the ENERGY lab

# E&P Focus

Fall 2015 Oil & Natural Gas Program Newsletter

NETL

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U.S. DEPARTMENT OF ENERGY

# Chemical Control of Fluid Flow and Contaminant Release in Shale Microfractures

Current tight gas and oil production technologies are estimated to recover less than 30% of natural gas and less than 5% of oil from unconventional shale reservoirs. The introduction of fracture fluids into shales has the potential to initiate myriad geochemical reactions that can oxidize inorganic and organic species, release toxic metals and radionuclides, weaken shales, and precipitate solids (e.g., iron hydroxides) that inhibit or block hydrocarbon migration and ultimately reduce production. For example, dissolved oxygen in fracture fluid is expected to oxidize pyrite (abundant in shales), releasing insoluble $Fe^{3+}$ and leading to the formation of iron hydroxides, which can accumulate as coatings as well as precipitates in necks between pores and occlude microfracture networks. Oxidation reactions also can release contaminants such as arsenic, selenium, mercury,

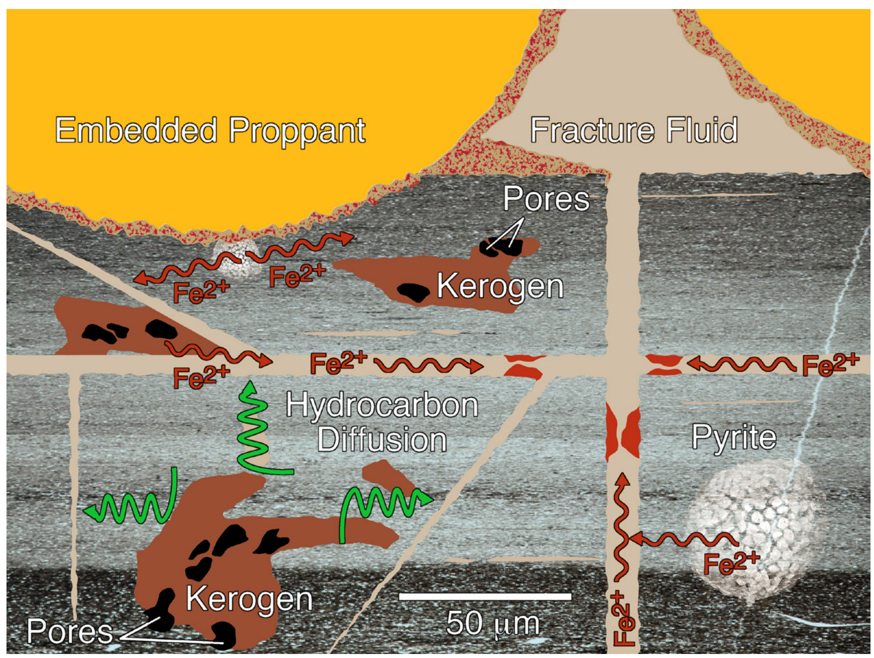


*Figure 1. Schematic illustration of pore- and fracture-scale geochemical processes that can cause formation damage in the altered zones proximal to propped fractures in hydraulically fractured shales. Green arrows illustrate transport of hydrocarbons and red arrows illustrate transport of Fe(II) ("$Fe^{2+}$" in the image) through the shale matrix and fracture network. During hydraulic fracturing, fracture fluids are imbibed into these fracture networks or driven in by strong hydraulic pressure gradients. Low pH conditions in fracture fluids can cause dissolution of Fe(II) from pyrite or other minerals including siderite, chlorite, and clays. Fracture fluids typically contain dissolved oxygen and organic components that react with this dissolved Fe(II) pool, causing oxidation and precipitation of Fe(III)-hydroxides (represented by red fracture fillings), which can clog the fracture network and block escape of hydrocarbons to propped fractures. Coatings on proppant grains are expected to contain aluminosilicates, carbonates, sulfates, and/or Fe(III)-hydroxides. Fracture fluid can also cause weakening of proppant and shale, resulting in proppant embedment, precipitation of minerals on proppant grains, and release of contaminants such as uranium to solution.*

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# Editor's Letter

## Understanding Subsurface Parameters

The last three decades have seen significant advances across the oil and gas exploration, drilling and production sectors. From deep and ultra-deep water enabling technologies to advanced fracturing technologies and capabilities, these advances, many funded by NETL, have allowed the country to once again become a key producer of oil and gas. Perhaps nowhere, however, has as much progress been made as in our understanding of subsurface parameters. Advanced seismic, downward looking VSP, cross-well tomography and electromagnetic imaging have allowed the industry to look at formations and reservoirs in a way, and with a resolution, never before possible. This, in turn, has spawned a new research emphasis on understanding the basics of subsurface mechanics.

NETL has, and continues, to fund research to increase subsurface understanding, from fluid flow in permeable environments to fracture generation mechanics to chemical interactions in various formation types. A number of these research projects, undertaken in conjunction with academic institutions and national laboratories, are detailed in this issue of E&P Focus. You can find full descriptions of each of these projects at http:/www.netl.doe.gov/research/oil-and-gas/project-summaries/enhanced-oil-recovery.

As always, we hope you enjoy the issue.

*The Editor*

and uranium into flowback water, creating the potential to introduce contamination into shallow groundwater aquifers and surfaces waters.

A fundamental challenge posed by fracture fluid-shale reactions is the formation of mineral precipitates and coatings inside of fine fracture networks, which has the potential to cause "formation damage", i.e., to reduce permeability and choke the supply of hydrocarbons to propped fractures that are fed by these fine-scale fracture networks (Figure 1). With the passage of time, coatings and fracture fillings are expected to become more abundant and permeability is expected to continually decrease. Although such processes are expected to occur and may constitute a first-order problem in unconventional oil and gas production, virtually no research has been done to examine, quantify, and predict them. There is a basic need to understand the geochemical reactions that occur when fracture fluids react with shale. Such knowledge is a prerequisite for improving long-term hydrocarbon production and efficiency, as well as minimizing environmental impact.

The research program being carried out by SLAC National Accelerator Laboratory is responding to this need. The team at SLAC, which includes several faculty and graduate students at Stanford University (see Research Team), is investigating the reaction of fracture fluids with economically important tight shales (Marcellus, Barnett, and Eagle Ford). The overall objectives of the program are to characterize products formed by the reaction of fracture fluids with whole shale and shale components (minerals and kerogen) and to assess the compositions and morphologies of coatings and aperture-clogging precipitates at spatial scales down to that of individual fracture coatings (i.e. nm level). The SLAC/Stanford team is studying shale-fracture fluid reaction products using synchrotron x-ray techniques to penetrate into rock and determine the 3D internal structures and mineralogical compositions over scales ranging from individual pores (tens to hundreds of nm) to fracture networks (hundreds of microns). Synchrotrons produce much higher intensity beams of x-rays that exhibit naturally low divergence as compared to most commonly available laboratory-based x-ray generators. Synchrotron x-rays also cover a wide range of energies, which contrasts to the narrow energy ranges available with laboratory x-ray sources. These synchrotron properties uniquely make it possible to combine imaging methods such as x-ray computed tomography (x-CT) with x-ray spectroscopy to map the 3D distributions of fluids, microfractures, pore spaces (isolated and connected), and minerals inside of rock at spatial resolution down to sub-100 nm. The SLAC team is combining these approaches with laboratory reactor studies, reactive transport modeling, and additional powerful analytical techniques including FIB-SEM (Focused Ion Beam Scanning Electron Microscopy) and surface-sensitive x-ray photoelectron spectroscopy, which can be used to identify low concentrations of surface phases. By integrating these approaches, it is possible to gather unprecedented 3D information on the internal pore structure and mineralogy of shales and how they change following reaction with fracture fluids. Information provided by these studies is feeding the development of geochemical models that will allow the researchers to quantitatively understand the coupling between chemical reactions and transport, and subsequently to predict the chemical evolution of hydraulically fractured shales over time. In addition, researchers will characterize the impact of fracture fluid-rock interactions on uranium mobilization from shales as a proxy for toxic redox-active trace metal and radionuclide mobilization. Knowledge gained from these studies will help hydrocarbon producers to improve well completion and management practices, improve hydrocarbon production, and reduce environmental impact.

One of the most important observations that has emerged from this work is that hydrochloric acid, often injected into shales in the initial stages of stimulation, liberates iron as Fe(II), which subsequently can be oxidized and precipitated as insoluble Fe(III)-hydroxides. The SLAC research program has shown that this process is accelerated by the abundant organic compounds present in fracture fluid such as kerosene and polyethylene glycol. Iron hydroxide precipitation is a concern because the particulates can clog fracture and pore apertures, leading to reductions in permeability. If present as reactive colloids, Fe(III)-hydroxides can be transported and accumulate elsewhere in the fracture system, contribute to near-wellbore clogging, and drive undesirable chemical reactions. This finding is being investigated in greater depth through studies of whole shale-fracture fluid interactions, geochemical reactive transport modeling, and synchrotron-based characterization activities.

**Whole shale-fracture fluid interactions:** This research thrust investigates the impact of fracture fluids on bulk shale samples with emphasis on alteration of shale surfaces and chemical factors contributing to Fe(II) oxidation. Economically important shales from different geological environments representing a wide range of clay, carbonate, and kerogen contents are reacted with simplified fracture fluids (containing the most common additives, including kerosene, guar gum, and polyethylene glycol) in batch reactors at reservoir-representative temperatures. The shales being evaluated include Marcellus, Eagle Ford, and Barnett. Changes in both fluid and solid compositions are tracked to gauge reaction progress and provide input to geochemical transport models. The SLAC/Stanford team is focusing in particular on iron oxidation reactions, which can be driven by multiple factors common in fracture fluid-shale systems, notably the presence of dissolved oxygen, changes in solution pH, and reaction of iron with organic additives.

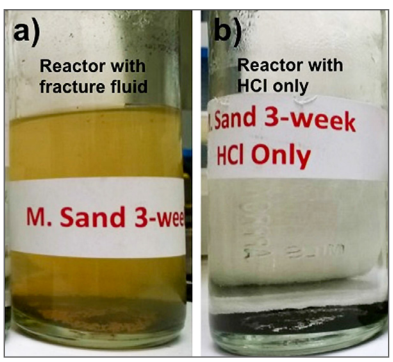
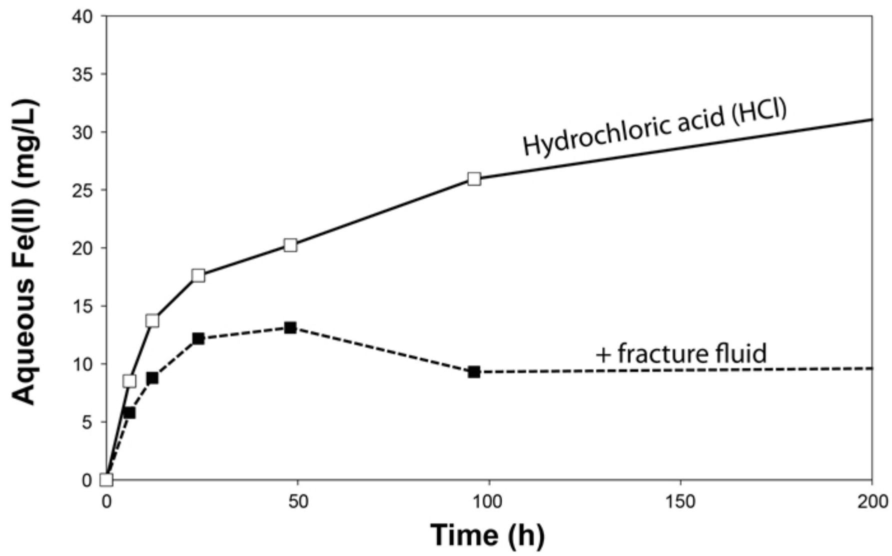



*Figure 2. Photograph of reactors with Marcellus shale after approximately two weeks of reaction with HCl and fracture fluid (a) and with HCl only (b). Note the presence of yellow Fe(III) hydroxide precipitates in the fracture fluid experiment, which indicates oxidation of Fe(II) to Fe(III).*

**Results.** Analysis of solution compositions is revealing that reaction progress is strongly dependent on both the initial shale and fluid compositions. In particular, the initial presence of HCl was observed to cause release of Fe(II) by dissolving pyrite, iron-rich clay minerals, and siderite in the shale matrix. Moreover, in the presence of typical organic components present in fracture fluids, dissolved Fe(II) was found to oxidize to insoluble Fe(III)-hydroxides, as indicated by the visual appearance of reddish-orange precipitates in suspension and coating reactor walls (Figure 2a). The total amount of Fe(II) dissolved in solution was sharply reduced in the presence of fracture fluid (Figure 3), consistent with oxidation and precipitation as Fe(III)-hydroxides. Synchrotron-based X-ray nano-computed tomography (nano-CT) measurements also show that Fe-rich coatings form on the surfaces of Marcellus shale following reaction with HCl (Figure 4). These observations suggest that reaction progress in fractured shales will depend on both lithology (susceptibility to dissolution and iron mineralogy) and the composition of the fracture fluid. In particular, the use of HCl is likely to induce the greatest changes in porosity and permeability by driving mineral dissolution, which increases porosity, and by facilitating greater Fe release. Fracture fluids that contain reactive organic compounds can then facilitate oxidation of the dissolved iron pool, forming Fe(III)-hydroxides and incurring increased risk for clogging of pore throats and fractures. Ongoing work is characterizing pore- and fracture-scale modifications to shale caused by these dissolution-precipitation. These changes will be correlated to measured induced variations in whole-rock permeability.

**Reactive transport modeling:** The research team is developing geochemical and reactive transport models to support 2-D and 3-D representations of fractured shale at pore and fracture scales in order to

Figure 3. Plot showing the dissolved concentrations of Fe from Marcellus shale as a function of reaction time with HCl (solid line) or HCl with fracture fluid (dashed line). In the presence of HCl, iron accumulates in solution in the form of dissolved Fe(II). However, in the presence of fracture fluid, which contains abundant organics, a significant fraction of Fe(II) is lost to oxidation and precipitation as Fe(III) hydroxides.




predict the evolution of shales over time following reaction with fracture fluids. Important processes incorporated into the model framework include redox reactions, uranium transformations, porosity-permeability changes, fluid migration, and transport of dissolved species. The SLAC team is presently developing and evaluating the model using the experimental data to support future work coupling transport and geochemical processes. Geochemical models also require that oxidative dissolution of Fe-bearing minerals is coupled with Fe(III)-hydroxide precipitation. Two key needs have been identified from model development: (i) better data are needed regarding mineral dissolution-precipitation kinetics in the presence of hydraulic fracturing fluids, particularly in the presence of organic-Fe(II)/Fe(III) reactions, and (ii) more knowledge is needed regarding the impact of Fe(II) oxidation and precipitation on shale porosity and permeability.

