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Title: Probing fluid behavior in rock nanopores under dynamic pressure conditions using small-angle neutron scattering

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Probing fluid behavior in rock nanopores under dynamic pressure conditions using small-angle neutron scattering

Dr. Chelsea W. Neil
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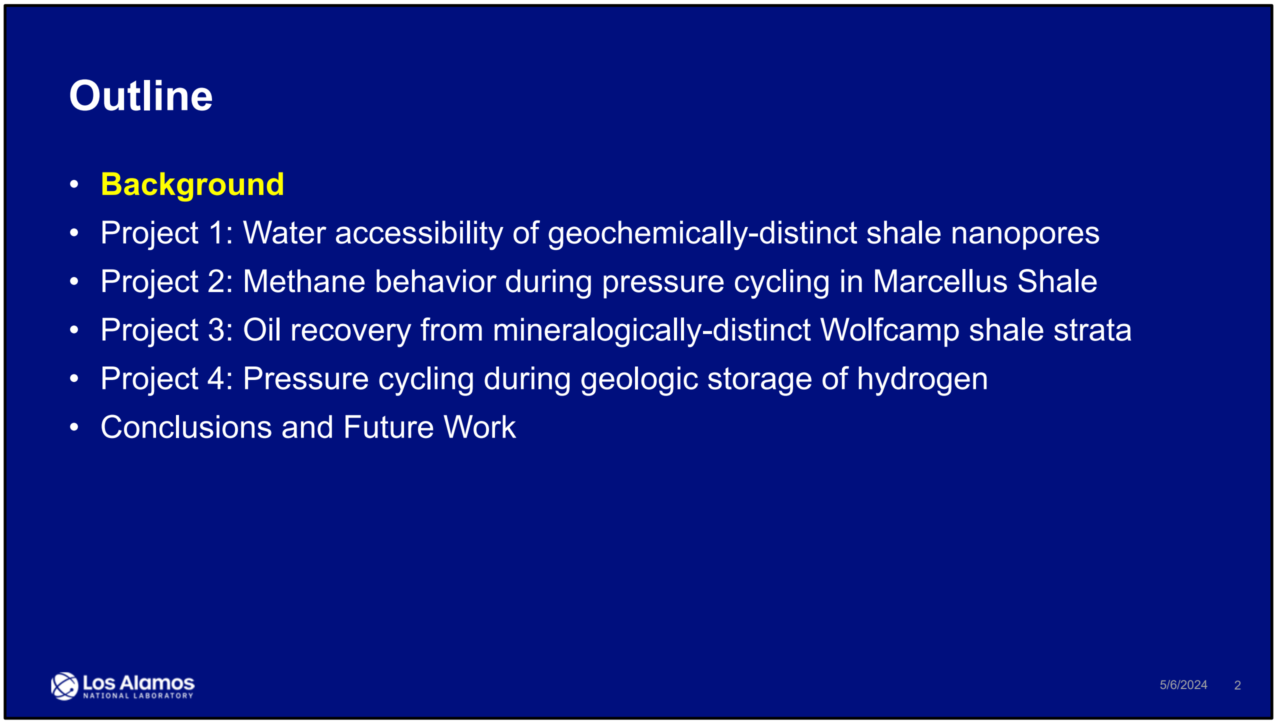
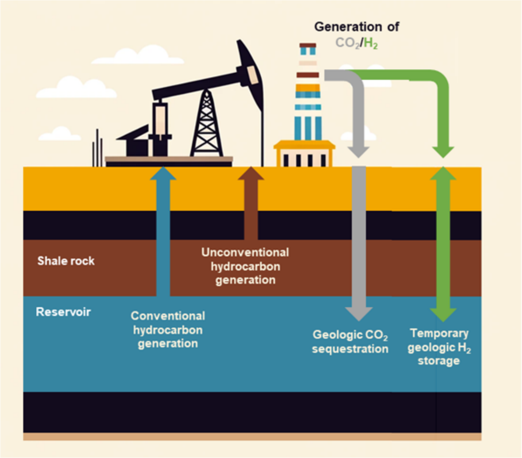


Outline

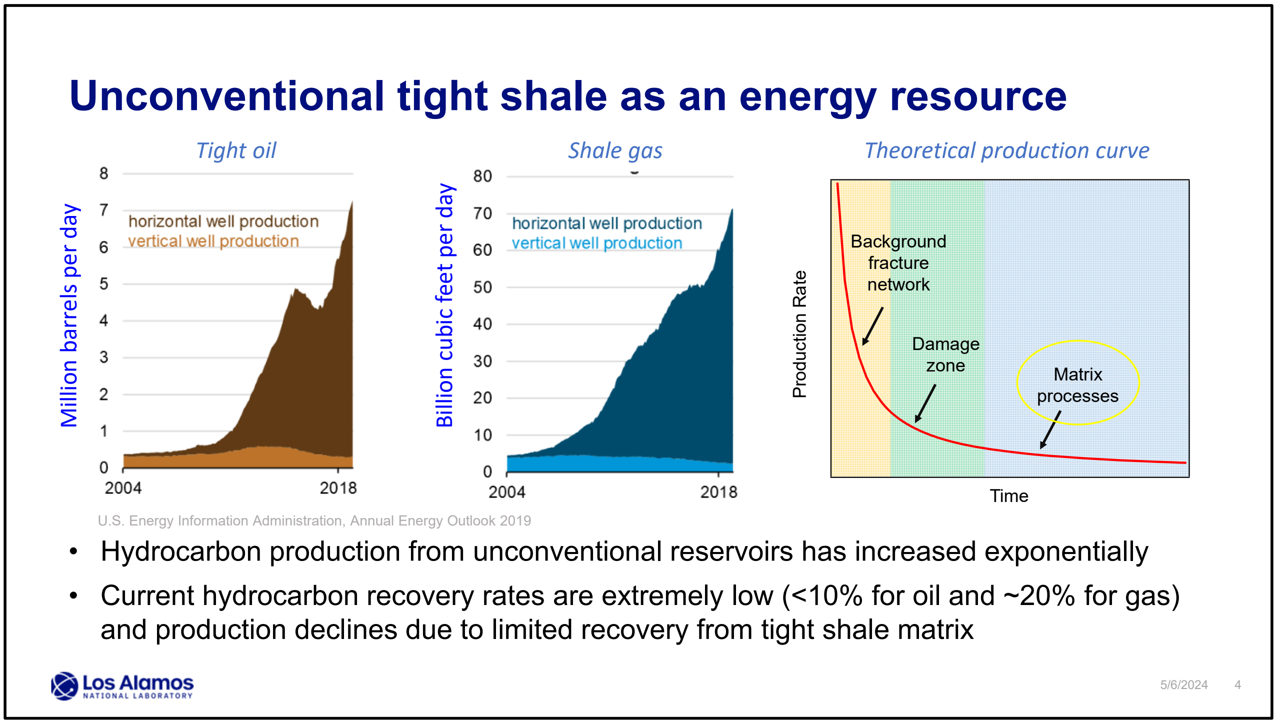
- **Background**
- Project 1: Water accessibility of geochemically-distinct shale nanopores
- Project 2: Methane behavior during pressure cycling in Marcellus Shale
- Project 3: Oil recovery from mineralogically-distinct Wolfcamp shale strata
- Project 4: Pressure cycling during geologic storage of hydrogen
- Conclusions and Future Work

Energy applications in nanoporous geomedia

- Subsurface formations provide vast resource for energy generation, energy storage, and carbon sequestration
- Sustainable energy generation from shale oil/gas and integrity of long-term storage necessitate understanding fluid behavior in nanoporous geomedia (e.g., shale caprock) under dynamic pressure conditions



The subsurface provides vast reservoirs which can be used for energy generation, energy storage, and carbon sequestration to meet zero emission goals. Efficiently and effectively utilizing these systems necessitates understanding how fluids behave in the ubiquitous nanopores of the subsurface.



Unconventional tight shale as an energy resource

Tight oil

Shale gas

Theoretical production curve

U.S. Energy Information Administration, Annual Energy Outlook 2019

- Hydrocarbon production from unconventional reservoirs has increased exponentially
- Current hydrocarbon recovery rates are extremely low (<10% for oil and ~20% for gas) and production declines due to limited recovery from tight shale matrix

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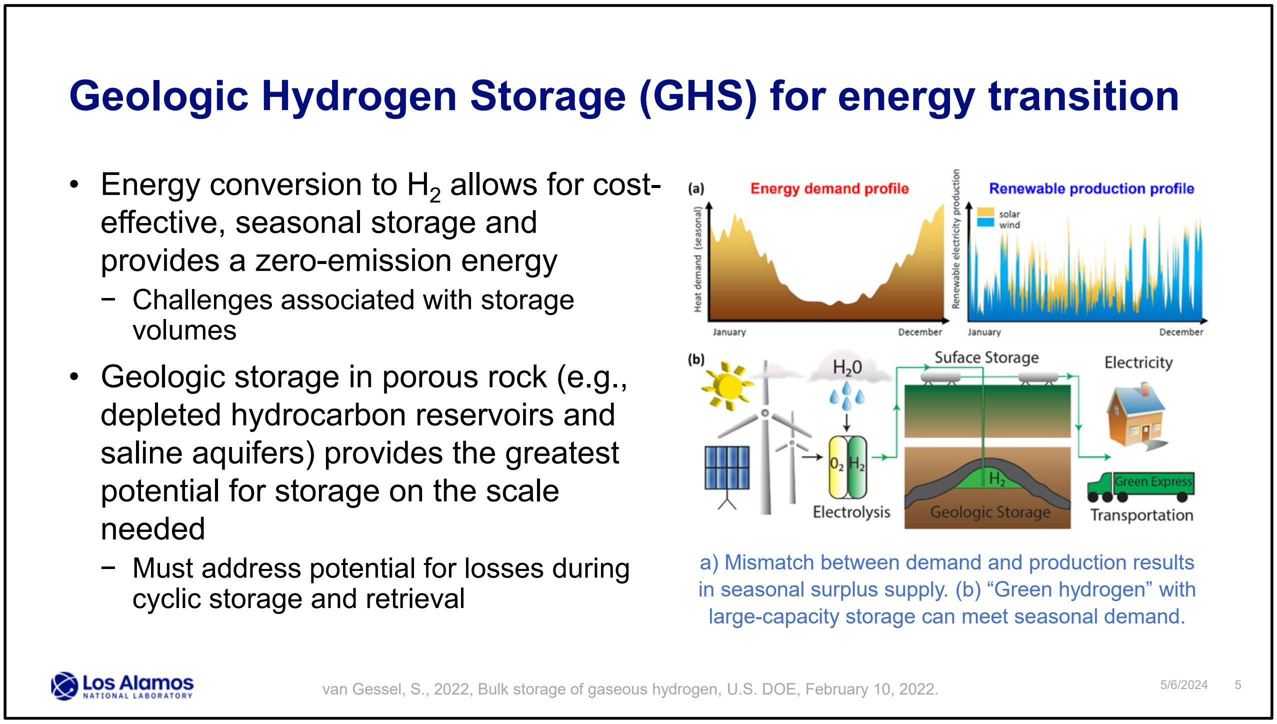
One example are unconventional hydrocarbon reservoirs, which produce gas and oil from that present in the tight shale matrix. The utilization of this resource has increased exponentially in the past decade, but recovery rates are still extremely low due to transport limits in the nanoporous matrix following the initial flushing of the fracture network.



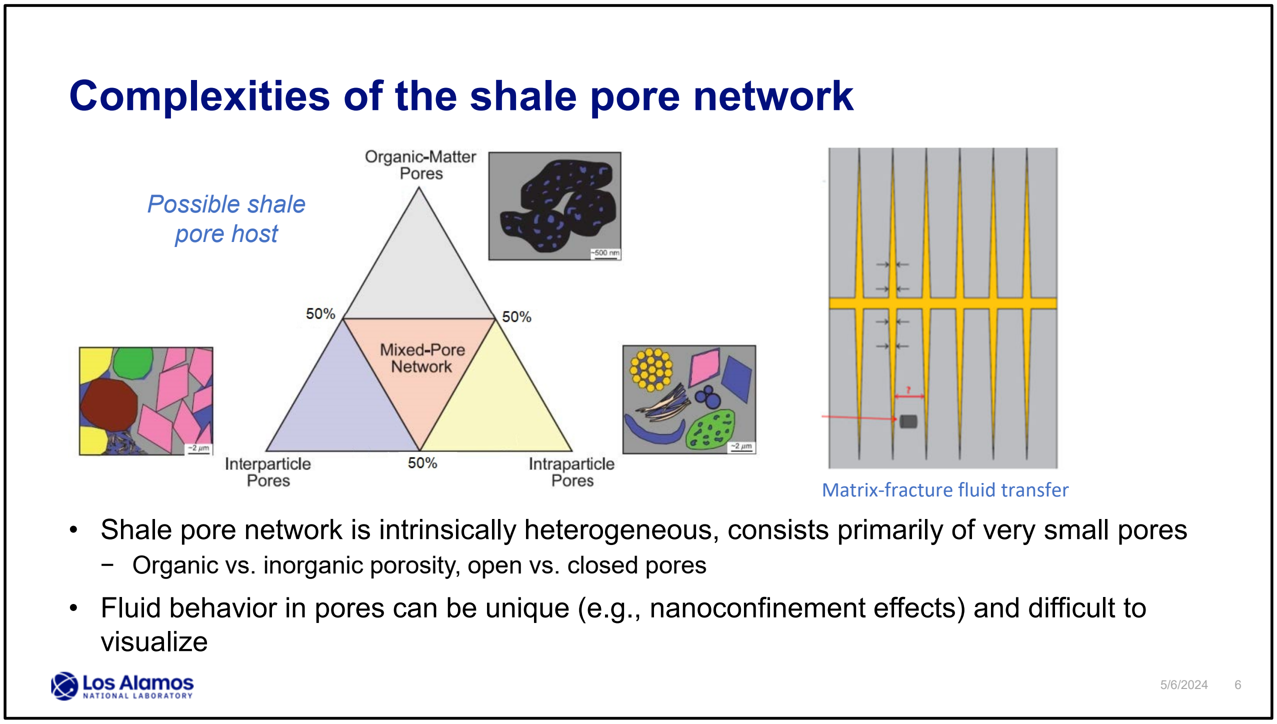
Geologic Hydrogen Storage (GHS) for energy transition

- Energy conversion to H_2 allows for cost-effective, seasonal storage and provides a zero-emission energy
  - Challenges associated with storage volumes
- Geologic storage in porous rock (e.g., depleted hydrocarbon reservoirs and saline aquifers) provides the greatest potential for storage on the scale needed
  - Must address potential for losses during cyclic storage and retrieval

a) Mismatch between demand and production results in seasonal surplus supply. (b) “Green hydrogen” with large-capacity storage can meet seasonal demand.

van Gessel, S., 2022, Bulk storage of gaseous hydrogen, U.S. DOE, February 10, 2022.

Another examine is hydrogen behavior in the subsurface during geologic storage. While GHS has been conducting successfully in impermeable domal salt, new proposed approaches include temporary storage in depleted oil and gas reservoirs and saline aquifers. It is critical in this scenario to ensure that hydrogen loss through the caprock is minimal during cyclic storage and retrieval.

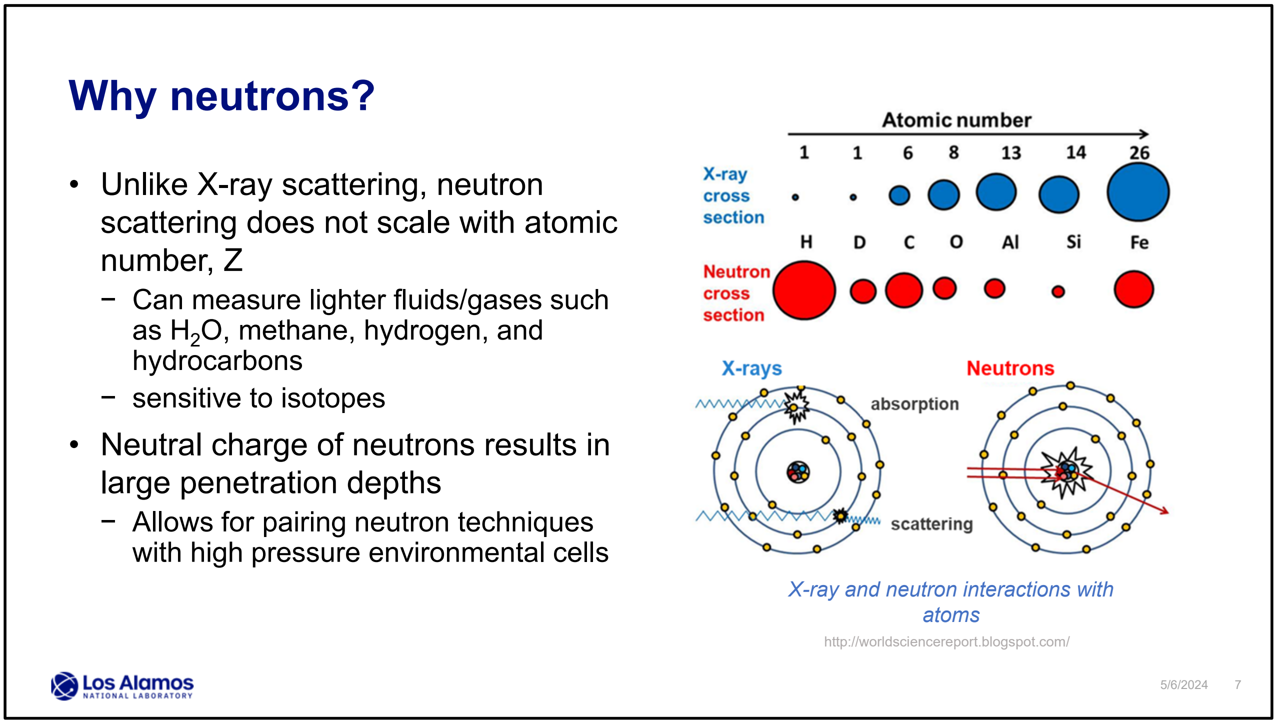


Complexities of the shale pore network

Matrix-fracture fluid transfer

- Shale pore network is intrinsically heterogeneous, consists primarily of very small pores
  - Organic vs. inorganic porosity, open vs. closed pores
- Fluid behavior in pores can be unique (e.g., nanoconfinement effects) and difficult to visualize

For both examples, fluid/gas behavior within shale nanopores and how the matrix interacts with surrounding fractures is critical. Understanding this system can be complicate due to the heterogeneous nature of shale nanoporosity. Pores can be hosted by organic mater, inorganic minerals, or between mineral grains. Pore can also be connected through a pore network (i.e., open) or closed off from the network. It is also difficult to visualize these pores due to their small size.



