



The effect of analytical particle size on gas adsorption porosimetry of shale



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ABSTRACT

Gas storage capacity and gas producibility of shale gas reservoirs are critically limited by shale porosity. In spite of its importance, porosimetric characterization of shale remains challenging due to highly heterogeneous structures, small average pore sizes, and wide pore size distributions. This study utilizes low-pressure N₂ and CO₂ gas adsorption porosimetry to investigate the evolution of micro- and mesopores in a suite of 11 New Albany Shale samples across a wide range of thermal maturity corresponding to vitrinite reflection R₀ values from 0.35 to 1.41%. Mesopore volumes follow a nonlinear evolutionary path starting with a maximum in immature shale (sample 472-1). Subsequent intermittent minima in mesopore volumes during early and late maturity are consistent with the transformation of kerogen during the early mature stage (sample 554-2) and secondary cracking of bitumen/oil at the late mature stage (sample IL2), respectively. Micropore volumes display a varying trend throughout thermal maturation, and are significantly controlled by total organic carbon contents. Both meso- and micropore volumes are positively correlated with clay content and tend to decrease with an increase in feldspar content.

A reduction in grain size of shale samples 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 smaller particles are able to attain complete adsorption equilibrium quickly, which in turn reduces experimental artefacts during gas adsorption porosimetry. Crushing of shale not only alters the shape of gas adsorption hysteresis loops, but also tends to tighten the openings of hysteresis loops by enhancing the connectivity of pores and reducing the likelihood of gas being trapped during desorption.

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1. Introduction

Successful exploration and recovery of natural gas from low-permeability unconventional reservoirs such as shales require an understanding of rock porosity. In spite of this importance, accurate porosimetric characterization of shales remains challenging due to highly heterogeneous structures across macro- to microscales, small average pore sizes, and wide pore size distributions (Chalmers et al., 2012; Kuila and Prasad, 2013; Loucks et al., 2009; Mastalerz et al., 2012, 2013). The quantification of pores in shales by gas adsorption techniques is further complicated by limited pore connectivity and partial filling or blocking of pores with water or bitumen (Clarkson et al., 2012; Mastalerz et al., 2013).

Even bioturbated, seemingly homogeneous shales typically express heterogeneous distributions of organic and inorganic moieties with associated pores when viewed at a magnification that is commensurate

with the small pores in fine-grained rocks (Schieber, 2010, 2011). Spatial variations in mineralogical composition and organic matter (OM) content across short distances in sediment cores are typically paralleled by variances in pore volumes and pore size distributions. For instance, carbonate-rich intervals of Gordondale Shale (Lower Jurassic, north-eastern British Columbia, Canada) typically have lower total porosities than adjacent carbonate-poor and clay-rich mudrocks (Ross and Bustin, 2007). The presence of clays of the illite–smectite type is mainly responsible for micro- and mesopores in shales (Kuila and Prasad, 2013). Porous OM is an important contributor to total porosity in organic-rich shales and can host substantial micropore volumes that usually correlate positively with the total organic carbon (TOC) content (Chalmers et al., 2012; Loucks et al., 2009; Strąpoc et al., 2010). Mineral- and OM-associated pores show contrasting geometries and morphologies. For example, cross-sections of mineral-associated pores in Haynesville Shale are predominantly slit-like, whereas OM pores in the Barnett and Horn River shales are typically round or elliptical (Curtis et al., 2012).

Pores in OM have attracted growing interest as a significant component of pore systems in gas-bearing shales (Bernard et al., 2012; Curtis

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et al., 2012; Loucks et al., 2009; Mastalerz et al., 2013). While some OM pores are a legacy of the cellular structure of precursor biological tissues (Loucks et al., 2012), much OM-associated pore space seems to relate to thermal transformations of kerogen, (pyro)bitumen, and liquid and gaseous hydrocarbons (Jarvie et al., 2007; Mastalerz et al., 2012, 2013; Ross and Bustin, 2009; Strapoć et al., 2010). Understanding the evolution of OM porosity during thermal maturation is critical for predicting the ability of shales to produce and store fluid hydrocarbons (Curtis et al., 2012).

Pores are generally classified according to their diameters as micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm; Sing et al., 1985). Based on their associations with mineral and organic particles, pores can also be classified as intergranular mineral pores, intragranular mineral and OM pores, and fracture pores (Loucks et al., 2012). Limitations of individual porosimetric methods to sections of the wide spectrum of pore sizes in shales make it necessary to use more than one porosimetric method in order to measure pore sizes from micropores to macropores (Sing et al., 1985). Various gas adsorption techniques using helium, nitrogen (N₂) and carbon dioxide (CO₂) are available to quantify surface areas and pore characteristics of shales (Lowell et al., 2004). Additional porosimetric approaches include small angle X-ray and neutron scattering (SAXS, SANS, and USANS; Cui et al., 2009; Mastalerz et al., 2012), mercury intrusion capillary pressure (MICP) porosimetry (Clarkson et al., 2013; Mastalerz et al., 2013), high resolution scanning and transmission electron microscopy (SEM, TEM; Chalmers et al., 2012; Loucks et al., 2012; Schieber, 2010), and Nuclear Magnetic Resonance (NMR; Borchardt et al., 2013). Although traditional SEM and TEM can theoretically image nanopores with diameters down to 1 nm, in practice such small pores cannot be adequately imaged electron-microscopically (Walters, 2013). Porosimetry of small pores from 0.35 nm to 300 nm typically relies on gas adsorption techniques for assessment of pore sizes, including the complete range of micro-, meso-, and macropores (Cui et al., 2009; Mastalerz et al., 2013).