**Synchrotron techniques for investigating pore-scale geochemical reactions in shale:** An example of advanced synchrotron characterization of fracture fluid-reacted shales is provided in Figure 4. This technique known as x-ray nano-CT was performed at SLAC's Stanford Synchrotron Radiation Lightsource at beam line 6-2 using a full-field transmission x-ray microscope, which provides spatial resolution down to *ca* 30 nm, enabling nondestructive reconstruction and visualization of the 3D fine structures in shales. High x-ray fluxes provided by the synchrotron source allow such high-resolution data sets to be collected within minutes. Another unique and important feature of the synchrotron light source is the ability to vary the incident energy of the x-ray beam, making it far easier to image tracers such as bromide ion and krypton gas within shale matrices. Energy tunability also makes it possible to collect compositional and speciation information on metals, such as iron, in order to investigate the spatial distribution of iron oxide precipitates and identify chemical compositions within 3-D matrices. As shown in Figure 3, the nano-CT images provide renderings of kerogenic pore networks and pyrite framboids. The images also disclose the presence of Fe(III)-hydroxide precipitates, indicated by a thin bright coating on the external surfaces of the reacted shale. The SLAC/Stanford team is using this capability to help map out pore and fracture networks in shales, an important step for developing the pore-scale models, and to measure transport of tracers in real-time to determine parameters such as diffusivity.

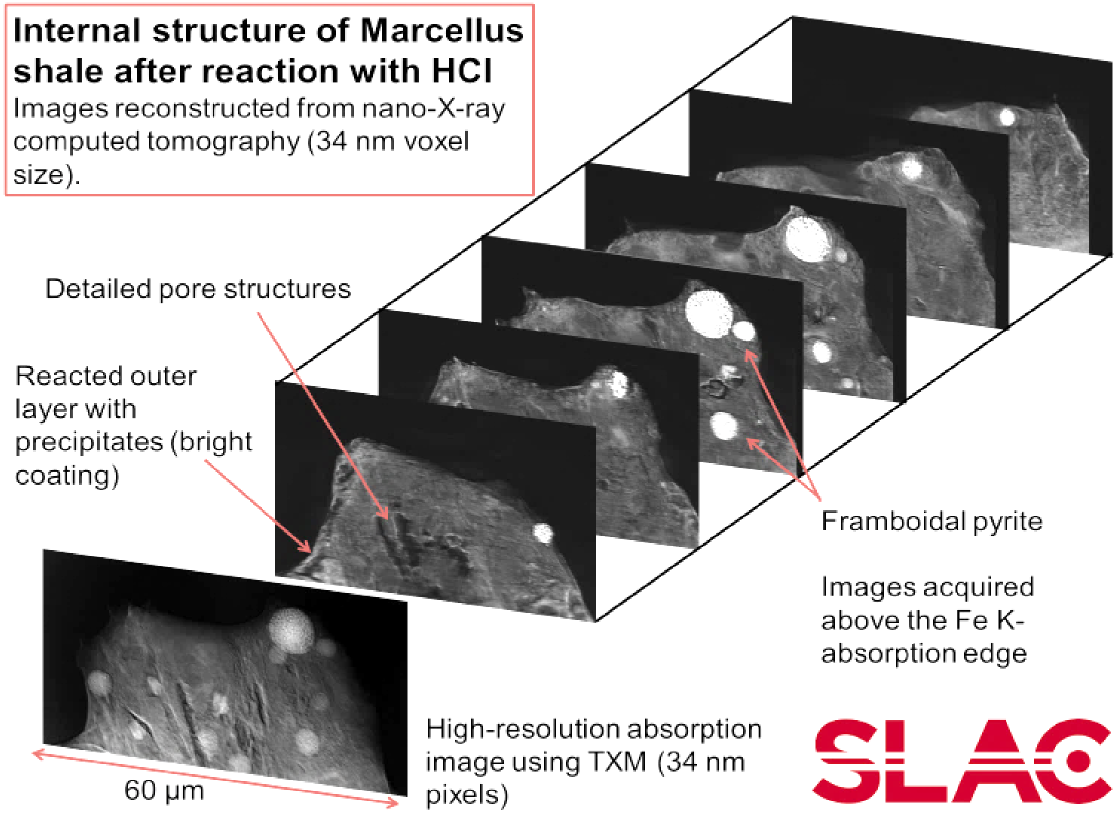



*Figure 4. Nano x-ray computed tomographic (CT) slice reconstructions of different elevations through a piece of Marcellus shale following reaction with HCl.*

For additional information on this project please contact David Cercone at NETL (david.cercone@netl.doe.gov or 412-386-6571) or John Bargar at SLAC (bargar@slac.stanford.edu or 650-234-9919).

**Summary.** Shales are chemically rich, reactive, and dynamic systems. They are electron rich, i.e. they contain elements and solids that are highly reduced, such as iron sulfides. In contrast, fracture fluids contain oxidants and organics that can interact strongly with species such as iron, as well as low-pH water (HCl). Introduction of these fluids into the rock matrix initiates suites of geochemical reactions that can ultimately decrease permeability and shut down hydrocarbon production. Iron seems to be particularly vulnerable to dissolution, oxidation, and precipitation. Experiments, analyses, and modeling by the SLAC/Stanford will provide valuable knowledge of these important processes, their evolution with time, and their impact on shale permeability.

**Research Team.** This project is being led by Dr. John Bargar (SLAC) and Prof. Gordon Brown (SLAC/Stanford), experts in mineral-water interface geochemistry and synchrotron spectroscopy techniques, Prof. Kate Maher (Stanford), an expert in uranium isotope geochemistry and reactive transport modeling, and Prof. Mark Zoback (Stanford), an expert on rock mechanics. SLAC postdocs Anna Harrison and Adam Jew are leading the experimental research. The NETL-funded program is leveraged by a SLAC Laboratory Directed Research and Development grant focused on developing x-ray nano- and micro-CT techniques to measure pore- and fracture-scale changes in shale, co-led by Dr. Yijin Liu (SLAC), an expert on synchrotron x-ray imaging. The LDRD project supports postdocs Andrew Kiss and Arjun Kohli. Additional input for this project is provided by Prof. Sally Benson (Stanford), an expert on carbon capture and sequestration; and Prof. Anthony Kovscek (Stanford), an expert on fluid flow in fractured media and 3D CT imaging of fractured rocks. This work is also leveraged by the participation of several Stanford graduate students who are helping with characterization studies, including Megan Dustin, Claresta Joe-Wong, and Dana Thomas.

# Laboratory and Numerical Investigation of Hydraulic Fracture Propagation and Permeability Evolution in Heterogeneous and Anisotropic Shale

For more information about this project, please contact Stephen Henry at NETL (stephen.henry@netl.doe.gov or 304-285-2083) or Seiji Nakagawa at Lawrence Berkeley National Laboratory (snakagawa@lbl.gov or 510-486-7894).

The overall goal of this project undertaken by Lawrence Berkeley National Laboratory (LBNL) is to understand the relationships between initial rock heterogeneity, such as natural fractures, grain inclusions, and anisotropy, and the dynamic propagation properties and static mechanical and hydrological properties of hydraulic fractures in shales. Researchers will use a combination of high resolution visualization experiments in the laboratory and coupled mechanical-hydrological simulations of the discrete fracturing processes.

The increase in oil and gas production from organic-rich shales has generated significant interest by the oil and gas industry and academia regarding the interaction between hydraulic fractures and heterogeneities in the rock. Laboratory investigations of fracture heterogeneities usually concentrate on the interactions between a single propagating fracture and preexisting fractures and discontinuities. This is largely because the scale of heterogeneities in shale that affect the overall geometry of hydraulic fractures requires rock samples that are much larger than standard geomechanical test cores, which are typically only several inches in size. Also, the behavior of hydraulic fractures is dominated by the stress anisotropy; the heavy, metallic coreholder required for core samples restricts observations through physical methods. Recent numerical modeling efforts to investigate the effect of preexisting fractures on hydraulic propagation have shown that interactions between preexisting fractures and weak interfaces result in a complex fracture network. Although numerical simulations indicate the significant impact of rock heterogeneity and anisotropy on hydraulic fracture propagation, detailed quantitative observations of complex fracture network development in the field and the laboratory have not been realized. Laboratory experiments that can provide quantitative, high-resolution images of the evolution of fracture geometry during fluid injection must be conducted in order to investigate the fundamental processes of the interaction between rock heterogeneity/anisotropy and hydraulic fracturing. This information will provide insight into the development of complex fractures and fracture networks. In addition, the experimental results need to be interpreted using an efficient numerical method for solving coupled geomechanical-hydrological problems. The model must be capable of modeling propagation of fractures with a sufficient degree of meshing freedom to accommodate the quickly evolving fracture geometry.

## Impact

Understanding how hydraulic fractures propagate in complex, anisotropic, and heterogeneous shale can help optimize fracturing operations in the field and subsequent oil and gas production. This will lead to (1) a reduction in the number of oil and gas wells required to develop the field; (2) a reduction in the total volume of fracturing fluid injected; and (3) mitigation of unexpected fracture propagation, which may cause a seal rock breach and/or fault activation.

## Accomplishments

The LBNL researchers prepared a polyaxial loading frame for optical visualization and a triaxial pressure vessel for X-ray CT visualization. An existing triaxial pressure vessel was modified with redesigned and fabricated platens that are 50% thicker to accommodate high-elastic-moduli test materials (e.g., glass, shale) used in the current experiments. This vessel was pressure tested and CT imaged with a mock sample to confirm experimental readiness.

Initially planned methods of producing synthetic fractured samples containing preexisting fractures were found to be unreliable and difficult to control fracture properties. Therefore, two alternate methods were developed: (1) fractures in quartz-rich polycrystalline rocks and analogue samples (glass blocks) are thermally produced by leveraging the differential thermal expansion between mineral grains and the rapid thermal shrinkage of heated glass and (2) fractures in synthetic/analogue samples are created by a laser engraving method in which designed fracture geometry can be reproduced and fracture strength can be altered by varying crack engraving density. Using the described methods, experimental samples have been prepared with multiple fracture densities and geometries (Figure 1).

Using the synthetic fractured samples, preliminary hydraulic fracturing experiments were conducted. For the experiments with X-ray CT imaging using a medical CT scanner, however, the induced fractures could not be imaged with sufficient clarity, in spite of heavy-density, liquid metal being used as the fracturing fluid. In contrast, optical visualization experiments using the polyaxial frame successfully produced images of hydraulic fractures generated in transparent samples (Figure 2). In both experiments, visualization of rapidly growing hydraulic fractures was very difficult when

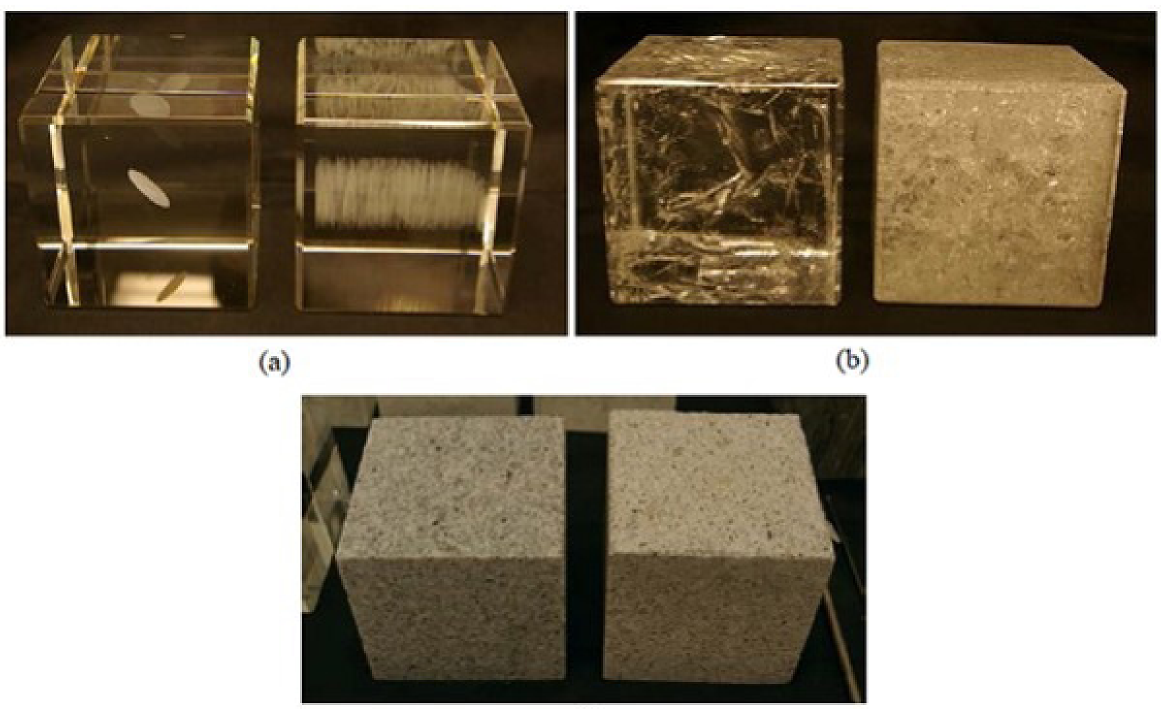
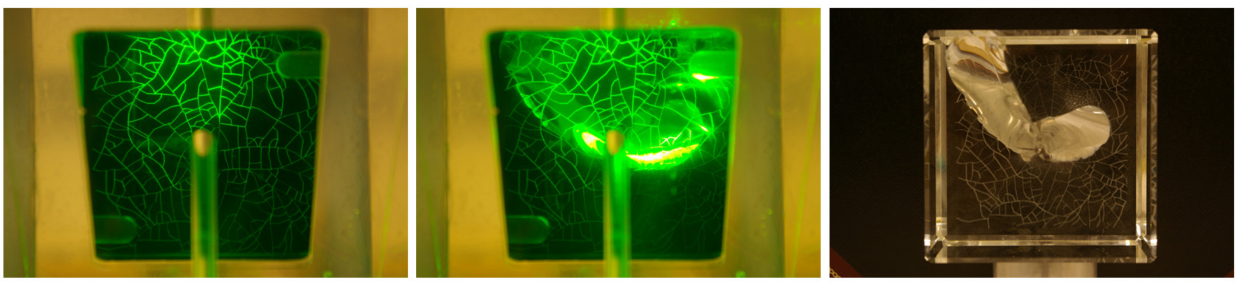



*Figure 1. Analogue/rock samples prepared using the following techniques for producing preexisting fractures: (a) 3D laser engraved fractures, (b) Thermal-shrinkage-induced fractures, and (c) Phase-transition-induced cracks in granite (block on the right was heated above the α–β quartz transition point)*

low-viscosity fluid was used as the fracturing fluid. This problem was solved by (1) developing a low-compressibility, low-flow rate fluid injection system, (2) using liquid metal as driving fluid, and (3) pre-fracturing the borehole wall, which involved a technique for introducing small, stable cracks before the fluid injection. The resulting, reduced fracture growth rate observed in the laboratory (Figure 3) was also reproduced by numerical simulations.

