wt. % of original rock)	1.26	1.65	1.97	2.16

Table 4. Average mesopore size distribution before and after sequential DCM and toluene extractions of 60-mesh fractions.

	MM4 ₆₀			NA2 ₆₀		
	original	after DCM extraction	after toluene extraction	original	after DCM extraction	after toluene extraction
Average pore width (nm)	14.28	13.67	11.56	15.12	12.68	12.99
	IL-5 ₆₀			IL-1 ₆₀		
	original	after DCM extraction	after toluene extraction	original	after DCM extraction	after toluene extraction
Average pore width (nm)	13.25	8.38	9.89	13.12	12.57	9.81

Table 5. BET surface areas (m^2/g) after sequential DCM and toluene extractions of 60-mesh fractions.

	MM4 R_o 0.55%	NA2 R_o 0.65%	IL-5 R_o 1.15%	IL-1 R_o 1.41%
Original BET surface area	4.45	4.10	4.11	3.06
BET surface area (m^2/g) after DCM extraction	5.36	4.61	6.25	3.90
BET surface area (m^2/g) after toluene extraction	5.48	5.82	8.65	9.42
Increase of the BET surface area (m^2/g) caused by toluene extraction	0.12	1.21	2.40	5.52