Quantifying Hydrophilic and Hydrophobic Pore Networks of the Bakken Shale*

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Abstract

Understanding rock wettability behavior from micrometer to nanometer scale is of great significance to in-situ hydrocarbon volume calculation and oil recovery improvement in tight-rock reservoirs. In this study, comprehensive rock-fluid experiments were performed to investigate wettability of three members of the Bakken Formation. The contact angle of selected specimens was measured by applying four types of hydrophilic and hydrophobic fluids (i.e., DI water, API brine, IPA isopropyl alcohol, and n-decane) to observe rock wettability at the millimeter scale. Then through a spontaneous imbibition test, different fluid flow behaviors in the shale were compared. As capillary-pressure greatly controls fluid migration in micro- and nano-pores, mercury injection capillary pressure (MICP) analysis, using non-wetting fluid mercury, was conducted to obtain pore system characteristics with multiple connected pore networks at the pore-throat size ranging in mm-nm scale. Furthermore, the wettability at nano-pore scale was qualified through a small-angle neutron scattering technique, by comparing the volume fraction of intruded fluids.

The results suggest a distinct difference in the rock wettability between the Upper/Lower Bakken and Middle Bakken, which is mainly caused by mineralogical composition and organic matter content. Multiple and complementary approaches enable us to quantify the proportion, and size distribution of hydrophilic vs. hydrophobic pore networks in the Bakken Shale.

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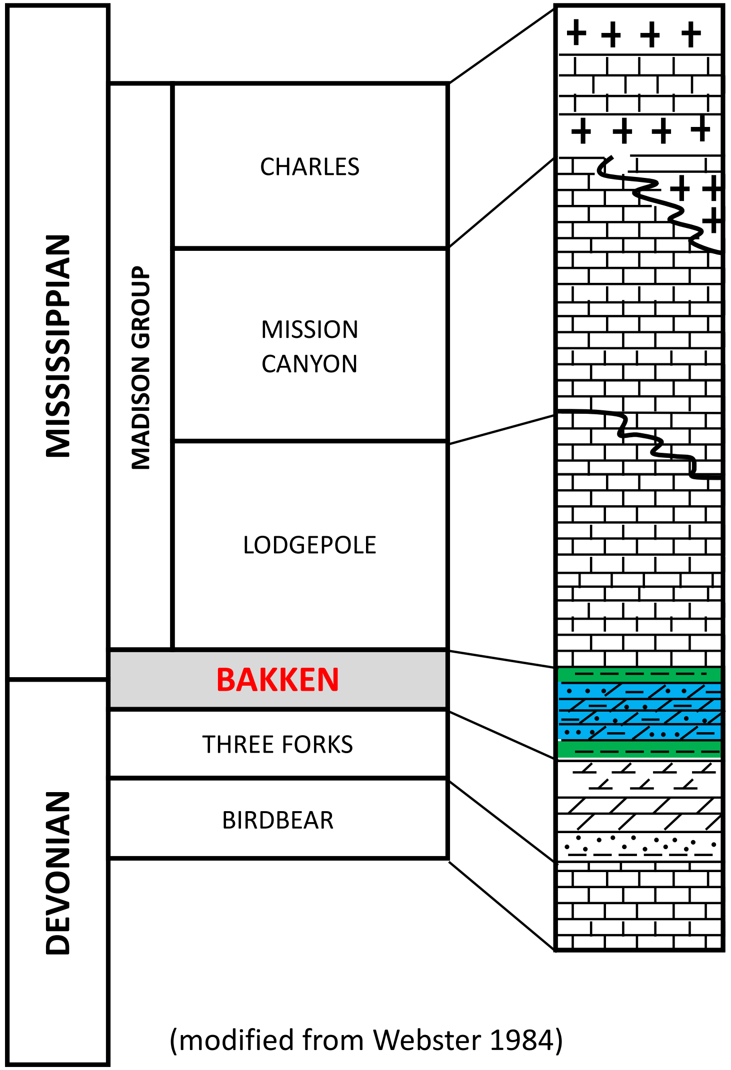
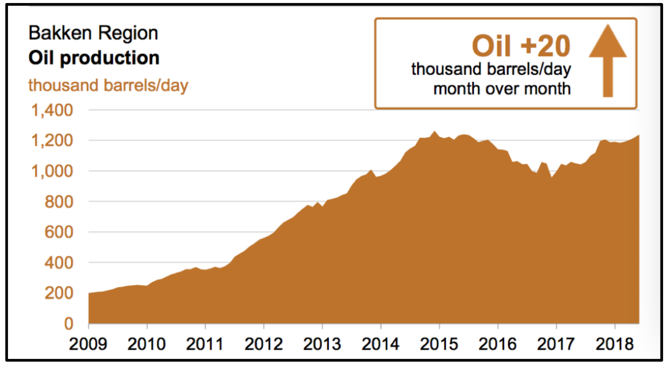
ACE 2018 ANNUAL CONVENTION & EXHIBITION
ACE 101: Bridging Fundamentals and Innovation

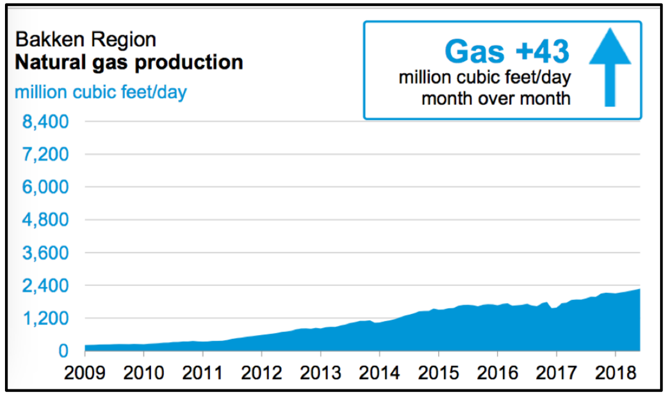
Background & Motivation

(Pitman et al., 2001)



(modified from Webster 1984)



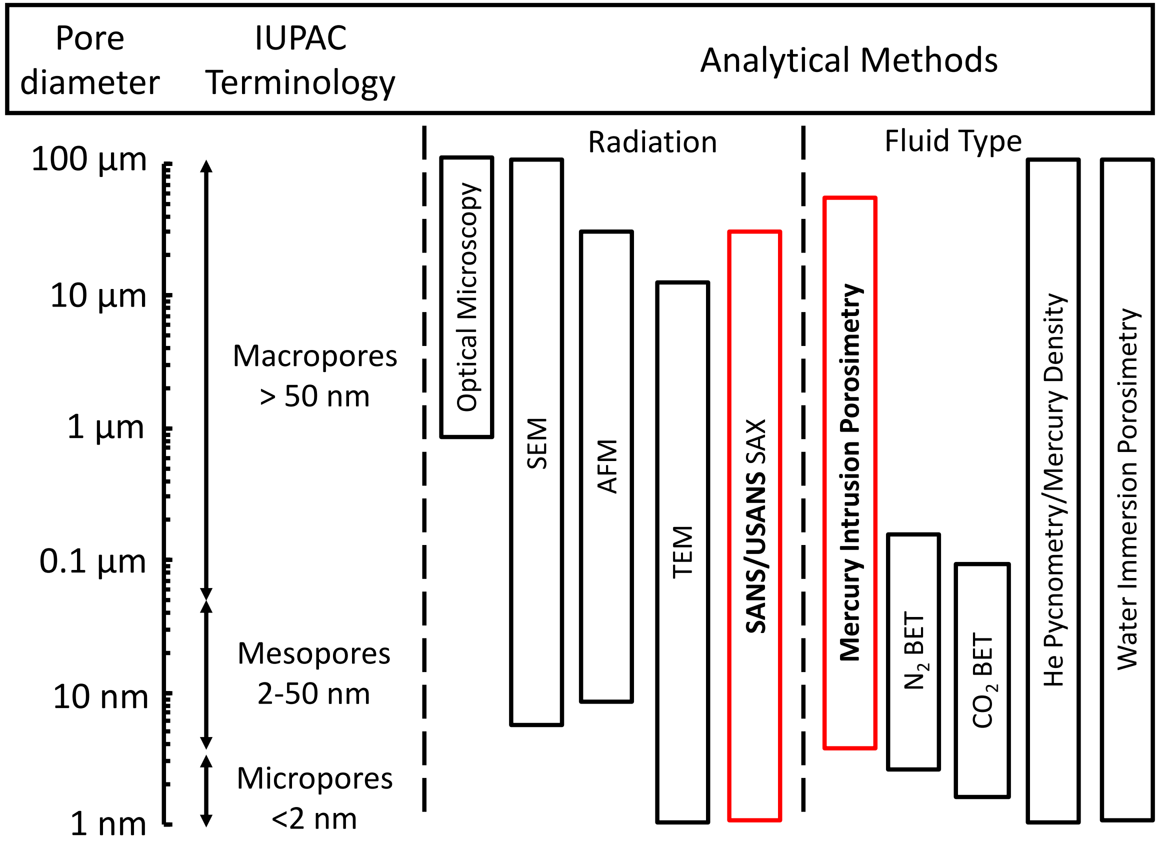


(EIA Report, May 2018)