The TOUGH-RBSN code was modified and tested for hydraulic fracturing in complex fractured rock. The elastic and strength anisotropy algorithms were tested and verified for modeling of laboratory scale samples under compression. The code modification and testing for modeling existing fractures subjected to compressive stresses was also completed. Subsequently, the numerical code was tested for fluid-driven fracture propagation of a single fracture. Modeling sensitivity analyses was completed to determine input parameters for future modeling experiments. A number of model grids were set up to represent the exact heterogeneity features of the 3D-laser engraved synthetic samples (Figure 4). Initial simulations of the synthetic samples were completed using expected anisotropic confining stress and injection rates. Preliminary



a) Before b) After c) Fractured sample

*Figure 2. Hydraulic fractures and their optical visualization. Synthetic fractured rock model (c) was hydraulically fractured while the growth of the fractures were visualized optically. The images of the fractures illuminated by laser (green light) are reflected and can be viewed in a diagonal mirror embedded in a transparent block on top of the sample (a,b).*

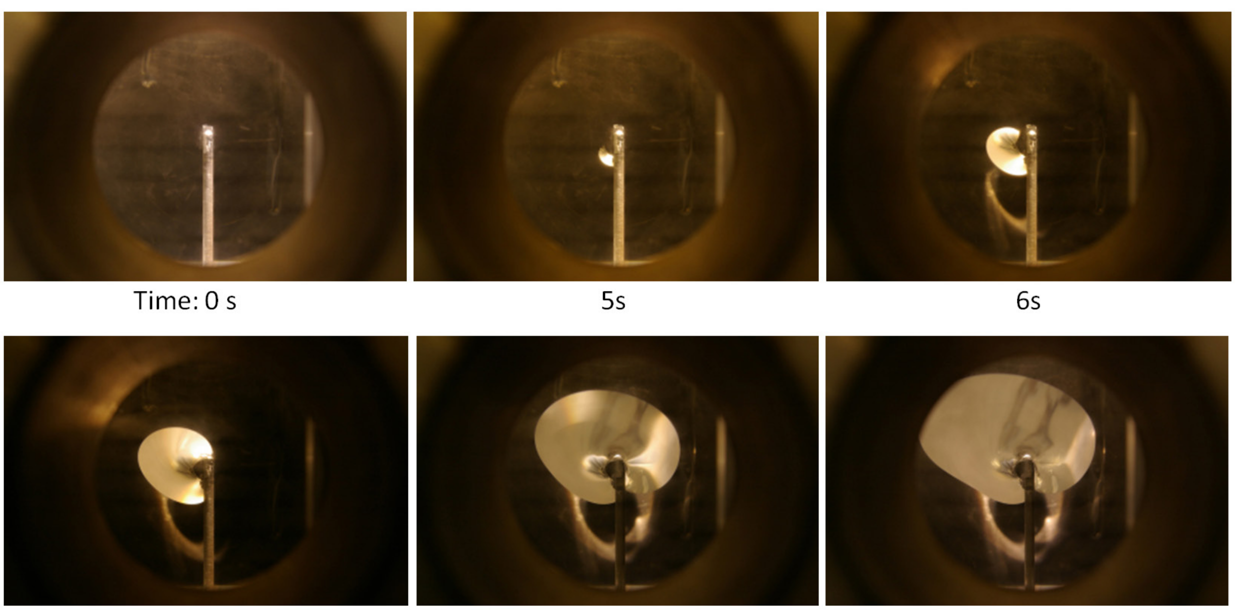


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*Figure 3. Reduced-growth-rate hydraulic fracture propagation from small initial flaws within a homogeneous glass cube. The reduction of the propagation speed allowed time-lapse imaging of the fracture growth. The size of the port hole is ~2 inches.*

results indicate hydraulic fracturing occurs in preferred directions due to the anisotropic stress conditions and the degraded mechanical properties of the pre-existing fracture network. Additionally, the numerical simulations successfully reproduced the laboratory-observed changes in the fracture growth rate occuring due to initial flaws around the borehole wall, increasing the confidence in the capability of the numerical model to simulate laboratory experiments (Figure 5).

## Current Status

Laboratory work is ongoing to investigate the impact of different fluid injection rates and viscosities on the interaction of the induced fractures and the preexisting fractures. Although X-ray CT has not been able to image fractures in glass blocks successfully, more experiments are being prepared using real rocks (granite, shale) which are less brittle than glass and therefore would result in thicker fractures that are more visible to X rays. Modeling work is also ongoing, focusing on interpretive modeling of laboratory experiments, field scale model preparation, and simulation of the Mont Terri hydraulic fracturing experiment.

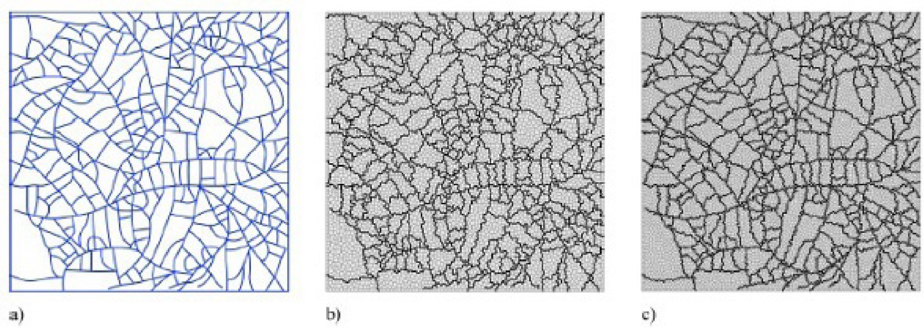
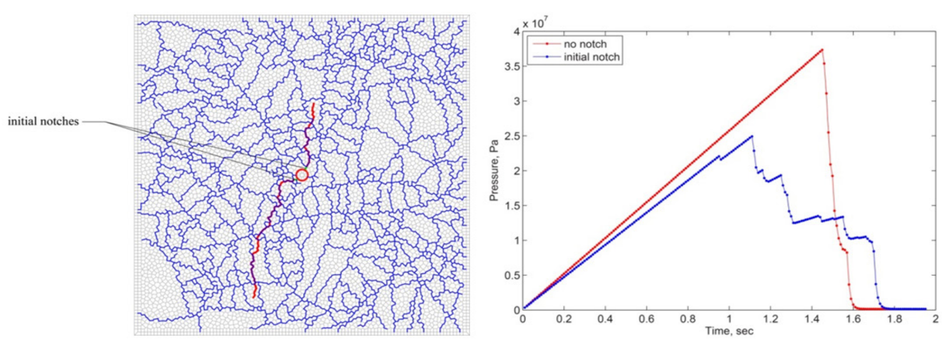
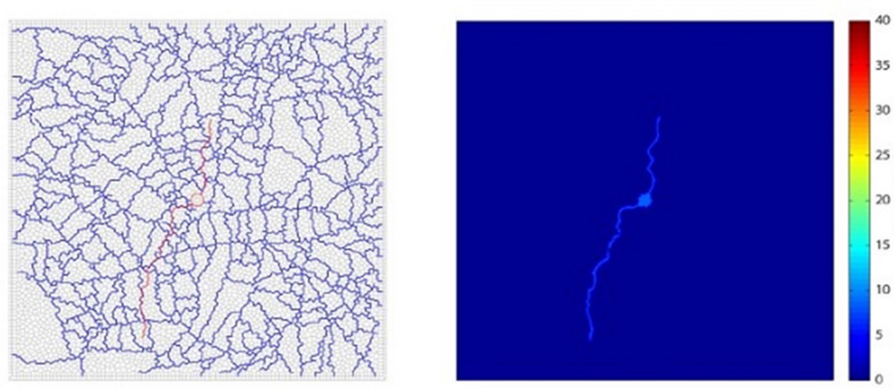



*Figure 4. a) Discrete fracture network of a glass samples; and mapping of the fracture geometry onto unstructured Voronoi grids with different mesh density: b) 5000 cells and c) 10000 cells, approximately.*




a) Geometry of hyraulic fractures

b) Pressure-time histroy of hydraulic fracture growth




a)

b)

*Figure 5. Hydraulic fracturing simulation using discrete fracture network of the 3D laser engraved analogue samples. Hydraulic fracturing mostly follows the pre-existing fractures, starting from the initial flaws around a borehole and propagating in the maximum principle stress direction (a). Comparison to the case without these flaws show reduced breakdown pressure and propagation speed (b).*

# Probing Hydrocarbon Fluid Behavior in Nanoporous Formations to Maximize Unconventional Oil/Gas Recovery

For addition information on this project, please contact Adam Tew at NETL (adam.tew@netl.doe.gov or 304-285-5409) or Hongwu Xu at Los Alamos National Laboratory (hxu@lanl.gov or 505-665-9266).

The overarching objective of this project is to gain fundamental understanding of the fluid phase behavior and flow properties in nanoporous shale formations. Hydrocarbon fluids, as well as water (the primary component of fracking fluids), exhibit significantly different behavior in unconventional reservoirs due to nanopore confinement effects and complex, heterogeneous fluid-rock interactions. The traditional, continuum models used for describing fluid behavior and for developing production strategies for conventional reservoirs are inadequate for shale and other tight formations. Hence, acquiring new knowledge of fluid flow properties and phase behavior in nanoporous media is essential for developing effective strategies to enhance the ultimate oil/gas recovery from unconventional reservoirs.

Researchers at Los Alamos National Laboratory (LANL) employ an integrated experimental and numerical approach to investigate fluid behavior and fluid-solid interactions in nanoporous media. Experimentally, they characterize the compositions and microstructures of oil- and gas-rich shale samples using a suite of analytical techniques. Small-angle neutron scattering (SANS), combined with custom-designed high-pressure cells, are used to examine in situ the fluid behavior and related changes in nanopores at reservoir pressure (P) and temperature (T) conditions. The Lattice Boltzmann method (LBM) is utilized to develop physics-based relationships between permeability, nanopore structure, and flow conditions examined by experiments.

## Background

Although shale oil/gas production in the US has increased exponentially, its low recovery (less than 10 percent for oil and 30 percent for gas in recovery rates) is a daunting problem that needs to be solved for continued growth. A prerequisite for mitigation of the low oil/gas recovery rates is to gain a better understanding of the fluid behavior in shale nanopores. This information is critical for estimating effective permeability of tight rocks, assessing potential for multi-phase flow, and optimizing operational parameters such as well spacing, bottom hole pressures and pumping rate, to maximize hydrocarbon recovery. Predictive models based on the new knowledge of nanopore fluid behavior are required to realize this goal.

LANL combines experimental characterization and observation with pore-scale modeling in this project. Integration between laboratory measurements and numerical calculations facilitates the understanding of nanoscale fluid behavior and development of effective predictive relationships that can be ultimately used to design better production approaches. Previous integrated experimental/modeling studies have been scarce and have focused on description of nanopore topologies and connectivities at ambient conditions. The integration of SANS measurements with LBM modeling is the first-of-its-kind in examining nanoscale fluid behavior at reservoir P-T conditions.

This project consists of two phases, each lasting nine months. In phase 1, LANL characterized the compositions and microstructures of an oil-rich shale sample using various analytical techniques, measured shale nanopores and their interactions with fluids (water and hydrocarbon) as a function of P-T using SANS, and simulated single-phase hydrocarbon transport behavior with LBM.

In phase 2, LANL will characterize a gas-rich shale sample, complete analyses of obtained SANS data, and examine the fluid flow behavior in nanoporous shales under in-situ loading conditions with SANS. LBM modeling will be extended to simulate hydrocarbon phase change and multiphase flow, and integrated with the experiments (Figure 1).

## Impact

This project will lead to a fundamental understanding of the fluid phase behavior and flow properties in nanoporous shale formations. More specifically, successful completion of both the experimental and modeling tasks on fluid behavior, nanopore characterization and fluid-nanopore interactions will provide important insights into the fundamental mechanisms underlying shale matrix diffusion and will ultimately help develop effective strategies for long-term unconventional oil/gas production.

## Accomplishments

LANL acquired a Wolfcamp core sample from Chevron (an industrial partner) and characterized the sample using a variety of analytical methods including quantitative X-ray diffraction, X-ray fluorescence, differential scanning calorimetry/thermogravimetry, and scanning electron microscopy (SEM) coupled with the focused ion beam (FIB) technique. The results reveal that the core is made of organic-matter (OM)-rich and OM-lean layers that exhibit different chemical and mineral compositions, and microstructural characteristics.

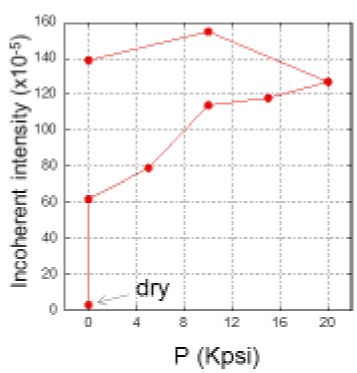
Using the custom-built hydrostatic pressure system and gas-mixing setup, LANL researchers conducted several sets of in-situ, high-pressure SANS experiments at pressures up to 20 kpsi with water and methane as the pressure media. Initial data processing has been completed, and further analyses are ongoing.

LANL researchers performed the first numerical study to calculate the correction factor (ratio of apparent permeability to intrinsic permeability) for complex kerogen nanoporous structures using LBM. The results show that the correction factor is always greater than one, indicating that the non-Darcy effects play an important role in the gas flow in kerogen nanopores. In addition, the correction factor increases with decreasing pore size, intrinsic permeability and pressure, which is in good agreement with the nanopore Knudsen correction.