Why neutrons?

- Unlike X-ray scattering, neutron scattering does not scale with atomic number, Z
  - Can measure lighter fluids/gases such as H_2O, methane, hydrogen, and hydrocarbons
  - sensitive to isotopes
- Neutral charge of neutrons results in large penetration depths
  - Allows for pairing neutron techniques with high pressure environmental cells

X-ray and neutron interactions with atoms

http://worldsciencereport.blogspot.com/

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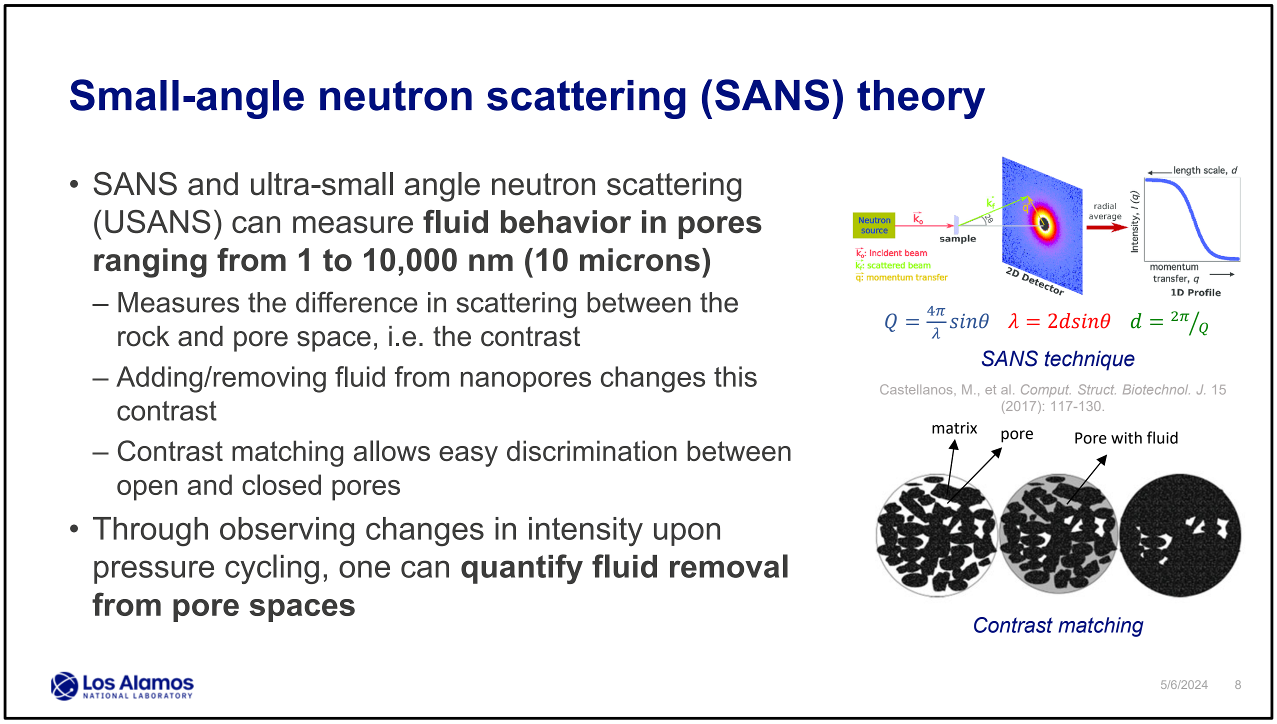
Neutron-based techniques are uniquely suited to measure these systems. This is because unlike X-ray scattering, neutron scattering does not scale with atomic number, Z, meaning that these techniques can measure lighter fluids and gases including water, methane, hydrogen, and hydrocarbons. It is also very sensitive to the isotopic composition of the fluid. Lastly, the neutral charge of neutrons results in large penetration depths, allowing for neutron techniques to be pair with high pressure environmental cells for in situ measurement at field-relevant pressures.



Small-angle neutron scattering (SANS) theory

- SANS and ultra-small angle neutron scattering (USANS) can measure **fluid behavior in pores ranging from 1 to 10,000 nm (10 microns)**
  - Measures the difference in scattering between the rock and pore space, i.e. the contrast
  - Adding/removing fluid from nanopores changes this contrast
  - Contrast matching allows easy discrimination between open and closed pores
- Through observing changes in intensity upon pressure cycling, one can **quantify fluid removal from pore spaces**

$$Q = \frac{4\pi}{\lambda} sin\theta \quad \lambda = 2dsin\theta \quad d = {}^{2\pi}/_{Q}$$

SANS technique

Castellanos, M., et al. *Comput. Struct. Biotechnol. J.* 15 (2017): 117-130.

Contrast matching

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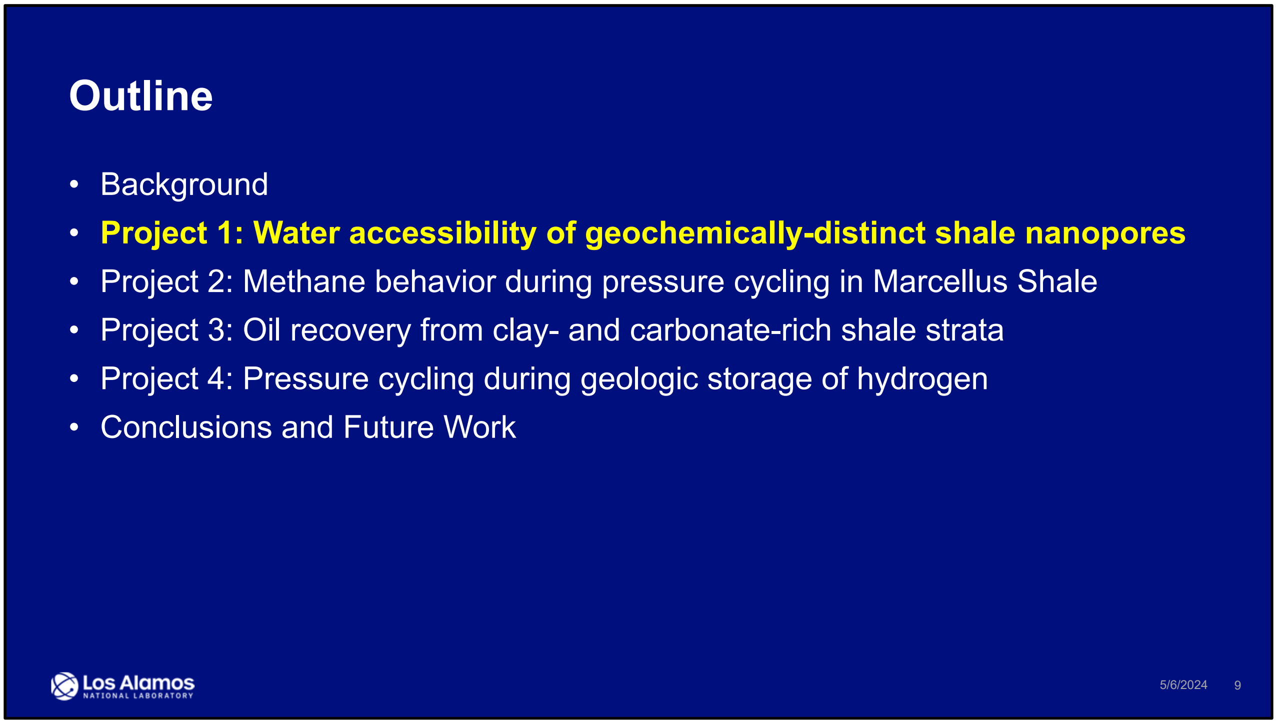
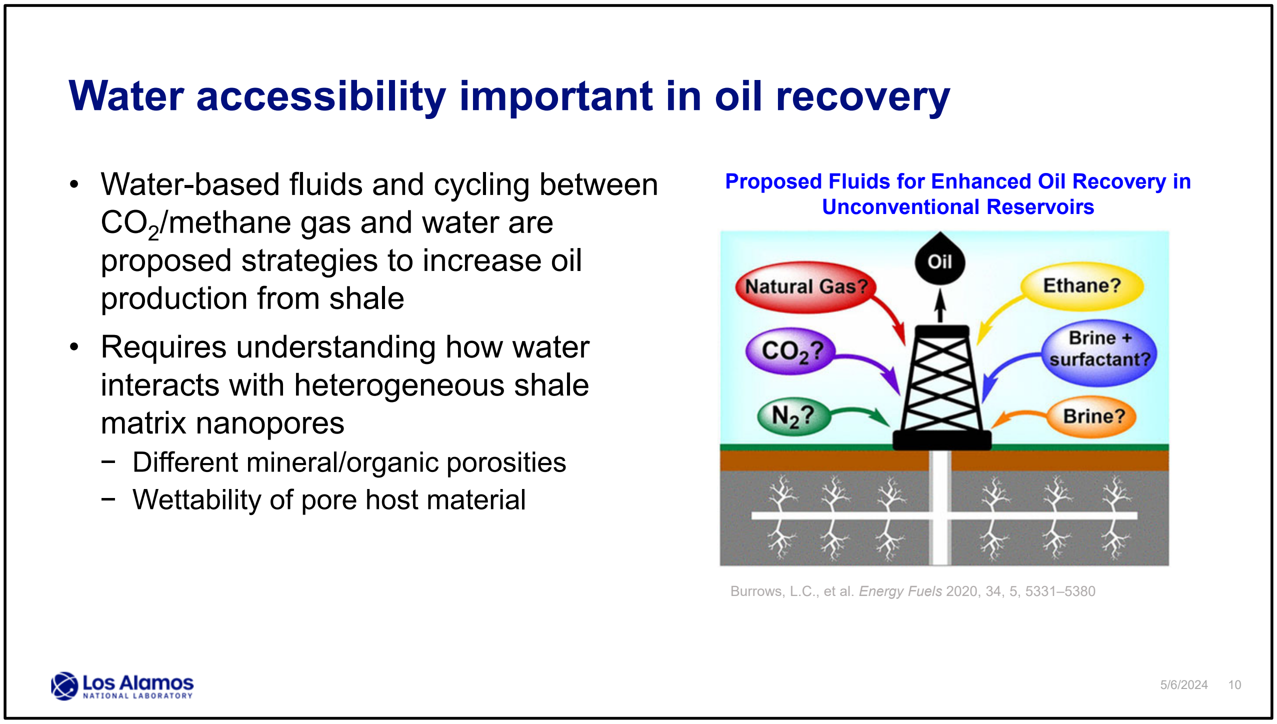
The technique we used was small-angle X-ray scattering (SANS). During SANS, a neutron beam is passed through the sample where it is scattering characteristically based on the sample composition and the number and size of pores in a given volume. Additionally, by filling or removing fluid from these pores, the scattering behavior will change, leading to a technique known as contrast matching, where a fluid composition is altered using different isotopes to match the scattering of the rock (see image). Contrast matching allows easy discrimination between open and closed pores. Combining this technique with fluid pressurization allows us to quantify fluid removal from nano-sized pores under different pressurization scenarios.



Outline

- Background
- **Project 1: Water accessibility of geochemically-distinct shale nanopores**
- Project 2: Methane behavior during pressure cycling in Marcellus Shale
- Project 3: Oil recovery from clay- and carbonate-rich shale strata
- Project 4: Pressure cycling during geologic storage of hydrogen
- Conclusions and Future Work



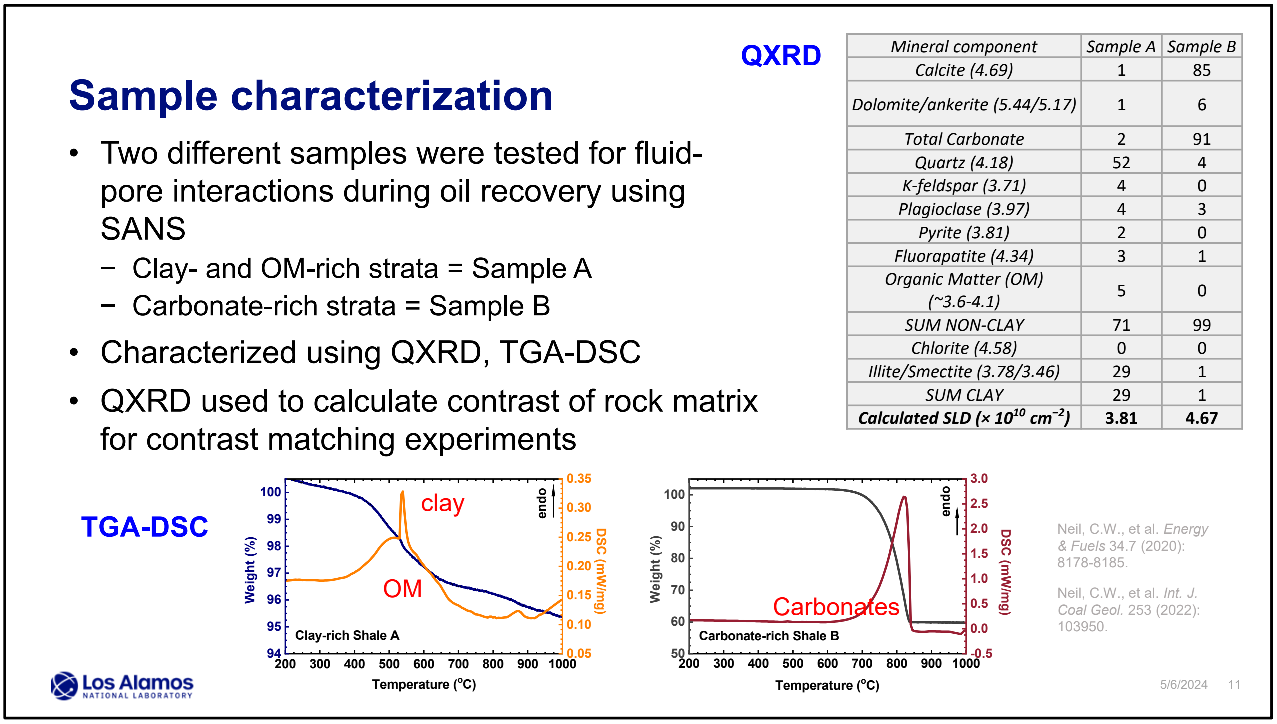
Water accessibility important in oil recovery

- Water-based fluids and cycling between CO_2/methane gas and water are proposed strategies to increase oil production from shale
- Requires understanding how water interacts with heterogeneous shale matrix nanopores
  - Different mineral/organic porosities
  - Wettability of pore host material

Proposed Fluids for Enhanced Oil Recovery in Unconventional Reservoirs

Burrows, L.C., et al. *Energy Fuels* 2020, 34, 5, 5331–5380

The first project is focused on the water accessibility of geochemically-distinct shale nanopores. Water accessibility is important because water-based fluids and cycling between CO2/methane gas and water are proposed strategies to increase oil production from shale. Maximizing recovery in these cases requires understanding how water interacts with heterogeneous shale matrix nanopores, especially considering the pore host materials will have very different wettabilities.



