Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Solvent-pore interactions in the Eagle Ford shale formation \star

Victoria H. DiStefano^{a,b}, Joanna McFarlane^a, Andrew G. Stack^a, Edmund Perfect^c, David F.R. Mildner^d, Markus Bleuel^d, Steve J. Chipera^e, Kenneth C. Littrell^a, Michael C. Cheshire^a, Katherine E. Manz^b, Lawrence M. Anovitz^{a,*}

^a Oak Ridge National Laboratory, Oak Ridge, TN 37830-6110, USA

^b Bredesen Center, University of Tennessee, Knoxville, TN 37996-3394, USA

^c Department of Earth and Planetary Science, University of Tennessee, Knoxville, TN 37996-1410, USA

^d Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

^e Chesapeake Energy, Oklahoma City, OK 73154-0496, USA

ABSTRACT

The effect of solvent extraction on pore space was examined on a suite of samples from the Eagle Ford Shale Formation with varying lithologies and maturities. Several solvents —toluene, cyclohexane, methanol, dichloromethane, and hydrochloric acid— were contacted with shale samples, extracting the compatible organic matter. The porosity in these extracted shale samples was compared to unmodified samples. The amount and type of organic matter extracted were determined using Gas Chromatography — Mass Spectrometry, and the porosity was determined by (Ultra) Small Angle Neutron Scattering. Mostly alkanes and aromatics were detected in the extracts, but other portions of bitumen may also have been present. Only higher molecular weight alkanes were extracted with hydrochloric acid, suggesting that physical dissolution of carbonate minerals may have liberated this portion of organic matter and the solvent was not able to penetrate the bitumen and kerogen to extract the lower molecular weight alkanes. Additionally, a decrease in porosity with extraction was observed and attributed to a dominant mechanism of kerogen swelling due to kerogen-solvent interaction.

1. Introduction

Hydraulic fracturing involves injecting large amounts of water with organic and inorganic additives into shale formations to break them apart and liberate oil and gas. Shale is a complex rock, composed of multiscale pore systems, multi-mineral interfaces, and organic matter. Fluid interactions within shale can alter pore structures and affect oil and gas mobility by increasing or decreasing porosity. Understanding the mechanisms of such fluid/pore interaction is, therefore, key to improving extraction efficiency.

Although solvents are used in a wide range of processes in oil and gas recovery, from hydraulic fracturing fluids to determining critical parameters for recovery, such as permeability, the interaction of solvents with shale pore space is poorly understood. To evaluate true permeability, the oil and gas industry uses solvent cleaners (such as CO_2 -toluene) on reservoir rocks, cycling the solvent through the rock numerous times, with the intent of removing oil that is blocking the entrance to pores. Like many methods used in the industry, this approach has been extended from conventional reservoir rocks, such as sandstones and carbonates, to unconventional shale reservoirs with much lower porosity and permeability [38]. These tests have yielded results that are not, as yet, fully explained; most notably, a decrease in permeability after solvent interaction [55].

Shale contains a host of minerals mixed with organic matter and multiscale pore systems [4,6,17,59]. The organic matter found in shale is classified into two portions, kerogen and bitumen, distinguished by their solubility. Kerogen is the portion of organic matter that is insoluble in organic solvents, mostly due to its structural complexity and high molecular weight (> 1000 Da). This definition of kerogen is based on the industrial classification of organic matter, but it may be better defined petrographically as a mixture of kerogen, solid bitumen, and pyrobitumen [33]. For simplicity, it will be referred to hereafter as kerogen. Bitumen is soluble in organic solvents, and is composed of a mixture of asphaltenes, resins, and crude oil (or hydrocarbons), which can be distinguished from one another by their molecular weight and solubility [56]. Asphaltenes and resins have larger molecular weights than crude oil, the most important component for energy generation, which generally has a molecular weight less than 600 Da [56,45,22]. In

. .

https://doi.org/10.1016/j.fuel.2018.10.010

Received 24 July 2018; Received in revised form 28 September 2018; Accepted 1 October 2018 Available online 29 October 2018 0016-2361/ © 2018 Elsevier Ltd. All rights reserved.



Full Length Article



^{*} This manuscript has been co-authored by UT-Battelle, LLC, under contract DE-AC05-00OR22725 with the US Department of Energy (DOE). The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan). * Corresponding author.

addition to organic matter, a wide range of minerals can be present in shale, including carbonates, clays, tectosilicates (quartz and feldspars), sulfides, iron oxides, and other heavy minerals [59]. The organic matter and mineral phases present are dependent on the depositional environment as well as the burial history of the shale (maturity).

Several studies have tried to remove all the organic matter from shale using solvents in order to evaluate the organic-matter-filled porosity. Kuila et al. [27] extracted organic matter from five shale formations (including the Haynesville and the Marcellus Shale in North America) with sodium hypochlorite, evaluating porosity before and after extraction with low pressure nitrogen adsorption, with the goal of differentiating porosity in clay from that in organic matter. They observed an increase in pore volume at some size ranges and a decrease at others. The decrease was attributed to obliteration of porosity in organic matter with extraction, although the amount of organic matter removed did not correlate to the observed porosity changes. Mohnhoff et al. [39] determined porosity changes with helium pycnometry in the Posidonia Shale (Germany) with flow-through experiments using dichloromethane. They found that porosity increased among the four samples examined. Sun et al. [53] used several solvents in succession to extract organic matter from the Shahejie Formation (China) and then evaluated porosity with small angle X-ray scattering (SAXS). However, they did not explain their procedure for determining pore size distributions. Additionally, shale samples have been submerged in aqueous solvents to determine solvent-accessible pores versus inaccessible pores with (ultra) small angle neutron scattering ((U)SANS) [51,20,9,52]. Results from these studies could be impacted by solventpore interactions.

DiStefano et al. [17] removed different portions of organic matter in samples of the Eagle Ford Shale with targeted solvent extraction to determine porosity development. They found that porosity did not always increase with extraction. In some cases, it decreased at all length scales, implying that organic matter removal was not the only process occurring. They suggested that the observed decrease in porosity may have been caused by clay swelling due to solvent interactions.

It is clear from the above results that analysis of organic matter porosity by extraction is not a simple procedure. However, since organic matter removal is key in determining how porosity and organic matter are distributed in shale, understanding the mechanisms that govern pore-solvent interactions will improve interpretation of results. This work, therefore, seeks to understand how solvents interact with the multiscale porosity in shale. Several solvents-organic and aqueous-were used to extract different portions of organic matter in a maturity suite of Eagle Ford Shale with varying lithologies. The porosity of each sample was then evaluated using (U)SANS and compared to a sample that was not contacted with any solvent. The type and amount of organic matter extracted with each solvent was analyzed with Gas Chromatography - Mass Spectrometry (GC-MS), and the amounts of extracted organic matter were compared to the changes in porosity of the rocks. DiStefano et al. [17] also evaluated pore space with SANS after extraction with organic solvents, but this study extends the range of pores examined by measuring larger pores with USANS and evaluates additional solvents, including an aqueous solvent. The effects of solvent extraction and interaction on pore space with various solvents provide insight into the mechanisms of pore-solvent interactions.

2. Materials and methods

2.1. Sample preparation

Samples from six cores of Eagle Ford Shale were obtained from Chesapeake Energy Corporation.¹ Fig. 1 shows the approximate locations in Texas from which the cores were recovered at depth. The Supplementary material details how the samples were classified. Four carbonate-rich (CARB 2, CARB 3, CARB 4, and CARB 5) and two clayrich samples (CLAY 2 and CLAY 5) were analyzed, with the numbers corresponding to increasing maturity (reported as R₀, an indication of thermal maturity). Descriptions of each core, including sample designation, depth recovered, and maturity are provided in Table 1, and the mineralogical compositions of the samples are given in Table 2. A schematic of sample preparation and treatment is presented in Fig. 2 and further detailed in The Supplementary material. Five shale slices from each sample were soaked in one of five solvents: toluene, cvclohexane, methanol, dichloromethane, and 0.01 M hydrochloric acid (pH = 2) for 11 days. Solvent properties are shown in Table 3. A sixth slice was not contacted with any solvent and was used as a control. Shale is extremely heterogenous, with mineralogy differing across various bedding. In order to limit the variation among sample slices, the six consecutive slices were cut, perpendicular to bedding. The porosity in the shale samples were analyzed with (U)SANS and scanning electron microscopy/backscattered electron (SEM/BSE) imaging. The remaining solutions containing extracted organic material were analyzed using GC-MS.