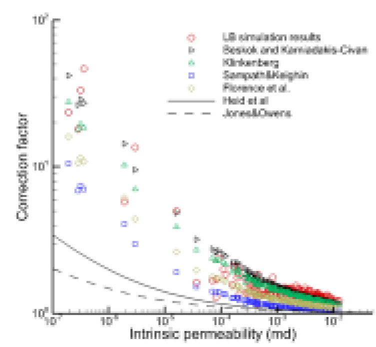
## Current Status

For comparison with the above studied, oil-rich, Wolfcamp sample, a gas-rich shale sample from Marcellus formation will be characterized. In particular, to directly image the nanopore structures, FIB/SEM/TEM (transmission electron microscopy) will be performed. To examine fluid flow behavior under uniaxial strain conditions, an oedometer will be designed and fabricated, and in-situ SANS measurements will be carried out. LBM modeling will be conducted to determine the effect of methane sorption on flow behavior (continuation of the ongoing modeling task) and to simulate the hydrocarbon phase change and multiphase flow behavior at reservoir conditions.

*Figure 1. Shale nanopores and their interactions with fluids (water and hydrocarbon) as a function of P-T using SANS, and simulated single-phase hydrocarbon transport behavior with LBM*




High-pressure SANS measurements of a Wolfcamp shale sample with water as the pressure medium: With increasing pressure, more water filled into shale nanopores (the water content scales with the incoherent neutron scattering intensity). Upon decreasing pressure, water remained in the nanopores.




LBM simulations of methane now in a reconstructed kerogen nanostructure: With decreasing the intrinsic permeability, the correction factor, which is the ratio of the apparent permeability to the intrinsic permeability and reflects nanopore confinement effect, increases dramatically. Our numerical results (red circles) are in good agreement with earlier empirical studies (other symbols).

# Petrophysics and Tight Rock Characterization for the Application of Improved Stimulation and Production Technology in Shale

To assist the characterization and development of shale reservoirs, Oklahoma State University is leading a two-year study called "Petrophysics and Tight Rock Characterization for the Application of Improved Stimulation and Production Technology in Shale." Partners in this research include the Geological Survey of Alabama and the University of Alabama at Birmingham. This research program is designed to improve understanding of how stimulation fluids and additives interact with shale matrix. Achieving this goal requires a fundamental understanding of petrology, petrophysics, and fluid-rock interactions. The project is designed to find ways to minimize formation damage caused by fracturing fluids, improve the effectiveness of hydraulic fracturing, and decrease the need for refracturing.

This study focuses on Paleozoic shale formations (Figure 1) and employs a systematic, multidisciplinary workflow that begins with the geologic and petrologic characterization of cores. The workflow employs a broad range of petrologic and petrophysical techniques that are directed at

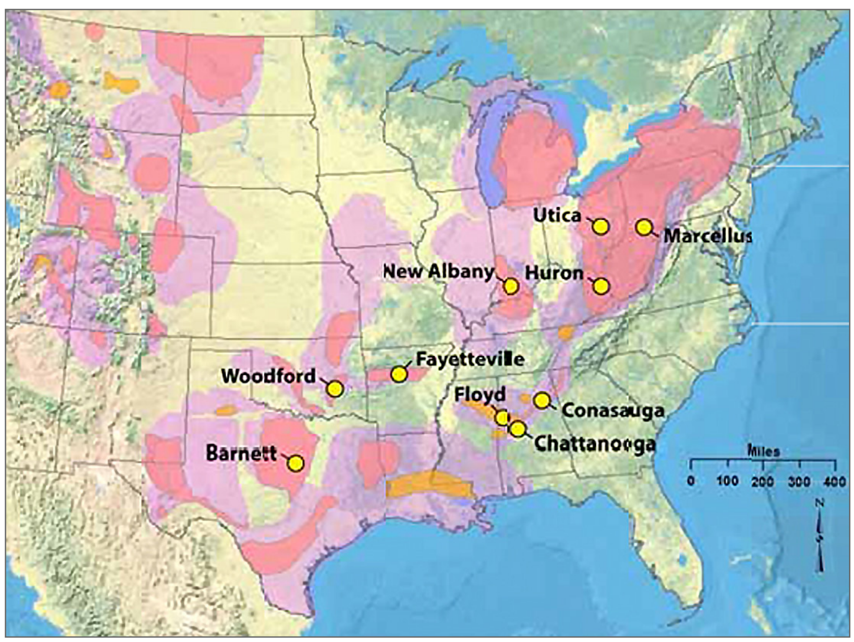



*Figure 1. Map of major Paleozoic shale plays in the Eastern and Southern. U.S. Yellow circles highlight areas that will be targeted for study in the project.*

understanding the fabric and pore structure of shale, how fluids move through shale, and how fluids react with shale. Petrophysical techniques to be employed include porosimetry, permeametry, and adsorption research. An important objective is to propose analytical standards for petrophysical characterization of shale, as well as new methods that can reduce cost and increase the reproducibility and reliability of analytical results. Investigation of fluid-rock interactions will be conducted under reservoir conditions using experimental techniques designed to establish protocols for laboratory testing and the evaluation and screening of stimulation fluids and additives. This research is intended to benefit operations in active shale plays by lowering risk and uncertainty, thereby bringing emerging and marginal plays to market, which will be required for the natural gas industry to meet long-term production forecasts and market demand.

As part of a RPSEA-funded program focusing on shale gas exploration, Pashin et al. (2011) developed a systematic workflow for the evaluation of shale formations that begins with stratigraphic and sedimentologic characterization, continues with characterization of structural geology, petrology, geochemistry, gas storage, and permeability, and concludes with estimation of resources and reserves. This new research focuses on petrology, geochemistry, gas storage, and permeability and is designed to develop a workflow that employs a battery of petrophysical and tight-rock characterization techniques.

The workflow (Figure 2) begins with the selection of cores and geological characterization. This step places the cores in geological context through basic description of rock types and sedimentary structures, facies modeling, and the development of stratigraphic and sedimentologic interpretations. Indeed, the composition, thickness, and continuity of shale formations were determined largely in the original depositional environment, and the quality of shale reservoirs can be related directly to transient redox conditions and sea-level changes in the host basin (e.g., Ettensohn, 1985; Schieber et al., 1998).

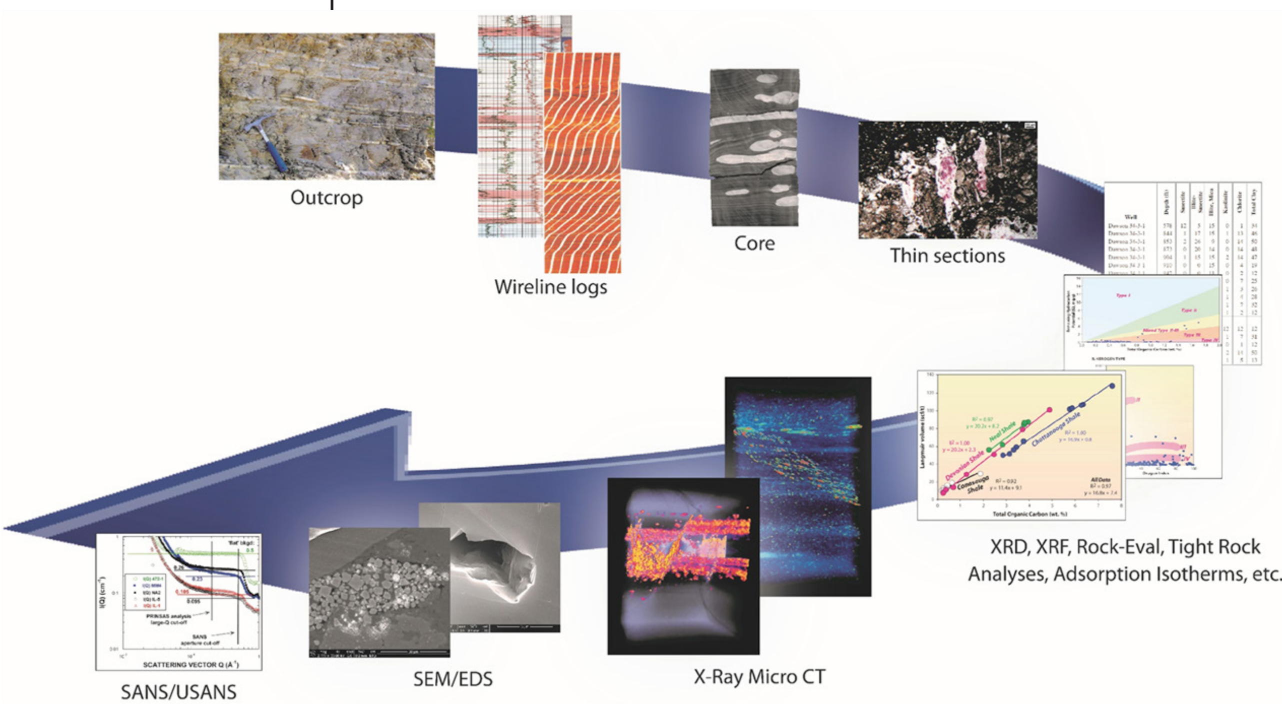



*Figure 2. Petrophysics and Tight Rock Characterization for the Application of Improved Stimulation and Production Technology in Shale Project work flow.*

**Specific objectives within the study are to:**

- Develop techniques, workflows and best practices for the petrologic and petrophysical characterization of shale;
- Propose analytical standards for porosity and permeability measurement in shale;

- Explore techniques to characterize shale microstructure; and,
- Develop techniques to rapidly evaluate stimulation fluids and additives.

The project included five major tasks. All but the final task, Fluid Evaluation and Optimization, have been completed, as listed in the table below.

| | |
|---|---|
| Task 4.0 Geological Characterization<br>Core selection and characterization<br>Geologic interpretation & modeling | Cores secured and analyzed:<br>Barnett-OSU; Woodford-OSU; Caney-OSU; Chattanooga-GSA,<br>Floyd-GSA; Lewis-GSA; Conasauga-GSA;<br>Parkwood-GSA; Wolfcamp-OSU |
| Task 5.0 Petrologic Characterization<br>Rock composition and authigenesis<br>Rock fabric and pore structure | Rock composition complete:<br>Woodford-OSU; Barnett-OSU;<br>Conasauga-GSA;<br>Fabric and pore structure ongoing |
| Task 6.0 Petrophysical Characterization<br>Porosity and permeability<br>Adsorption research (OSU) | Porosity and permeability measurements complete or in progress:<br>Woodford and Barnett-UAB<br>Adsorption tests complete:<br>New Albany - $CH_4$<br>Woodford - $CH_4$, $CO_2$, $N_2$<br>Caney – $CH_4$, $CO_2$, $N_2$ |
| Task 7.0 Fluid Rock Interaction | Ongoing fluid-rock studies:<br>Polymer-shale - OSU |
| Task 8.0 Fluid Evaluation and Optimization | Ongoing OSU |

**The list of specific accomplishments includes:**

- Core samples and bit cuttings from multiple basins were secured for Paleozoic shales including the Barnett, Caney, Chattanooga, Conasauga, Floyd, Lewis, New Albany, Parkwood, Wolfcamp and Woodford.
- Selected samples were characterized using a variety of methods including thin section petrography, SEM, XRF and XRD to determine authigenic components that influence reservoir properties.
- Gas-adsorption tests, nuclear- magnetic resonance imaging were used to establish the types of adsorbed compounds, permeability to single phase and multiphase fluids, and determine adsorption isotherms for selected samples.
- A function was fit to measurements of effective permeability versus pressure during determination of the minimum capillary displacement pressure of an unfractured brine-saturated mudstone having absolute permeability of 3 microdarcy.

For addition information about this project, please contact Skip Pratt at NETL (skip.pratt@netl.doe.gov or 304-285-4396) or Jim Puckette at Oklahoma State University (jim.puckette@okstate.edu or 405-744-6374).

- A method has been developed that can be used to test the strength of the interaction of friction reducers in fracturing fluids (polymers) and host shale using rheological techniques.
- Cell designed and constructed to measure, simultaneously, both the axial and radial permeabilities of a cylindrical core plug cut perpendicular to bedding.
- Characterized shales from 5 different regions based on their interaction with higher molecular weight anionic and cationic polyacrylamide from highly interacting to non-interacting shales.
- Micro x-ray Computed Tomogography (Micro CT) was used to characterize, fabric, composition, and microscale porosity and fracture networks in selected Paleozoic shale samples as well as identify areas for higher resolution scanning electron microscopy (SEM) analyses.
- A shale characterization workflow was developed that integrates investigations that range in scale from the outcrop and wireline well log scale to thin-section petrography, elemental analysis, maturity and adsorption determination, fluid-rock interaction, x-ray micro CT scanning, and scanning electron microscopy.
- A nuclear magnetic resonance (NMR) technique to estimate the ratio of bitumen to kerogen in shale was developed that is based on integrating results of cross-polarization magic angle spinning (CP-MAS) and direct polarization magic angle spinning (DP-MAS).
- Fracture aperture in shale was determined after corrections for inertial effects on gas flow and simplifying assumptions of low matrix porosity and smooth fracture walls. Correction for inertial effects resulted in good agreement of permeability measurements that were previously inconsistent.

# Understanding Basic Mechanisms in Natural Gas Production Using Reservoir-Scale Modeling

Production of natural gas and other hydrocarbons from unconventional sources involves hydraulic fracturing and horizontal drilling, to establish connectivity and increase the permeability. The current recovery rates are low with the production rapidly declining in the first couple of years. This inefficient extraction leads to drilling of multiple wells, which in turn increases the environmental footprint. The hypothesis is that there are several transport mechanisms that are responsible for hydrocarbon recovery, and a fundamental physics-based understanding of these mechanisms and the production curves will provide information on improving recovery efficiencies. The primary objective of this project is to develop a combined process-level and systems-level reservoir-scale modeling approach that will isolate the key process parameters and their influence on the production curve. This reservoir-scale modeling approach will be built on high-performance computing tools that have been developed at the U.S. Department of Energy (DOE) national laboratories.

## Background

Unconventional hydrocarbon reservoirs (e.g., tight shale) have naturally existing fractures with very low matrix permeability (nanodarcy). The discrete fracture network (DFN) approach, where fractures are modeled as two dimensional planes in three dimensional planes, is known to be an effective approach in characterizing such reservoirs, provided the fracture stochastics are known. The process-level part of the approach is based on dfnWorks, which is a workflow built on the DFN approach. This workflow involves: a DFN generator – dfnGen; meshing toolkit – LaGriT; flow simulator – PFLOTRAN (Figure 1); and a particle-tracking toolkit - dfnTrans. The challenge with this approach is characterizing fractures at smaller scale (damage) and other smaller scale processes such as matrix diffusion and desorption.