Sample characterization

- Two different samples were tested for fluid-pore interactions during oil recovery using SANS
  - Clay- and OM-rich strata = Sample A
  - Carbonate-rich strata = Sample B
- Characterized using QXRD, TGA-DSC
- QXRD used to calculate contrast of rock matrix for contrast matching experiments

QXRD

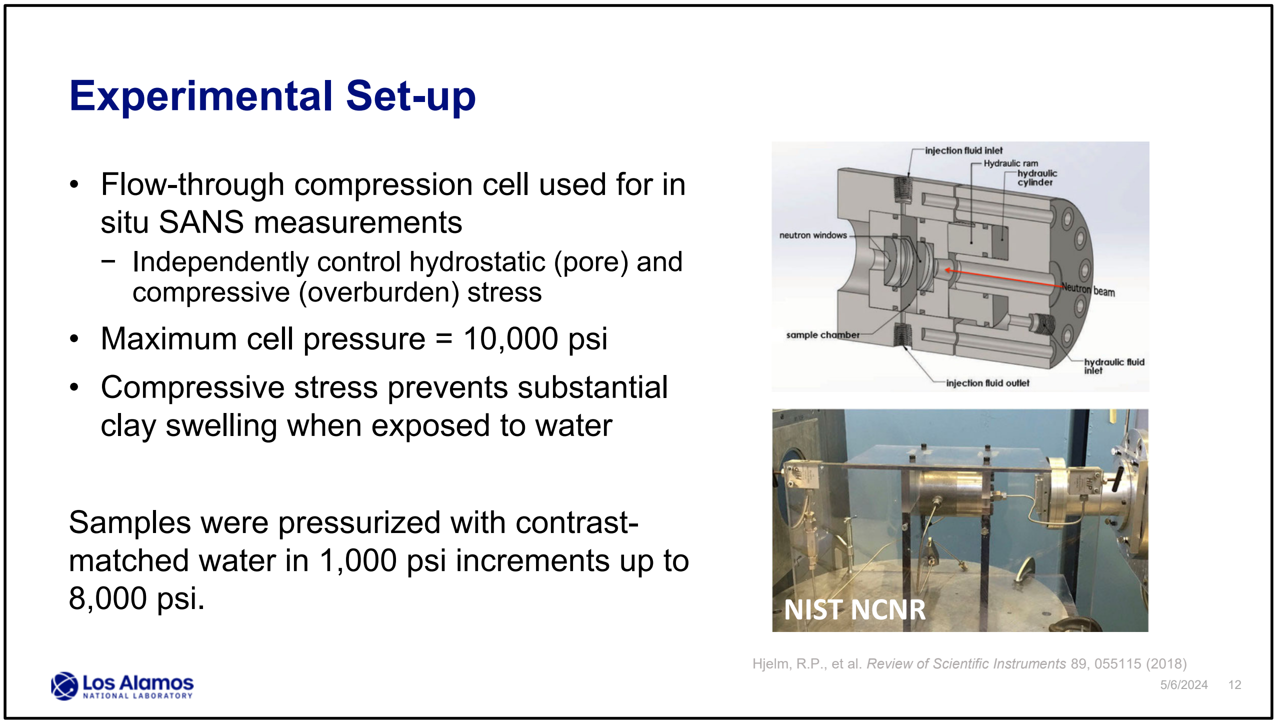
Mineral component	*Sample A*	*Sample B*
Calcite (4.69)	1	85
Dolomite/ankerite (5.44/5.17)	1	6
Total Carbonate	2	91
Quartz (4.18)	52	4
K-feldspar (3.71)	4	0
Plagioclase (3.97)	4	3
Pyrite (3.81)	2	0
Fluorapatite (4.34)	3	1
Organic Matter (OM) (~3.6-4.1)	5	0
SUM NON-CLAY	71	99
Chlorite (4.58)	0	0
Illite/Smectite (3.78/3.46)	29	1
SUM CLAY	29	1
Calculated SLD (× 10^{10} cm^{-2})	**3.81**	**4.67**

TGA-DSC

Neil, C.W., et al. *Energy & Fuels* 34.7 (2020): 8178-8185.

Neil, C.W., et al. *Int. J. Coal Geol.* 253 (2022): 103950.

For these experiment, we used two different Permian basin shale samples provided by our collaborators at Chevron. These were characterized using quantitative X-ray diffraction (QXRD), and thermogravimetric analysis with differential scanning calorimetry (TGA-DSC). It was determined that one, Shale A, was rich in clay and organic matter, while the other, Shale B, was rich in carbonates. The compositional analysis was used to calculate the scattering density of the rock, which was used to tune the water scattering density by changing the ratio of hydrogen to deuterium.



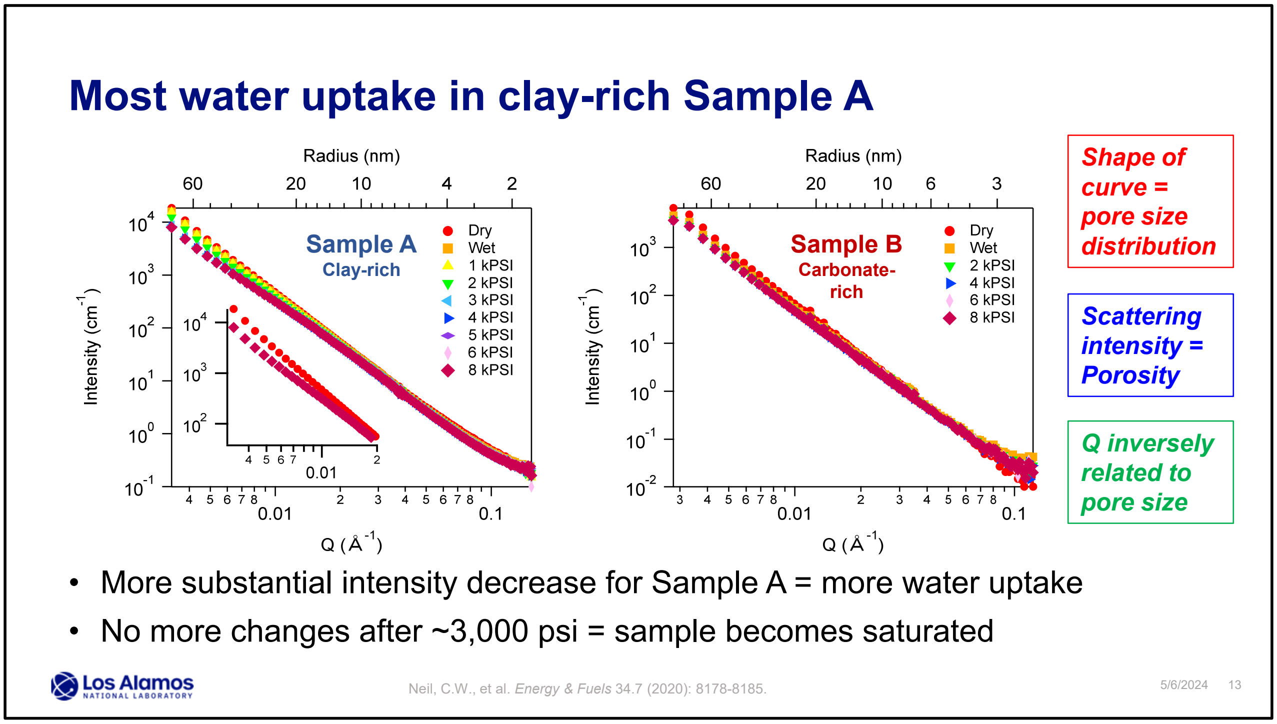
Experimental Set-up

- Flow-through compression cell used for in situ SANS measurements
  - Independently control hydrostatic (pore) and compressive (overburden) stress
- Maximum cell pressure = 10,000 psi
- Compressive stress prevents substantial clay swelling when exposed to water

Samples were pressurized with contrast-matched water in 1,000 psi increments up to 8,000 psi.

Hjelm, R.P., et al. *Review of Scientific Instruments* 89, 055115 (2018)

Pressurization of the shale sample was accomplished using a LANL-designed flow-through compression cell, which allows for a maximum pressure of 10,000 psi while minimizing clay swelling. During the experiment, samples were pressurized with contrast-matched water in 1,000 psi increments up to 8,000 psi.



Most water uptake in clay-rich Sample A

Shape of curve = pore size distribution

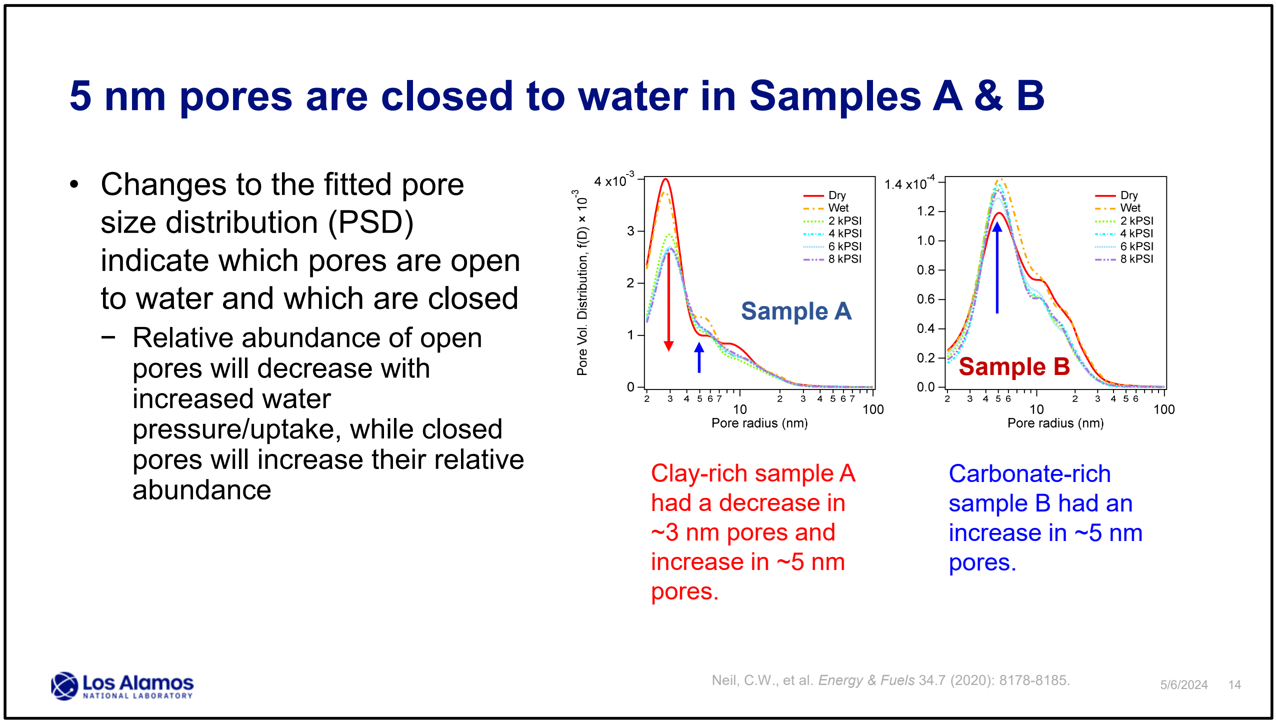
Scattering intensity = Porosity

Q inversely related to pore size

- More substantial intensity decrease for Sample A = more water uptake
- No more changes after ~3,000 psi = sample becomes saturated

Neil, C.W., et al. *Energy & Fuels* 34.7 (2020): 8178-8185.

This slide shows the SANS scattering spectra. To interpret this data, briefly the intensity is positively related with the overall porosity/number of pores, the scattering vector, Q, is inversely related to the pore size. Thus, the shape of the curve can be fit to determine the relative abundance of pores of different sizes, i.e. the pore size distribution. Even without fitting, it is clear from the SANS spectra that sample A had more water update due to its substantial intensity decrease. This is because as the contrast-matched water fills accessible pores, removing scattering interfaces. Additionally, the data shows that the sample becomes saturated at ~3,000 psi, as changes after that point are minimal.



5 nm pores are closed to water in Samples A & B

- Changes to the fitted pore size distribution (PSD) indicate which pores are open to water and which are closed
  - Relative abundance of open pores will decrease with increased water pressure/uptake, while closed pores will increase their relative abundance

Clay-rich sample A had a decrease in ~3 nm pores and increase in ~5 nm pores.

Carbonate-rich sample B had an increase in ~5 nm pores.

Neil, C.W., et al. *Energy & Fuels* 34.7 (2020): 8178-8185.

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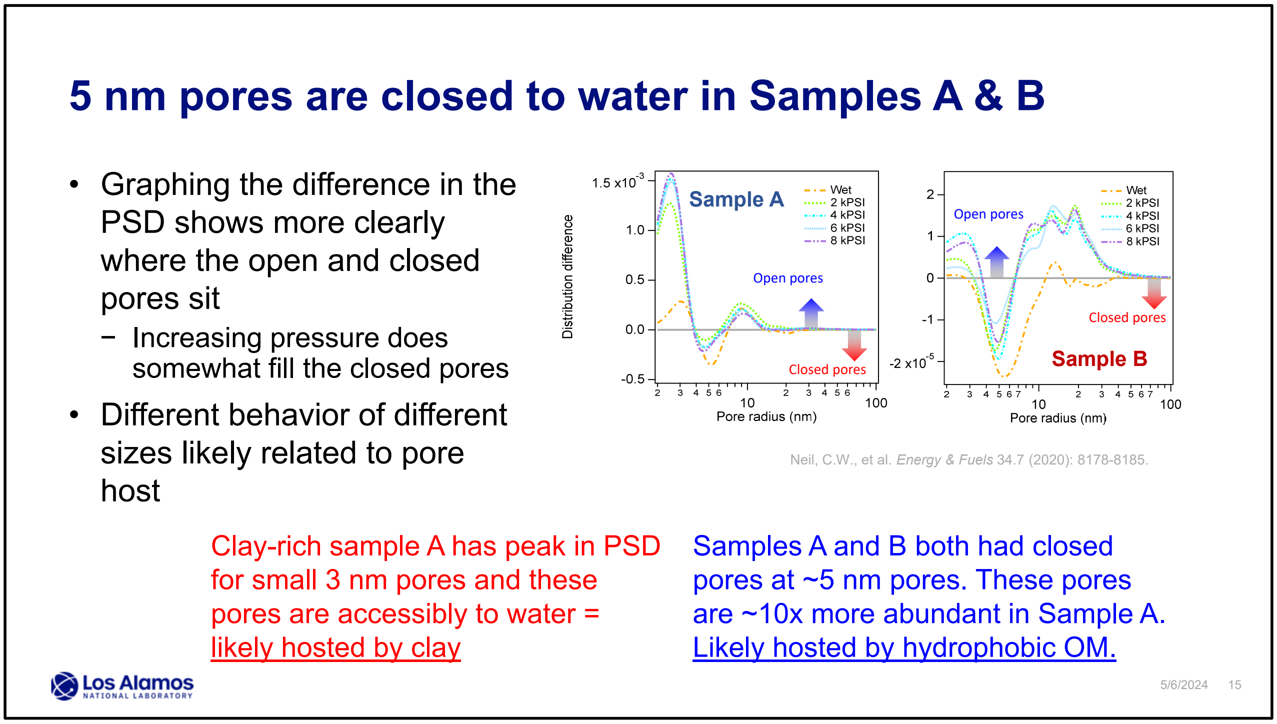
These plots show the fitted pore size distribution. Changes to this distribution indicate which pores are open to water and which are closed. The relative abundance of open pores will decrease with increased water pressure/uptake, while closed pores will increase their relative abundance. For clay-rich Sample A, the abundance of 3 nm pores decreased, while for both samples there was an increase in the abundance of 5 nm pores.



5 nm pores are closed to water in Samples A & B

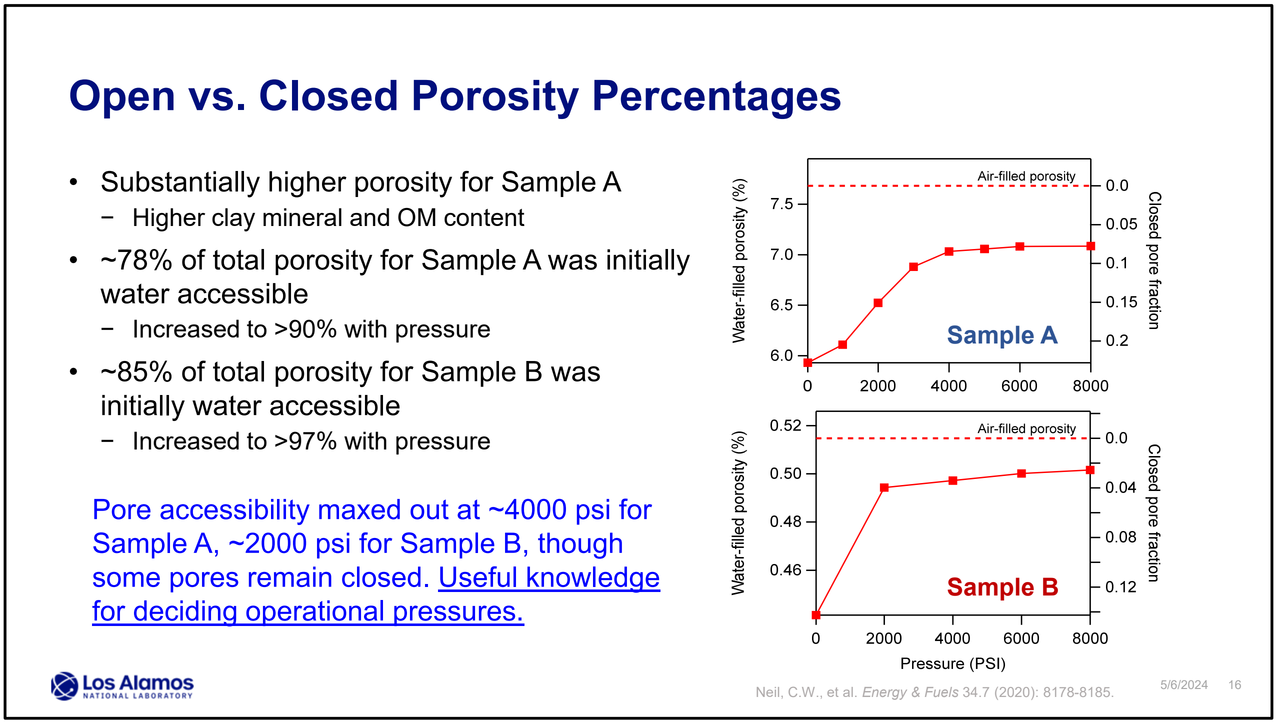
- Graphing the difference in the PSD shows more clearly where the open and closed pores sit
  - Increasing pressure does somewhat fill the closed pores
- Different behavior of different sizes likely related to pore host

Neil, C.W., et al. *Energy & Fuels* 34.7 (2020): 8178-8185.