2.2. Analysis of solvent extracts with gas chromatography-mass spectrometry

The solvents were analyzed by gas chromatography (GC) using an Agilent 7890B gas chromatograph with a 5977A mass selective detector (MSD) running Agilent MassHunter Acquisition software (version B.07.00). Details of the analytical method are given in Table 4 and The Supplementary material. The total ion chromatograms (TIC) were used to quantify and compare the amount of organic matter extracted from each sample. In order to quantify the amount extracted per gram of shale and account for any solvent evaporation, amounts were normalized to an internal standard, recovery standard, and the mass of the shale extracted, discussed in The Supplementary material. The uncertainty (\pm 30%) was quantified based on the variation (standard deviation) of the peak areas of the internal standard in all the sample chromatograms. Organic compounds detected ranged in mass from undecane (156.31 amu) to pentatriacontane (492.96 amu). More complex, higher molecular weight bitumen compounds, such as asphaltenes and resins, may have been present in the samples but would not have been observed in the GC-MS as their low volatility would have prevented elution.

2.3. Scanning electron microscopy/backscattered electron (SEM/BSE) imaging

Both the reacted samples and polished thin sections prepared from them for (U)SANS analysis were imaged using a Hitachi S4800 scanning electron microscopy in backscattered electron mode (SEM/BSE). Comparison of the uncontacted and contacted samples provided insight into porosity before polishing and the internal structure of the shale samples. SEM images give us a qualitative understanding of the effects of solvents on porosity and additional detail can be found in the Supplementary material.

2.4. (Ultra)small angle neutron scattering porosity measurements

(U)SANS can be used to characterize pore structures of geological material at scales ranging from 1 nm to $20 \,\mu$ m [49,48,7,5,4]. For this

¹ Certain commercial equipment, instruments or materials are identified in this paper to foster understanding. Such identification does not imply

⁽footnote continued)

recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.



Fig. 1. Approximate location of samples spanning the oil and gas windows. The circles represent the approximate location of the samples, with increasing numbers corresponding to increasing maturity. These numbers also correspond to the sample designations in Table 1. The sample location designated with the 1 refers the location of CARB 1 which will be investigated in a later study. As can be seen on the map, the samples span the petroleum window. This map was modified from the original EIA version (U.S. Energy Information Administration (EIA), [57]).

Table 1

Samples.

I

ncreasing Maturity	Carbonate- Rich Samples	Depth Recovered (ft)	Maturity (R ₀)	Clay-Rich Samples	Depth Recovered (ft)	Maturity (R ₀)
	CARB 2	5512	0.77	CLAY 2	5701	0.77
	CARB 3	6366	0.96			
	CARB 4	8747	1.18			
	CARB 5	7923	1.57	CLAY 5	8158	1.57

Table 2 Sample lithology.

-						
Sample	%Clay	%Carbonate	%Quartz	% TOC	%Other	%Illite/Smectite*
CARB 2	11.8	74.5	3.3	2.7	7.6	5.9
CARB 3	4.4	84.3	4.7	0.7	5.9	0.2
CARB 4	3.0	89.4	5.0	0.6	2.1	0.9
CARB 5	4.0	85.4	6.5	0.5	3.6	2.4
CLAY 2	21.1	51.8	15	7	5.1	10.4
CLAY 5	25.6	42.1	12.6	3.4	16.4	13.3

 \ast %Illite/Smectite refers to the percentage of mixed clay mineral in the shale.

experiment, SANS measurements were performed on the NGB 30 m instrument [19] at the National Institute for Standard and Technology (NIST) Center for Neutron Research (NCNR). USANS measurements were performed on the BT5 USANS [11] instrument at the NCNR and

the BL-1A USANS instrument at the Oak Ridge National Laboratory (ORNL) Spallation Neutron Source (SNS). The Supplementary material details the conditions used for each instrument for analysis. The porosity of the samples was determined from the scattering curves assuming a two-phase system, with the majority of scattering occurring at the pore/mineral interface [48]. Cumulative porosity and pore size distributions (PSD) were determined using Irena, a computer software [12,62,35,42,23,61]. Additional details are provided in the Supplementary material.

3. Results

3.1. Gas chromatography-mass spectrometry results

Chromatograms of specific ion masses detected with mass-spectrometry can be extracted from the TIC of each solvent and used to identify compounds. Several key chromatograms for the organic matter



Fig. 2. Schematic of sample preparation. All six samples were prepared according to this schematic. Shale cores are not to scale.

Table 3				
Solvent and	organic	matter	characteristics.	

Solvent/Organic matter	Classification	Dipole moment [•] (D)	Solubility parameter ^{•, +} (MPa) ^{0.5}
Water	polar protic	1.85	47.87
Methanol	polar protic	1.70	29.52
Hydrogen Chloride	acidic	1.08	22.00
Dichloromethane	non-polar	1.60	20.38
Acetone	polar aprotic	2.88	20.05
Toluene	non-polar	0.36	18.35
Cyclohexanes	non-polar	0.61	16.93
anthracene			19.173
n-undecane			15.989
n-heptadecane			15.925
2-methyltetradecane			15.258
2-methylpentadecane			15.227
2-methylheptadecane		15.148	
n-docosane		14.767	
2,6,10,14-tetramethylpen	tadecane (Pristar	ne)	14.173
triacontane		13.654	

• Values taken from Yaws [60].

⁺ Solubility parameters are calculated as the square root of the heat of vaporization divided by molal volume [24].

Table 4	
GC-MSD	method

Component	Settings
Injector	250 °C
	Splitless
	2.5 μL
Detector	340 °C
Column	DB-1, 30 m length, 0.250 mm ID, 0.25 µm film
	thickness
Solvent delay	5.0 min
Carrier gas	UHP helium @ 16.37 psi
Oven Temperature program	50–325 °C @ 15° min ⁻¹
	Hold at 325 °C for 5 min

extracted with each solvent from the CARB 4 samples are shown in Figs. 3-5. The chromatograms of all the other shale samples were qualitatively similar. For each solvent, a progression of linear alkanes, also called n-paraffins, was observed. This can be readily visualized in the mass/charge (m/z) = 57 ion chromatogram representing the C₄H₉⁺ fragment (Figs. 3 and 4). The molecular weight range of the extracted nparaffins differed among the solvents, and the greatest concentration of components peaked at different chain lengths, indicating a preferential extraction based on molecular weights. Methanol extracted some of the lightest hydrocarbons, from tridecane (nC_{13}) to tetracosane (nC_{24}) , with the peak around octadecane (nC_{18}) . Dichloromethane extracted a greater range of molecular weights, from undecane (nC_{11}) to hentriacontane (nC31), with a peak around nonadecane (nC19). Cyclohexane and toluene extracted similar portions of n-alkanes, with cyclohexane extracting a slightly lighter range than the toluene, from pentadecane (nC_{15}) to triacontane (nC_{30}) versus heptadecane (nC_{17}) to dotriacontane (nC_{32}) . Both peaked around docosane (nC_{22}) . Finally, hydrochloric acid extracted some of the heaviest n-paraffins from heneicosane (nC21) to dotriacontane (nC32), with a peak around tetracosane or pentacosane (nC24/25).