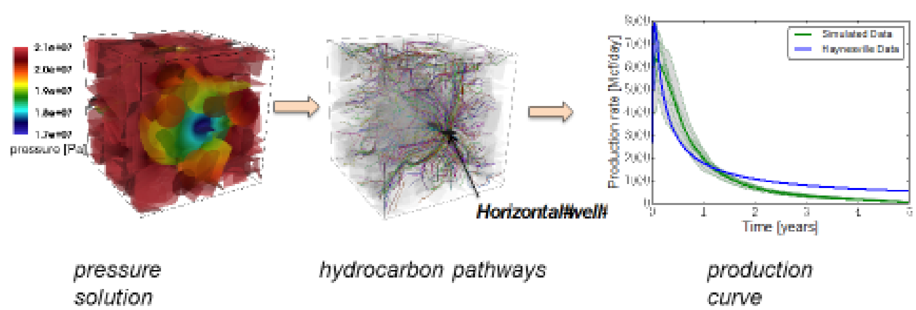



*Figure 1. (Left) Discrete frature network used in the work and the pressure solution computed using PFLOTRAN on the DFN. (Center) Transport pathlines of hydrocarbon packets represented by 1000 dynamically inert and indivisible tracer parcels (particles) traveling to the horizontal well. (Right) Comparison of the production curves produced pathlines for ten independent realizations. Shade gray area shows min and maximum values, and the thick green line is the average production rate. The maximum value of the production curves has been calibrated to the Haynesville production data from Moniz et al. 2011.*

Using the systems-level decision support toolkit (MADS) in the framework, the aim is to characterize these smaller scale phenomena using site data (geology, fractures) and production data from different sites (for instance, using data from our collaborator Apache Corp and from the Texas Railroad Commission). This approach can lead to multiple solutions for the process parameters when calibrating with the site production data. The results from the other two LANL projects (Experimental Study of In Situ Fracture Generation and Fluid Migration in Shale, Bill Cary, and Probing Hydrocarbon Fluid Behavior in Nanoporous Formations to Maximize Unconventional Oil/Gas Recovery, Hongwu Xu) will enable further constraining of some of these parameters (e.g., diffusion coefficient from Xu's project). Additionally, using the combined process-level and systems-level framework, the researchers will be able to perform sensitivity analysis and identify how the production curves depend on the transport process parameters.

### Impact

The tasks in place will help to identify and isolate the key process parameters, and analyze how the production curve depends on these parameters.

For additional information on this project, please contact Adam Tew at NETL (adam.tew@netl.doe.gov or 304-285-5409) or Satish Karra at Los Alamos National Laboratory (satkarra@lanl.gov or 505-606-1894).

### Accomplishments (most recent listed first)

The project consists of two phases, each lasting nine months. The first phase is focused on capability development: implementing the small scale processes into the flow simulator PFLOTRAN; implementing multi-phase flow for flow-blocking analysis; and implementing the systems-level decision support toolkit (MADS) into the overall framework with the process-level workflow (dfnWorks). Figure 1 illustrates the work flow for obtaining the production curve for a sample DFN. The second phase is focused on using the combined process-level and systems-level framework to perform calibration on the various site datasets (from literature, Apache Corp and Texas Railroad Commission), performing sensitivity analysis on the process parameters, identifying the key parameters and then summarizing recommendations for improving production efficiency.

The accomplishments to date are as follows:

- Project researchers have successfully implemented the various smaller-scale process mechanistic models in the flow simulator PFLOTRAN that is part of dfnWorks.
- The project team has successfully added the systems-level decision support toolkit (MADS) to the overall workflow. This gives a powerful tool for performing production curve analysis in Phase II.
- The team successfully implemented the methane-water equation of state in PFLOTRAN for performing multi-phase flow blocking analysis. Flow blocking is where the water injected in the fracturing phase can block the hydrocarbon from moving to the fracture pathways. They have applied the multi-phase flow for preliminary test cases and are currently working on applying the multi-phase flow implementation to the DFN reservoir domain (that was used for other processes).

### Current Status

In Phase I, the researchers incorporated the small scale processes damage due to small fractures, matrix diffusion, and desorption in PFLOTRAN and calculated the production curves for each process. In Phase II, researchers will calculate the combined production curves using the implemented process models. The models will then be calibrated with different field datasets (from literature e.g., Moniz et al. 2011, Apache Corp and Texas Railroad Commission). The calibration approach will help to characterize the small-scale processes. Particle tracking for water-hydrocarbon multi-phase flow will identify the paths of water packets and hydrocarbon packets, providing insights on the effect of flow blocking on the production curve.

Sensitivity analysis of the different process model parameters will be performed to identify the key parameters that influence the production curve.

Based on the calibration method and sensitivity analysis, the researchers will summarize their findings and provide recommendations for production efficiency improvement.

# Experimental Study of In Situ Fracture Generation and Fluid Migration in Shale

Hydraulic fracturing of unconventional oil and gas resources is inefficient, with recoveries at less than 15 percent. One of the limitations to improving efficiency is the lack of knowledge of the fundamental properties of the fracture network generated by hydraulic fracturing operations. In the field, the ability to observe fracture and flow consists mostly of microseismic data on the number and location of fracture events. As valuable as these data are in delimiting the location and extent of fracture clouds, they provide neither the resolution nor the detail required to provide an understanding of processes occurring in unconventional reservoirs. This project, undertaken by Los Alamos National Laboratory (LANL), will conduct experiments at reservoir conditions that provide fundamental insights into fracture growth, penetration, permeability, and surface area as essential components of developing methods of improving hydraulic fracturing performance in the field.

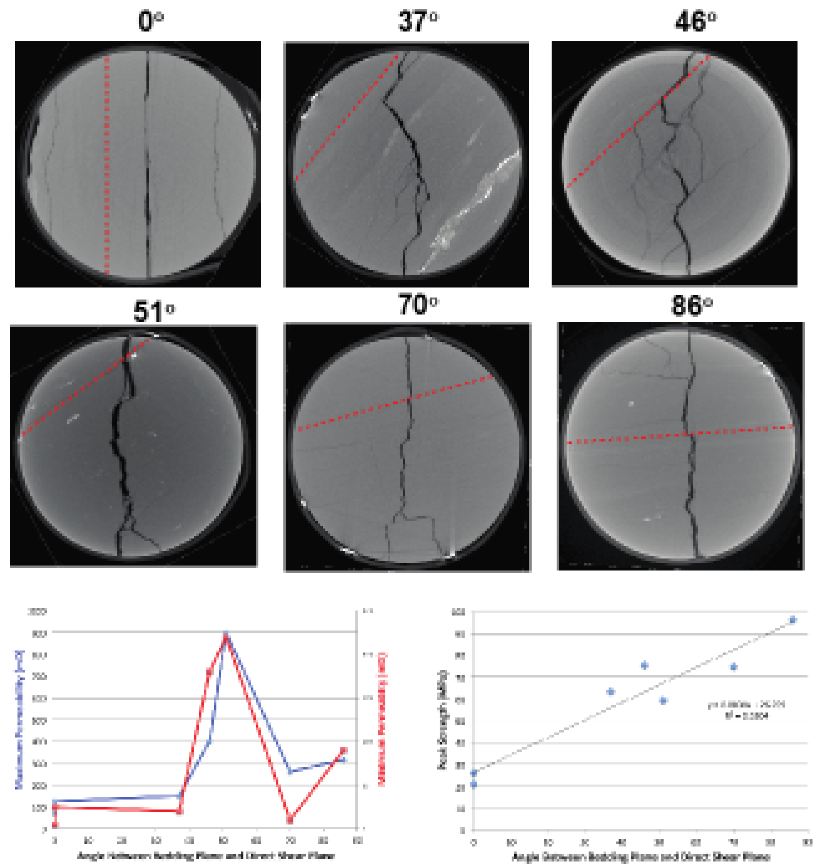
**Key objectives:**

- Conduct Fracture Property Analysis: In situ observation and characterization of fracture properties using integrated acoustic emission and x-ray tomography
- Determine Permeability of Fractures: In situ measurements of permeability on laboratory-generated hydraulic fractures in relation to acoustic emission and x-ray tomography
- Measure Fracture Surface Area: Measurement of fracture surface areas and comparison between geometric and reactive surface areas
- Characterize Fluid Penetration: Direct optical observations of fluid penetration of fracture networks in relation to surface area measurements

## Background

Experimental studies of fracture-permeability relations generated under in situ reservoir conditions are limited. Most studies of hydraulic fracturing have used triaxial devices to examine rock mechanics (stress-strain behavior) and acoustic emission associated with rock damage. Key features of hydraulic fracturing remain unexplored in these experimental studies. What are fracture properties (aperture and geometry) at reservoir conditions? How permeable are these fractures and how does permeability evolve with fluid flow and time? What is the surface area of fractures in relation to the amount of matrix and hydrocarbon that can easily diffuse into the fractures? How does the injected working fluid migrate into, and sweep hydrocarbon out of, the fracture system?

LANL will make use of unique experimental capabilities that include a triaxial coreflood system integrated with at-conditions x-ray tomography (Figure 1) and high-pressure microfluidics. These allow the research team to overcome limitations of earlier work by making direct observations at in situ conditions so that fractures are generated and characterized without changing the environment. This removes the ambiguity created by ex situ analyses where fracture properties may change following decompression (e.g., apertures may open or fractures may even be created). The research team uses these in situ observations to characterize fracture density, connectivity, surface areas, and permeability.




Fracture-permeability relations in shale: Fracture aperture and geometry changes as a function of the angle between the shear and bedding planes as shown by x-ray tomography. Permeability peaks at an angle near 45°, while strength increases linearly with angle. (Carey et al., 2015, Amer. Rock Mech. Assoc. Conf.)

*Figure 1. X-ray tomography of fracture permeability relations in shale.*

## Impact

This project will yield new insights into how applied stress, fluid pressure, and injection dynamics impact fracture penetration, apertures, and permeability. The project will correlate acoustic emission activity with tomographic observations of fracture growth to enhance field understanding of microseismic surveys. Finally, this study will yield basic understanding of how to effectively displace and mobilize hydrocarbon from complex fracture networks.

## Accomplishments

The first phase of the project focused on sample acquisition and characterization, fracture generation and characterization, and fracture permeability studies. LANL has made significant progress on these three subtasks and has notable insights involving the experimental study of fractured shale at reservoir conditions.

Subtask 1. Sample acquisition and characterization. Research partner Chesapeake Energy has supplied Utica shale core from the unconventional plays in Ohio and Pennsylvania. The researchers have data on the mineralogy, porosity, and organic carbon content of these samples. In addition, they have acquired Marcellus shale in outcrop through a collaboration with Dustin Crandall of the National Energy Technology Laboratory (NETL).

Subtask 2. Fracture characterization. LANL developed a novel technique for inducing hydraulic fractures in a triaxial device (Frash et al., submitted, Int. J. Rock Mechanics & Mining Sci.). Previous studies have required specialized equipment or sample geometries, but this approach works with conventional triaxial systems and allows permeability measurements of the fracture system. The researchers have conducted simultaneous fracturing of shale in a triaxial device while conducting x-ray tomography imaging, an experimental first that will be key to understanding in situ fracture properties. They have developed and implemented an acoustic emission system to monitor fracture development.

Subtask 3. Fracture permeability. Researchers have made numerous measurements of fracture permeability of Utica shale conducted in traditional compression experiments and using direct shear methods (Carey et al., 2015, J. Unconventional Oil & Gas Resources). These have provided detailed information on the effect of confining stress (or depth) and time on fracture permeability and evolution.

Subtask 5. Fracture Penetration. The researchers have conducted preliminary sweep efficiency experiments with a high-pressure microfluidics system to characterize hydrocarbon removal during water injection.

## Current Status

LANL will apply new capabilities discussed above to a larger suite of shale samples as they pursue the goal of developing a fundamental understanding of shale fracture processes.

For additional information about this project, please contact Adam Tew at NETL (adam.tew@netl.doe.gov or 304-285-5409) or Bill Carey (bcarey@lanl.gov or 505-667-5540).

# Understanding Water Controls on Shale Gas Mobilization into Fractures

The goal of this project, underway at Lawrence Berkeley National Laboratory (LBNL) is to understand and predict the dynamics of water-gas interactions within regions of unconventional shale reservoirs stimulated by water-based hydraulic fracturing fluids. Laboratory tests and modeling studies will be performed on gas shales under reservoir conditions. The knowledge gained through these efforts will contribute to the growing scientific basis for designing more effective hydraulic fracturing strategies that may ultimately maximize gas production while utilizing significantly less water.

The enabling technologies of horizontal drilling and hydraulic fracturing have proven effective in recovery of natural gas trapped within shales, facilitating rapid development of shale gas and tight gas reservoirs in the U.S. over the past decade. Although major advances have been made in modeling large-scale gas production from unconventional shale formations, understanding matrix processes and their interactions with fractures underlying reservoir productivity remains qualitative and limits confidence in long-term gas production predictions. The common problems of formation damage and water-blocking cannot be reliably predicted, with some wells being highly productive despite little water recovery while others have low productivity despite good fracture fluid recovery. Reservoir heterogeneities over many scales and complex nanopore structures have been investigated to a considerable extent, yet quantitative linkages to reservoir responses are unclear. The presence of water, both native and injected (as the main component in hydraulic fracturing fluids), greatly complicates gas transport over all scales of interest, from nanopores to reservoir scales. Despite the controlling role of water in shale gas production, surprisingly few direct measurements of the multiphase behavior of water and gas in unconventional reservoir rocks are currently available. Because of the scarcity of experimental data indicating relationships among water saturation, capillary (disjoining) pressure, and permeabilities (to both gas and water) in unconventional reservoirs, models still rely heavily on scaling-based extrapolations from more permeable media. Spatial variability of material properties, complexity of pore networks, kerogen distributions, and fracture distributions have become well-recognized factors affecting the flow of gas in tight reservoirs. While further investigation into complex systems and processes such as these will certainly lead to better predictions concerning unconventional shale reservoirs, note that water is a key factor in these issues as well. Moreover, unlike the inherent highly variable structural complexity of rock over multiple scales, water is a potentially controllable parameter in well field operations. However, control of water in unconventional reservoirs will first require a better understanding of the relationships between water and the rock matrix.