Clay-rich sample A has peak in PSD for small 3 nm pores and these pores are accessibly to water = likely hosted by clay

Samples A and B both had closed pores at ~5 nm pores. These pores are ~10x more abundant in Sample A. Likely hosted by hydrophobic OM.

Graphing the difference in the PSD shows more clearly where the open and closed pores sit. It also shows that these two types of pores are present in both samples, though to a lesser extent in sample B, and that increasing pressure did fill even closed pores to a certain extent. The peak at 3 nm shows pores that are accessible to water and abundance in Shale A. These are likely hosted by clay, which is more hydrophilic. The 5 nm closed pores are likely hosted by hydrophobic organic matter.



Open vs. Closed Porosity Percentages

- Substantially higher porosity for Sample A
  - Higher clay mineral and OM content
- ~78% of total porosity for Sample A was initially water accessible
  - Increased to >90% with pressure
- ~85% of total porosity for Sample B was initially water accessible
  - Increased to >97% with pressure

Pore accessibility maxed out at ~4000 psi for Sample A, ~2000 psi for Sample B, though some pores remain closed. <u>Useful knowledge for deciding operational pressures.</u>

Neil, C.W., et al. *Energy & Fuels* 34.7 (2020): 8178-8185.

Finally, the SANS spectra can be used to calculate the overall porosity of shale samples. As expected, Shale A has a substantially higher porosity due to its high clay and organic matter content. The water accessible porosity increased with pressure to >90% for Shale A and >97% for shale B. Interestingly, pore accessibility maxed out at ~4000 psi for Sample A, ~2000 psi for Sample B. This can be useful knowledge for deciding on operational pressures in the field, as there may be diminishing returns and high costs associated with over-pressurization.

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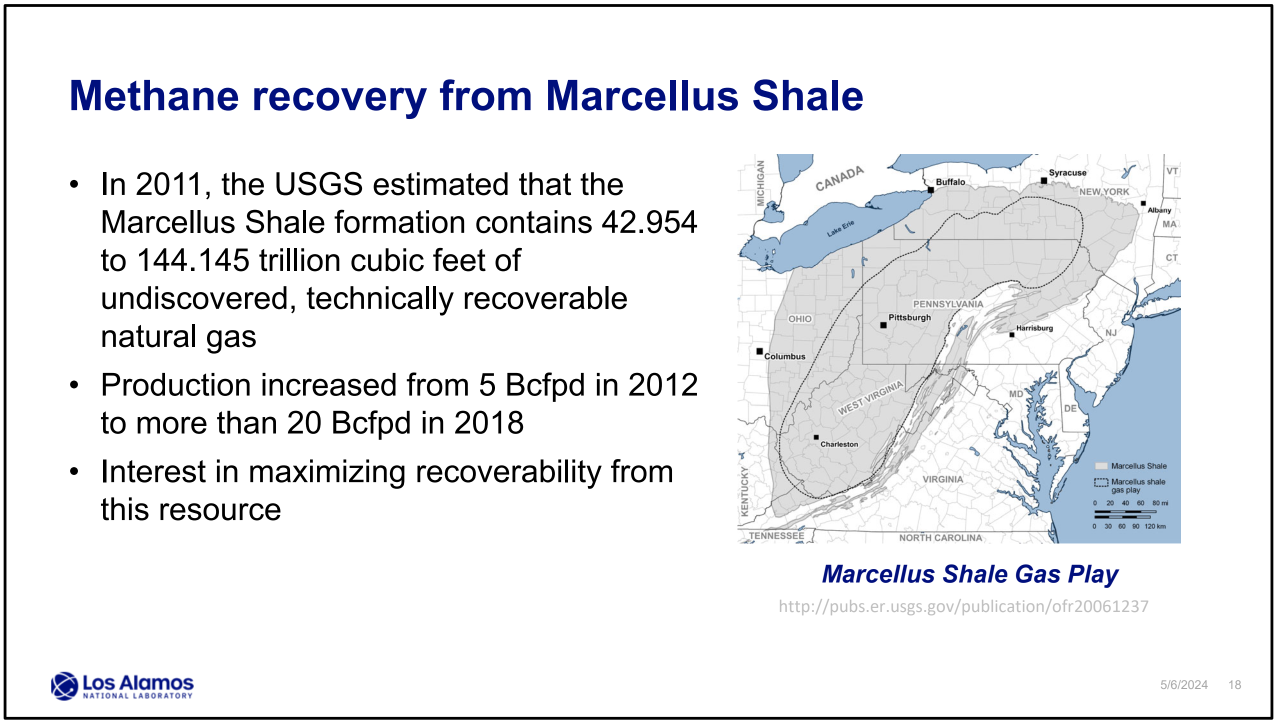

Methane recovery from Marcellus Shale

- In 2011, the USGS estimated that the Marcellus Shale formation contains 42.954 to 144.145 trillion cubic feet of undiscovered, technically recoverable natural gas
- Production increased from 5 Bcfpd in 2012 to more than 20 Bcfpd in 2018
- Interest in maximizing recoverability from this resource

Marcellus Shale Gas Play

http://pubs.er.usgs.gov/publication/ofr20061237

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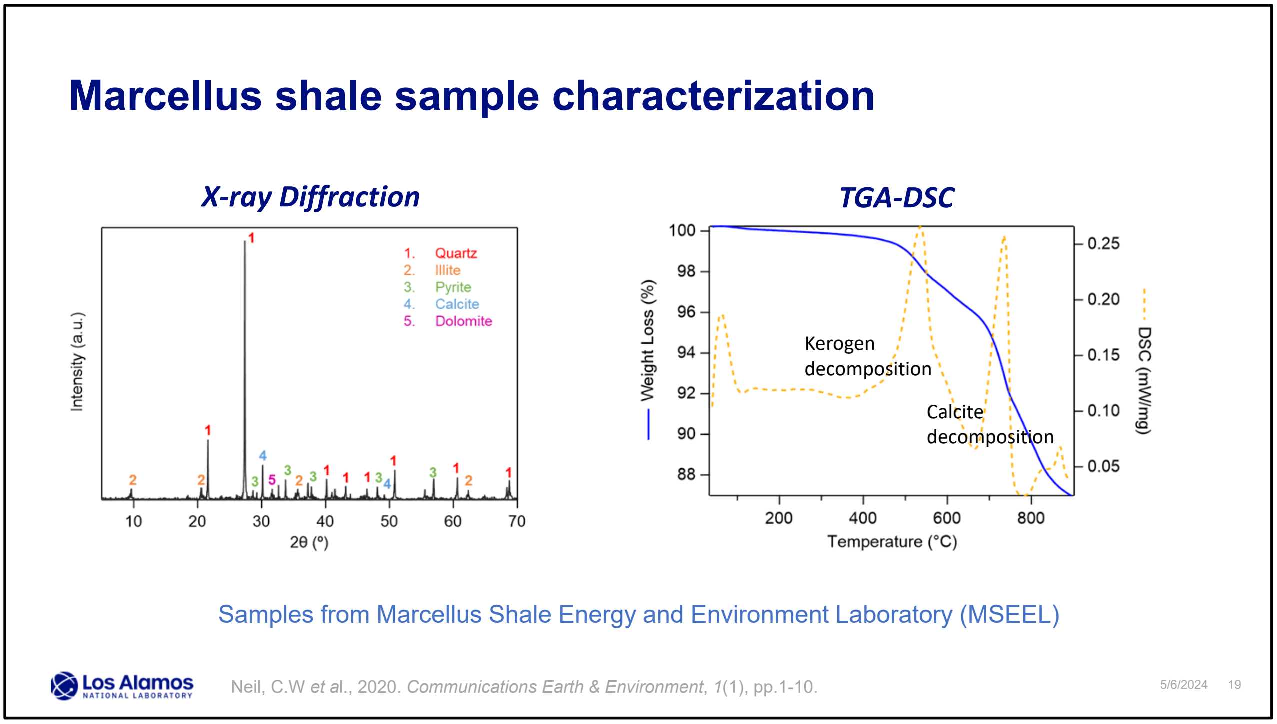
For the second project, we focused on the mobility of methane gas in nanopores of Marcellus shale. Marcellus is one of the largest plays supplying natural gas to the US and there is interest in maximizing recoverability from this resource.



Marcellus shale sample characterization

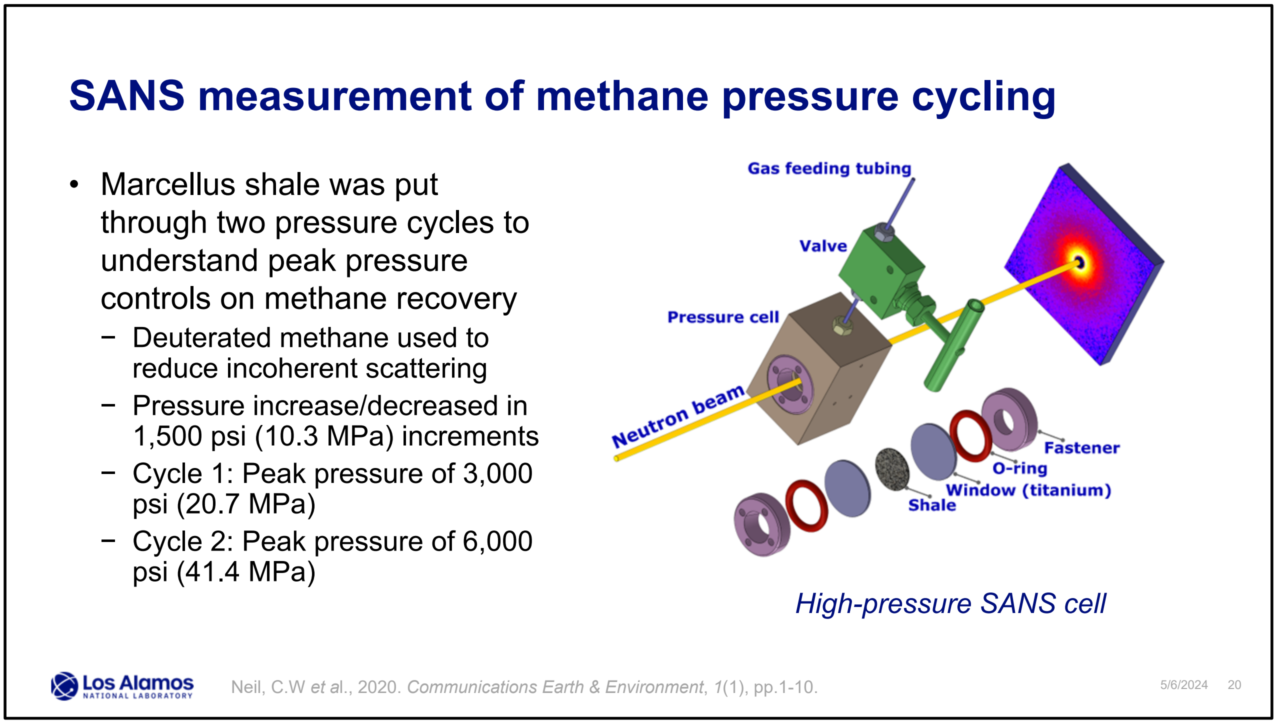
X-ray Diffraction

TGA-DSC

Samples from Marcellus Shale Energy and Environment Laboratory (MSEEL)

Neil, C.W *et al.*, 2020. *Communications Earth & Environment*, *1*(1), pp.1-10.

Samples were supplied from the MSEEL lab, which has done a lot of characterization on this play.



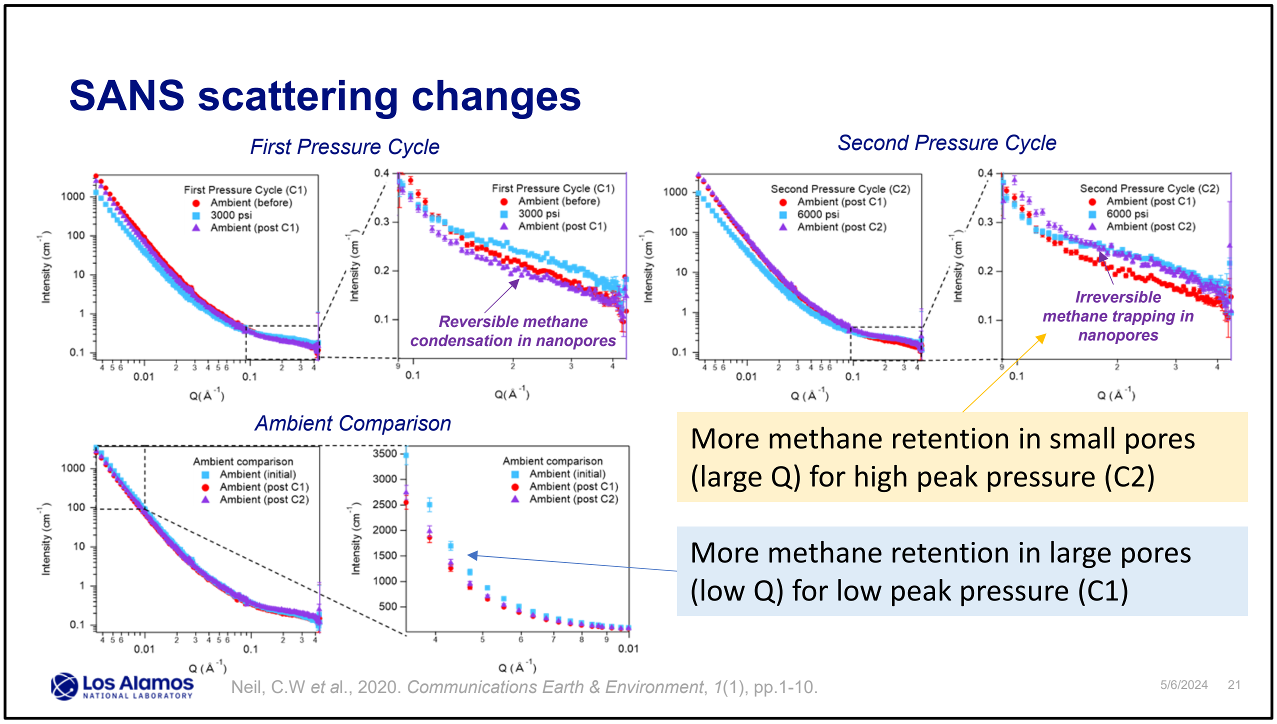
SANS measurement of methane pressure cycling

- Marcellus shale was put through two pressure cycles to understand peak pressure controls on methane recovery
  - Deuterated methane used to reduce incoherent scattering
  - Pressure increase/decreased in 1,500 psi (10.3 MPa) increments
  - Cycle 1: Peak pressure of 3,000 psi (20.7 MPa)
  - Cycle 2: Peak pressure of 6,000 psi (41.4 MPa)

High-pressure SANS cell

Neil, C.W *et al*., 2020. *Communications Earth & Environment*, *1*(1), pp.1-10.

For these experiments, we used a different high-pressure cell which is capable of pressurizing gases. The shale sample was put through two pressure cycles, one with a peak of 3,000 psi and one with a peak of 6,000 psi.



SANS scattering changes

First Pressure Cycle

Second Pressure Cycle

Ambient Comparison

More methane retention in small pores (large Q) for high peak pressure (C2)

More methane retention in large pores (low Q) for low peak pressure (C1)

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Neil, C.W *et al.*, 2020. *Communications Earth & Environment*, *1*(1), pp.1-10.