Purpose

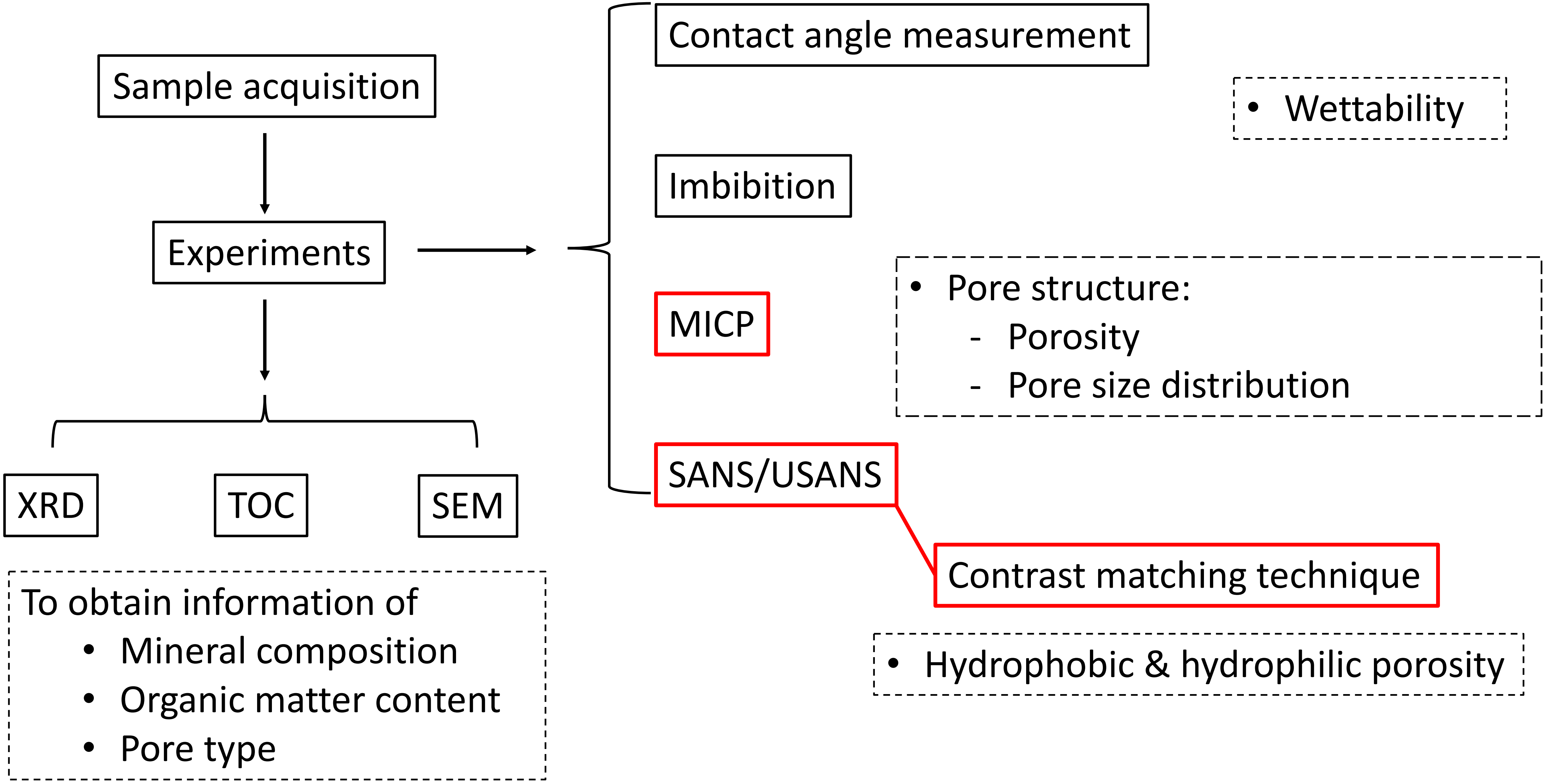
Study Purpose:
Characterize pore geometry, connectivity, and wettability of the Bakken Shale from nanometer to micrometer scales

Main techniques:
1. Mercury injection capillary pressure (MICP) analysis
2. Small angle and ultra-small angle neutron scattering (SANS and USANS) measurements

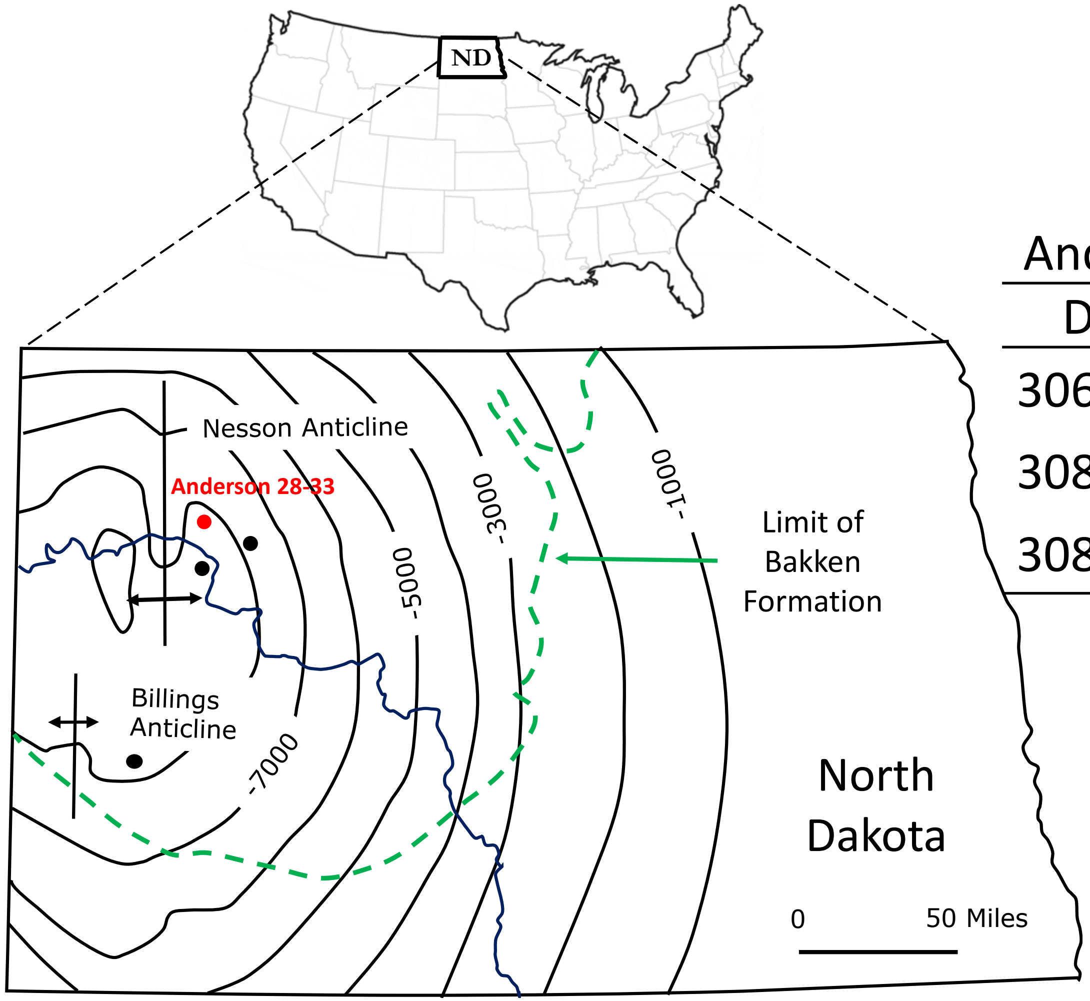


(modified from Anovitz and Cole, 2015)