Along with linear alkanes, branched alkanes are also common components of oil and gas. The main branched species are isoalkanes, in which a methyl group is attached to the second carbon [22]. Dichloromethane extracted the most isoalkanes, including 2-methylte-tradecane (iC_{15}), 2-methylpentadecane (iC_{16}), and 2-methylheptadecane (iC_{18}). Methanol also extracted some isoalkanes, including iC_{16} and iC_{18} ; however, some of these were not quantifiable due to the fronting peak of the standards, discussed in further detail in the section entitled Total Amount of Extracted Material.

Another group of branched alkanes extracted from the samples was the isoprenoids, in which a methyl group is located every fourth carbon. In all the organic solutions, pristane and phytane, common isoprenoid biomarkers, were detected. Biomarkers are stable molecules derived from formerly living organisms that are chemically and structurally similar to the parent organic molecule. These are usually more resistant to degradation and thus can be used to geochemically identify source organic matter, depositional environment, and maturity. Pristane and phytane are diterpanes (contain four isoprene subunits) and are thought to be the remains of the side chain of chlorophyll [22].

Some aromatic compounds were also extracted from the shale



Fig. 3. Ion chromatogram (m/z = 57) for organic solvent extractions from CARB 4. A) Toluene, B) Cyclohexane, C) Methanol, and D) Dichloromethane. The compounds identified in gray were not included in quantification because they were impurities, byproducts of the standards, standards themselves, or were obscured by the standards peak in the total ion chromatogram (TIC). Pr stands for pristane and Ph stands for phytane. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

samples, especially in the those contacted with toluene and cyclohexane. The aromatic portion extracted by each solvent is apparent in the m/z = 77 ion chromatogram representing the $C_6H_5^+$ fragment (with mass = 77, Figs. 4 and 5). Many of the peaks visible in these spectra are not from the samples, but from the internal and recovery standards. While the $C_6H_5^+$ fragment is only a small component of the mass spectra of these standards, the large standard concentrations make them clearly distinguishable. Additionally, the byproducts of the recovery standard, 2,4,6-tribromophenol discussed in The Supplementary material, are apparent, including a bromobenzene compound in the organic extractions, and several phenol compounds in the hydrochloric acid extractions.

In the organic solvent extractions an additional compound was identified as a polycyclic aromatic hydrocarbon (PAH). This could be ethyl-anthracene, ethyl-phenanthrene, or phenyl-naphthalene. PAHs are common components of bitumen and can have a range of attached functional groups such as alkyl, nitro, and amino groups [46,43]. These compounds are very similar chemically, so it is not possible to distinguish between them using the techniques employed here.

Toluene and cyclohexane extracted very similar portions of aromatics, mirroring their alkane extraction behavior, although cyclohexane appears to have extracted more aromatics than toluene. However, analysis of the cyclohexane blank showed evidence of contamination, including some methylated benzene rings, 1,1'-Bicyclohexyl, phthalate, and silane. This is not surprising as 1,1'-Bicyclohexyl and phthalate have previously been identified as impurities in cyclohexane solvents in the 0.1 ng per mL range [36]. The silane compound may be a byproduct of column breakdown [40].

A high molecular weight compound appeared in both the m/z = 57 (Fig. 3A and B) and the m/z = 77 chromatograms in all of the toluene and cyclohexane extractions (Fig. 5A and B). The mass spectrum for this compound is shown in the Supplementary material. Its main components include m/z = 57, 191, 316, and 647. The m/z = 57 indicates the presence of $C_4H_9^+$ fragments while the m/z = 191 indicates tri-, tetraor pentacyclic terpane, all common biomarkers in oil [58,22,30]. A demethylated tetracyclic terpane, with a molecular ion at m/z = 316, has also been identified in severely biodegraded oils [63,2] Finally, the m/z = 647 could be due to two molecular ions (m/z = 316) connected

by an oxygen atom. As demonstrated by Laakia et al. [30] in the identification of unusual biomarker compounds in oil, co-elution of biomarkers can make identification of specific molecules difficult, especially without employing advanced gas chromatography techniques such as two-dimensional gas chromatography-time of flight mass spectrometry (GC x GC-TOFMS) [30].

3.1.1. Total amount of material extracted

As described in The Supplementary material, the amount extracted from each sample was quantified using the peak area in the total ion chromatogram (TIC), normalized by the recovery standard, internal standard, and initial rock mass. The amounts extracted with each solvent from each rock sample are presented in Figs. 6 and 7. There are, however, some limitations to these data. Unfortunately, quantification of peaks in the TIC requires that a high concentration of the component be present relative to background. Thus, some of the components observable in the m/z = 57 and m/z = 77 chromatograms (Figs. 3–5) were not observable in the TIC. Additionally, some hydrocarbons in the methanol solutions were not quantified because their peaks could not be resolved from those of the standards due to peak broadening. This could be because the nonpolar standards were not completely dissolved in the methanol and thus eluted earlier than samples with a nonpolar solvent as the mobile phase. The components that were not quantified in the TIC are marked in gray in Figs. 3-5.

3.2. (U)SANS porosity

3.2.1. Cumulative porosity

The cumulative porosity was calculated from the PSD curves, again using Irena [23] (Supplementary material). The cumulative porosity represents pores in the size range examined, about 2.5 nm to $8.2 \,\mu$ m in diameter. Fig. 8 shows the measured and normalized (to 100%) cumulative porosities of the uncontacted samples, with the Irena [23] calculated uncertainty. Additional uncertainty in the cumulative porosity is introduced due to the variation of organic matter present in the samples. Fig. 9 shows the change in porosity after contact with the solvents; negative numbers correspond to decreases in porosity with extraction, which has previously been observed in shale samples



Fig. 4. Ion Chromatograms (m/z = 57 and 77) from Hydrochloric acid Extraction for CARB 4. A) m/z = 57 and B) m/z = 77. The compounds identified in blue were not included in quantification because they were impurities, byproducts of the standards, standards themselves, or were obscured by the standards peak in the total ion chromatogram (TIC). PAH stands for polycyclic aromatic hydrocarbon. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

contacted with organic solvents [17,27].

In order to better understand the differences in pore sizes among the uncontacted samples as a function of maturity and composition, the cumulative porosity is displayed by breaking the total porosity into several pore size ranges (Table 5) similar to those defined by DiStefano et al. [17]. Samples CLAY 2 and CLAY 5 have the largest total porosities, but the relative porosities of all samples (Fig. 8B) are relatively consistent for all of the samples.

Significant changes were observed in the cumulative porosities of the shale samples after contact with solvents (Fig. 9). Total cumulative porosity decreased with extraction across all solvents for the clay-rich samples, with dichloromethane causing the greatest decrease in porosity for both. Organic extraction in the carbonate-rich samples increased total porosity in some samples while decreasing it in others, and in CARB 3 and CARB 5 some solvents increased porosity, while others caused little change. For CARB 2, the only solvents that caused a significant change were methanol and, to a lesser extent, cyclohexane, which increased and decreased the porosity, respectively. Porosity in CARB 4 was only affected by toluene, which caused a decrease.

3.2.2. Pore size distributions (PSD)

The distribution of pore sizes was primarily bimodal in all samples in the range examined, which is typical for shale [16,26,54] although it is evident that a series of larger, somewhat distinct pore sizes also exist,

which clearly make up a large fraction of the total porosity as shown in Fig. 8. Fig. 10 shows the PSD of one representative sample as an example. The smaller peaks in Fig. 10 at larger sizes indicate that the number of such pores is fewer than that of the smaller pores, but their larger diameters contribute proportionately more to the total volume. The first peak in the PSD of the shale samples had medians ranging from 3.1 nm in CLAY 2 contacted with methanol to 7.43 nm in CLAY 5 contacted with dichloromethane. The median pore size in the second peak had a much greater variation between samples and will not be discussed in detail. The porosity of the first peak in the distributions correlates to the percentage of clays in the samples (P-value < 0.05), so it may be due to broken edges of elementary clay layers in tactoid stacks [8,14,41,28]. Fig. 11 shows the porosity in this range for each sample and solvent. There was no significant change in porosity for CARB 3, CARB 4, and CARB 5 with extraction, but there was a decrease with solvent extraction in CARB 2, CLAY 2, and CLAY 5.