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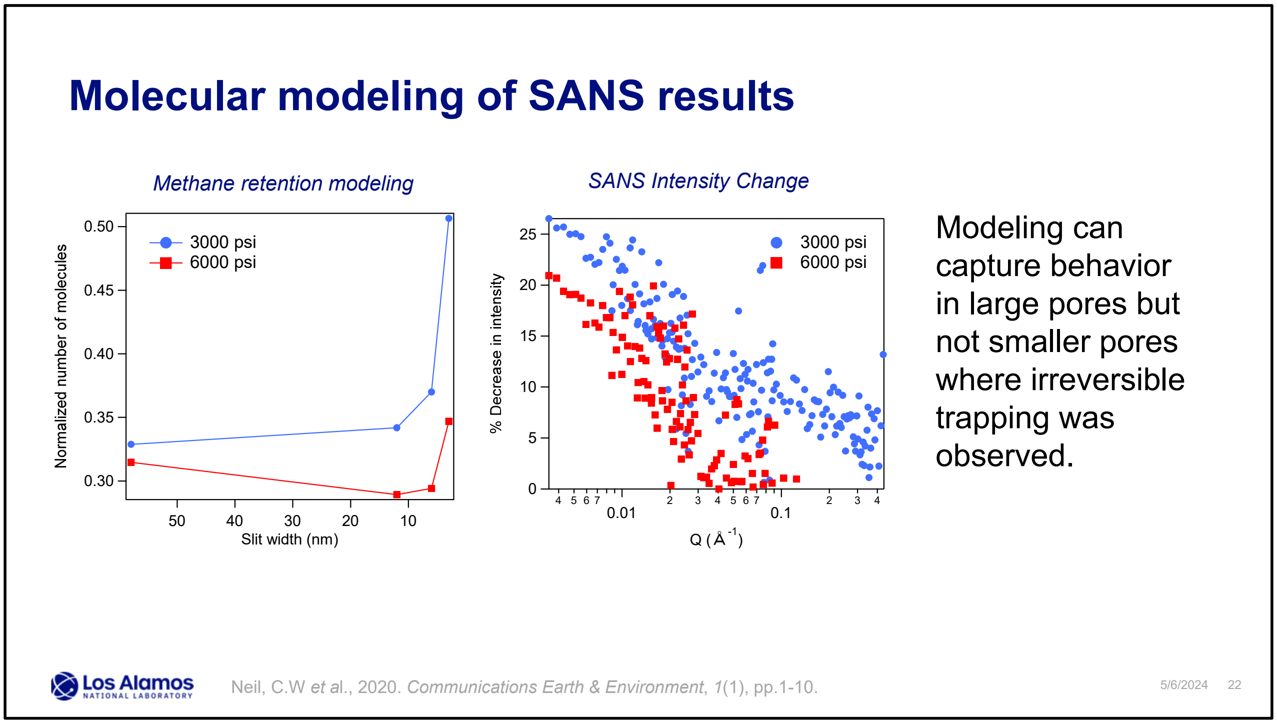
These plots show the SANS spectra before and after the two pressure cycles and for the ambient measurements. Increases in the scattering intensity in the high Q range are due to the condensation of methane in shale nanopores. For the lower pressure cycle, depressurization cleared the methane from these pores. However, for the second pressure cycle, methane remained trapped in the pores. Meanwhile, for the low Q range (larger pores), the higher pressure cycle resulted in less methane retention.



Molecular modeling of SANS results

Methane retention modeling

SANS Intensity Change

Modeling can capture behavior in large pores but not smaller pores where irreversible trapping was observed.

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Neil, C.W *et al*., 2020. *Communications Earth & Environment*, *1*(1), pp.1-10.

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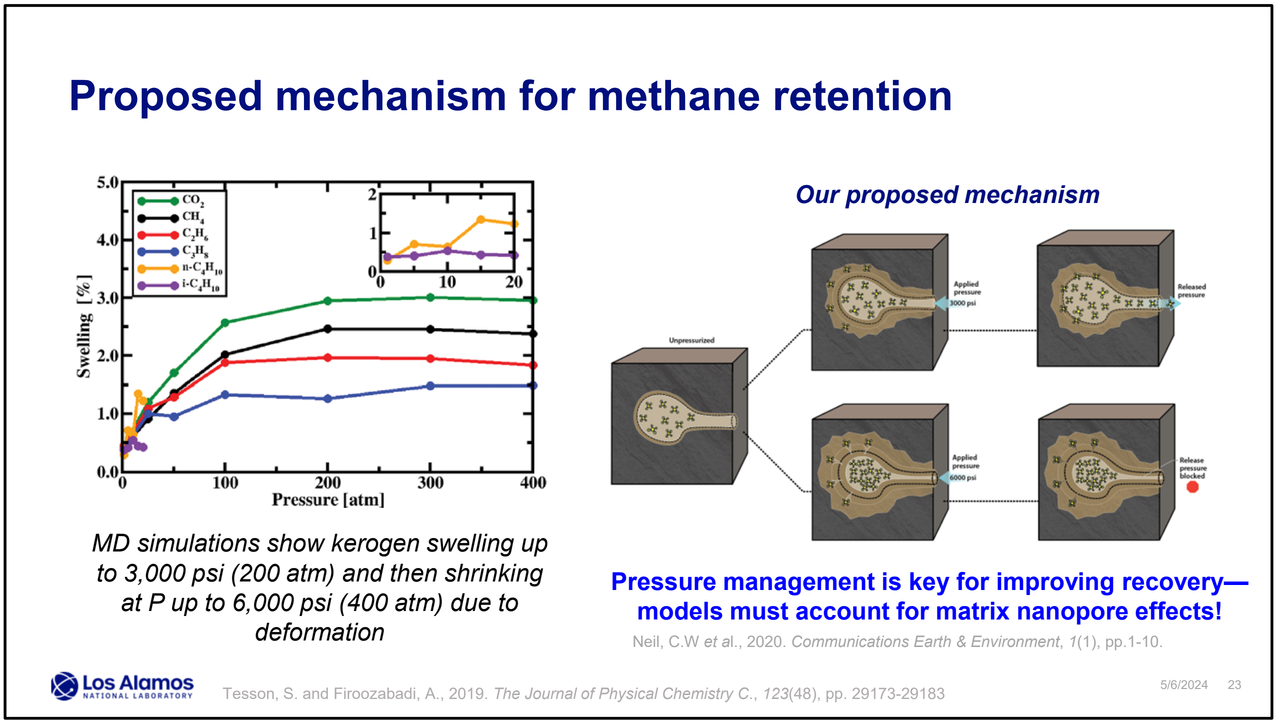
Molecular modeling was used to try to mimic SANS results. However, these models could only capture the behavior of methane in the larger pores and did not capture the irreversible trapping observed in the smaller pores.



Proposed mechanism for methane retention

MD simulations show kerogen swelling up to 3,000 psi (200 atm) and then shrinking at P up to 6,000 psi (400 atm) due to deformation

Our proposed mechanism

Pressure management is key for improving recovery—models must account for matrix nanopore effects!

Neil, C.W *et al.*, 2020. *Communications Earth & Environment*, *1*(1), pp.1-10.

Tesson, S. and Firoozabadi, A., 2019. *The Journal of Physical Chemistry C.*, *123*(48), pp. 29173-29183

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Instead, we turned to the literature. We found that in simulations of kerogen behavior in the presence of methane, the kerogen swelled upon exposure up to 3,000 psi. Further pressure increases led to deformation. Thus, we hypothesis that the initial uptake of methane and kerogen swelling up to 3,000 psi is reversable, which allows methane to be later recovered from pores. However, further increases to 6,000 psi led to deformation, which was irreversible and trapped methane in pores. This finding supports that pressure management is key to recovery.

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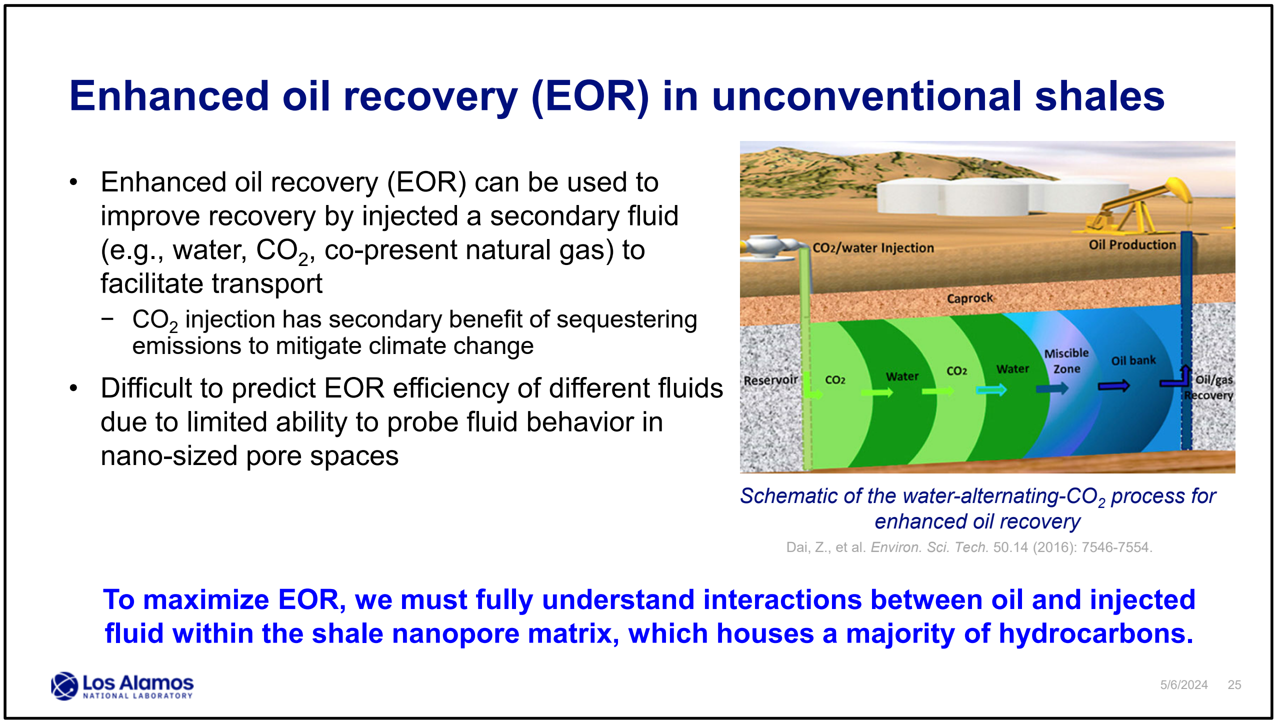


Enhanced oil recovery (EOR) in unconventional shales

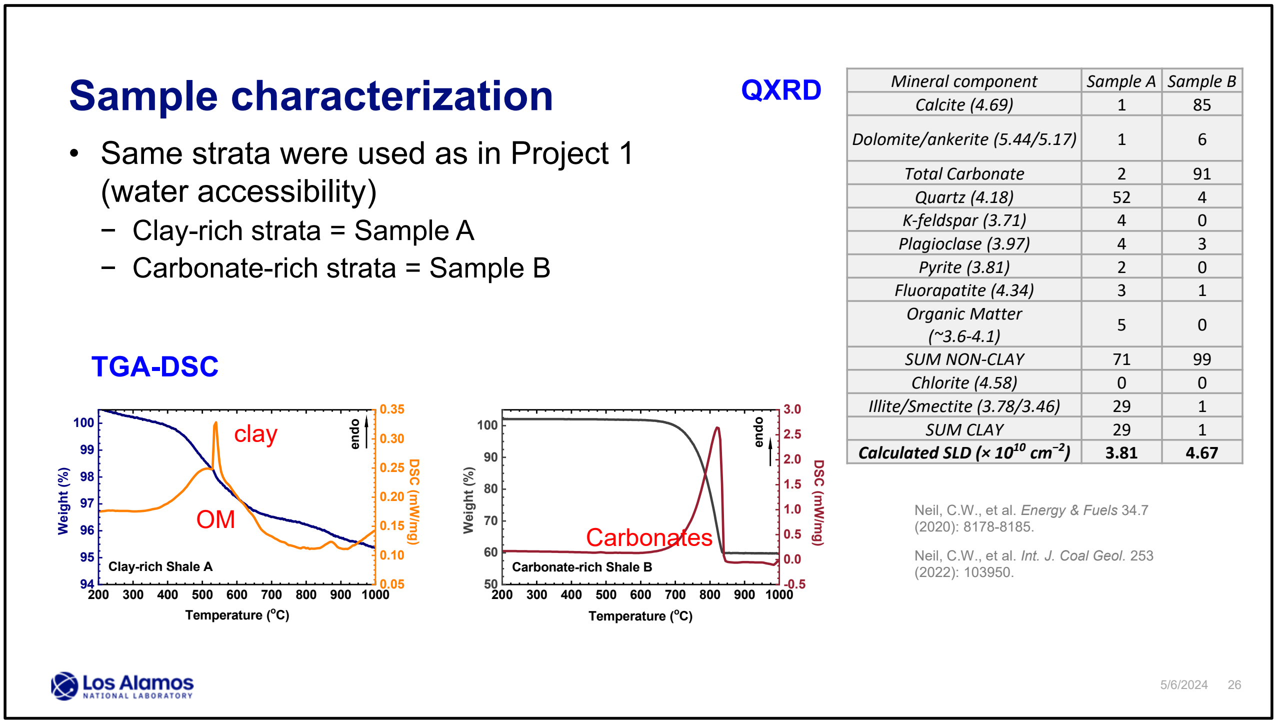
- Enhanced oil recovery (EOR) can be used to improve recovery by injected a secondary fluid (e.g., water, CO_2, co-present natural gas) to facilitate transport
  - CO_2 injection has secondary benefit of sequestering emissions to mitigate climate change
- Difficult to predict EOR efficiency of different fluids due to limited ability to probe fluid behavior in nano-sized pore spaces

Schematic of the water-alternating-CO_2 process for enhanced oil recovery

Dai, Z., et al. *Environ. Sci. Tech.* 50.14 (2016): 7546-7554.

To maximize EOR, we must fully understand interactions between oil and injected fluid within the shale nanopore matrix, which houses a majority of hydrocarbons.

Out third neutron-based study of shale focuses on enhanced oil recovery (EOR). EOR is a technique whereby a secondary fluid is injected into the subsurface to facilitate the transport of oil. However, it is difficult to predict EOR efficiency of different fluids due to limited ability to probe fluid recovery from nano-sized pore spaces. This is where SANS can be a powerful probe.



Sample characterization

- Same strata were used as in Project 1 (water accessibility)
  - Clay-rich strata = Sample A
  - Carbonate-rich strata = Sample B

TGA-DSC

QXRD

Mineral component	*Sample A*	*Sample B*
Calcite (4.69)	1	85
Dolomite/ankerite (5.44/5.17)	1	6
Total Carbonate	2	91
Quartz (4.18)	52	4
K-feldspar (3.71)	4	0
Plagioclase (3.97)	4	3
Pyrite (3.81)	2	0
Fluorapatite (4.34)	3	1
Organic Matter (~3.6-4.1)	5	0
SUM NON-CLAY	71	99
Chlorite (4.58)	0	0
Illite/Smectite (3.78/3.46)	29	1
SUM CLAY	29	1
Calculated SLD (× 10^{10} cm^{-2})	**3.81**	**4.67**

Neil, C.W., et al. *Energy & Fuels* 34.7 (2020): 8178-8185.

Neil, C.W., et al. *Int. J. Coal Geol.* 253 (2022): 103950.

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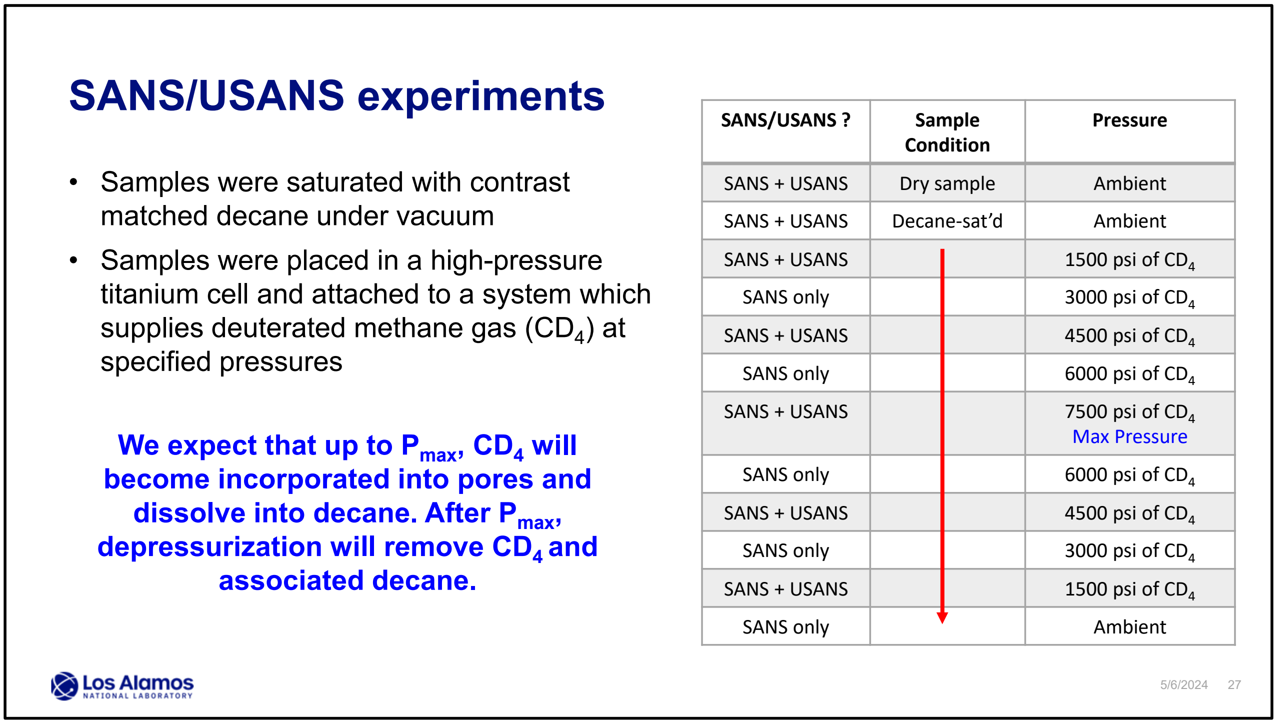
For these experiments, we utilized the same carbonate-rich and clay/organic matter-rich samples from the first study on water accessibility.