Workflow


Sample acquisition
Experiments
XRD
TOC
SEM
To obtain information of
• Mineral composition
• Organic matter content
• Pore type
Contact angle measurement
Imbibition
MICP
SANS/USANS
• Wettability
• Pore structure:
- Porosity
- Pore size distribution
Contrast matching technique
• Hydrophobic & hydrophilic porosity

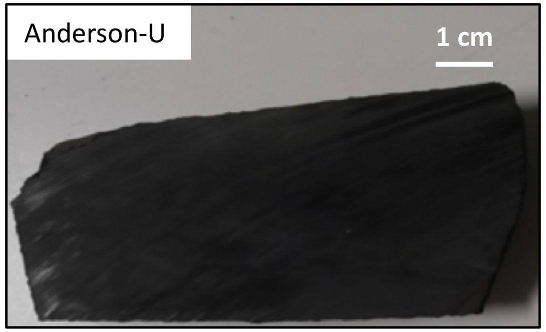
Experiments - sample acquisition

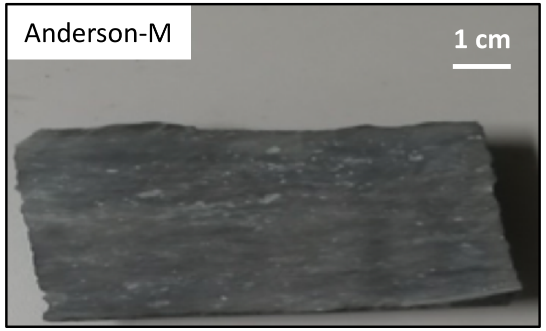


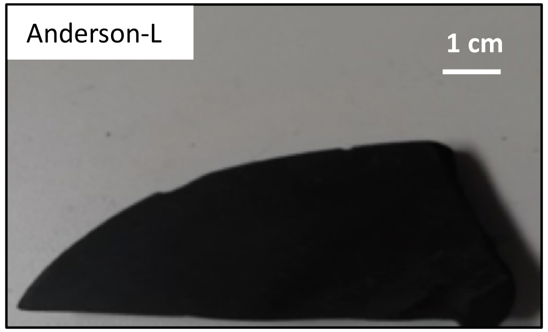
(modified from Webster 1984)

Anderson 28-33

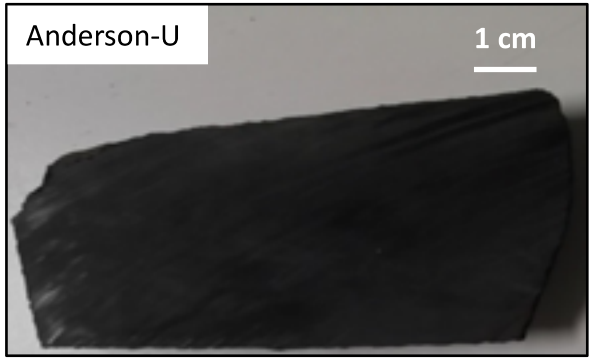
Depth m (ft)	Formation
3067.5 (10064)	Upper Bakken
3084.9 (10121)	Middle Bakken
3085.8 (10124)	Lower Bakken