4. Discussion

4.1. GC-MS analysis of extracted organic matter

As expected, the type of organic matter extracted with each solvent varied as a function of the solvent properties, including polarity and the solubility parameter (calculated as the square root of the heat of

0.4



Fig. 5. Ion chromatogram (m/z = 77) for organic solvent extractions from CARB 4. A) Toluene, B) Cyclohexane, C) Methanol, and D) Dichloromethane. The compounds identified in red were not included in quantification because they were impurities, byproducts of the standards, standards themselves, or were obscured by the standards peak in the total ion chromatogram (TIC). Pr stands for pristane and Ph stands for phytane and PAH stands for polycyclic aromatic hydrocarbon. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

vaporization divided by molal volume) [24,60]. This is most clearly shown by the portions of alkanes and aromatics extracted. Methanol, the only polar solvent, and the solvent with the highest solubility parameter, was only able to extract short-chain n-paraffins, which also have higher solubility parameters (Table 3). It did not extract much of the longer, heavier n-paraffins, which are more nonpolar and hydrophobic, and immiscible in methanol, which explains the small extraction amounts observed (Fig. 6).

The nonpolar solvents— dichloromethane, toluene, and cyclohexane— extracted more material than methanol (cf. [17]) (Fig. 6). Except for CLAY 2, the amount extracted with the various solvents followed similar trends. Dichloromethane extracted the greatest amount of material from all the samples, with the largest range of nparaffins (Fig. 3). Dichloromethane is commonly used to extract Total Petroleum Hydrocarbons (TPH) in sediment and water due to its miscibility with petroleum hydrocarbons [1]. Toluene and cyclohexane have very similar properties with solubility parameters in the range of the n-paraffins (Table 3), and they extracted similar portions of alkanes and aromatics and similar total amounts of organic matter. The exception is sample CLAY 2, in which cyclohexane extracted much more material than the other nonpolar solvents (Fig. 6). Comparison of the chromatograms, however, reveals that the all three nonpolar solvents extracted similar compounds in CLAY 2. The difference was only about 0.05 µg, which is within analytical error. Thus, the nonpolar solvents all behaved similarly.

The total amount of alkanes and aromatics extracted with the organic solvents from each of the samples does not show any observable trends with maturity. However, as expected, there was a positive correlation (P-value < 0.05) between the initial TOC and the amount extracted by each solvent (Fig. 12), which explains why so much more

Fig. 6. Organic matter extracted with organic solvents. The amount of organic matter extracted, in micrograms, with the organic solvents per gram of shale. The boxes above the bars indicate the starting amount of total organic carbon (TOC). The error bars are calculated by the variation (standard deviation) in the peak area of the internal standard across all samples.





Fig. 7. Organic matter vs. initial organic carbon content in the samples contacted with hydrochloric acid. The amount of organic matter extracted, in micrograms, with the hydrochloric acid per gram of shale as a function of TOC. The error bars are calculated by the variation (standard deviation) in the peak area of the internal standard across all samples. P-value < 0.05.



Fig. 8. Porosity of the Uncontacted Samples across the Ranges of Porosity. A) shows the total porosity across the ranges of pore sizes and B) shows the normalized porosity. Uncertainties in porosity were calculated in Irena by running multiple fits to the data, varying the data by adding Gaussian noise.

organic matter was extracted from CLAY 2 (TOC = 7%). This was less pronounced in the methanol extraction, but methanol was the least compatible organic solvent with the organic matter present in the samples. Besides the initial organic carbon, small differences in the amounts extracted could be due to accessibility of the hydrocarbons or the miscibility of the solvents with the organic matter present in the



Fig. 9. Change in cumulative porosity after contact with solvents. Uncertainties in porosity were calculated in Irena by running multiple fits to the data, varying the data by adding Gaussian noise.

samples.

The hydrochloric acid showed the highest amount of extraction among all the solvents (Fig. 7). However, the difficulty in quantifying the recovery standard for normalization, discussed in The Supplementary material, prevents direct comparison between the hydrochloric acid and the organic solvent data. Since byproducts of the standard were used to normalize the amount extracted, the totals are probably overestimated. Additionally, the aqueous hydrochloric acid solution only extracted long chain, high molecular weight hydrocarbons (Fig. 4) which have low solubility parameters and are more hydrophobic and are thus expected to be the least compatible with hydrochloric acid (Table 3). The Eagle Ford Shale is very carbonate-rich compared to other shale gas plays, and the interaction of hydrochloric acid with this carbonate-rich matrix leads to the dissolution of the carbonate materials, altering the distribution of organic matter extracted. The lighter hydrocarbons extracted with the organic solvents were not extracted with the hydrochloric acid, suggesting that the hydrochloric acid was not able to penetrate the bitumen and kerogen to extract the lighter portion of organic matter. Just as with the organic solvents, there was a positive correlation (P-value < 0.05) between the amount of alkanes and aromatics extracted with the hydrochloric acid and the TOC of the uncontacted samples (Fig. 7).

In considering the relationship between the amounts of organics extracted and changes in porosity, it must be remembered that larger molecular weight molecules such as asphaltenes and resins would not be detected in the GC-MS because their elution times are much longer and they would be trapped in the injection port. Organic solvents have been shown to extract polyaromatic resins and asphaltenes using different methods of extract analysis. Mohnhoff et al. [39] extracted three shale samples from the Posidonia Shale in Germany with dichloromethane and analyzed the extracts with Thin-Layer Chromatography (TLC) utilizing a Flame Ionization Detector (FID). They determined that 30-60% of the amount extracted was resins and asphaltenes. While these were different shale samples that had been crushed to improve extraction, it is possible that some resins and asphaltenes were extracted in this work. The extraction of this organic matter likely altered the porosity but was not quantified in the extractants [17].

4.1.1. Solvent-clay interactions

The pore structure of shale may be affected by a number of chemical and physical processes between solvents and the matrix, including reactions between the clay interlayers, water, and organic and inorganic molecules in the solvents [25]. These interactions may be further complicated by organic matter stored in or sorbed to clay particles, which may play a role in the initial preservation of organic matter in sediments [21]. Understanding the alteration of pore space during solvent contact may shed light on the mechanisms of interaction

Table 5

Defined ranges with approximate pore diameters and porosity for uncontacted samples.

Pore diameter (Å)	Pore diameter (nm)	Porosity in une	Porosity in uncontacted samples (%)					
		CARB 2	CARB 3	CARB 4	CARB 5	CLAY 2	CLAY 5	
25-51.5	2.5-5.15	0.21	0.00	0.07	0.01	0.68	0.19	
51-92.6	5.1-9.26	0.06	0.07	0.10	0.05	0.20	0.22	
92.6–590	9.26–59	0.68	0.21	0.54	0.22	0.95	1.25	
590-2740	59–274	0.94	0.36	1.48	0.32	2.20	2.22	
2740-82,000	274-8200	3.37	0.80	3.68	0.92	7.77	8.51	

between the clay minerals in shale and solvents.

Smectite is a common clay mineral found in shale and its structure both allows exchange of interlayer cations and structural expansion due to intercalation of water or other fluids between the clay layers [3], decreasing surrounding porosity. Water solvates cations in the interlayer and bonds to external clay surfaces [15]. Additional expansion can occur in acidic solvents such as hydrochloric acid, from which hydrogen can exchange with interlayer cations. Cations in the solution, such as calcium from dissolved carbonate, can also exchange with interlayer cations [3].