## Impact

Laboratory tests at reservoir conditions and close integration between laboratory and modeling studies will enable a critical quantitative understanding of the dynamic processes controlling gas flow from shale into fractures.

Anticipated key results include (a) determining how water block dissipation times depend on shale properties and amounts of water imbibition; (b) understanding the shale surface chemistry of wetting and reduction of gas permeability; and (c) determining the role of initial native pore water saturations in shales and in water block formation and dissipation.

## Accomplishments

Experimental work has been ongoing to characterize Woodford Shale samples from five separate sample locations. Total organic carbon (TOC), total inorganic carbon (TIC), X-ray diffraction (XRD), and water adsorption/desorption isotherm analyses have been completed. TOC values of the five samples range from 2.7 to 7.1% on a mass basis. One sample location (WH1) exhibited high TIC (3.6%) which is consistent with XRD results that indicate the minerals quartz and illite are common to all samples while calcite was only identified in the high TIC sample (WH1). Water adsorption and desorption isotherms were completed on each sample using two grain sizes (500-800 µm and 250-500 µm) over a range of relative humidities (0 to ≥ 96%). Adsorption/desorption results indicate that grain size does not significantly impact the wetting and drying behavior of the shale. Adsorption measurements were completed at 30 and 50 ˚C with significant agreement between measurements (Figure 1). Desorption isotherms were only completed at 50 ˚C to reduce the excessive time required for duplicative results. Desorption isotherms are showing significantly higher water contents relative to levels obtained by adsorption at the same relative humidity, indicative of water blocking.

The pore-scale model has been developed based on the many-body dissipative particle dynamics (MDPD) method. After investigating several modeling approaches, MDPD was selected because it is more fundamental and easily applied relative to other approaches in terms of representing interactions with different minerals and organic matter in rock space, including but not limited to slip flow, wettability, and adsorption/desorption processes. The MDPD code has been tested and verified against existing model results in simple simulations (Figure 2).

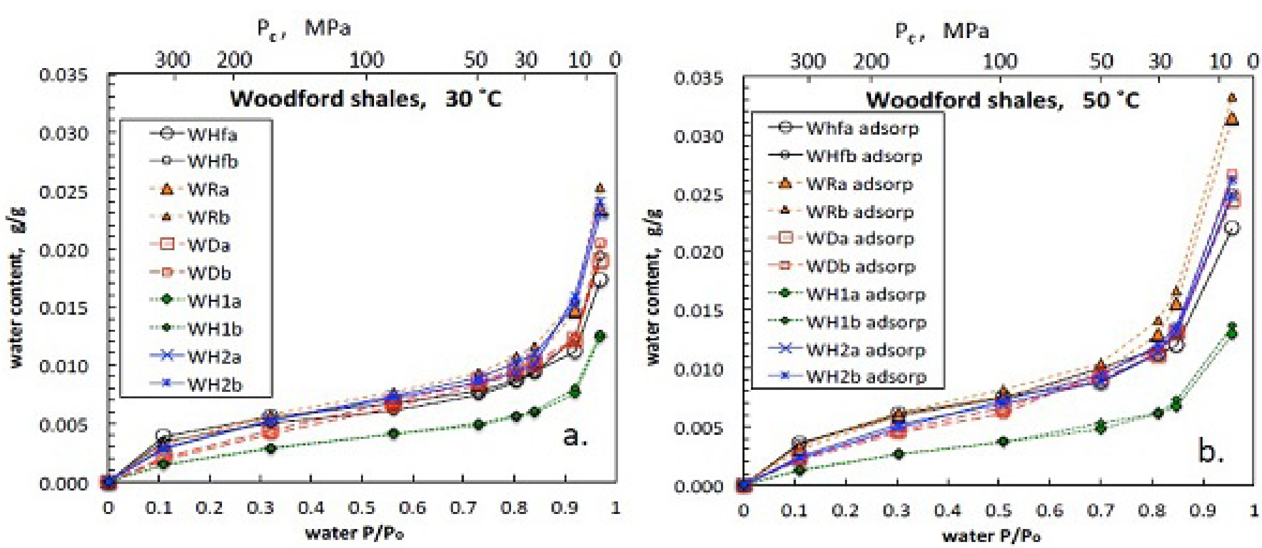



*Figure 1. Water vapor adsorption isotherms on Woodford Shale samples, conducted at 30 and 50 °C. P/Po is the relative humidity, controlled using saturated salt solutions. The "a" and "b" sample designations denote 500-800 µm and 250-500 µm grain-size ranges, respectively.*

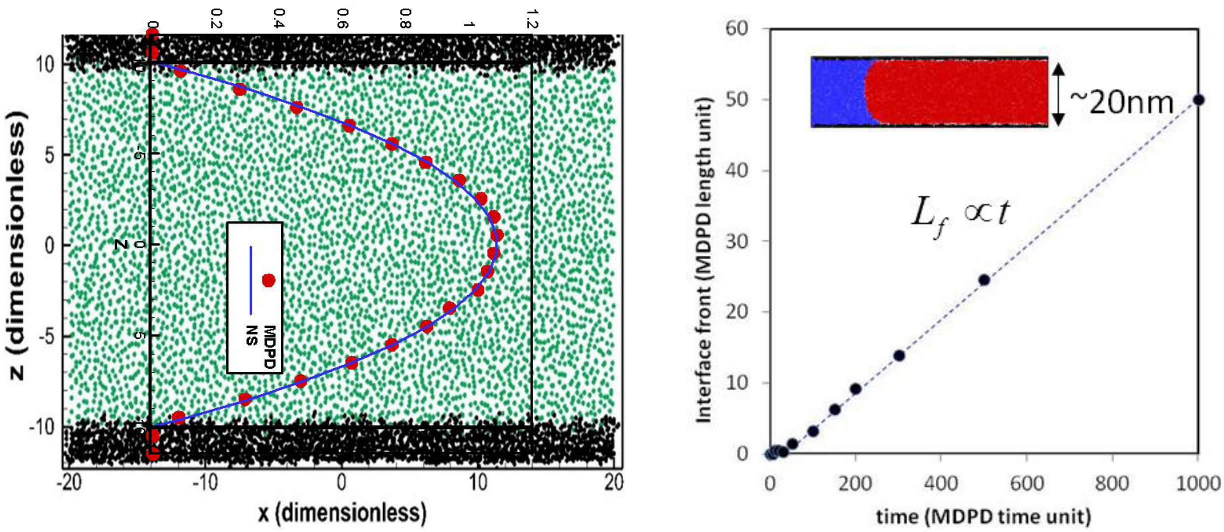



*Figure 2. (a) Initial model setup for the single-phase flow simulation in a capillary tube, black representing centers of solid/wall particles and green representing centers of MDPD fluid particles, overlaid with a comparison of the MDPD results with the existing model results (Navier-Stokes solution) for steady flow under no-flow boundary conditions at the channel walls. (b) Demonstration of the MDPD-predicted results for the interface front movement during the spontaneous imbibition in a nanotube. (Black=solid, blue=wetting fluid, red=nonwetting fluid). The interface moves proportional to the time in the nanotube except at very early times, deviating from the Lucas-Washburn (LW) equation prediction, L~t1/2, in capillary tubes. Similar results were observed in earlier studies on flow of partially wetting fluids in nanotubes, attributed to dynamic contact angle and fluid slip not taken into account by LW.*

## Current Status

Laboratory work is ongoing with Scanning Electron Microscope (SEM) analysis, X-ray fluorescence analyses, density and porosity measurements. Preliminary elemental compositions match XRD results of the previously identified dominant minerals in the shale samples. Laboratory measurements of shale gas permeability are underway, and will later include measurements at different levels of water saturation and measurements of $CH_4$ adsorption/desorption isotherms. The experimentally determined gas diffusivities and permeabilities at progressively higher water saturation and redistribution tests will be used to test and improve the models. Furthermore, meso-scale and macro-scale models will be utilized to investigate the impacts of heterogeneity and initial water saturations on water blocking and gas flow.

For additional information about this project, please contact (stephen.henry@netl.doe.gov or 304-285-2083) or Tetsu Takunaga at Lawrence Berkeley National Laboratory (tktokunaga@lbl.gov or 510-486-7176).

# Fundamental Understanding of Methane-Carbon Dioxide-Water ($CH_4$-$CO_2$- $H_2O$) Interactions in Shale Nanopores under Reservoir Conditions

Shale is characterized by the predominant presence of nanometer-scale (1-100 nm) pores. The behavior of fluids in those pores directly controls shale gas storage and release in shale matrices and, ultimately, the wellbore production in unconventional reservoirs. Recently, it has been recognized that a fluid confined in nanopores can behave dramatically differently from the corresponding bulk phase due to nanopore confinement (Wang, 2014). $CO_2$ and $H_2O$, either preexisting or introduced, are two major components that coexist with shale gas (predominately $CH_4$) during hydrofracturing and gas extraction. Limited data indicate that $CO_2$ may preferentially adsorb in nanopores (particularly those in kerogen) and, therefore, displace $CH_4$ in shale. Similarly, the presence of water moisture seems able to displace or trap $CH_4$ in shale matrix. Therefore, fundamental understanding of $CH_4$-$CO_2$-$H_2O$ behavior and their interactions in shale nanopores is of great importance for gas production and the related $CO_2$ sequestration. This project focuses on the systematic study of $CH_4$-$CO_2$-$H_2O$ interactions in shale nanopores under high-pressure and high temperature reservoir conditions.

## Accomplishments

Experimental Work: The P-V-T-X properties of $CH_4$-$CO_2$ mixtures with $CH_4$ up to 95 vol. %, and adsorption kinetics of various materials, were measured under the conditions relevant to shale gas reservoir.

Three types of materials were used: (I) model materials, (II) single solid phases separated from shale samples, and (III) crushed shale samples. The model materials are well characterized in terms of pore sizes. Therefore, the results associated with the model materials serve as benchmarks for the project's model development.

The P-V-T-X properties obtained in this study will be used to establish a high-precision equation of state (EOS) applicable to shale gas recovery in confined nano-pore environments. An EOS that can accurately describe interactions in the $CH_4$–$CO_2$–$H_2O$ system for a wide range of ionic strengths in a confined environment is an important and essential tool that enables efficient resource recovery from fewer and less environmentally impactful wells. However, such an EOS does not exist at present.

Sorption capacities, sorption and desorption kinetics are highly relevant to shale gas recovery. The project systematically measured sorption capacities and sorption and desorption kinetics for the three types of materials under reservoir relevant conditions. These results will be used for molecular dynamics (MD) modeling of the interactions in a multiple component system.

In Figure 1, a typical sorption curve using a thermal gravimetric analyzer (TGA) is presented. The linear portion of the curve is used for determination of sorption kinetics. The portion that indicates the sorption saturation has been attained is used for determination of sorption capacities. As an example, the sorption rate for montmorillonite is determined from the linear portion of the sorption curve as shown in Figure 2. We have used this methodology to measure the sorption capacities and kinetics for activated

*Figure 1. Sorption of $CH_4 + CO_2$ onto activated carbon at 25°C temperature and 1 bar*

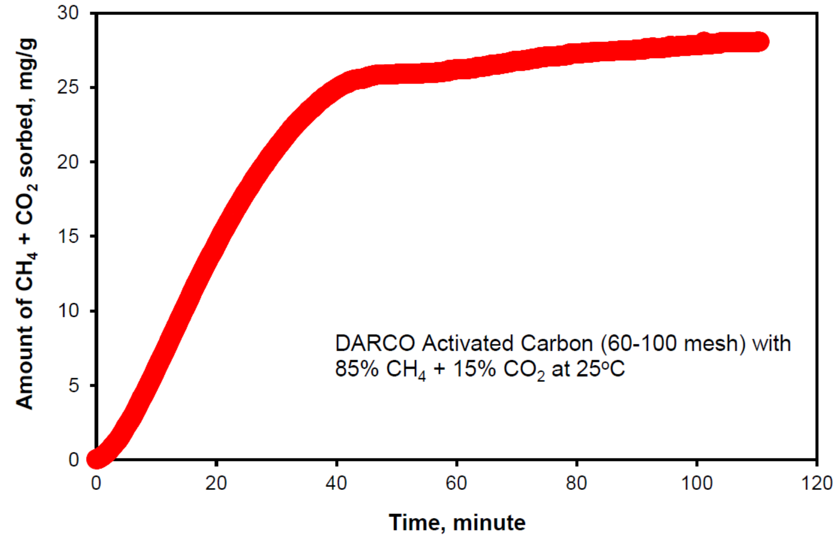



*Figure 2. Sorption kinetics with $CH_4 + CO_2$ for montmorillonite at 25°C temperature and 1 bar*

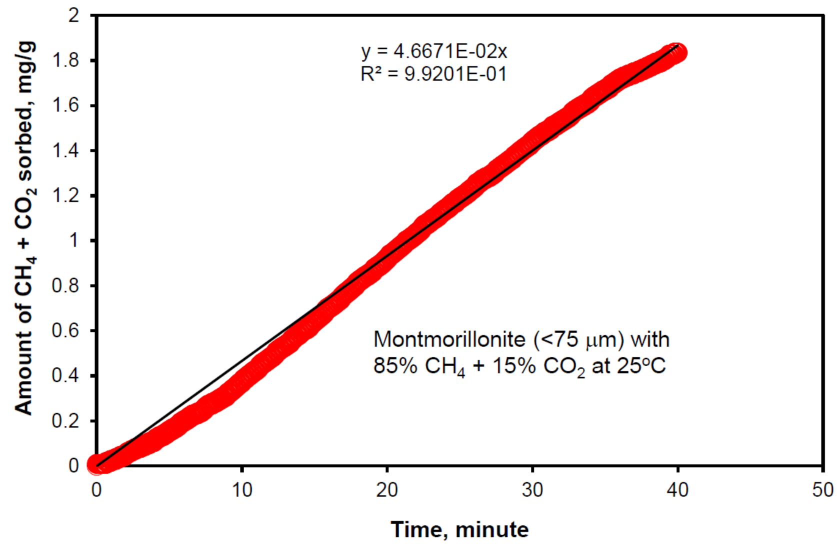
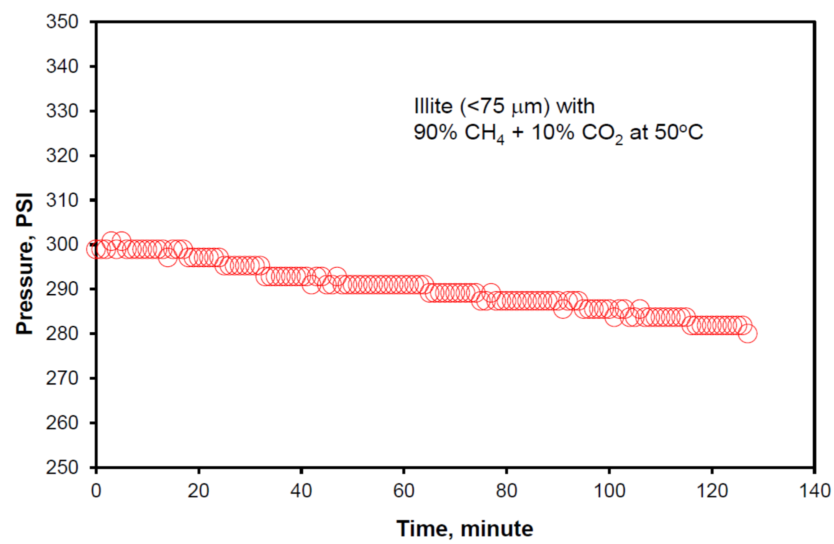



*Figure 3. Sorption of $CH_4 + CO_2$ onto illite at 50°C temperature and 300 psi*



carbon, crushed shale, mesoporous silica, illite and montmorillonite. We have obtained raw data for these materials up to 125°C.