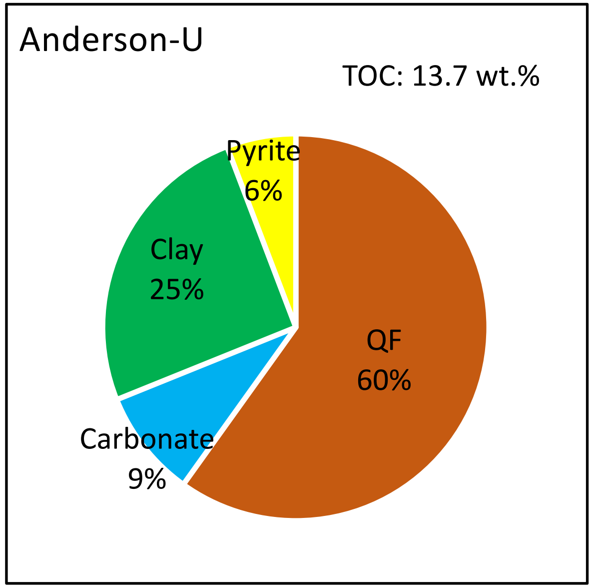


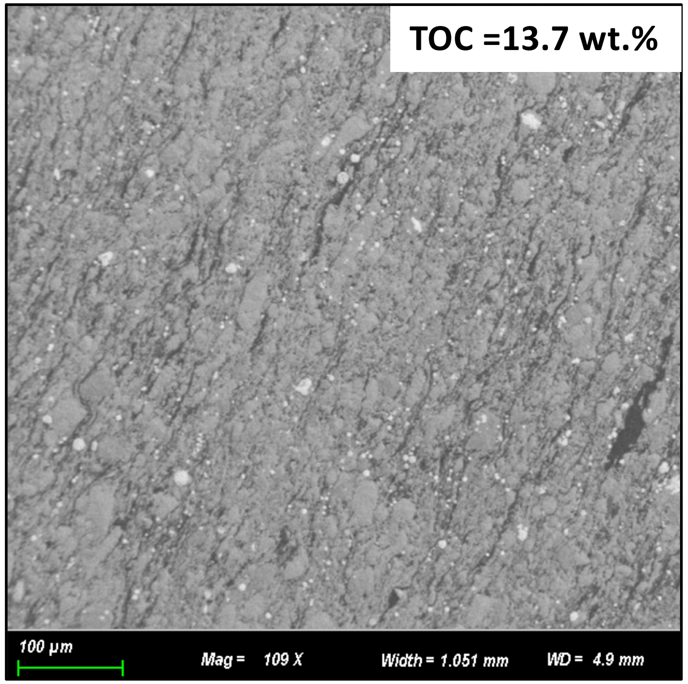


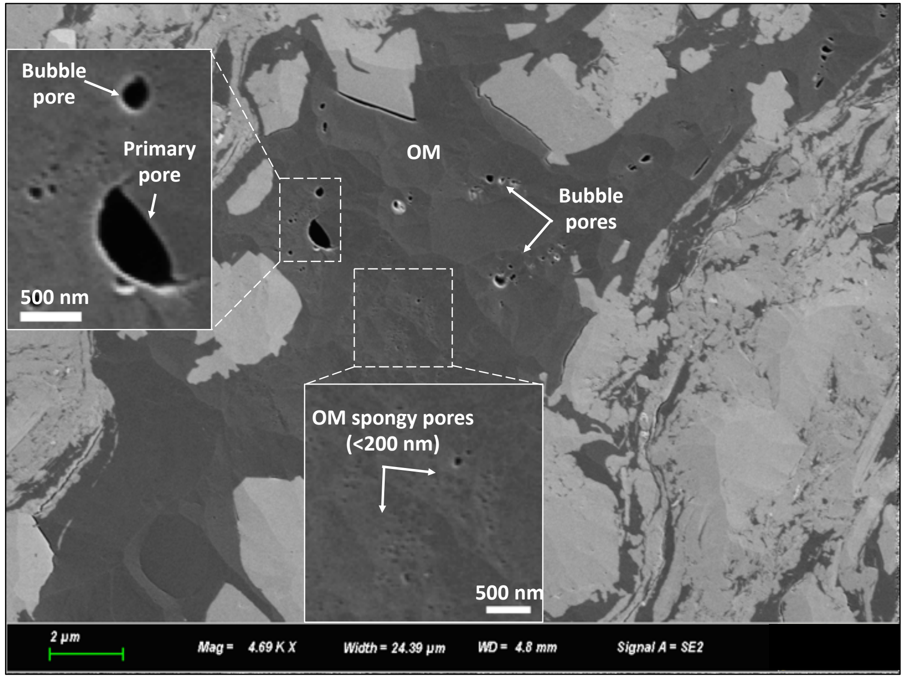


Experiments - XRD, TOC, SEM - Upper Bakken



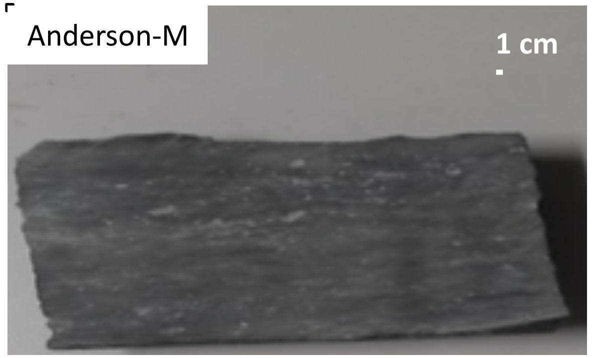


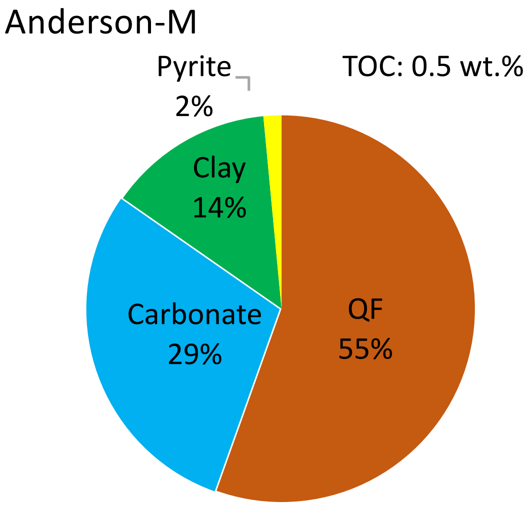


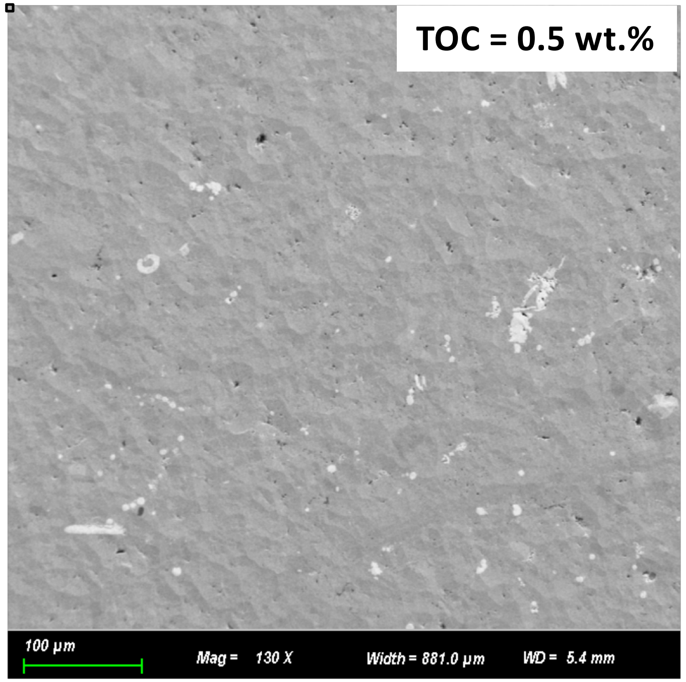


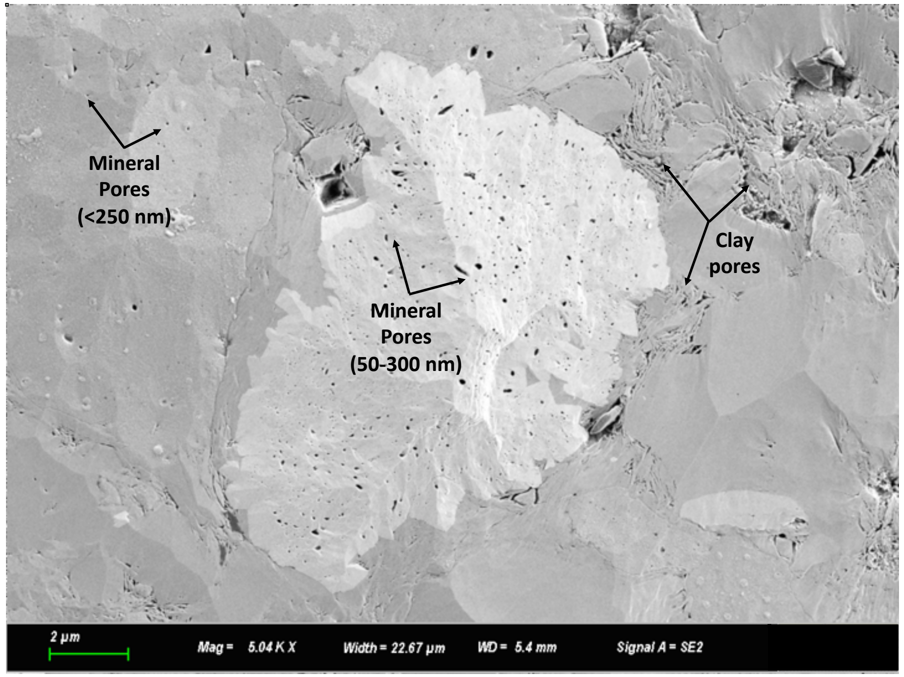
- Organic-rich black shales
- Various pore types (mineral pores, organic pores)