Organic solvents have also been demonstrated to expand clay layers, although to a lesser extent than aqueous solvents [25]. The chemical affinity between clays and organic solvents depends on the structure of the solvent (i.e. molecular weight, chain length, functional groups such as pi bonds in aromatic rings, and aqueous phases present) [25]. Solvation or coordination of interlayer cations and hydrogen bonding between silicate layers and hydroxyl functional groups in neutral organic molecules is possible if the energy of adsorption is large enough to overcome the interaction between clay layers [3]. This has been observed for benzene and toluene, which form stable complexes through pi bonds with the copper ion in copper (II) montmorillonite, a type of synthetic smectite [18]. However, this only occurred in clays with excess negative charge due to isomorphic substitution (i.e. Na^+ for Ca^{2+}) [18]. Additionally, alcohols have been demonstrated to expand clay layers [13] and chemically reduced smectites have been demonstrated to adsorb polychlorinated alkanes and alkenes [15].

DiStefano et al. [17] proposed that clay expansion was the dominant process causing the decreased porosity observed with solvent extraction. While clay-rich samples showed the greatest decrease across all solvents and length scales, if clay expansion controls porosity decrease, hydrochloric acid should cause the greatest decrease due to water



Fig. 11. Porosity due to pores in the first peak of the bimodal pore size distributions for the contacted and uncontacted samples.

intercalation and cation exchange. This was not observed in either the total porosity changes (Fig. 9) or in the changes in solvent extraction in the first PSD peak (Fig. 11). Additionally, total porosity also decreased



Fig. 10. Pore size distribution for a representative uncontacted sample (CLAY 2). This sample shows a bimodal distribution of porosity. Uncertainties in porosity were calculated in Irena by running multiple fits to the data, varying the data by adding Gaussian noise. Note: porosity is normalized by the diameter of the pores.



Fig. 12. Initial TOC vs. the amount of organic matter extracted in the organic solvents. P-values: cyclohexane < 0.005, methanol < 0.05, toluene < 0.005, and dichloromethane < 0.01.

in sample CARB 4 with toluene extraction, although it had the lowest clay content of all the samples (3.0%). As such, another mechanism must have contributed to the decrease.

4.1.2. Solvent-kerogen interactions

Kerogen cannot be extracted from shale with organic solvents due to its complex, cross-linked macromolecular network [10]. It is a complex polymeric material composed of non-repeating PAH units with bridging and side functional groups [10]. Both isolated kerogen and kerogen in oil shale swell extensively when immersed in organic solvents [31,10]. This has been shown to follow regular solution theory, which predicts a maximum in swelling at the solubility parameter of the polymer [10]. Kerogen swelling is therefore another possible mechanism for porosity decrease in shale.

To test the possibility that kerogen swelling affected porosity in our samples, the absolute decrease in porosity in CLAY 2 and CLAY 5 was plotted against the solubility parameters of the solvents. Excluding hydrochloric acid, the results seem to follow regular solution theory demonstrating a maxima of swelling (Fig. 18), which is similar to results reported by Ballice [10] and Larsen and Li [31]. The maxima, around 20 MPa^{0.5}, is near the reported solubility parameter of kerogen from other shale (19.43 MPa^{0.5}) [10]. Deviations may be due to clay layer expansion. This was discounted due to evidence that mineral matter does not decrease kerogen swelling [31], but the clays may have *increased* the effects of swelling on porosity. These results suggest that



Fig. 13. Increase in porosity due to shale composition. Uncertainties in porosity were calculated in Irena by running multiple fits to the data, varying the data by adding Gaussian noise. P-values: % Pyrite, TOC, & Clay < 0.05.

kerogen swelling is a key factor in the porosity decrease observed during shale interactions with solvents.

4.1.3. Hydrochloric acid interactions

The decrease in porosity in the samples reacted with HCl is not fully explained by either clay-layer expansion or kerogen swelling. Hydrochloric acid, as an aqueous solvent, is expected to expand clay layers and, as a hydrogen bonding solvent, to enhance kerogen swelling compared to predictions from regular solution theory [10]. However, the opposite appears to have been the case (Fig. 18), possibly because swelling was offset by carbonate dissolution or extraction of resins and asphaltenes, but the extent to which these processes altered porosity is unknown.

4.2. Porosity of the uncontacted samples

As shown above, the (U)SANS data can be used to determine porosity as a function of pore diameter, assuming only two phases are present in the rock. This assumes the square of the difference in neutron scattering length densities (the scattering contrast) between empty pores and the rock matrix is the greatest contribution to scattering, which is not always the case. Radlinski and Hinde [47] demonstrated that the neutron scattering length density in organic matter decreases with decreasing carbon to hydrogen ratios. As such, empty pores and pores filled with alkanes will contribute similarly to scattering, i.e. they have similar scattering length densities [47]. More complex organic matter has increasingly large scattering length densities, and thus may behave more like the rock matrix [47]. Thus, the porosity determined by (U)SANS is an apparent porosity, which includes pores filled with alkanes and aromatics.

The cumulative porosity of the uncontacted samples shows no distinguishable trend with maturity ($R_0 = 0.77-1.57$), although other studies have noted such trends over larger maturity ranges [34,6]. Mastalerz et al. [34] used gas adsorption to show a decrease in porosity from $R_0 = 0.35$ to 1.15, followed by a porosity increase to $R_0 = 1.41$. They attributed this increase to transformations within organic matter [34,50]. As just noted, porosity changes within bituminous organic matter are unlikely to be quantified with (U)SANS. Anovitz et al. [6] also observed a decrease in porosity from $R_0 = 0.58$ to 0.77 in both clay and carbonate-rich samples from the Eagle Ford shale, but a relatively constant porosity to $R_0 = 1.57$ using (U)SANS. This suggests that most of the porosity changes with maturity in shale observable with (U)SANS may occur at lower maturities than those in this study.

While trends with maturity were not identified, the mineralogical composition of the shale may have partially controlled the porosity. As demonstrated by Kuila et al. [29], clay minerals are a large source of shale porosity. Among our samples CLAY 5 had the most porosity with 12.4%, while CLAY 2 had 11.8%. This difference could be attributed to the amount of clay in the samples (25.6% in CLAY 5, 21.1% in CLAY 2). The porosities of the carbonate samples are all similar, but there are differences with maturity. CARB 2 (5.3%) and CARB 4 (5.9%) have similar cumulative porosities but, as noted by Anovitz et al. [6], the large TOC content of CARB 2 (2.7%) relative to CARB 4 (0.6%) could account for much of the reported porosity since pores filled with alkanes and aromatics would scatter like empty pores. Additionally, the higher maturity shale samples (CARB 4 and 5) had a greater proportion of large pores (\sim 0.3 µm) and the lower maturity shale samples (CARB 2 and 3) had a greater proportion of smaller pores. This could reflect both changes in clay mineral structure and the generation of petroleum, and the larger pores could be forming as oil and gas is generated and trapped or expelled from the source rock.

As exemplified by CARB 3 and CARB 5, the composition of the shale may play an important role in the total porosity. Figs. 13 and 14 show the correlation between total porosity and the percent clay, pyrite, carbonate, and TOC in the rock. There is a positive correlation (P-values < 0.05) between the total porosity and the percentage of clay,



Fig. 14. Decrease in porosity due to shale composition. Uncertainties in porosity were calculated in Irena by running multiple fits to the data, varying the data by adding Gaussian noise. P-value: < 0.005.

pyrite, and TOC, and a negative correlation (P-value < 0.05) with the percentage of carbonate. The relationship between clay and porosity is not surprising as pores between clay particles and clay aggregates are often observed in shale [27-29]. Additionally, in this case, it reasonable that any trend with respect to the percent of clay would be reversed in the carbonate percentage, since in all of the samples 70% of the minerals are clay and carbonate. Mastalerz et al. [34] saw similar trends when they excluded the most and least mature samples from their sample set. The trend of increasing porosity with increasing TOC is also reasonable. As noted, pores filled with alkanes and aromatics will appear in (U)SANS to be empty pores, although, other studies based on approaches other than (U)SANS have reported a similar correlation [44,37,27]. Finally, the pyrite only made up a small percent of the shale compositions, ranging from 0.2 to 2.8% (included % Other in Table 2), but the correlation between porosity and percent pyrite in the samples could be due to pores or organic matter within the pyrite framboids (4-28 µm) observed in the SEM/BSE images (Fig. 15). Pores between various sizes of pyrite aggregates have previously been reported to have an important effect on multiscale porosity observed in shale [32], and our results support that conclusion.