McElroy et al. (1989) measured the compressibility factors for $CH_4$+$CO_2$ mixtures at $CH_4$ percentages of 0, 25, 75 and 100 in the temperature range from 30°C to 60°C. We used their measured compressibility factor at 50°C to calculate the amounts absorbed and the sorption kinetics (Table 1).

*Table 1. Experimental measurements of sorption capacities and sorption rates for the model substances at elevated temperatures and pressures*

| Model Substances | Temp, °C | Gas Mixture, volume percent | Pressure, PSI | Sorption Capacity (mixture) mg/g | Sorption Rate, mg/g min-1 |
|---|---|---|---|---|---|
| Illite, <75 m | 50 | 90% $CH_4$ + 10% $CO_2$ | 300 | 160 | 6 × 10-1 |

The project has obtained raw data for the model materials up to 125°C and at the total pressures of 1000 psi by using the same method. Researchers are looking for the compressibility data for our system, and process our measured compressibility factors. The results will be provided in the next quarterly report.

## Modeling Work

Models for amorphous silica, montmorillonite and kerogen have been selected and created for simulation with individual and mixed gases. For kerogen, a representative suite of models that span a range of maturity have been developed by Ungerer et al. (2014). These models are now being studied with different force fields (e.g., OPLS, PCFF, CVFF) to determine which one will best predict the physical properties of both kerogen and methane as a function of temperature and pressure. Figure 4 illustrates an initial configuration containing kerogen molecules representative of the mature end member of the organic-rich Duvernay series. This conformation is being relaxed in successive NPT stages (900K, 700K, 500K, and 400K) in order to compare our software's results to that used by Ungerer et al. (2014). This will also result in one of the initial kerogen configurations to examine gas adsorption and diffusion. In August, a postdoctoral associate will join our team and conduct matrices of simulations using the force fields and models currently being tested.

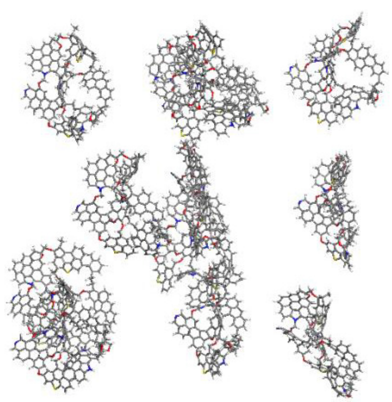


*Figure 4. Initial configuration containing kerogen molecules representative of the mature end member of the organic-rich Duvernay series*

## Outlook

The next steps will include:

Expanding the low pressure sorption measurements to a full cycle of adsorption- desorption measurements. The data to be obtained will help understand the possible hysteresis behavior of gas sorption in nanopores.

Continue performing high pressure and high temperature sorption measurements. Develop a highly accurate equation of state (EOS) for $CH_4$-$CO_2$ mixtures for data interpretation.

Starting a cDFT formulation for $CH_4$-$CO_2$ sorption in nanopores and trying to apply the model to both low and high pressure requirements.

For additional information on this project, please contact Joseph Renk at NETL (joseph.renk@netl.doe.gov or 412-386-6406) or Yifeng Wang at Sandia National Laboratories (ywang@sandia.gov or 505-844-8271).

# Connectivity Between Fractures And Pores In Hydrocarbon-Rich Mudrocks

## Goals and Objectives

The objective of this project is to determine the degree to which fracture systems induced prior to production form a network of connected flow pathways that access the surrounding matrix porosity. Both laboratory experiments and numerical simulation will be employed to understand fracture system development and characterization. This will require defining the rock properties and stress conditions necessary for these fracture systems to develop, and characterizing the size and distribution of fracture systems that do develop, as well as characterizing the unfractured matrix microstructure around fractures. The overall goal is to develop targeted methods for determining where the best production within a mudrock reservoir may be expected, and methods for exploiting favorable rock properties to enhance production rates and recovery.

## Existing Technologies

Imaging

Field emission scanning electron microscopy (FESEM) of ion-milled samples (e.g. Fig. 1c, d) can provide instructive, if not representative views of the SEM-visible porosity. Milliken et al. (2013) and references therein, describe a comprehensive method of conducting FESEM imaging of ion-mill polished thin sections. In fact, application of this milling method with mudrocks was largely pioneered at the BEG. Also in development at UT is a digitization routine to quantify the mudrock microstructure via mapping of both silt-grains and pores (some initial examples are found in Milliken and Reed, 2010 and Hayman et al., 2012).

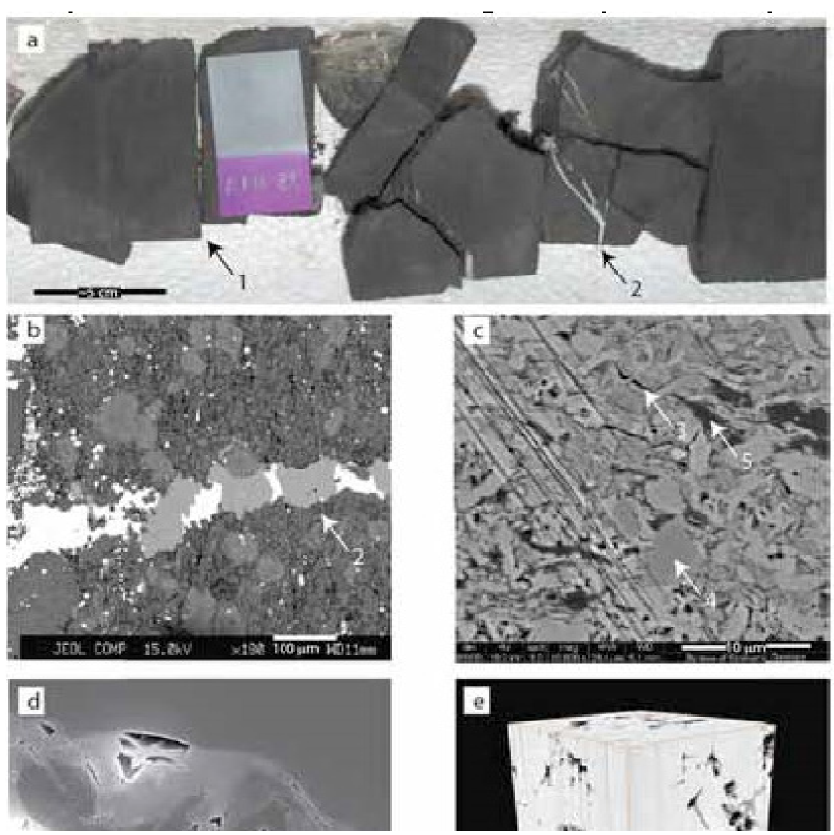



*Figure 1. Examples of natural mudrocks at a variety of scales. (a) Mudrock core with coring-induced fractures (1), and natural, cemented fractures (2). (b) SEM image of a natural fracture (2) (from Milliken et al., 2012). (c) Ion-milled (streaks on left side of image are artifacts of the ion-milling process) sample imaged in FESEM taken in the BEG microscopy laboratory showing silt-sized grains (3) creating inter- granular porosity (e.g., Loucks et al., 2009) (4). Note the organic material (5). (d) Organic material hosts porosity (center). (e) 3D rendering of multiple focused ion beam images (from Walls, 2011).*

Mudrock matrix deformation is undoubtedly a very three-dimensional process. Of the many techniques for capturing 3D structure, the one that appears to work best for mudrock analysis is Focused Ion Beam (FIB) wherein FESEM images are systematically recorded over many increments of ion-milling. A typical 3D rendering (e.g. Fig. 1e) might be constructed with ~45 images, each with a 5X5 micron area, taken every ~100 nm. Using FIB, companies such as "InGrain" (Fig. 1e) and workers at Lawrence Livermore Lab routinely produce such volumes and incorporate them into flow models (e.g., Silin and Kneafsey, 2012). What has not been done, to our knowledge, is a microstructural analysis of mudrocks to gauge the distribution of strain imparted by fracture. Such approaches have been done with metamorphic rocks using micro-CT data (e.g., Ketcham, 2005; Hirose and Hayman, 2008; Hayman, 2008). However, CT, in our experience, cannot routinely resolve the fine-scale details of the silt- and pore- microstructure. Therefore, we intend to adopt the methods of strain analysis of CT data volumes to 3D-renderings from FIB imaging from undeformed and experimentally deformed samples.

Experiments

In addition to direct imaging techniques, a number of technologies exist for analyzing pore structure and fluid flow in mudrocks. These include NMR, gas adsorption/desorption, acoustic velocity measurements performed during triaxial deformation tests, and permeability measurements by pulse-decay and steady-state gas flow techniques. NMR measures transverse relaxation times of hydrogen nucleus spin precession (T2), which is used to infer distribution of pore sizes (Fig. 2) (Kenyon et al., 1995). This technique has been used to characterize distribution of pore sizes as small as 3 nm (Sondergeld et al., 2010a; Sondergeld et al., 2010b). NMR is typically unable to detect pores smaller than ~3 nm due to the extremely fast relaxation of hydrogen in small pores. Correlating T2 with pore size requires comparing T2 distributions with pore size distributions measured by other techniques such as mercury injection or gas adsorption/desorption. NMR is valuable particularly for inferring the presence of fractures, which are typically many orders of magnitude larger than pores in mudrocks (e.g., Fig. 1b) and have correspondingly larger T2 values.

Gas adsorption/desorption can determine quantitative pore size distribution and surface area by measuring volume of gas injected or produced during pressurization or depressurization of a sample. Typical gases used for this analysis include $N_2$, Kr, Ar, and $CO_2$. $N_2$ adsorption/desorption has been used successfully to characterize pores in clays and mudrocks as small as 1.7 nm, but the technique is ineffective in pores larger than ~0.3 μm (Kuila and Prasad, 2011; Schmitt et al., 2013). However, this technique provides a means of determining pore volumes associated with pores below the detection limit of NMR or SEM imaging.

Measurements of compressional and shear wave velocity during triaxial deformation tests can provide information about crack development, grain rearrangement, and porosity changes. Velocities measured at different orientations (i.e., axial and radial) can be used to characterize the compliance tensor and monitor changes in elastic properties and anisotropy as the sample deforms. These measurements also provide vital information for correlating dynamic elastic properties such as those measured by acoustic well logs or seismic data with stress and deformation in the subsurface.

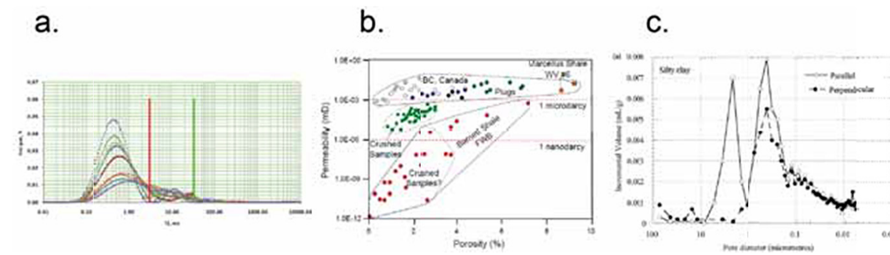



*Figure 2. Example experimental results. (a) NMR T2 distributions for as-received Barnett Shale samples showing typical T2 values in the range 0.1-1 ms corresponding to nanopores. From Sondergeld (2010a). (b) Permeability measurements on various shales showing enhancement of permeability in intact samples that is attributed to the existence of microcracks. From Wang and Reed (2009). (c) Mercury in section-derived pore size distributions for a marine mudstone measured by injection parallel and perpendicular to bedding. The peak around 2 microns for injection parallel to bedding is interpreted to represent bedding-parallel microcracks. From Bolton et al. (2000).*

## Geophysical modeling

Elastic modeling using effective medium models provides a single averaged set of elastic constants (Fig. 3). As the complexity of the material increases, effective medium models require more and more input parameters, of which many must be inferred or estimated. Anisotropic models appropriate for mudrocks require specifying either mineral, fluid, and pore stiffnesses (e.g., Chapman, 2003; 2009) or compliance and geometric parameters (e.g., Pervukhina et al., 2011; Sayers, 2013). Both types can be considered appropriate depending on the information to be extracted from measurements.