SANS/USANS experiments

- Samples were saturated with contrast matched decane under vacuum
- Samples were placed in a high-pressure titanium cell and attached to a system which supplies deuterated methane gas (CD_4) at specified pressures

We expect that up to P_{max}, CD_4 will become incorporated into pores and dissolve into decane. After P_{max}, depressurization will remove CD_4 and associated decane.

SANS/USANS ?	Sample Condition	Pressure
SANS + USANS	Dry sample	Ambient
SANS + USANS	Decane-sat'd	Ambient
SANS + USANS		1500 psi of CD_4
SANS only		3000 psi of CD_4
SANS + USANS		4500 psi of CD_4
SANS only		6000 psi of CD_4
SANS + USANS		7500 psi of CD_4 Max Pressure
SANS only		6000 psi of CD_4
SANS + USANS		4500 psi of CD_4
SANS only		3000 psi of CD_4
SANS + USANS		1500 psi of CD_4
SANS only		Ambient

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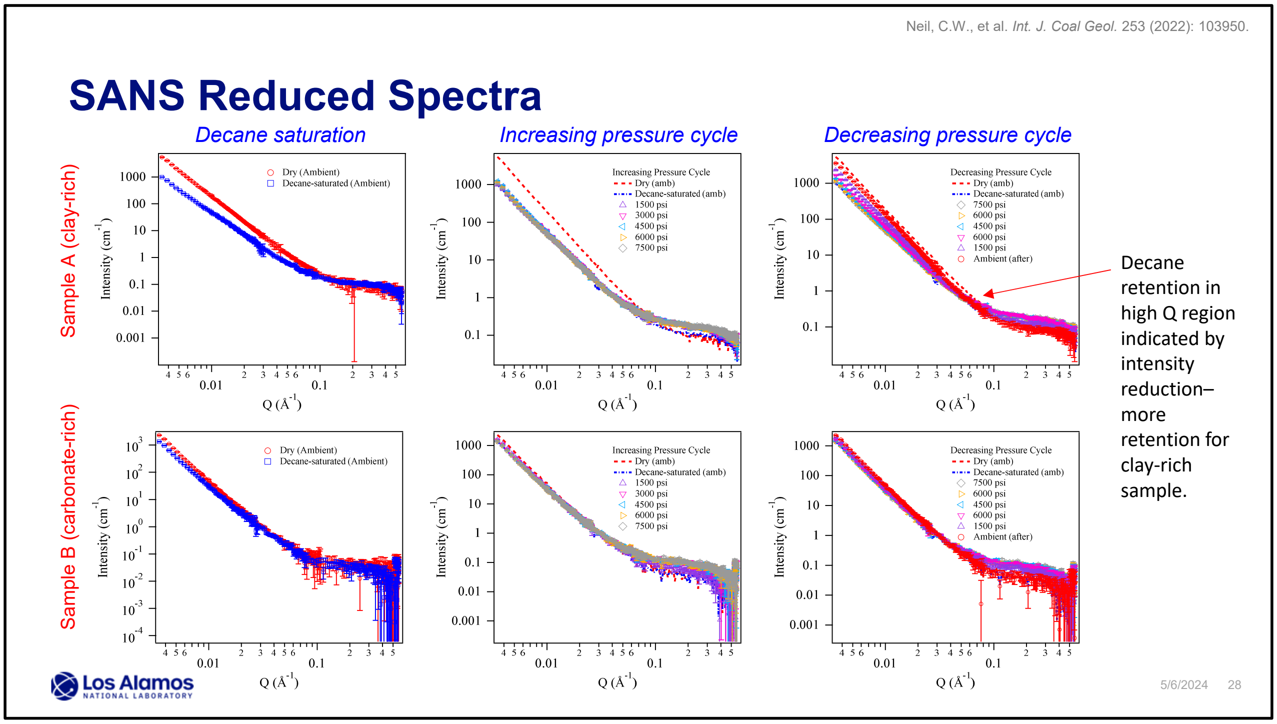
Samples were first saturated with decane, which was contrast matched to the pore matrix. Pressurization was carried out using the same pressure cell as in Project 2. The samples were pressurized to a maximum pressure of 7,500 psi and then depressurized back to ambient pressure.



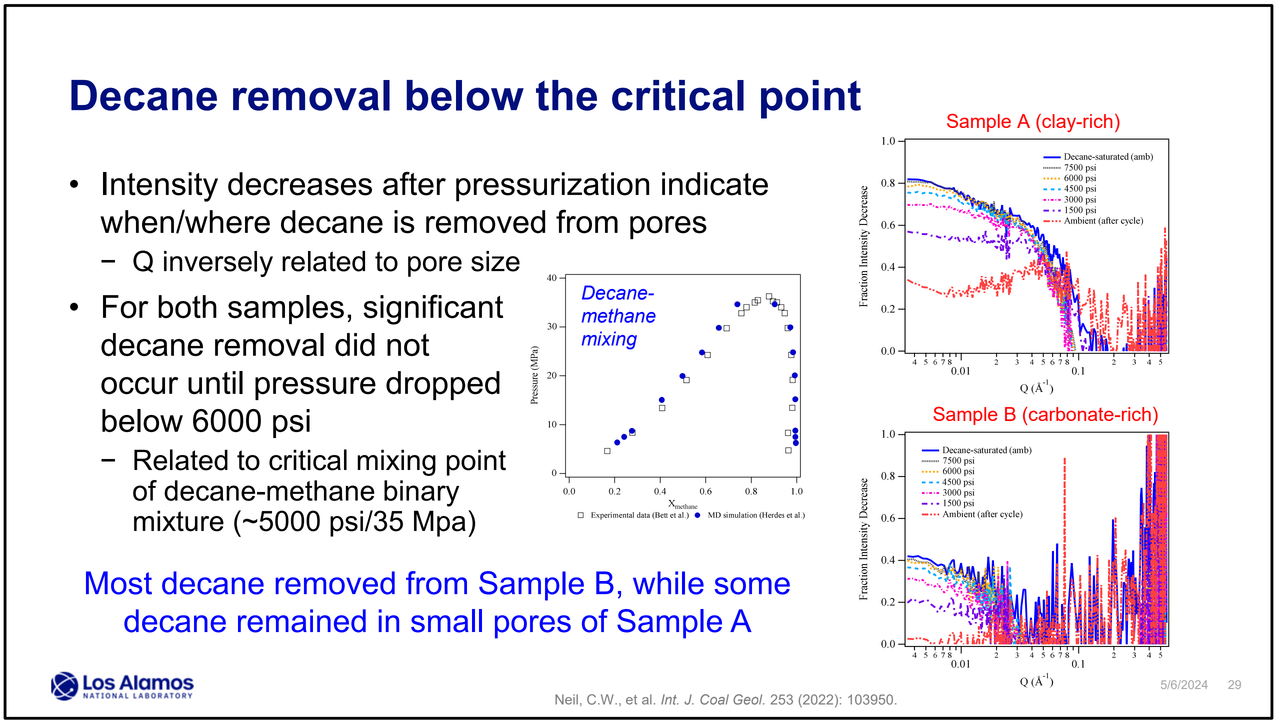
Neil, C.W., et al. *Int. J. Coal Geol.* 253 (2022): 103950.

SANS Reduced Spectra

Decane saturation | *Increasing pressure cycle* | *Decreasing pressure cycle*

Decane retention in high Q region indicated by intensity reduction– more retention for clay-rich sample.

These plots show the SANS spectra for the two samples. Sample A took up much more decane than sample B, as evidenced by the larger intensity drop. This makes sense given the much higher organic matter content of sample A. Pressurization with methane did not substantially change the scattering. Upon depressurization though, the scattering intensity clearly increases for both samples as decane is removed from the pore spaces. You can also observe for Shale A that there is still decane remaining in the pores, particularly at high Q/in the smaller pores.



Decane removal below the critical point

- Intensity decreases after pressurization indicate when/where decane is removed from pores
  - Q inversely related to pore size
- For both samples, significant decane removal did not occur until pressure dropped below 6000 psi
  - Related to critical mixing point of decane-methane binary mixture (~5000 psi/35 Mpa)

Most decane removed from Sample B, while some decane remained in small pores of Sample A

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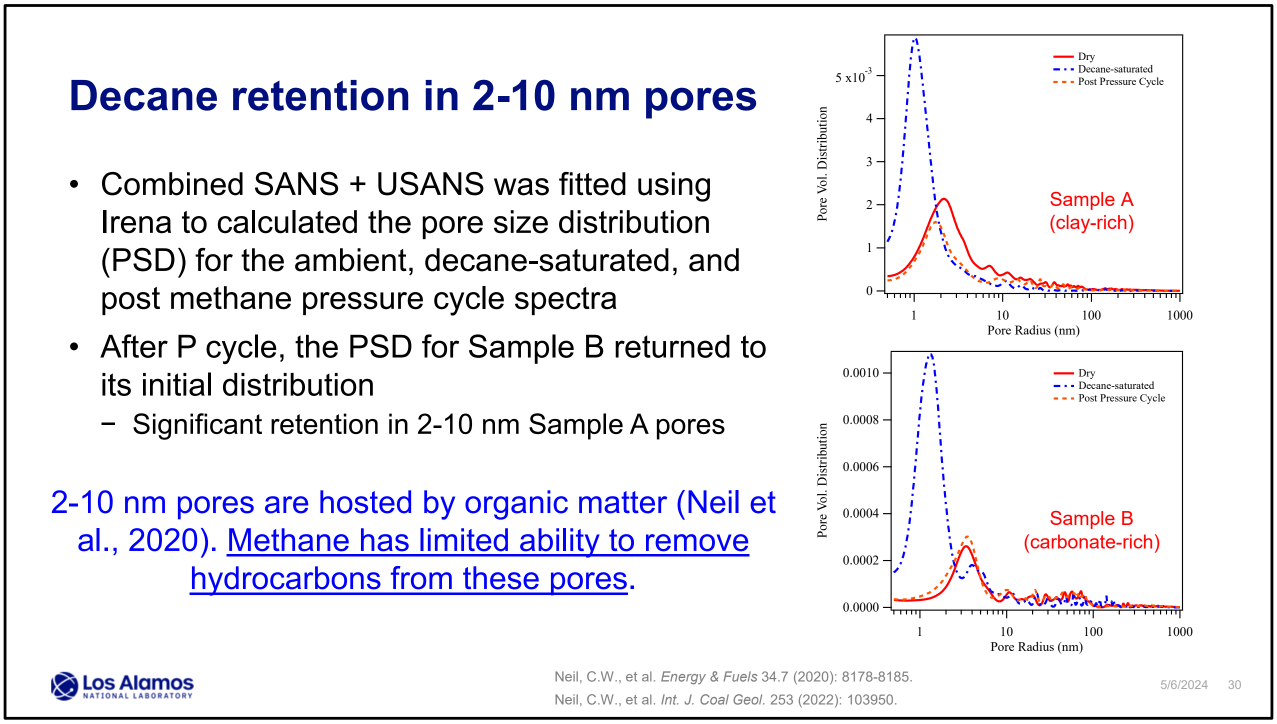
Neil, C.W., et al. *Int. J. Coal Geol.* 253 (2022): 103950.

This becomes more obvious when you plot the graphs as the change in intensity vs. Q, where decreases in intensity indicate where decane remains in the pores. For both samples, significant decane removal did not occur until pressure dropped below 6000 psi, which we think is related to the critical mixing point of decane-methane binary mixture (~5000 psi/35 Mpa). It's also clear that for sample A, there was significant retention in the small pores while for sample B, there was essentially no retention.



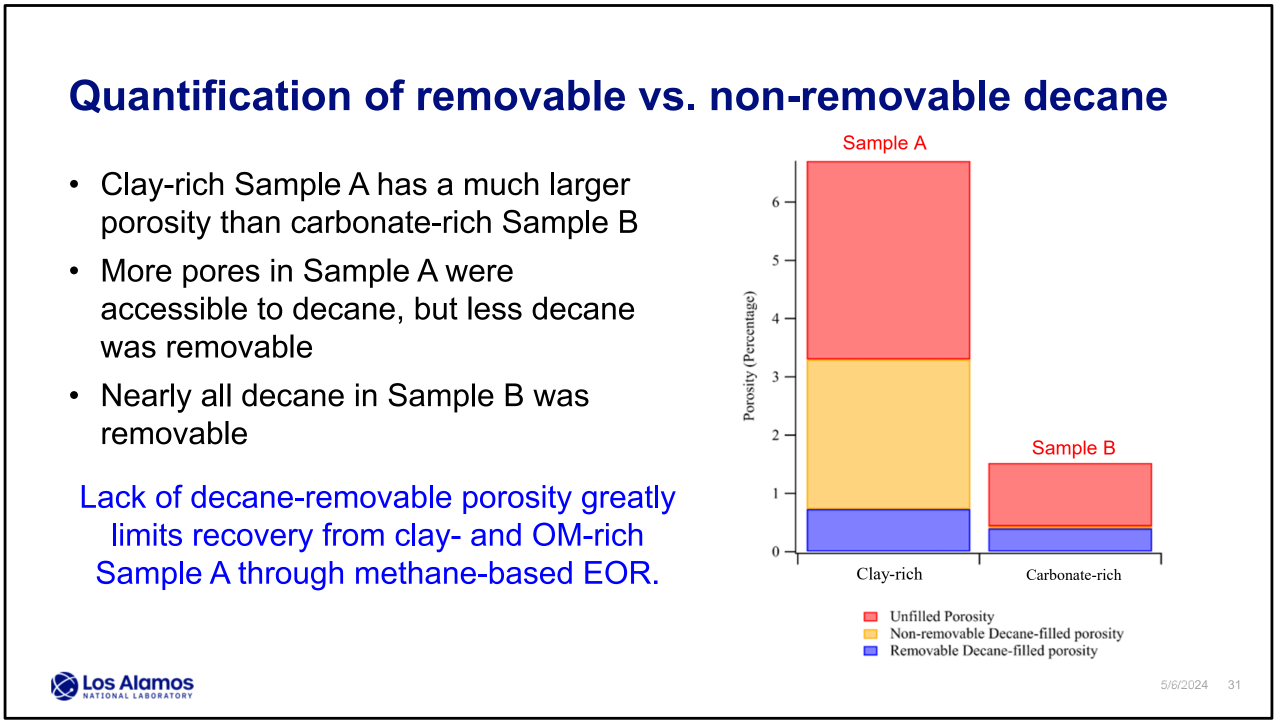
Decane retention in 2-10 nm pores

- Combined SANS + USANS was fitted using Irena to calculated the pore size distribution (PSD) for the ambient, decane-saturated, and post methane pressure cycle spectra
- After P cycle, the PSD for Sample B returned to its initial distribution
  - Significant retention in 2-10 nm Sample A pores

2-10 nm pores are hosted by organic matter (Neil et al., 2020). Methane has limited ability to remove hydrocarbons from these pores.

Neil, C.W., et al. *Energy & Fuels* 34.7 (2020): 8178-8185.
Neil, C.W., et al. *Int. J. Coal Geol.* 253 (2022): 103950.

SANS spectra at ambient conditions were fitted to further demonstrate which pores were host to retained decane. For both samples, decane saturation led to a relative abundance of very small pores, likely due to pore that were either inaccessible due to their size or not completely filled with decane. After pressurization and depressurization with methane, the PSD for Sample B returned to its initial distribution, while significant retention was observed in the 2-10 nm Sample A pores. We know from project 1 that these pores are likely hosted by organic matter, which is also the likely host of in place hydrocarbons within the shale matrix. Thus, it seems likely that methane has a limited ability to remove hydrocarbons from these pores.