Experiments - XRD, TOC, SEM - Middle Bakken



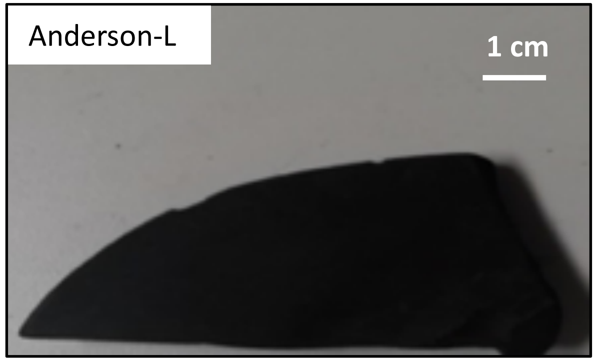


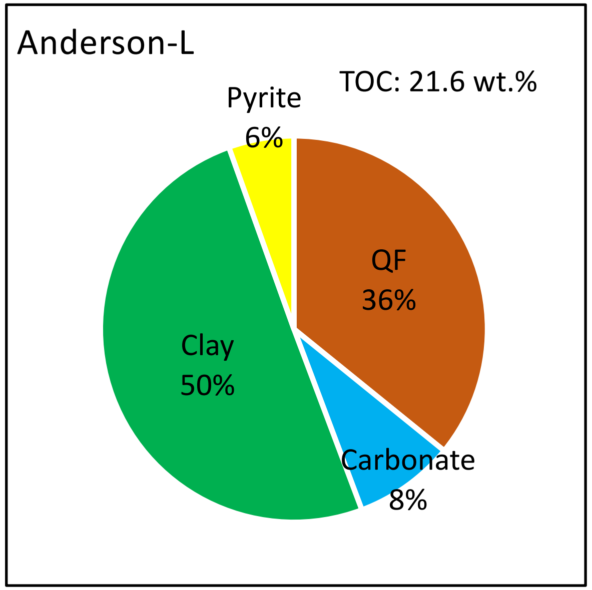


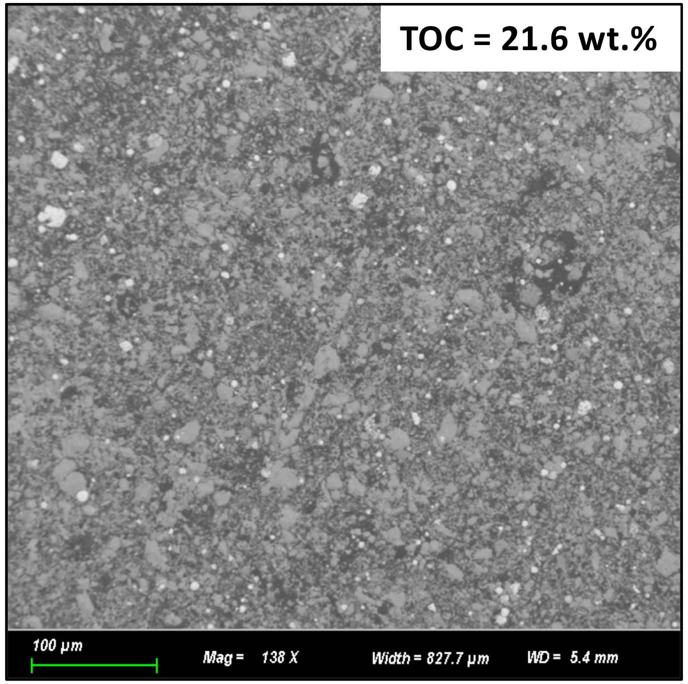


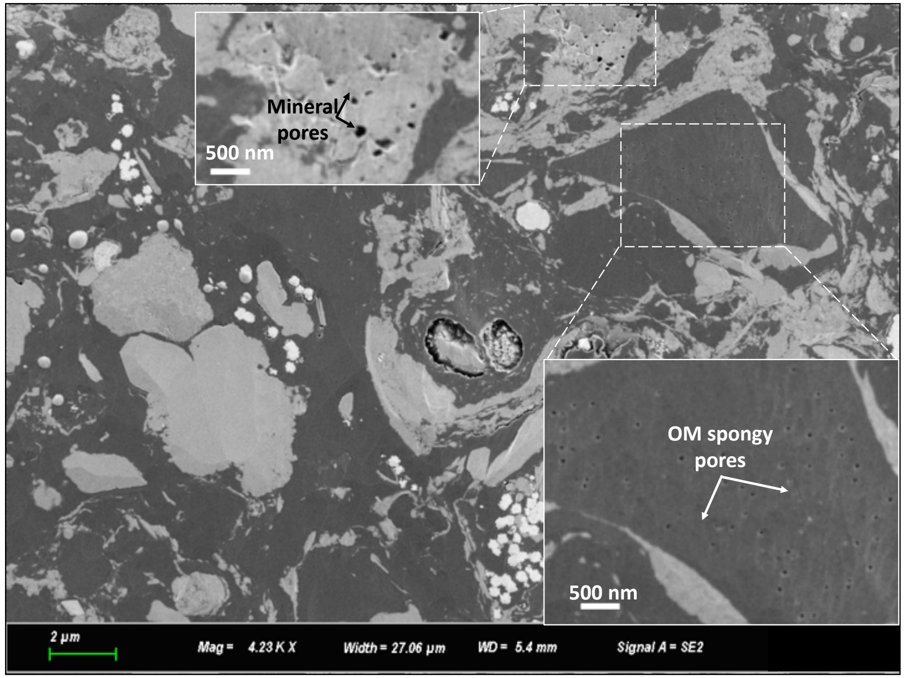
- Carbonate-rich
- Inter-particle and intra-particle meso/macropores

Experiments - XRD, TOC, SEM - Lower Bakken







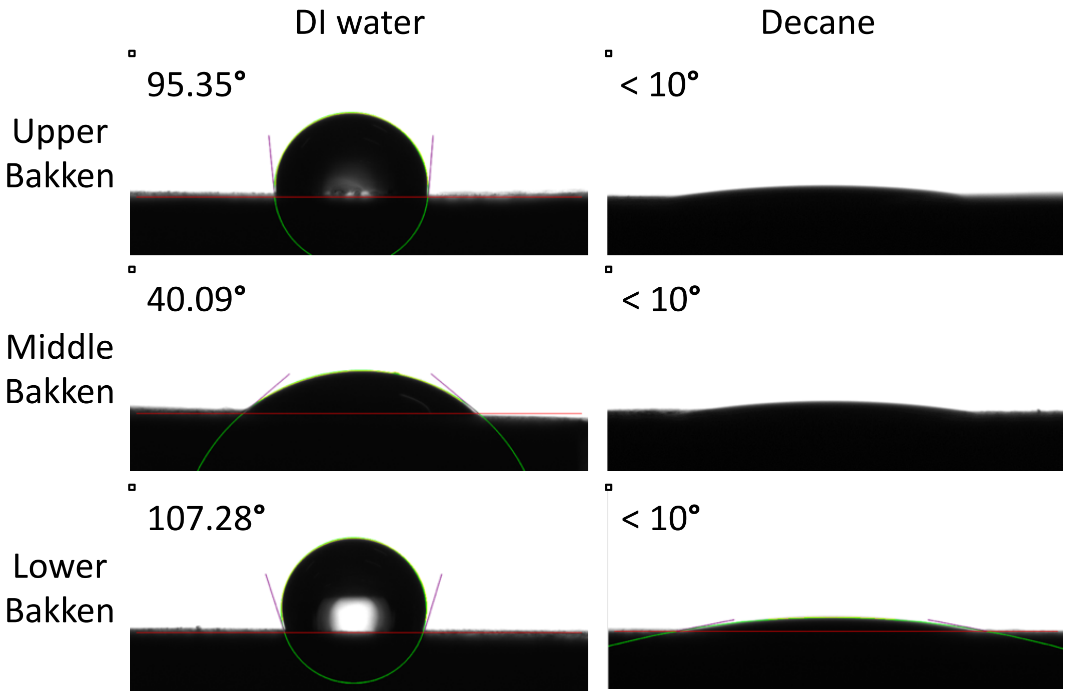


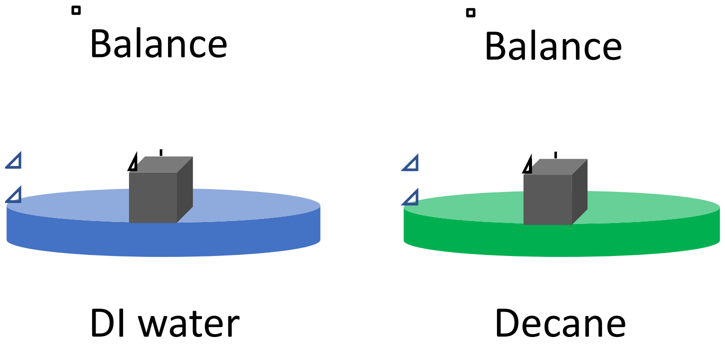
- Organic-rich black shales
- Various pore types (mineral pores, organic pores)

Experiments - contact angle measurement & imbibition

Two fluids:

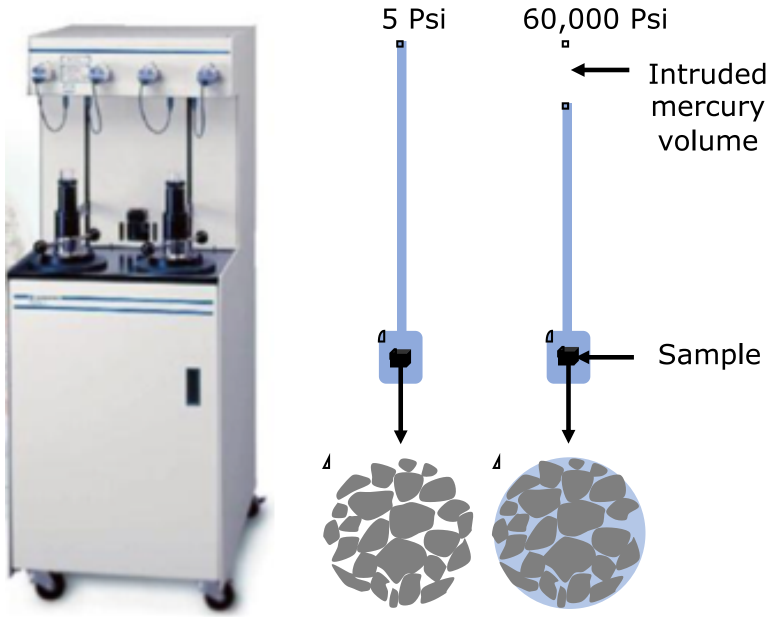
- DI water: H_2O
- Decane: $C_{10}H_{22}$ (hydrocarbon)