Existing technologies for wave propagation in fine-scale geologic media include staggered-grid finite-difference (FD) approaches (Madonna et al., 2013) and finite-element methods (FEM) (De Basabe et al., 2011). In a staggered-grid FD system, an extremely fine scale uniform grid must be defined to account for any small-scale features. The drawback is that the smallest feature dictates the grid size so that everywhere in the domain, the grid size must be small even when not necessary. As the grid becomes finer, the computational costs increase significantly. For FEM, an unstructured mesh represents the domain through which the wave

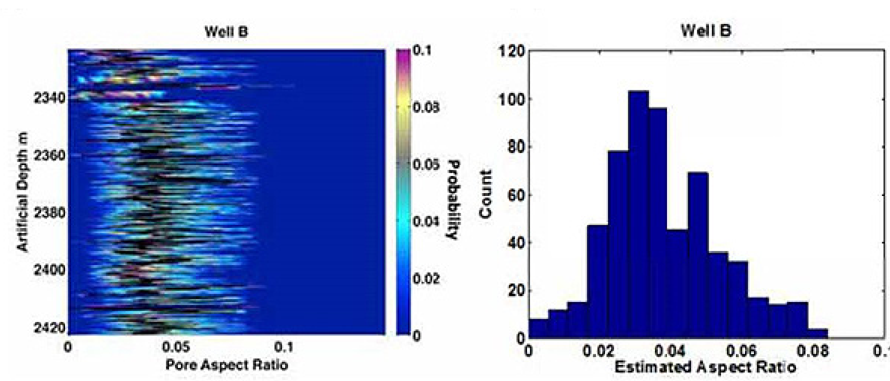



*Figure 3. Example of inverting an effective medium model for a distribution of pore aspect ratios from well log data (a) as a function of depth. (b) is the histogram of inverted aspect ratios shown in (a). To obtain this distribution, a rock physics model is calibrated to measured sonic well data taking into account composition from XRD analyses and estimates of total porosity. Best fit matches within some error between the modeled and measured velocities provide inverted distributions. Each wellbore sonic measurement passes through a volume of material, and presumably through a suite of pores, of which the distribution in (b) is an estimate.*

propagates. This mesh, however, is not uniform. In other words, for fine r scale features, the mesh adapts to a finer scale and remains large where needed.

FD methods rely on continuity of stress and displacement across all boundaries and at every location. Put in the context of a microstructural image, the propagating wave in a FD simulation cannot move from a solid to a void. The staggered grid approximates this, with associated error, by providing continuity of stress or displacement at every other node. A particular FEM method, the discontinuous Galerkin method, uses a weakened form of the wave equation to allow discontinuities in both the medium and the wavefield (Grote et al., 2006). Therefore, this FEM method speeds computation and better accommodates discontinuities in the wavefield created by fluid-solid and free-surface boundary conditions present at a pore-solid or fracture-solid interfaces (De Basabe, 2009; De Basabe et al., 2011).

<u>Highlights & Accomplishments</u>
Work was completed on Subtasks 5.1, 5.2, and 5.3 of the project. Nitrogen adsorption/desorption isotherms, as well as pore size distributions were determined from the adsorption isotherms. In general, all samples showed some amount of increase in pore volume in the failed material relative to the intact material. In the siliceous samples, the failed material had an increase in pore volume generally in the 10-100 nm size range, while in the Eagle Ford samples the increase in pore volume was much smaller and restricted to larger pores (>100 nm). The adsorption-desorption hysteresis loops in the siliceous samples generally retain the same width in the failed samples relative to the intact samples, while the hysteresis loops in the Eagle Ford grow wider upon failure. This may be an indication of a change in the overall connectivity of the pore network.

*Subtask 5.1:* NMR measurements to analyze at least 10 samples under increasing confining and axial stresses were taken to determine T2 distribution related to pore size distribution (Figure 4). Samples were obtained from an undisclosed siliceous mudrock and from Eagle Ford mudrock.

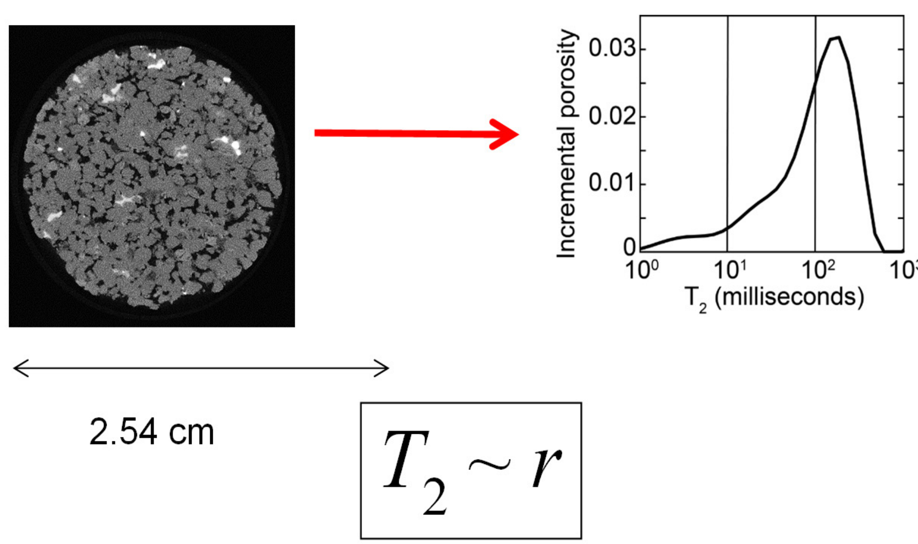



*Figure 4. T2 distribution is related to pore size distribution*

*Subtask 5.2:* Gas adsorption/desorption measurements were taken from 13 samples from material before and after deformation during NMR measurements, for a total of 26 samples, also from an unidentified siliceous mudrock and from Eagle Ford mudrock. Figures 5 – 8 below summarize findings from the samples.

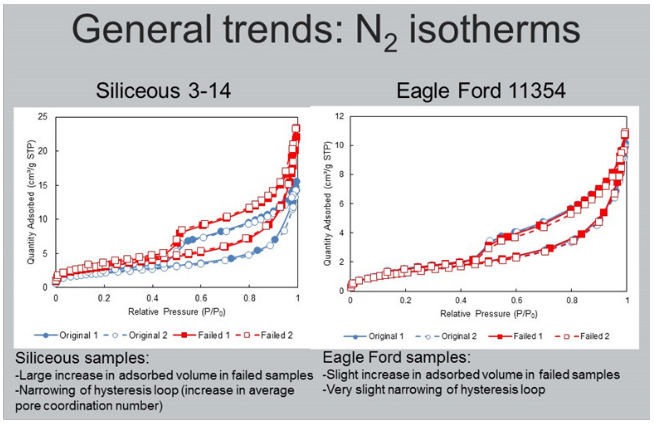



*Figure 5.*

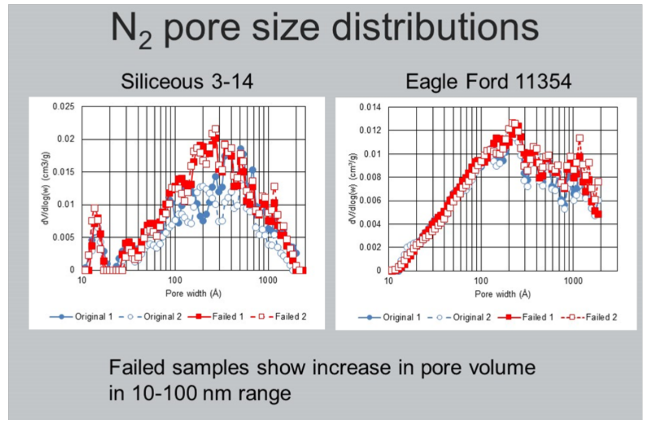



*Figure 6.*

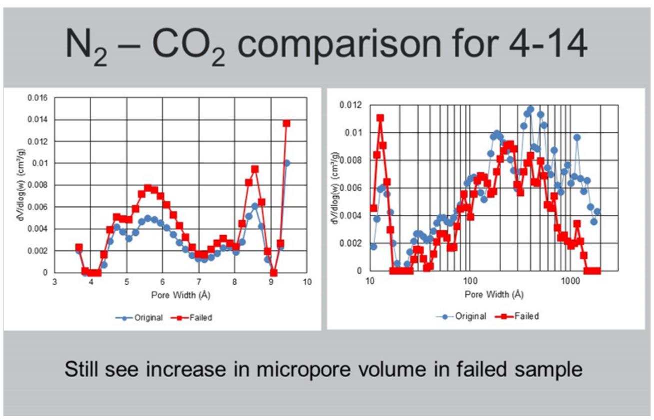



*Figure 7.*

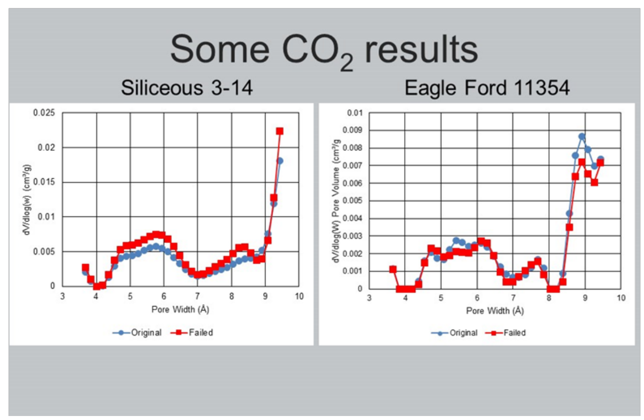



*Figure 8.*

*Subtask 5.3:* This subtask comprised measurement of compressional and shear velocities in axial and radial directions throughout the entire consolidation test on at least 4 samples, from the same sources as subtasks 5.1 and 5.2) that were consolidated to the point of failure. Examples of the data obtained in the measurements are contained in Figures 9 and 10 below.

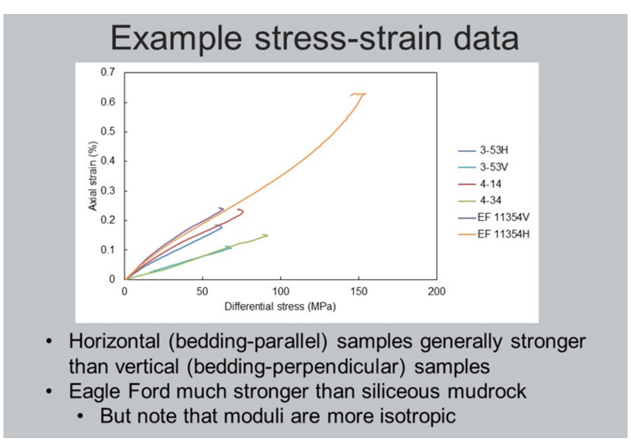



*Figure 9.*

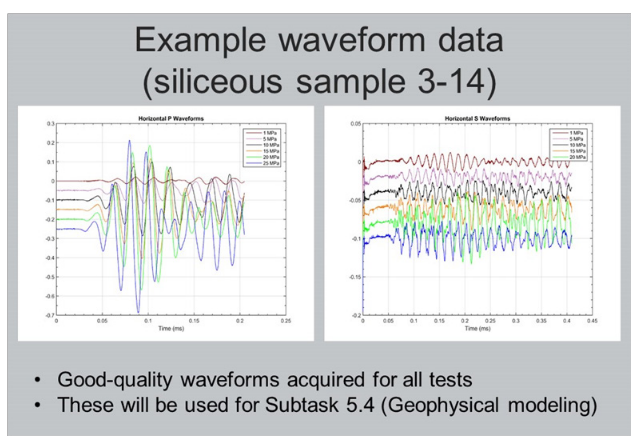



*Figure 10.*

For additional information on this project, please contact Skip Pratt at NETL (skip.pratt@netl.doe.gov or 304-285-4396) or Hugh Daigle at the University of Texas at Austin (daigle@austin.utexas.edu or 512-471-3775).

Additional measurement and analyses of mudrock samples are underway to determine:

*Subtask 5.4:* Geophysical modeling

- What do the waveforms recorded during deformation tell us about microstructural deformation?
- What rock properties are associated with permeability enhancement that might occur as a result of deformation?

*Subtask 5.5:* Imaging

- Where is the porosity enhancement occurring? Is it localized within certain components of the rock (e.g. organic matter)?
- Are existing pores being enlarged or are new pores being created?
- What are the rock properties associated with different amounts of porosity enhancement?

*Subtask 6.0:* Data integration and synthesis

- How does porosity enhancement correlate with other rock properties (TOC, clay content, etc.)?
- How does porosity enhancement change the connectivity of the pore system? (based on image analysis and $N_2$ isotherm analysis)
- What factors can we use to predict what parts of a wellbore or reservoir will respond better to hydraulic fracturing?

# E&P Snapshots

In addition to the projects discussed in this edition of E&P Focus, several additional projects funded by NETL target improvements in subsurface understanding. These include:

## Water Handling and Enhanced Productivity from Gas Shales:

Researchers will utilize a combination of computer modeling, field tests, and laboratory experiments to characterize Marcellus Shale core samples and gain a better understanding of the interactions between the shale matrix and fracturing fluids used to stimulate production wells. With a better understanding of the influence those interactions may have on well productivity, researchers will provide new guidelines and present optimal choices for the treatment and reuse of flow back water. Another focus is on the beneficial reuse of produced water through the application of various pre-treatment options.

## Conductivity Of Complex Fracturing In Unconventional Shale Reservoirs:

The objective of the proposed research is to conduct a systematic experimental study of fracture conductivity in shale oil and gas formations.  The study will focus on the conductivity behavior of shales from three formations, namely the Barnett shale, the Fayetteville shale and the Eagle Ford shale. Outcrops and cores from the three shales will be collected, systematic experimental condition will be designed, and conductivity under different closure stresses will be studied by flowing either gas or liquid through the test cells. Both propped and un-propped fracture conductivity will be examined, and the effect of proppant type, size and concentration will be analyzed in the study. The conductivity obtainable in unpropped fractures will be identified, and the mechanims of unpropped conductivity will be examined. The effect of natural fracture, proppant type, size and loading, closure stress, and rock mechanics properties, on fracture conductivity will be carefully examined in the project. Understanding of fracture conductivity behavior in different shales will be further evaluated by performance prediction with simple models to explain the observation and support the findings from the experimental study.

New procedures and more flexible experimental apparatus will be developed with accurate measurement equipment for fracture conductivity. The similarities and differences in the conductivity behavior among the three shale formations will be summarized from the findings of the study, and experimental observations will be compared with publically reported production history observations to confirm the findings, explain the causes of failures of fracture treatments and unexpected declines of production performance, and provide guidelines for future fracture practices in these shale formations.

## Numerical and Laboratory Investigations for Maximization of Production from Tight/Shale Oil Reservoirs:

The main goal of this project is to conduct multi-scale laboratory investigations and numerical simulations to (a) identify and quantify the various mechanisms involved in hydrocarbon production from tight systems; (b) describe the thermodynamic state and overall behavior of the various fluids in the nanometer-scale pores of tight media; (c) propose new methods for producing low-viscosity liquids from tight/shale reservoirs; and (d) investigate a wide range of such possible strategies, identify the promising ones, and quantitatively evaluate their performance. Laboratory research will include nano- to core-scale studies, and numerical simulations will examine molecular to field-scale conditions. By covering the spectrum from fundamental studies to technology development and evaluation, the project team proposes to gain a deeper understanding of the dominant processes that control production from tight reservoirs and to develop a compendium and document the effectiveness of appropriate production strategies.