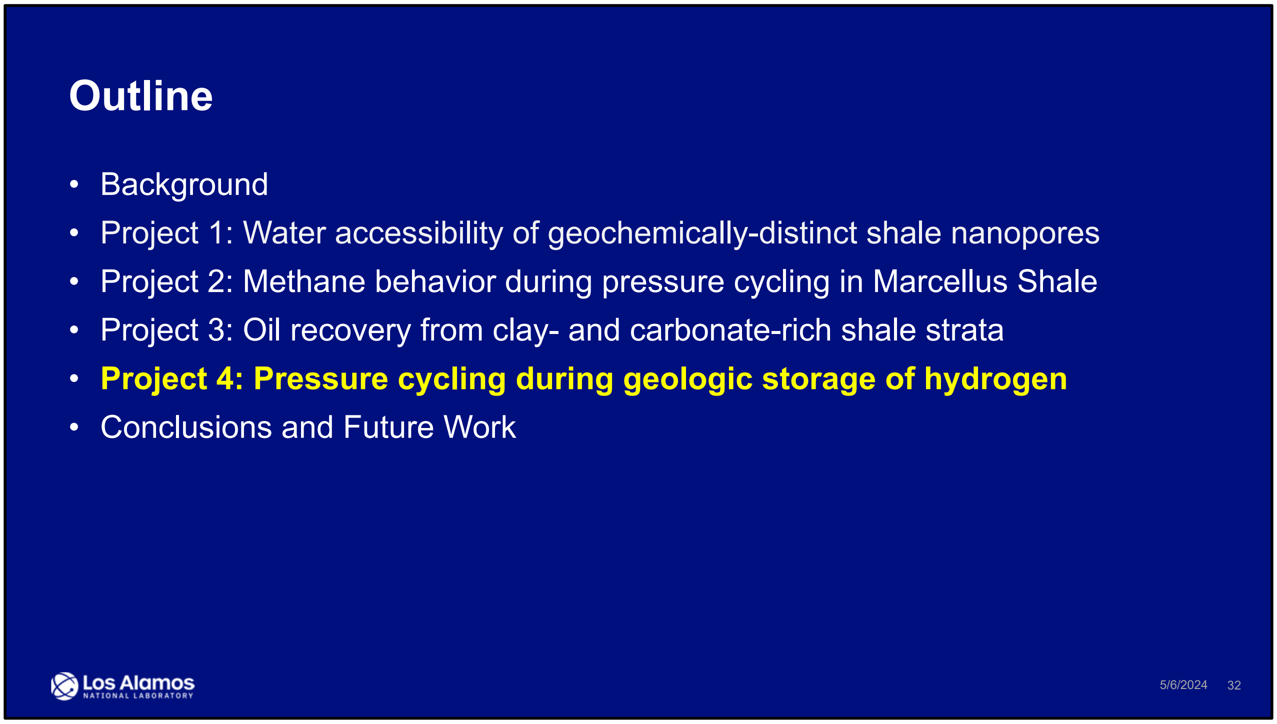


Quantification of removable vs. non-removable decane

- Clay-rich Sample A has a much larger porosity than carbonate-rich Sample B
- More pores in Sample A were accessible to decane, but less decane was removable
- Nearly all decane in Sample B was removable

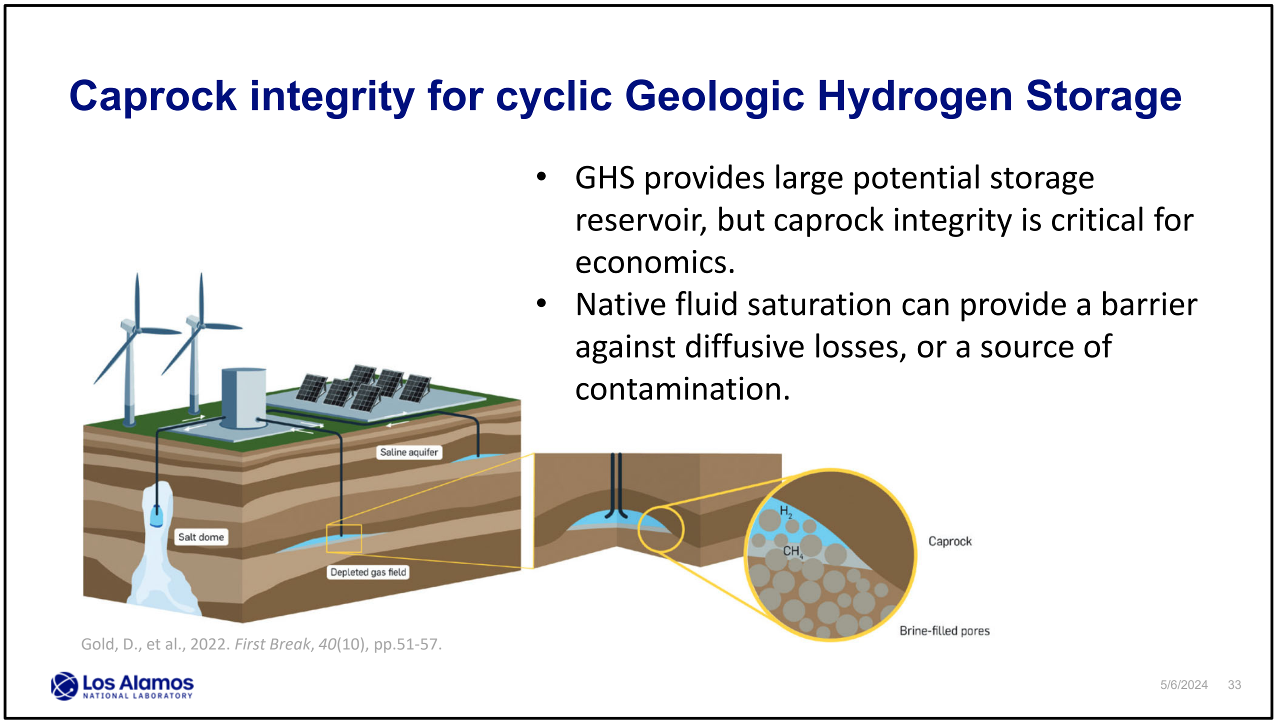
Lack of decane-removable porosity greatly limits recovery from clay- and OM-rich Sample A through methane-based EOR.

Finally, we took the SANS data and calculated the porosity to quantify removable vs. non removable decane. As we observed previously, Sample A has a much larger porosity than Sample B. We also found that while more pores in Sample A were accessible to decane, a smaller percentage of decane was removable, while for sample B nearly all decane was removable. Thus, a lack of decane-removable porosity greatly limits recovery from clay- and OM-rich Sample A through methane-based EOR.



Outline

- Background
- Project 1: Water accessibility of geochemically-distinct shale nanopores
- Project 2: Methane behavior during pressure cycling in Marcellus Shale
- Project 3: Oil recovery from clay- and carbonate-rich shale strata
- **Project 4: Pressure cycling during geologic storage of hydrogen**
- Conclusions and Future Work

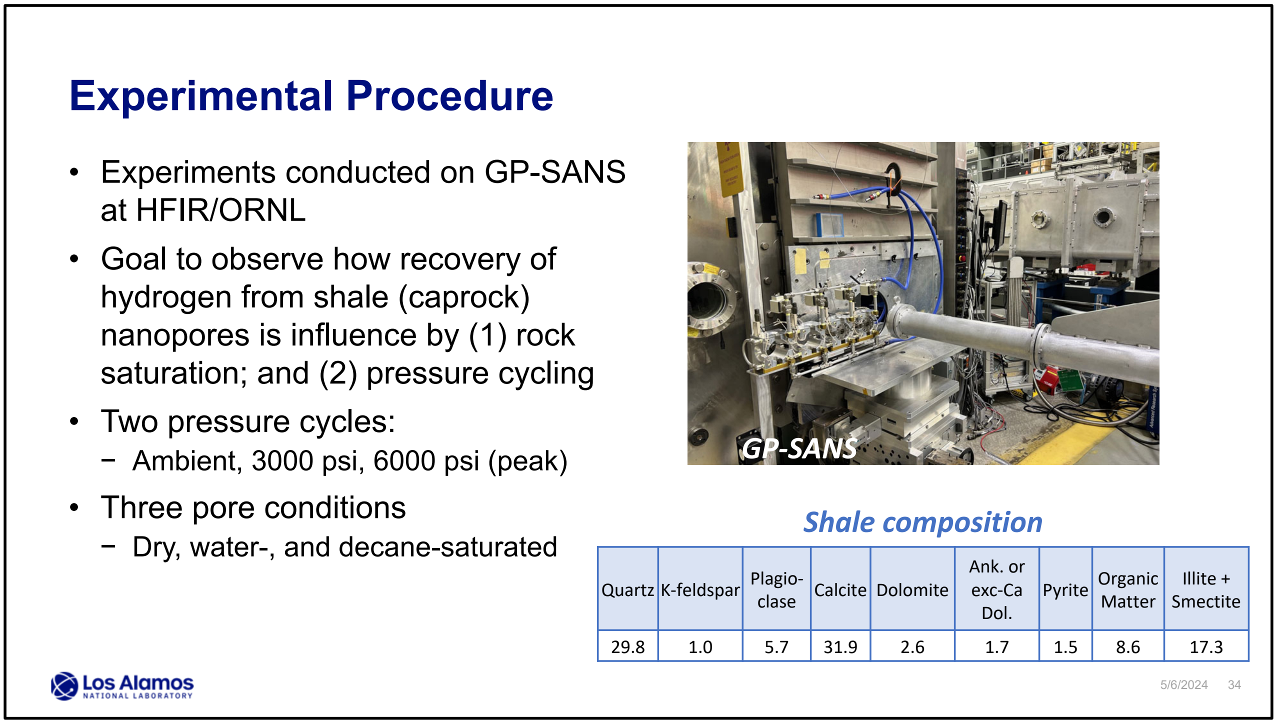


Caprock integrity for cyclic Geologic Hydrogen Storage

- GHS provides large potential storage reservoir, but caprock integrity is critical for economics.
- Native fluid saturation can provide a barrier against diffusive losses, or a source of contamination.

Gold, D., et al., 2022. *First Break*, *40*(10), pp.51-57.

For our last SANS study, we will shift focus to hydrogen behavior within shale. For proposed seasonal storage of hydrogen in subsurface reservoirs, caprock integrity is critical to ensure that injected hydrogen remains present for subsequent withdrawal. Hydrogen is an extremely small and buoyant molecule, making it difficult to contain. For our initial study, we focused on the impact of rock saturation. The saturation of shale with native fluid, be it either water or hydrocarbons, can provide a barrier against diffusive losses. However, it can also be a source of contamination.



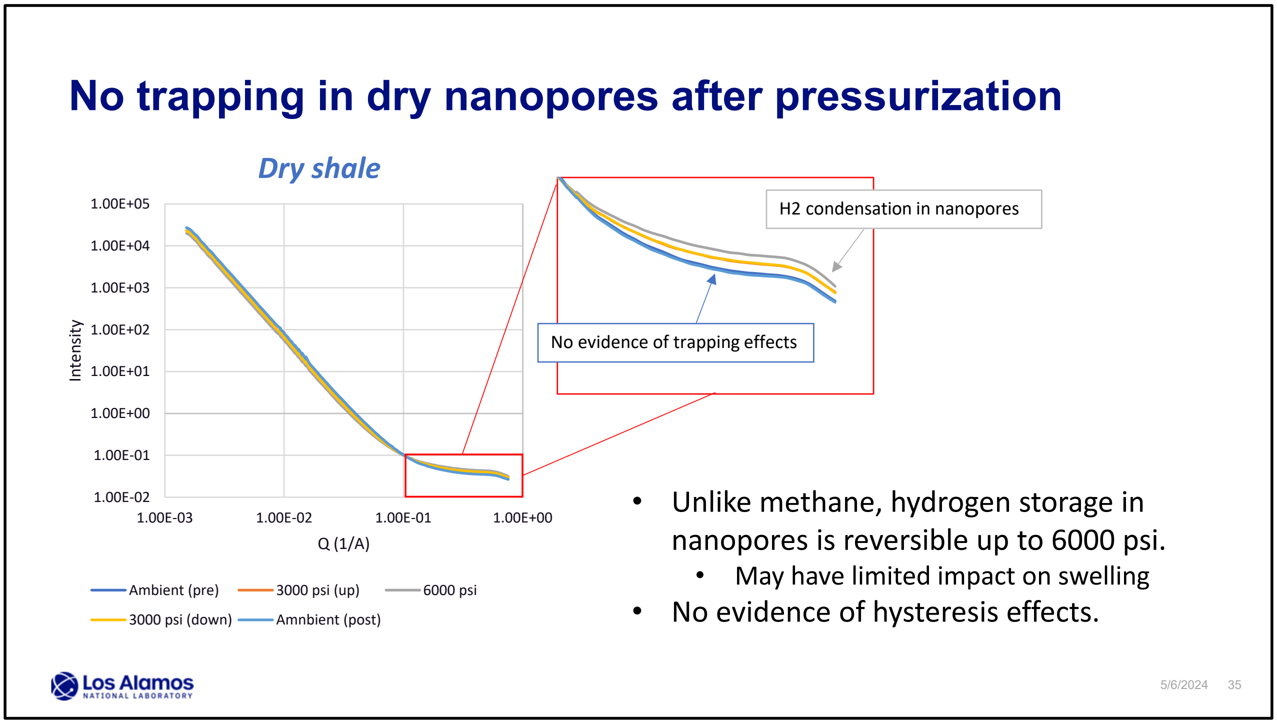
Experimental Procedure

- Experiments conducted on GP-SANS at HFIR/ORNL
- Goal to observe how recovery of hydrogen from shale (caprock) nanopores is influence by (1) rock saturation; and (2) pressure cycling
- Two pressure cycles:
  - Ambient, 3000 psi, 6000 psi (peak)
- Three pore conditions
  - Dry, water-, and decane-saturated

Shale composition

Quartz	K-feldspar	Plagio-clase	Calcite	Dolomite	Ank. or exc-Ca Dol.	Pyrite	Organic Matter	Illite + Smectite
29.8	1.0	5.7	31.9	2.6	1.7	1.5	8.6	17.3

Due to the cyclic nature of hydrogen storage, we were interested in measuring the behavior over multiple pressure cycles. We utilized shale rock which was either dry, water saturated, or decane saturated. The shale was pressurized to 6,000 psi then decreased to ambient pressure twice over two pressure cycles with the goal of observing how these factors impact hydrogen recovery from the caprock.



No trapping in dry nanopores after pressurization

- Unlike methane, hydrogen storage in nanopores is reversible up to 6000 psi.
    - May have limited impact on swelling
- No evidence of hysteresis effects.

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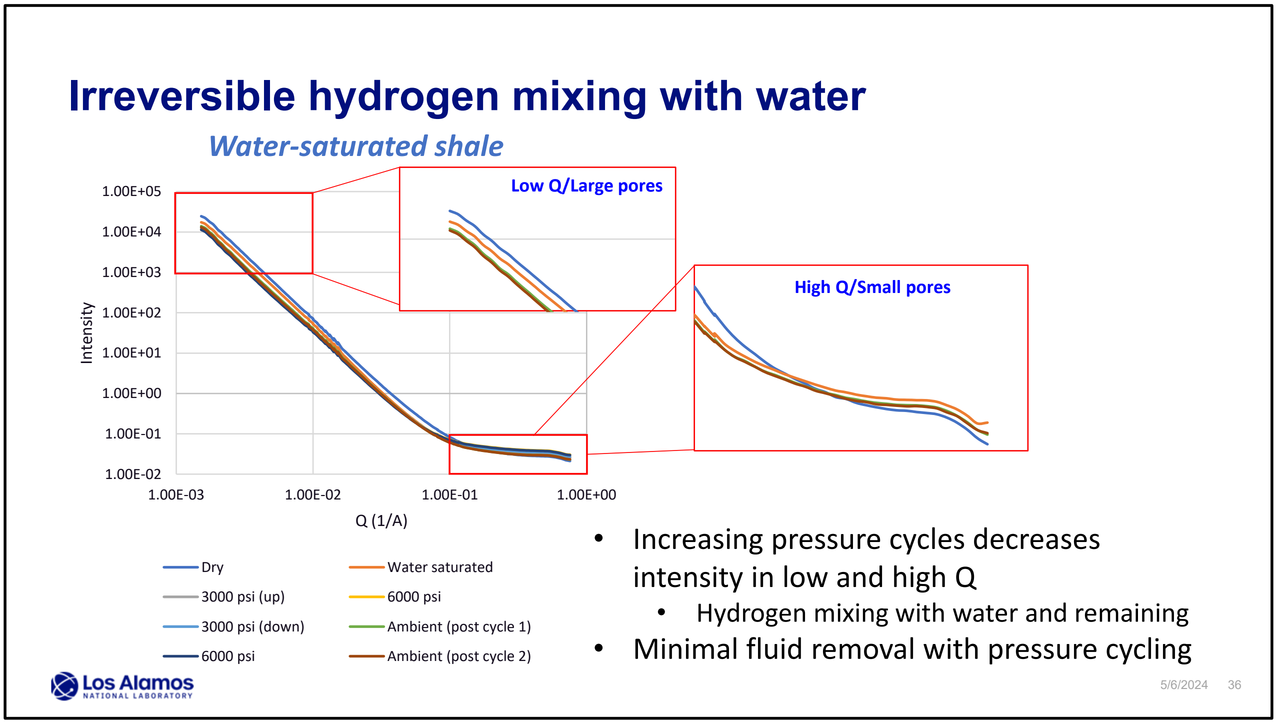
For the dry shale sample, hydrogen storage in nanopores is reversible up to 6000 psi with no evidence of hysteresis effects, a different finding compared with our methane study. This could be because of differences in the molecule (hydrogen vs. methane) impacting the degree of swelling, or could be because this sample is from an oil-producing play rather than a gas-producing play. This distinction could be important in future site selection.