An additional correlation (P-value < 0.07) between the amount of organic matter extracted and the initial porosity of the samples could be an artifact of these mineralogical relationships. However, it may



Fig. 15. SEM/BSE images of pyrite framboids in polished thin sections. A and B show pyrite framboids in the CARB 5 sample with diameters of 8 and 28 μ m, respectively. C shows a 12 μ m framboid found in the CARB 5 sample after contact with hydrochloric acid and D shows a 5 μ m framboid in CARB 3.

indicate that the initial accessibility of the pores can impact the amount of hydrocarbons extracted. Further investigation into this trend is necessary for substantiated conclusions.

4.3. Comparison to previous studies

The amount of organic matter extracted with the organic solvents in DiStefano et al. (2017), $\sim 2.5 \text{ mg/g}$, is an order of magnitude higher than the mass extracted here, $\sim 0.25 \,\mu g/g$, using some of the same solvents. Differences in the quantification of the organic matter can be attributed to the methods employed in the two studies. The recovery standards added to the solvents in this study was expected to improve the quantification of the organic matter extracted compared to the methods in DiStefano et al. (2017). The recovery standards were added to the solvents before the shale samples were extracted and the total amount of organic matter extracted was normalized to the initial concentration of the recovery standards. This accounted for any evaporation of solvent in the samples, which may have caused the quantification of organic matter extracted in DiStefano et al. (2017), without the recovery standard, to be higher. This explains the large differences in amount extracted determined from the two studies. While the mass of organics extracted in each chapter is not directly comparable, both studies showed that more organic matter was extractable in the clayrich samples than in the carbonate-rich samples and in DiStefano et al. (2017), the most organic matter was extracted from the low maturity samples. Additionally, in both studies, methanol extracted the least amount of organic matter.

The porosity of the uncontacted samples varied with maturity and lithology. While the porosity of the samples from DiStefano et al. (2017) and this work analyzed slightly different pore ranges, the measured porosities were in the range of the porosities determined from the same shale samples in other studies. Anovitz et al. [6] investigated all of the samples examined in DiStefano et al. (2017) and this work. excluding CLAY 5 (which replaced another high-maturity clay-rich sample that was no longer available). Porosities determined by Anovitz et al. [6] were reported in two orientations, the Z- and Y- orientations discussed in Supplementary material, for pore sizes that ranged from 1 nm to 20 µm (Fig. 16). As shown in Fig. 16, the porosities reported in DiStefano et al. (2017) and this work were in the range of or lower than the porosities from the two orientations reported by Anovitz et al. [6]. This lower porosity can be attributed to the smaller range of pore sizes examined, 2 nm to 1.4 µm in DiStefano et al. (2017) and 2.5 nm to 8.2 µm in this study. Anovitz et al. [6] showed a significant drop in porosity as maturity initially increased, followed by relatively constant porosity values across maturity. The drop in porosity observed in Anovitz et al. [6] was also observed in the carbonate-rich samples (CARB LM and CARB HM) in DiStefano et al. (2017), but it was observed in a lesser extent in the clay-rich samples (CLAY LM and CLAY HM). Additionally, in all three studies, the clay-rich samples exhibited greater overall porosity than the carbonate-rich samples (DiStefano et al., 2017; [6]). Finally, the similar porosities across various samples of the same shale indicate that, although shale is very heterogenous, the Eagle Ford Shale has similar porosity across the formation, thus the uncontacted samples may be compared to the contacted shale.

4.4. Solvent-pore interactions

Significant changes in porosity occurred after solvent extraction (Fig. 9). As noted by DiStefano et al. [17], extracting only alkanes and aromatics from shale may not significantly alter the porosity measured by (U)SANS. The GC-MS analyses of the solvent extracts revealed that alkanes were, indeed, the primary OM extracted and quantified, although as noted above larger bitumen molecules extracted would have been excluded from this quantification. Thus, no trends are to be expected between the amount extracted and the changes in porosity [17]. However, Fig. 17 shows that there was, indeed, a negative correlation



Fig. 16. Porosity comparison. Porosity is compared to the porosity determined on the same samples analyzed by DiStefano et al. and Anovitz et al. [6].

(P-value < 0.005) between change in the (U)SANS porosity and the amount of organic matter extracted. If larger bitumen molecules were extracted, an increase in porosity should have been observed, but many of the solvents yielded a decrease in porosity (Fig. 9), suggesting pore space closure. The mechanism for this decrease is not well understood but could be due to solvent-clay or solvent-kerogen interactions.

4.5. Porosity changes caused by solvent interaction

DiStefano et al. [17] proposed several mechanisms for the porosity changes observed in their (U)SANS experiments: (1) complete breakdown of asphaltenes and resins, (2) dissolution and migration of resins and asphaltenes, or (3) the incomplete or partial breakdown of organic matter. They suggest that a complete breakdown, dissolution, and migration of resins and asphaltenes are dominant. However, as alkanes and aromatics are removed and solvents interact with matrix-bound kerogen, kerogen may also swell into spaces previously occupied by the alkanes and aromatics. This may explain why porosity decreased with increased alkanes and aromatics extraction with the organic solvents (Fig. 17) and may be the dominant cause of porosity changes. Other



Fig. 17. Effect of extraction of alkanes and aromatics on porosity. uncertainties in porosity were calculated in Irena by running multiple fits to the data, varying the data by adding Gaussian noise.



Fig. 18. Decrease in porosity as a function of solubility parameter. The triangles (\blacktriangle) represent CLAY 2 extractions and the circles (\bullet) represent the CLAY 5 extractions. The swelling roughly follows regular solution theory, except the hydrochloric acid extractions outliers (open triangle and circle, see the text).

mechanisms that may influence porosity change include clay layer expansion, extraction of resins and asphaltenes, and mineral dissolution, as in the case of hydrochloric acid.

5. Conclusions

In this work the effects of solvent extraction on porosity in the Eagle Ford Shale was examined by comparing solvent-extracted to unextracted samples, and the type and amount of organic matter extracted were compared to the porosity changes. The effects of mineralogy, organic matter type, and maturity were considered. Additionally, the effects of maturity and lithology on unaltered pore space was examined in the uncontacted samples.

A range of solvents was used to determine how solvent properties affected the amount and type of organic matter extracted. Only alkanes and aromatics were detected in the extract using Gas Chromatography – Mass Spectrometry (GC-MS); however, other results suggested that heavier hydrocarbons were also extracted. The methanol extract contained mostly light alkanes and extracted the smallest amount as methanol is the organic solvent least compatible with the organic matter present in the samples. The other organic solvents, dichloromethane, toluene, and cyclohexane, all extracted similar amounts of organic matter, with toluene and cyclohexane extracting more aromatics. Dichloromethane may have extracted slightly more than the other solvents due to its compatibility with the organic matter present. The aqueous solvent, hydrochloric acid, extracted the longest alkane chains. This portion of organic matter is the most hydrophobic and thus chemically incompatible with the aqueous hydrochloric acid, thus, physical dissolution of carbonate minerals may have liberated heavier organic matter. The lighter hydrocarbons were not extracted with the hydrochloric acid, suggesting that the hydrochloric acid was not able to penetrate the bitumen and kerogen to extract the lighter portion of organic matter. The amount of alkanes and aromatics extracted also correlated (P-values < 0.05) with the amount of total organic carbon (TOC) present.

For the uncontacted samples, composition, rather than maturity, controlled total porosity. There were statistically significant positive correlations (P-values < 0.05) between the amount of porosity and the TOC, clay, and pyrite content. Porosity between clay stacks, in organic matter, and within pyrite framboids is most likely the cause of these trends. Additionally, there was a correlation (P-values < 0.07) between initial porosity and the amount of alkanes and aromatics extracted with the solvents. This could be due to the pore accessibility or reflect the dependence of porosity and amount extracted on TOC.