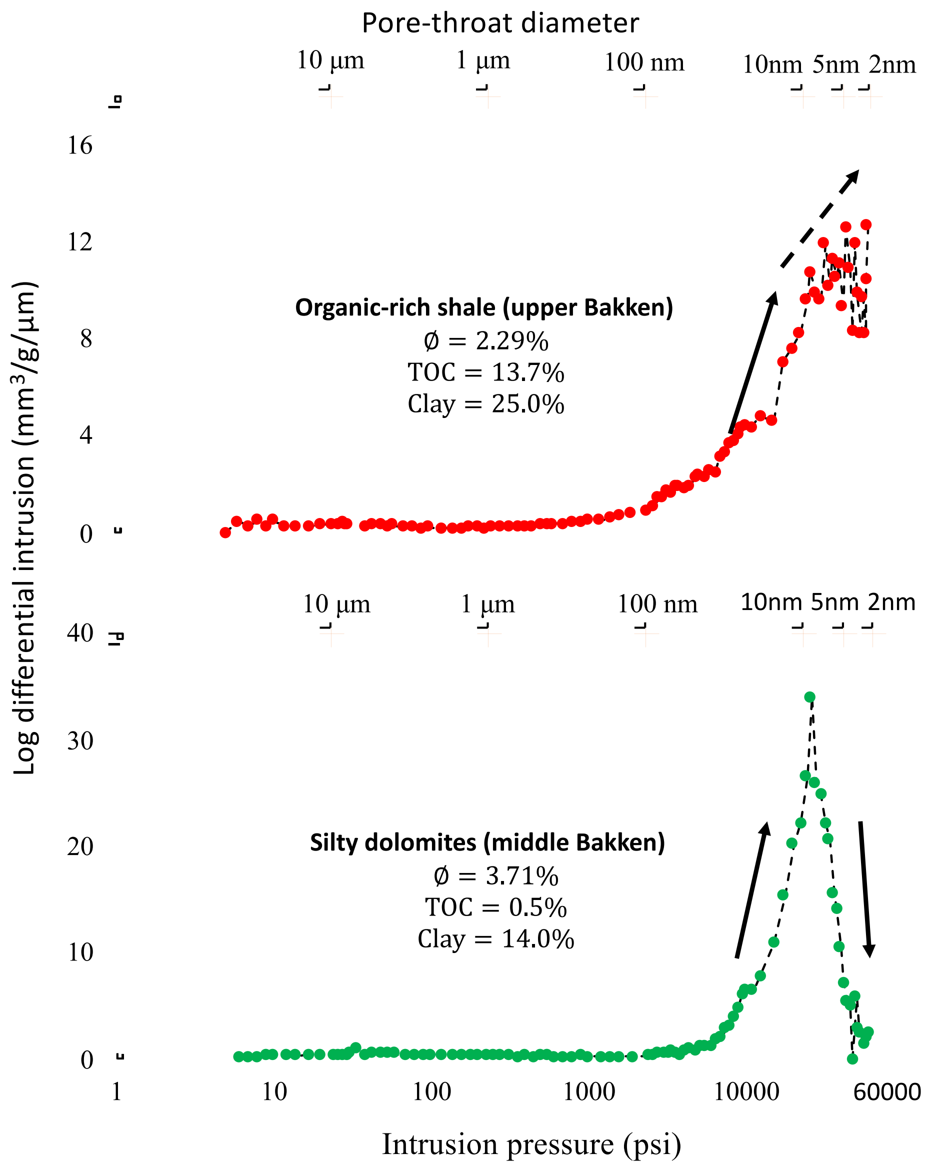




	DI water (mg/cm^3)	Decane (mg/cm^3)
Upper Bakken	9.55	16.85
Middle Bakken	26.86	16.73
Lower Bakken	14.52	18.44

Experiments - MICP





Washburn Equation:

$$D = -\frac{4\gamma \cos \theta_c}{P}$$

D : Pore-throat diameter (cm)

γ: Surface tension (485 dyne cm^{-1})

θ_c: Contact angle (130°)

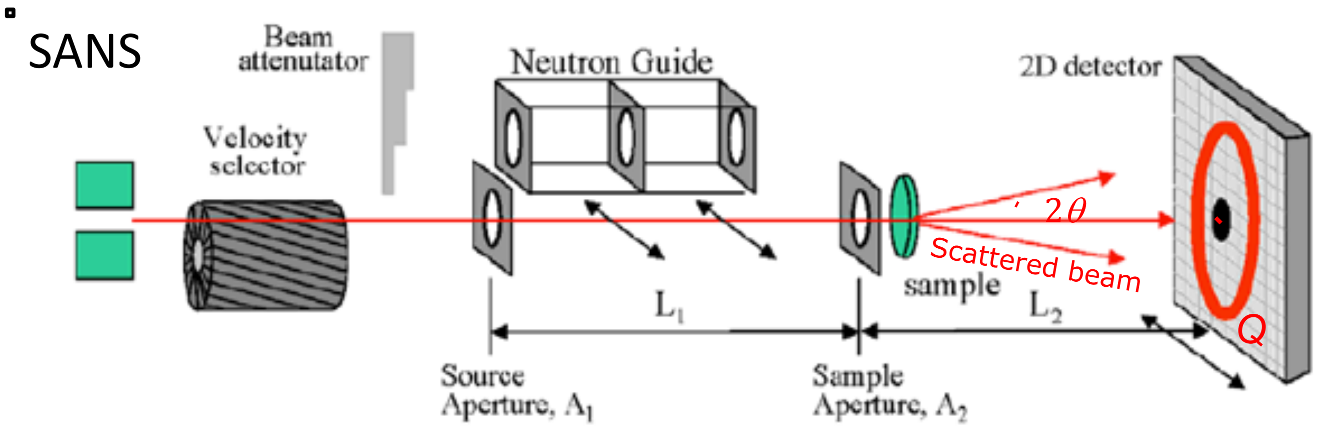
P: Applied pressure (dyne cm^{-2})

(Washburn, 1921)

Experiments - SANS&USANS - theory

Why neutron scattering?