Irreversible hydrogen mixing with water

Water-saturated shale

- Increasing pressure cycles decreases intensity in low and high Q
    - Hydrogen mixing with water and remaining
- Minimal fluid removal with pressure cycling

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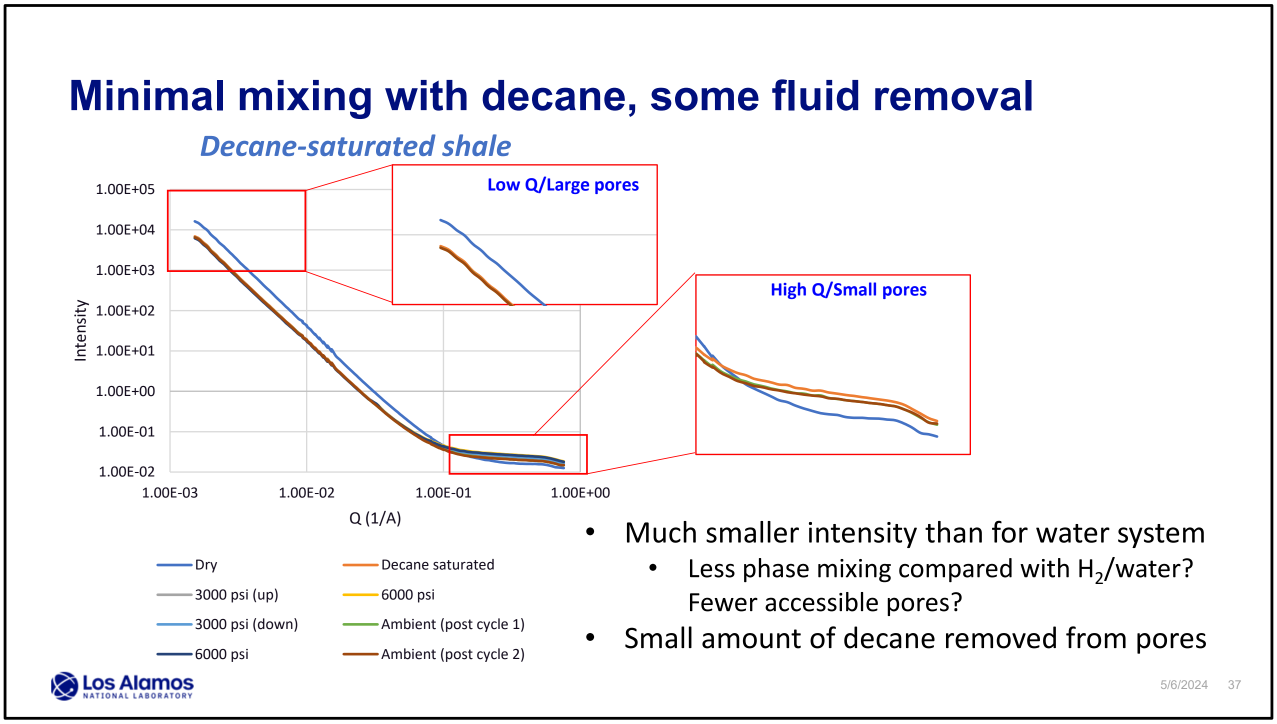
Once water is present in the pores, we observed that upon H2 introduction the intensity decreased across the entire Q range and remained nearly constant even with multiple pressure cycles. This indicates that hydrogen may be mixing with water and that this mixing is irreversible. Additionally, there is not strong evidence that water is removed from the pores during pressure cycling.



Minimal mixing with decane, some fluid removal

Decane-saturated shale

- Much smaller intensity than for water system
  - Less phase mixing compared with H_2/water? Fewer accessible pores?
- Small amount of decane removed from pores

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For decane saturated shale, there was a much smaller intensity drop when H2 was introduced, which could be due to less phase mixing compared with H2/water or possibly fewer accessible pores. It did appear that following pressurization, there was a small amount of decane removed from pores.

Nanopore transport impacts on GHS

- Preliminary SANS observations indicate important processes which can impact long term GHS
  - Hydrogen loss to water-saturated caprock
  - Contamination by removable decane
- Minimal water removal indicated that water saturation can prevent hydrogen diffusion through caprock
- Ongoing work
  - PSD analysis of experimental results
  - Neutron imaging
  - Reservoir rock characterization

SANS results indicate that there were some interactions between hydrogen and pore fluid, including hydrogen loss to the saturated caprock and potentially some contamination of hydrogen by removable decane. However, there was minimal fluid removal over multiple pressure cycles, meaning that in place fluid may be stable enough to prevent substantial hydrogen diffusion into the caprock.

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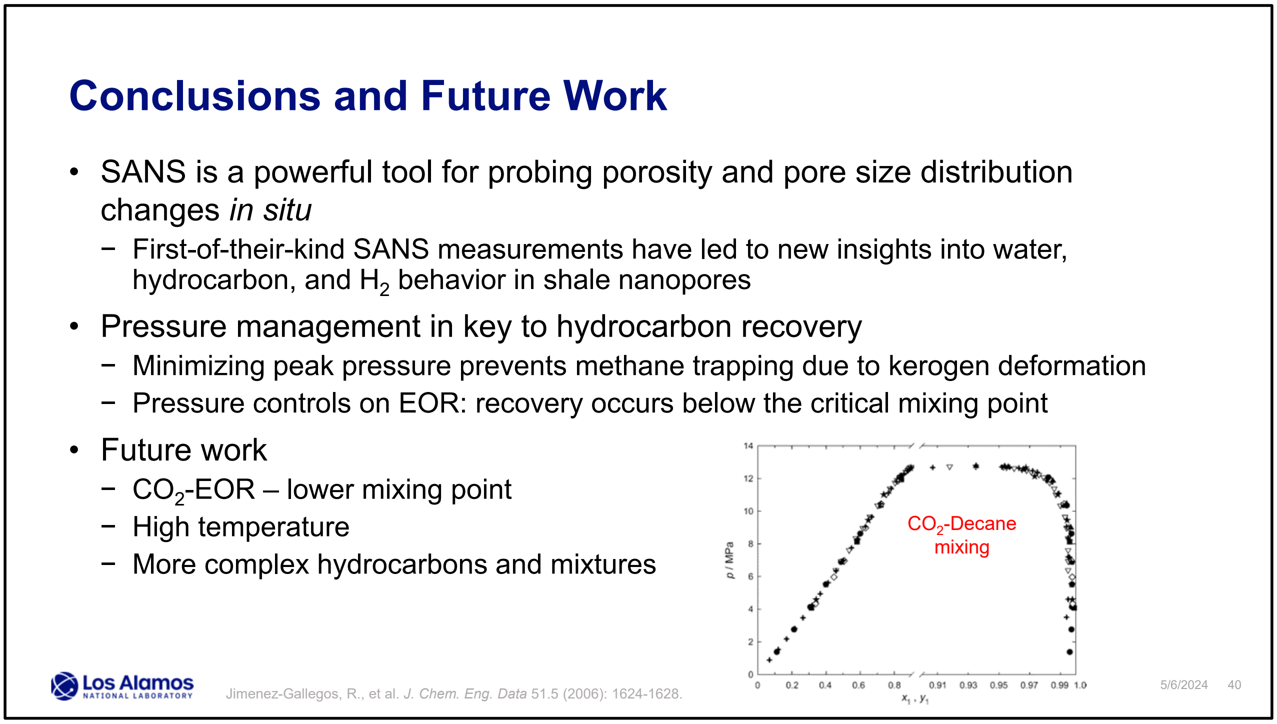

Conclusions and Future Work

- SANS is a powerful tool for probing porosity and pore size distribution changes *in situ*
  - First-of-their-kind SANS measurements have led to new insights into water, hydrocarbon, and H_2 behavior in shale nanopores
- Pressure management in key to hydrocarbon recovery
  - Minimizing peak pressure prevents methane trapping due to kerogen deformation
  - Pressure controls on EOR: recovery occurs below the critical mixing point
- Future work
  - CO_2-EOR – lower mixing point
  - High temperature
  - More complex hydrocarbons and mixtures

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Jimenez-Gallegos, R., et al. *J. Chem. Eng. Data* 51.5 (2006): 1624-1628.

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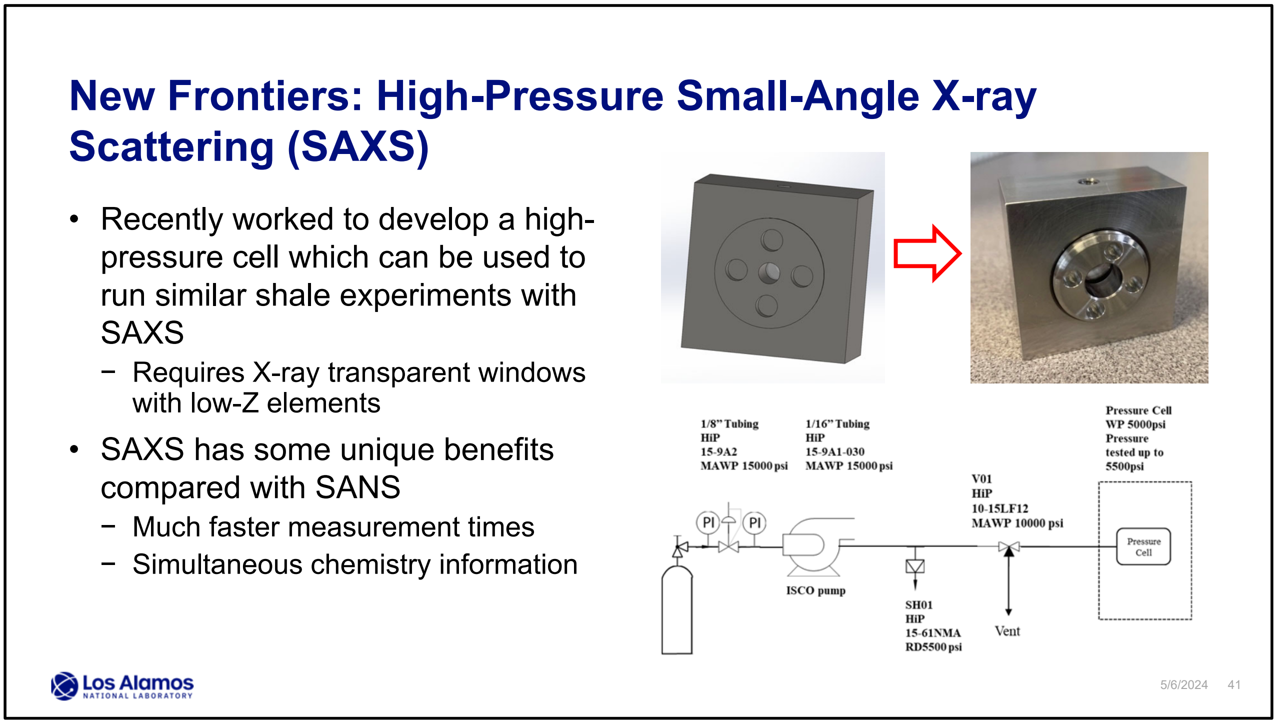
In conclusion, SANS is a powerful tool for probing porosity and pore size distribution changes in situ. Our first-of-their-kind SANS measurements have led to new insights into water, hydrocarbon, and H2 behavior in shale nanopores, and these results indicate that pressure management is key for controlling fluid and gad behavior in these systems. We are expanding our work into looking at CO2 use for EOR, making measurements at high temperature, and looking at more complex hydrocarbons and mixtures.



New Frontiers: High-Pressure Small-Angle X-ray Scattering (SAXS)

- Recently worked to develop a high-pressure cell which can be used to run similar shale experiments with SAXS
  - Requires X-ray transparent windows with low-Z elements
- SAXS has some unique benefits compared with SANS
  - Much faster measurement times
  - Simultaneous chemistry information

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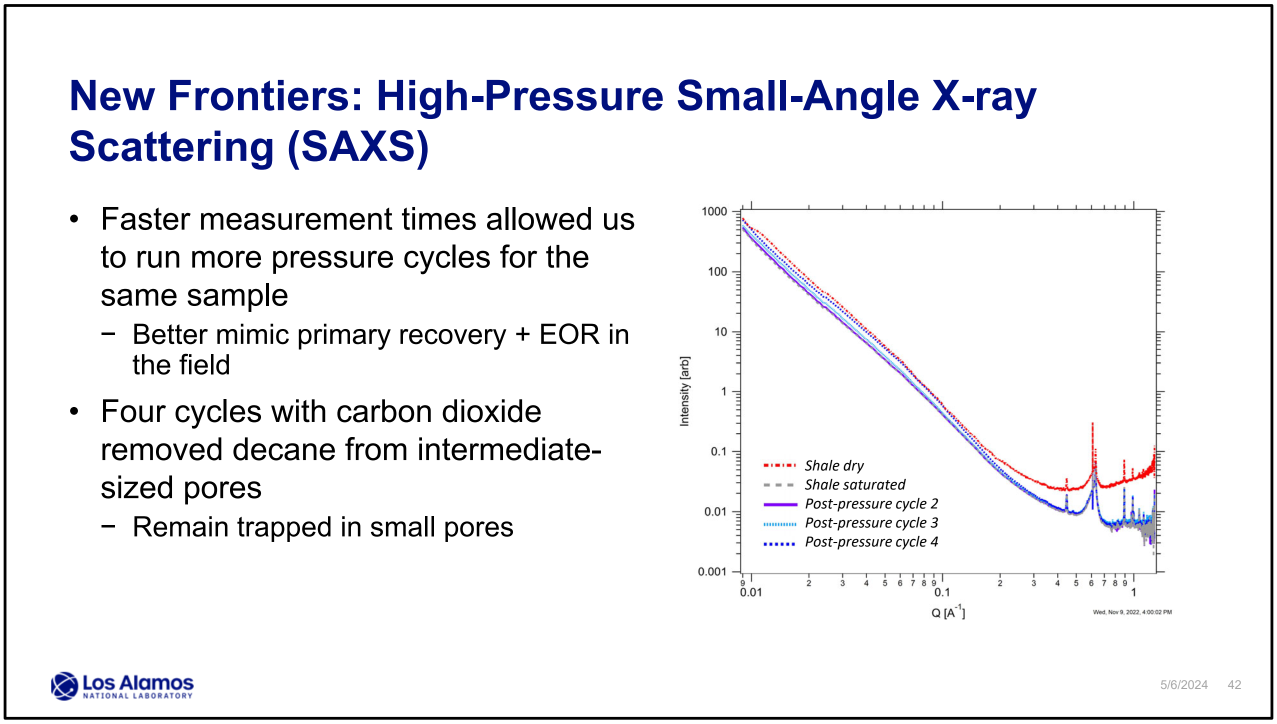
Additionally, we are working on applying this technique for high-pressure small-angle X-ray scattering (SAXS). SAXS has some unique benefits compared with SANS, including much faster measurement times and the ability to measure changes in chemistry simultaneously.



New Frontiers: High-Pressure Small-Angle X-ray Scattering (SAXS)

- Faster measurement times allowed us to run more pressure cycles for the same sample
  - Better mimic primary recovery + EOR in the field
- Four cycles with carbon dioxide removed decane from intermediate-sized pores
  - Remain trapped in small pores

Using SAXS, we were able to run more pressure cycles, which would otherwise be time prohibitive for SANS. We observed that four cycles with CO2 removed decane from intermediate-sized pores, but it remained trapped in small pores.

SANS Publications

- Neil, C.W., Hjelm, R.P., Hawley, M.E., Watkins, E.B., Cockreham, C., Wu, D., Mao, Y., Fischer, T.B., Stokes, M.R. and Xu, H., 2020. Small-angle neutron scattering (SANS) characterization of clay-and carbonate-rich shale at elevated pressures. *Energy & Fuels*, *34*(7), pp.8178-8185.
- Neil, C.W., Mehana, M., Hjelm, R.P., Hawley, M.E., Watkins, E.B., Mao, Y., Viswanathan, H., Kang, Q. and Xu, H., 2020. Reduced methane recovery at high pressure due to methane trapping in shale nanopores. *Communications Earth & Environment*, *1*(1), pp.1-10.
- Neil, C.W., Hjelm, R.P., Hawley, M.E., Watkins, E.B., Cockreham, C., Wu, D., Mao, Y., Cheshire, M., Burger, J., Fischer, T.B. and Stokes, M.R., 2022. Probing oil recovery in shale nanopores with small-angle and ultra-small-angle neutron scattering. *International Journal of Coal Geology*, *253*, p.103950.
- Mehana, M., Santos, J.E., Neil, C., Carey, J.W., Guthrie, G., Hyman, J., Kang, Q., Karra, S., Sweeney, M., Xu, H. and Viswanathan, H., 2022. Shale fundamentals: Experimental and modeling insights. *Energy Reports*, *8*, pp.11192-11205.
- Neil, C.W., Hjelm, R.P., Hawley, M.E., Watkins, E.B., Mao, Y., Pawar, R. and Xu, H., 2023. Small-Angle Neutron Scattering Investigation of Oil Recovery in Mineralogically Distinct Wolfcamp Shale Strata. *Energy & Fuels*, 37(7), pp.4937-4947.

Thank you!

Questions or comments?

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