After extraction, shale porosity increased with some solvents and decreased with others. Mechanisms of pore-solvent interaction, especially with aqueous solvents, include clay layer expansion, extraction of bitumen, and mineral dissolution. However, as more alkanes and aromatics were extracted from the samples, the change in porosity decreased, possibly because matrix-bound kerogen swelled to fill spaces once filled with bitumen. This mechanism seems to dominate poresolvent interactions in the Eagle Ford Shale.

This study has shown how minerals and organic matter in shale may interact with solvents producing unintended consequences, such as decreases in porosity. Any decrease in porosity may be detrimental to oil and gas recovery by sealing off escape pathways. Solvents and fluids that are injected underground may be used to reduce these effects. To improve the efficiency of oil and gas extraction, kerogen swelling, as the main mechanism determined in this work to govern porosity decreases, may be controlled by using solvents with targeted solubility parameters to decrease swelling. For example, solvents such as cyclohexane and toluene can be used instead of dichloromethane as they tend to swell shale less while extracting a comparable amount of organic matter. Additionally, solvent-free fluids may be utilized for oil and gas recovery to prevent or lessen kerogen swelling, such as inert gases. This greater understanding of the Eagle Ford Shale formation can hopefully improve the efficiency of oil and gas extraction.

Acknowledgments

This material is primarily based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. VHD acknowledges a graduate fellowship through the Bredesen Center for Interdisciplinary Research at the University of Tennessee in Knoxville. JM funding came from the Research Partnership to Secure Energy for America, contract NFE-11-03260. E.P. was sponsored by the Army Research Laboratory and was accomplished under Grant Number W911NF-16-1-0043. E. P. also acknowledges support from the Tom Cronin and Helen Sestak Faculty Achievement award. A portion of this research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. Access to both the SANS and USANS instruments was provided by the Center for High Resolution Neutron Scattering, a partnership between the National Institute of Standards and Technology and the National Science Foundation under agreement No. DMR-1508249. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2018.10.010.

References

- Adeniji A, Okoh O, Okoh A. Analytical methods for the determination of the distribution of total petroleum hydrocarbons in the water and sediment of aquatic systems: a review. J Chem 2017.
- [2] Aguiar A, Júnior AIS, Azevedo DA, Neto FRA. Application of comprehensive twodimensional gas chromatography coupled to time-of-flight mass spectrometry to biomarker characterization in Brazilian oils. Fuel 2010;89(10):2760–8.
- [3] Aldridge S, Downs AJ. The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities. John Wiley & Sons; 2011.
- [4] Anovitz LM, Cole DR. Characterization and analysis of porosity and pore structures. Rev Mineral Geochem 2015;80:61–164. https://doi.org/10.2138/rmg.2015.80.04.
- [5] Anovitz LM, Cole DR, Rother G, Allard LF, Jackson AJ, Littrell KC. Diagenetic changes in macro- to nano-scale porosity in the St. Peter Sandstone: an (ultra) small angle neutron scattering and backscattered electron imaging analysis. Geochim Cosmochim Acta 2013;102:280–305. https://doi.org/10.1016/j.gca.2012.07.035.
- [6] Anovitz LM, Cole DR, Sheets JM, Swift A, Elston HW, Welch SA, et al. Effects of maturation on multiscale (nanometer to millimeter) porosity in the Eagle Ford shale. Interpretation 2015;5(3):SU59–70. https://doi.org/10.1190/INT-2014-0280.1.
- [7] Anovitz LM, Lynn GW, Cole DR, Rother G, Allard LF, Hamilton WA, et al. A new approach to quantification of metamorphism using ultra-small and small angle neutron scattering. Geochim Cosmochim Acta 2009;73(24):7303–24.
- [8] Aylmore LAG, Quirk JP. Domains and quasi-crystalline regions in clay systems. Soil Sci Soc of Am J 1971;35:652–4.
- [9] Bahadur J, Ruppert LF, Pipich V, Sakurovs R, Melnichenko YB. Porosity of the marcellus shale: a contrast matching small-angle neutron scattering study. Int J Coal Geol 2018;188:156–64.
- [10] Ballice L. Solvent swelling studies of Göynük (Kerogen Type-I) and Beypazarı oil shales (Kerogen Type-II). Fuel 2003;82(11):1317–21. https://doi.org/10.1016/ S0016-2361(03)00026-7.
- [11] Barker J, Glinka C, Moyer J, Kim M, Drews A, Agamalian M. Design and performance of a thermal-neutron double-crystal diffractometer for USANS at NIST. J Appl Crystallogr 2005;38(6):1004–11.
- [12] Beaucage G. Approximations leading to a unified exponential/power-law approach to small-angle scattering. J Appl Crystallogr 1995;28(6):717–28.
- [13] Bradley WP. Molecular associations between montmorillonite and some polyfunctional organic liquids1. J Am Chem Soc 1945;67(6):975–81.
- [14] Cases JM, Berend I, Besson G, Francois M, Uriot JP, Thomas F, et al. Mechanism of adsorption and desorption of water vapor by homoionic montmorillonite. 1. The sodium-exchanged form. Langmuir 1992;8:2730–9.
- [15] Cervini-Silva J. Coupled hydrophilic and charge-transfer interactions between polychlorinated methanes, ethanes, and ethenes and redox-manipulated smectite clay minerals. Langmuir 2004;20(22):9878–81. https://doi.org/10.1021/ la0491089.
- [16] Clarkson CR, Solano N, Bustin RM, Bustin AMM, Chalmers GRL, He L, et al. Pore structure characterization of North American shale gas reservoirs using USANS/ SANS, gas adsorption, and mercury intrusion. Fuel 2013;103:606–16. https://doi. org/10.1016/j.fuel.2012.06.119.
- [17] DiStefano VH, McFarlane J, Anovitz LM, Stack AG, Gordon AD, Littrell KC, et al. Extraction of organic compounds from representative shales and the effect on porosity. J Nat Gas Sci Eng 2016;35:646–60.
- [18] Doner H, Mortland M. Benzene complexes with copper (II) montmorillonite. Science 1969;166(3911):1406–7.
- [19] Glinka CJ, Barker JG, Hammouda B, Krueger S, Moyer JJ, Orts WJ. The 30 m smallangle neutron scattering instruments at the National Institute of Standards and Technology. J Appl Crystallogr 1998;31(3):430–45.
- [20] Gu X, Mildner DFR, Cole DR, Rother G, Slingerland R, Brantley SL. Quantification of organic porosity and water accessibility in marcellus shale using neutron scattering. Energy Fuels 2016;30:4438–49.
- [21] Hedges JI, Keil RG. Sedimentary organic matter preservation: an assessment and speculative synthesis. Mar Chem 1995;49(2–3):81–115.
- [22] Huc A-Y. Geochemistry of Fossil Fuels: From Conventional to Unconventional Hydrocarbon Systems. Paris, France: Editions Technip; 2013.
- [23] Ilavsky J, Jemian PR. Irena: tool suite for modeling and analysis of small-angle scattering. J Appl Crystallogr 2009;42(2):347–53.
- [24] Kamlet MJ, Carr PW, Taft P, Abraham MH. Linear solvation energy relationships. 13. Relationship between the Hildebrand solubility parameter, delta. H, and the solvatochromic parameter, pi. J Am Chem Soc 1981;103(20):6062–6.
- [25] Kowalska M, Guler H, Cocke DL. Interactions of clay minerals with organic pollutants. Sci Total Environ 1994;141:223–40.
- [26] Kuila U, McCarty DK, Derkowski A, Fischer TB, Prasad M. Total porosity measurement in gas shales by the water immersion porosimetry (WIP) method. Fuel 2014;117:1115–29. https://doi.org/10.1016/j.fuel.2013.09.073.
- [27] Kuila U, McCarty DK, Derkowski A, Fischer TB, Topór T, Prasad M. Nano-scale texture and porosity of organic matter and clay minerals in organic-rich mudrocks.