Although gas adsorption porosimetry has been used broadly for the characterization of porosity in shales, mudrocks and other porous materials, surprisingly little is known about the influence of some fundamental parameters like the grain size of used rock material. Lab-based standardizations of grain size by individual research groups serve to generate reproducible data within each lab. Unfortunately, the use of different standard grain sizes calls into question direct comparisons of published data from different laboratories. A compilation of findings from recent gas adsorption-related studies (Table 1) documents conflicting conclusions from laboratories that used different particle sizes.

Following our previous investigation on porosity in New Albany Shale (NAS; Mastalerz et al., 2013), this study aims to (1) systematically explore the influence of particle size on porosimetric characterization of NAS via gas adsorption. Additional goals are to (2) improve the characterization on the evolution of NAS's porosity across a wider range of thermal maturity by including additional NAS samples with

intermediate maturities, and (3) to characterize the influence of mineralogical and organic compositions on the NAS pore system.

2. Experimental section

This study utilizes 11 NAS samples across wide ranges of thermal maturity (R_o 0.35 to 1.41%) and TOC contents (2.37 to 21.5 wt.%) for porosimetric measurements, X-ray diffraction (XRD), organic petrography, and other analyses. Total porosity of the samples ranges from 1.0 to 9.1 vol.% (Table 2). NAS samples originate from coring locations shown in Fig. 1. Cores without signs of weathering or oxidation have been archived by the Indiana Geological Survey and the Illinois State Geological Survey.

2.1. Low-pressure gas adsorption measurements

Each of the 11 shale samples was carefully hand-crushed and sieved to generate three size fractions of 4, 20 and 60 mesh. The resulting 33 samples were subsequently analyzed via N₂ and CO₂ low-pressure gas adsorption on a Micromeritics ASAP-2020 apparatus to obtain information about mesopores and micropores, respectively. Shale samples were automatically degassed at ~110 °C in vacuo for about 14 h to remove adsorbed moisture and volatile matter. Degassed sample aliquots weighing 1–2 g were exposed to N₂ at the temperature of liquid nitrogen (–196 °C) or to CO₂ near 0 °C along a series of precisely controlled gas pressures. N₂ and CO₂ adsorption volumes were measured over the relative equilibrium adsorption pressure (P/P_o) range of 0.050–0.995, where P_o is the condensation pressure of N₂ or CO₂ at laboratory conditions, and P is the actual gas pressure.

N₂-based adsorption data collected on shale size fractions were interpreted using Brunauer–Emmett–Teller (BET) analysis for surface area and Barrett–Joyner–Halenda (BJH) analysis for pore size distributions (Mastalerz et al., 2013). CO₂-based adsorption data were interpreted using Dubinin–Astakhov (D–A), Dubinin–Radushkevich (D–R), and density functional theory (DFT) pore size distribution models (Gregg and Sing, 1982). These calculations can be generated automatically by the instrument's computer software.

2.2. Organic petrography and X-ray diffraction analysis

Vitrinite reflectance R_o (%) measurements (maximally 25 points) were performed with a Leica optical microscope and an MSP200 photometry system. Total organic carbon (TOC) concentrations were quantified using a Leco analyzer. Independent quantitative mineralogical analyses of pulverized shale samples (ground wet with a micronizer to a grain size 5 μm) were performed with a Bruker D8 Advance XRD in the Department of Geological Sciences at Indiana University. The XRD was equipped with a Sol-X solid-state detector and a Cu X-ray tube operated at 40 kV and 30 mA. Shale powders were scanned from

Table 1
Summary of recent porosimetry via low-pressure N₂ and CO₂ gas adsorption techniques.

Literature	Particle size	Sample information	Relationship with total organic carbon (TOC)
Mastalerz et al. (2013)	4 mesh (4.75 mm)	New Albany Shale, USA	No relationship between TOC content and pore volume D–A micropore volume and total gas content correlate positively with TOC content
Strapoć et al. (2010)	60 mesh (250 μm)	New Albany Shale, USA	
Ross and Bustin (2009)	60 mesh (250 μm)	Western Canadian Sedimentary Basin, Canada	Significant correlation between micropore volume and TOC content for Devonian–Mississippian shale but not for Jurassic shale.
Chalmers et al. (2012)	60 mesh (250 μm)	Barnett, Woodford, Haynesville, Marcellus, and Doig shales	No correlation between TOC content and micropore volume
Chalmers and Bustin (2012)	60 mesh (250 μm)	Shaftesbury Formation in northeastern British Columbia, Canada	Positive correlation between TOC content and porosity
Tian et al. (2013)	60–80 mesh (250–178 μm)	Lower Silurian shales in the Chuangdong Thrust Fold Belt, southwestern China	Total porosity increases with increasing TOC and clay contents
Mastalerz et al. (2012)	60 mesh (250 μm)	Springfield coal and New Albany Shale	Mesopore and micropore volumes increase with increasing TOC content

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