

Solvent-pore interactions in Eagle Ford shale by ultra and small-angle neutron scattering

J. McFarlane,¹ L. M. Anovitz,¹ V. H. DiStefano,^{1,2} A. G. Stack,¹ E. Perfect,³ D. F. R. Mildner,⁴ M. Bleuel,⁴ S. J. Chipera,⁵ K. C. Littrell,¹ M. C. Cheshire,¹ and K. E. Manz²

The interaction of fluids with porous materials is of interest for many applications including extraction of hydrocarbons from shales. In the field, shale fracturing can be done with pressurized water, hydrocarbons, or gases, depending on the depth and mineralogy of the formation. Although the technology is mature, the process is not well understood, leading to inefficiencies in fluid usage during fracturing and decreases in hydrocarbon production over time. In this study, we examined the effect of organic solvents and acidic aqueous solutions on rock porosity using small and ultra-small angle neutron scattering (U)SANS. The extracted material was analyzed by gas chromatography-mass spectrometry (GC-MS) to determine if there is a correlation between the type of organic extracted, shale maturity, and how the extraction process affected porosity.

Chesapeake Energy Corporation provided six cores taken from the Eagle Ford Shale formation as shown in Figure 1 [1]. Five slices from each, cut perpendicularly to bedding to minimize variation, were soaked for ≈ 2 weeks in one of five solvents: toluene, cyclohexane, methanol, dichloromethane, or 0.01 mol/L HCl (pH = 2). Total ion chromatograms from GC-MS were used to quantify and compare the amount of organic matter extracted from each sample. Chromatograms of specific ion masses were used to identify classes of chemical compounds: linear alkanes by the mass/charge $m/z = 57$ for $C_4H_9^+$ and aromatic compounds by $m/z = 77$ for $C_6H_5^+$. Most of the hydrocarbons extracted were n-alkanes, (nC_{11} to nC_{31}), although significant amounts of branched alkanes and aromatics were observed. The molecular weight distribution of the extracted hydrocarbons changed with the solvent. Methanol mostly dissolved light alkanes and extracted the smallest overall amount of hydrocarbon because it has the lowest compatibility with the organic matter. The other organic solvents—dichloromethane, toluene, and cyclohexane—all extracted similar amounts of organic matter, although toluene and cyclohexane extracted more aromatics and dichloromethane extracted more branched alkanes. The only aqueous solvent tested, HCl, surprisingly extracted the longest alkane chains, possibly because physical dissolution of carbonate minerals liberated heavier organics. Lighter

hydrocarbons were not extracted with HCl, suggesting the acid could not penetrate the hydrophobic bitumen and kerogen. Overall, the amount of extracted material correlated with the amount of total organic carbon present.

The porosity of the shale samples in the 1 nm to 20 μm range was analyzed by (U)SANS. Porosity was determined assuming a two-phase system and that scattering primarily occurs at the pore/mineral interface [2]. Because neutron scattering length density (SLD) of organic matter declines with decreasing carbon-to-hydrogen ratios, empty pores and pores filled with alkanes contribute similarly to scattering [3]. More complex organic matter has increasingly larger SLDs, behaving more like the rock matrix. Hence, the apparent porosity determined by (U)SANS includes pores filled with alkanes and aromatics. It is clear from Figure 2 that most of the change in porosity, as well as the reduction in asymmetry, occurs at low maturities – in this case between about 0.56 and 0.77 – although the reduction in asymmetry is much less in clay-rich than in carbonate-rich samples. At higher maturities there is little observable trend in porosity with maturity [4].

The mineral composition of the shale plays an important role in the total porosity. We found a positive correlation between the total porosity and the percentage of clay, pyrite, and total organic carbon. The distribution of pore sizes was bimodal in all samples in the range examined, which is typical for shale. The number distribution of smaller diameter pores (maximum 3 nm to 7 nm) corresponds to the percentage of clays, in agreement with the literature [5]. There were far fewer larger pores but, volumetrically, they contribute a large fraction of the total porosity.

Significant changes were observed in the cumulative porosities of the shale samples after solvent contact. Total cumulative porosity decreased with extraction across all solvents for clay-rich samples (Figure 3), with the greatest decrease attributed to dichloromethane. Organic extraction in carbonate-rich samples increased total porosity in some samples and decreased it in others. A positive correlation between the amount of organic matter extracted and the initial sample porosity may indicate that initial pore accessibility can affect hydrocarbon extraction.

¹ Oak Ridge National Laboratory, Oak Ridge, TN 37830

² Bredeben Center, University of Tennessee, Knoxville, TN 37996

³ Department of Earth and Planetary Science, University of Tennessee, Knoxville, TN 37996

⁴ NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899

⁵ Chesapeake Energy, Oklahoma City, OK 73154

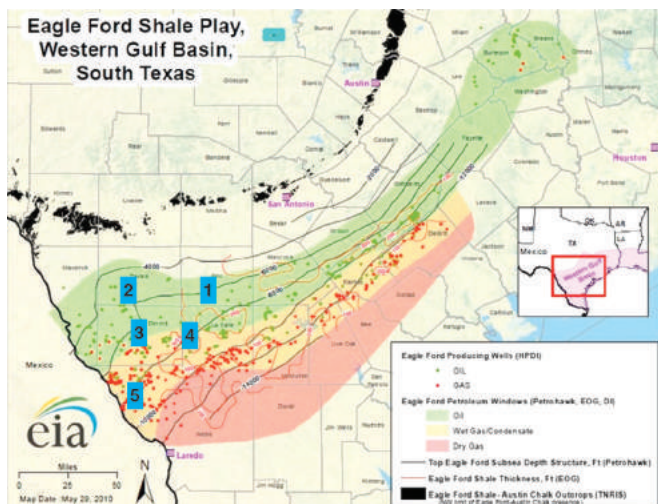


FIGURE 1: Collection sites for sample cores. (The underlying map was taken from the Energy Information Administration, www.eia.gov/maps/maps.htm, 9-30-2011.)