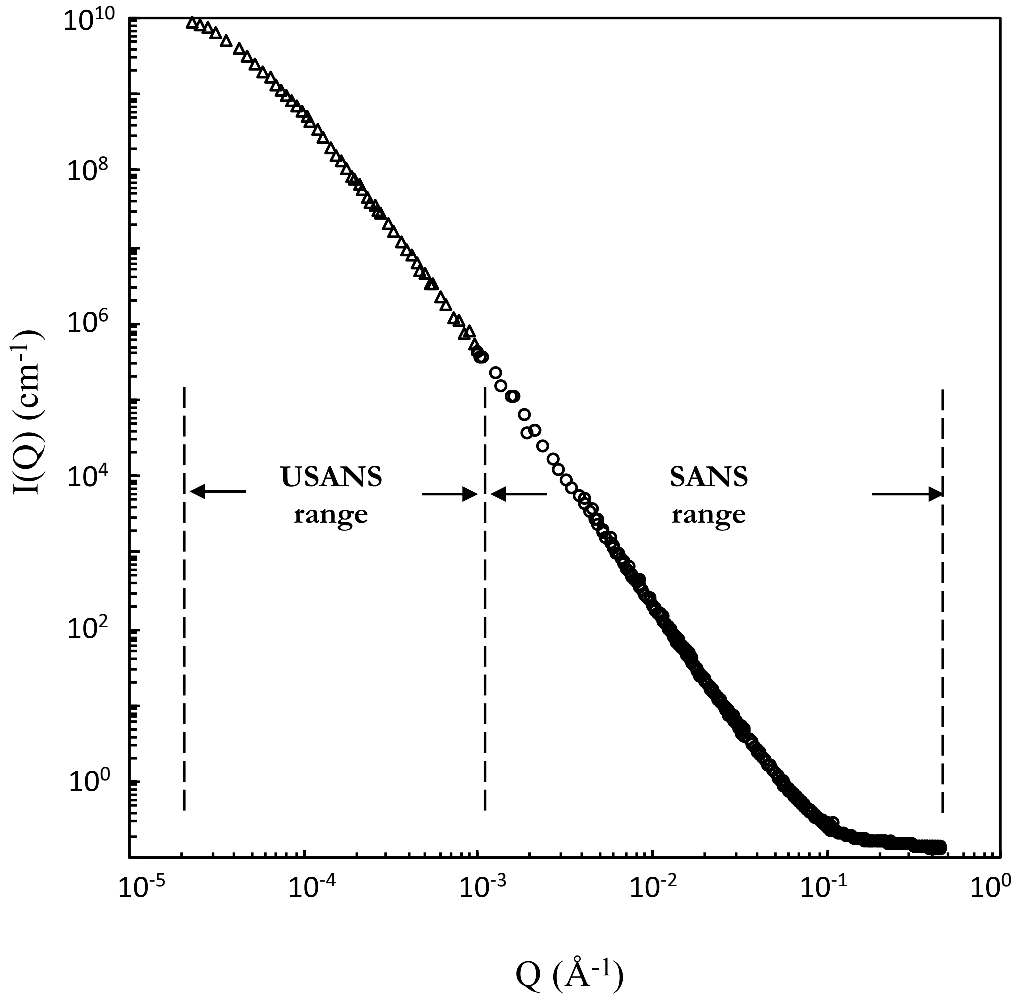
- Penetrating (low adsorption)
- Nondestructive
- Detect accessible pores and inaccessible (closed) pores



$$Q = 4\pi\lambda^{-1}\sin\theta$$

- **Q**: momentum transfer or scattering vector
- **λ**: neutron wavelength
- **2 θ**: scattering angle

Experiments - SANS&USANS - theory



$$I(Q) \sim (\Delta\rho)^2 = (\rho_1 - \rho_2)^2$$

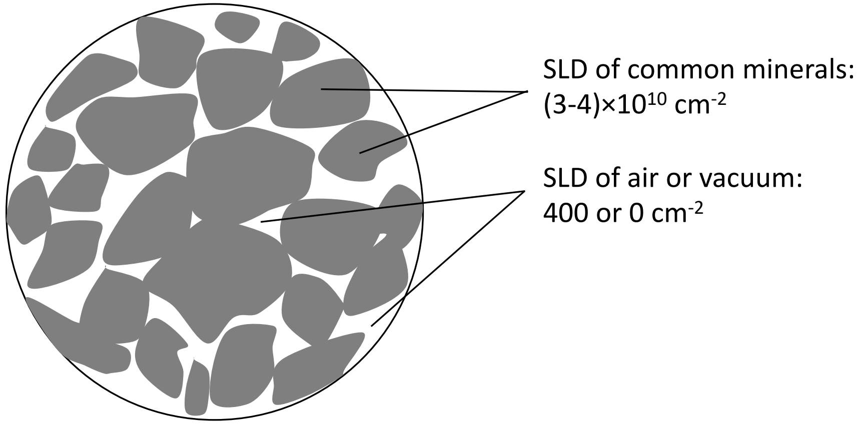
ρ_1, ρ_2: scattering length density (SLD)

$$r = 2.5/Q$$

r: size of the scattering object (e.g., pores in rocks)

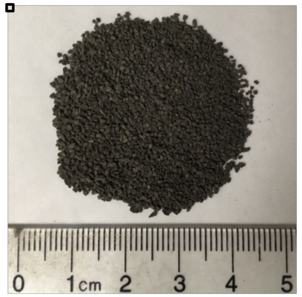
(Radlinski, 2000)

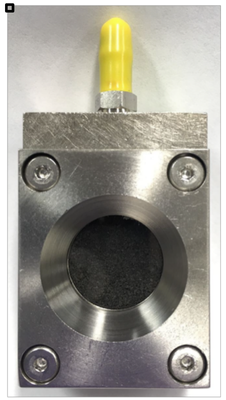
Detecting size range: ~1 nm – 20 μm (diameter)

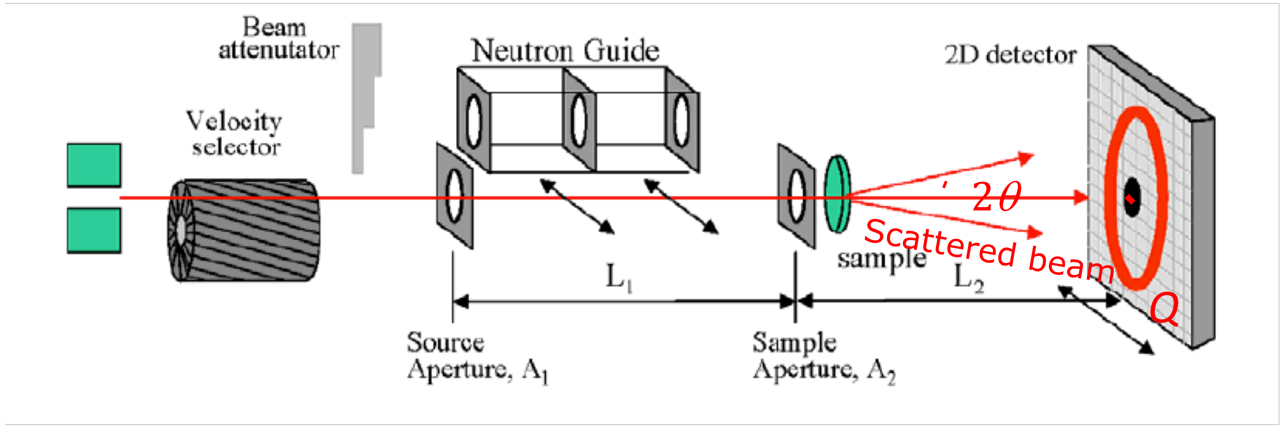


Experiments - SANS&USANS – experiments & model

Grain size: 177 – 500 µm







PDSP Model
(polydisperse spherical pore model)

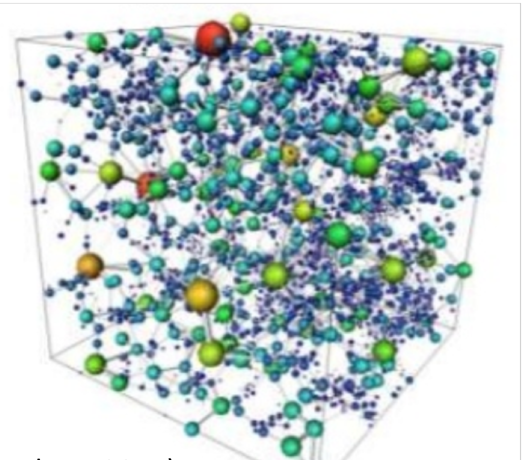
$$I(Q) = \frac{d\Sigma}{d\Omega}(Q) = (\rho_1 - \rho_2)^2 \frac{\phi_p}{\bar{V}_r} \int_{R_{min}}^{R_{max}} {V_r}^2 f(r) F_{sph}(Qr)\, dr$$

$\bar{V}_r = \int_0^\infty V_r^2 f(r) dr$: averaged pore volume

$f(r)$: power-law pore size distribution factor

R_{min} & R_{max}: minimum and maximum pore radii

ϕ_p: porosity



(Martin Blunt, 2015)

Results – Porosity, Pore (throat) size distribution

	MICP (Cube)	(U)SANS (Grains)*
Anderson-U	2.29%	11.69%
Anderson-M	3.71%	8.83%
Anderson-L	2.91%	12.80%