Fuel 2014;135:359-73.

- [28] Kuila U, Prasad M. Specific surface area and pore-size distribution in clays and shales. Geophys Prospect 2013;61:341–62. https://doi.org/10.1111/1365-2478. 12028.
- [29] Kuila U, Prasad M, Derkowski A, McCarty, DK, Compositional controls on mudrock pore-size distribution: An example from Nibrara formation. Paper presented at the SPE Annual Technical Conference and Exhibition, 2012, San Antonio, TX.
- [30] Laakia J, Casilli A, Araújo BQ, Gonçalves FT, Marotta E, Oliveira CJ, et al. Characterization of unusual tetracyclic compounds and possible novel maturity parameters for Brazilian crude oils using comprehensive two-dimensional gas chromatography-time of flight mass spectrometry. Org Geochem 2017;106:93–104.
 [31] Larsen JW, Li S. Solvent swelling studies of Green River kerogen. Energy Fuels
- [31] Larsen JW, Li S. Solvent swelling studies of Green River kerogen. Energy Fuels 1994;8(4):932–6.
 [32] Loucks RG, Reed RM, Ruppel SC, Jarvie DM. Morphology, genesis, and distribution
- of nanometer-scale pores in siliceous mudstones of the Mississippian Barnett shale. J. Sedimen Res 2009;79:848–61. https://doi.org/10.2110/jsr.2009.092.
- [33] Mastalerz M, Drobniak A, Stankiewicz AB. Origin, properties, and implications of solid bitumen in source-rock reservoirs: a review. Int J Coal Geol 2018.
- [34] Mastalerz M, Schimmelmann A, Drobniak A, Chen Y. Porosity of devonian and mississippian new albany shale across a maturation gradient: insights from organic petrology, gas adsorption, and mercury intrusion. AAPG Bull 2013;97(10):1621–43. https://doi.org/10.1306/04011312194.
- [35] Merritt M, Zhang Y. Interior-point gradient method for large-scale totally nonnegative least squares problems. J Optim Theory Appl 2005;126(1):191–202.
- [36] Middleditch B. Analytical Artifacts-GC. MS, HPLC, TLC and PC: Springer; 1989.
 [37] Milliken KL, Rudnicki M, Awwiller DN, Zhang T. Organic matter-hosted pore system, marcellus formation (Devonian) Pennsylvania. AAPG Bull 2013;97(2):177–200.
- [38] Mitchell-Tapping HJ, Porosity and permeability relationship to cleaning effectiveness in whole core analyses, 1982.
- [39] Mohnhoff D, Littke R, Krooss BM, Weniger P. Flow-through extraction of oil and gas shales under controlled stress using organic solvents: implications for organic matter-related porosity and permeability changes with thermal maturity. Int J Coal Geol 2016;157:84–99.
- [40] Morrey EL, Knutsen L, Analysis and identification of the breakdown products of potential extinguishing agents subjected to flaming combustion, 2002.
- [41] Neaman A, Pelletier M, Villieras F. The effects of exchanged cation, compression, heating and hydrationon textural properties of bulk bentonite and its corresponding purified montmorillonite. Appl Clay Sci 2003;22:153–68.
- [42] Nelson A. Co-refinement of multiple-contrast neutron/X-ray reflectivity data using MOTOFIT. J Appl Crystallogr 2006;39(2):273–6.
- [43] Pampanin DM, Sydnes MO. Polycyclic Aromatic Hydrocarbons a Constituent of Petroleum: Presence and Influence in the Aquatic Environment Hydrocarbon. InTech; 2013.
- [44] Passey QR, Bohacs K, Esch WL, Klimentidis R, Sinha S, From oil-prone source rock to gas-producing shale reservoir-geologic and petrophysical characterization of unconventional shale gas reservoirs. Paper presented at the International Oil and Gas Conference and exhibition in China, 2010.

- [45] Pepper AS, Corvi PJ. Simple kinetic models of petroleum formation. Part I: oil and gas generation from kerogen. Mar Pet Geol 1995;12(3):291–319.
- [46] Poirier M-A, Das BS. Characterization of polynuclear aromatic hydrocarbons in bitumen, heavy oil fractions boiling above 350 °C by g.c.-m.s. Fuel 1984;63(3):361–7. https://doi.org/10.1016/0016-2361(84)90013-9.
- [47] Radlinski A, Hinde A. Small angle neutron scattering and petroleum geology. Neutr News 2002;13(2):10–4.
- [48] Radliński AP. Small-angle neutron scattering and rock microstructure. Rev Mineral Geochem Neutron Scatter Earth Sci 2006:363–97.
- [49] Radliński AP, Ioannidis MA, Hinde AL, Hainbuchner M, Baron M, Rauch H, et al. Angstrom-to-millimeter characterization of sedimentary rock microstructure. J. Colloid Interface Sci 2004;274:607–12.
- [50] Radlinski AP, Mastalerz M. Neutron scattering study of vitrinite: insights into submicrometer inclusions in North American Carboniferous coals of bituminous rank. Int J Coal Geol 2018;186:145–54.
- [51] Ruppert LF, Sakurovs R, Blach TP, He L, Melnichenko YB, Mildner DFR, et al. A USANS/SANS study of the accessibility of pores in the Barnett Shale to methane and water. Energy Fuels 2013;27(2):772–9. https://doi.org/10.1021/ef301859s.
- [52] Sakurovs R, Koval L, Grigore M, Sokolova A, Ruppert LF, Melnichenko YB. Nanometre-sized pores in coal: variations between coal basins and coal origin. Int J Coal Geol 2018;186:126–34.
- [53] Sun C, Yao S, Li J, Liu B, Liu H, Xie Z. Characteristics of pore structure and effectiveness of shale oil reservoir space in Dongying Sag, Jiyang Depression, Bohai Bay Basin. J Nanosci Nanotechnol 2017;17(9):6781–90.
- [54] Swift AM, Anovitz LM, Sheets JM, Cole DR, Welch SA, Rother G. Relationship between mineralogy and porosity in seals relevant to geologic CO2 sequestration. Environ Geosci 2014;21(2):39–57. https://doi.org/10.1306/eg.03031413012.
- [55] Teklu TW., Park D, Jung H, Amini K, Abass H., Effect of Dilute Acid on Hydraulic Fracturing of Carbonate Rich Shales – Experimental Study. Paper presented at the SPE Liquids-Rich Basins Conference – North America, 2017, Midland, Texas, USA.
- [56] Tissot BP, Welte DH. Petroleum Formation and Occurrence. Berlin, Germany: Springer-Verlag; 1984. (Vol. Second Revised and Enlarged Edition).
- [57] U.S. Energy Information Administration (EIA). Updates to the EIA Eagle Ford Play Maps. US Energy Information Administration; 2015.
- [58] Wang Z, Stout SA, Fingas M. Forensic fingerprinting of biomarkers for oil spill characterization and source identification. Environ Forensics 2006;7(2):105–46.
- [59] Wood DA, Hazra B. Characterization of organic-rich shales for petroleum exploration & exploitation: a review-Part 1: bulk properties, multi-scale geometry and gas adsorption. J Earth Sci 2017;28(5):739–57.
- [60] Yaws CL. Yaws' Thermophysical Properties of Chemicals and Hydrocarbons. Knovel; 2009.
- [61] Zhang F, Ilavsky J, Long GG, Quintana JP, Allen AJ, Jemian PR. Glassy carbon as an absolute intensity calibration standard for small-angle scattering. Metall Mat Trans A 2010;41(5):1151–8.
- [62] Zhang Y. Interior-Point Gradient Methods with Diagonal-Scalings for Simple-Bound Constrained Optimization: CAAM Technical Report TR04-06. Rice University; 2004.
- [63] Zhusheng J, Fowler M, Lewis C, Philp R. Polycyclic alkanes in a biodegraded oil from the Kelamayi oilfield, northwestern China. Org Geochem 1990;15(1):35–46.