Solvent-pore interactions (solvent-clay or solvent-kerogen) were considered to see if they could explain the significant changes, primarily decreases, in porosity after extraction. The pore structure may be affected by a number of chemical and physical solvent/matrix interactions, including reactions between the clay mineral interfaces, trapped hydrocarbons, and solvents [6]. Smectite layers in clay minerals can expand by exchange of interlayer cations due to intercalation of water or other fluids [7]. Acids like HCl can provide a hydrogen ion for that exchange. To a lesser extent, organic solvents have also been demonstrated to expand clay layers [6]. However, by this mechanism HCl should have caused the greatest decrease in porosity from water intercalation and cation exchange and this was not observed, so a different mechanism caused the pore volume decrease.

Kerogen swelling may also have caused some of the pore volume changes. Kerogen is a complex polymeric material based on a lattice of polyaromatic hydrocarbons. It can swell extensively when immersed in organic solvents. Hence, the measured change in porosity from the solvent contact was compared to its solubility parameter. The largest effect was observed at 20 MPa^{0.5}, which is close to a previously reported solubility parameter of kerogen (19.43 MPa^{0.5}) [8]. This suggests that kerogen swelling was the likely cause of the porosity decrease. The decrease in porosity in the samples contacted with HCl was not adequately explained by either clay-layer expansion or kerogen swelling, but kerogen swelling may have been offset by carbonate dissolution.

This study had the goal of investigating changes in porosity as a consequence of the extraction of organic matter from shale minerals using organic and acidic solvents. (U)SANS measurements showed that mineralogy, rather than maturity, controlled the measured total porosity in these Eagle Ford shales. Porosity distributions and total porosity in extracted shale samples were compared to samples from the same formations that had not been contacted with fluids. There was

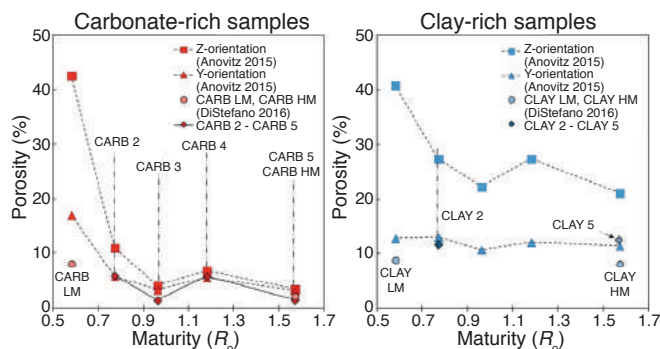


FIGURE 2: Porosity as a function of maturity, determined for carbonate- and clay-rich samples, with Y-orientation parallel to bedding, and Z-orientation perpendicular to bedding.

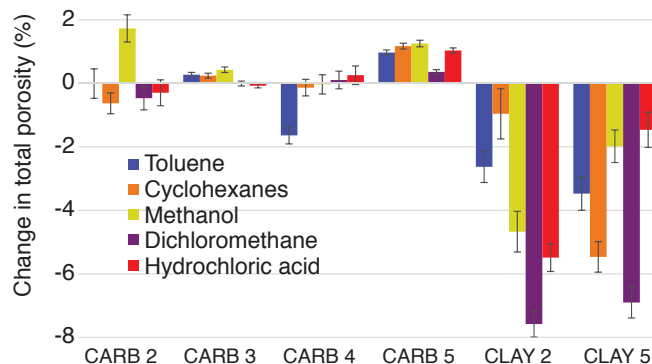


FIGURE 3: Effect of extraction of hydrocarbons on total porosity.

a positive correlation between initial porosity and the extraction of alkanes and aromatics, likely arising from the number and type of pores in the shale samples. A decrease in porosity with extraction is thought to have primarily arisen from kerogen swelling upon exposure to organic solvent(s). The extraction of hydrocarbons with exposure to HCl probably arose from the dissolution of carbonate minerals in the acid. These results contribute to our understanding of the fluid-rock interactions affecting the efficiency of oil and gas extraction.

References

- [1] V. H. DiStefano, et al., *Fuel* **238**, 298 (2018).
- [2] A. P. Radliński, *Rev. Mineral. Geochem., Neutron Scattering in Earth Sciences*, 363–397, (2006).
- [3] A. Radlinski, A. Hinde, *Neutron News*, **13**(2), (2002).
- [4] L. M. Anovitz, et al., *Interpretation*, **5**(3), SU59-SU70 (2015).
- [5] U. Kuila, et al., *Fuel*, **135**, 359 (2014).
- [6] M. Kowalska, H. Guler, D. L. Cocke, *Sci. Total Environ.* **141**, 223 (1994).
- [7] S. Aldridge, A. J. Downs, *The group 13 metals aluminum, gallium, indium and thallium: Chemical patterns and peculiarities*. John Wiley & Sons, (2011).
- [8] L. Ballice, *Fuel*, **82**(11), 1317 (2003).