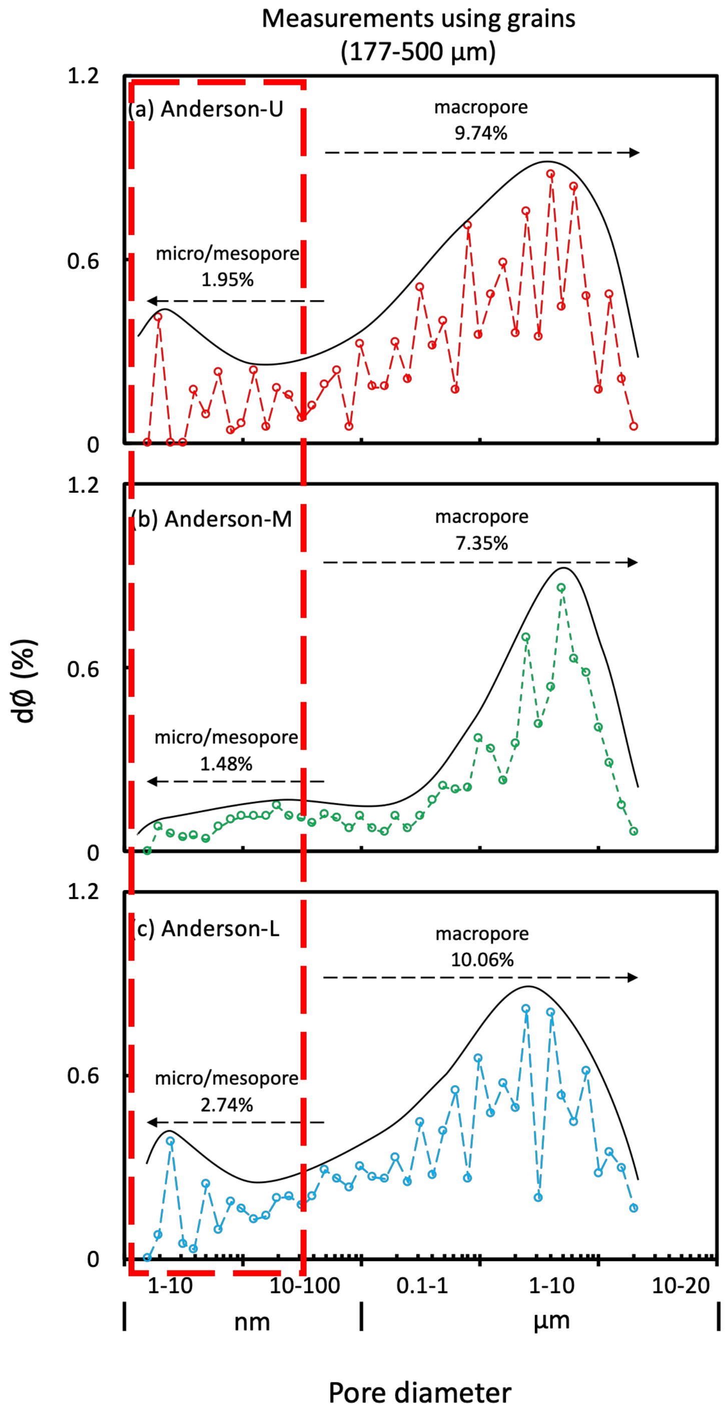
* Averaged value

MICP-Porosity:
middle Bakken > upper/lower Bakken

(U)SANS-Porosity:
middle Bakken < upper/lower Bakken

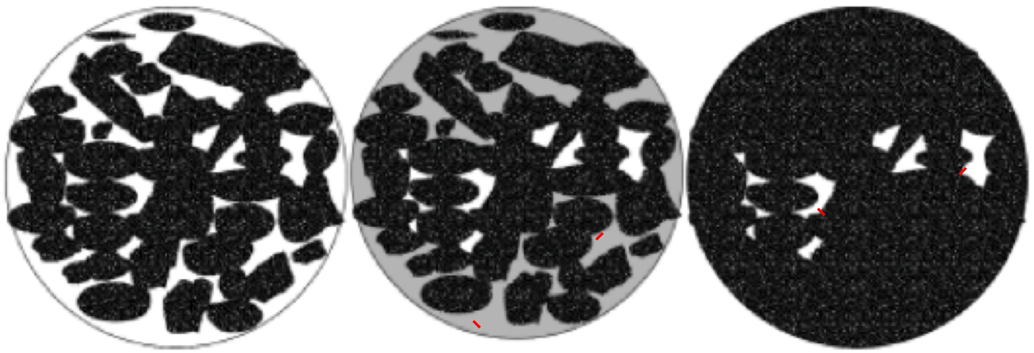
WHY?

(U)SANS measures closed porosity
Upper/lower Bakken have many inaccessible pores (micropores, mesopores, macropores) – OM pores?



Experiments - SANS&USANS - contrast matching

Mineral/pore system:

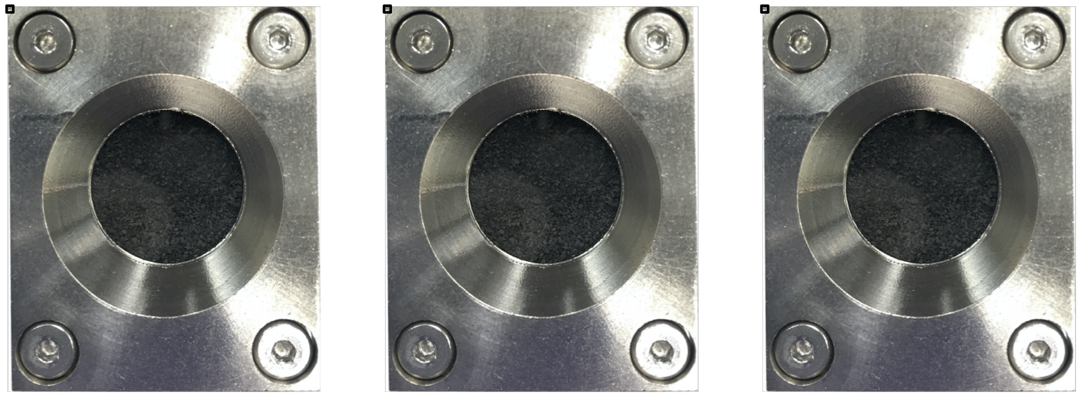


Accessible pores (grey)

Inaccessible pores (white)

An very useful technique in SANS studies to separate connected from unconnected porosity

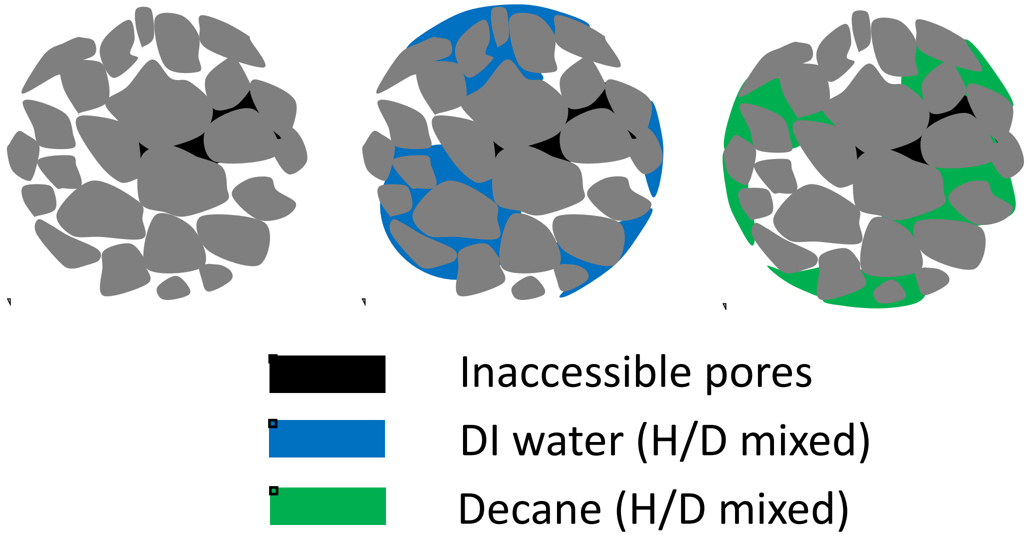
(Anovitz and Cole, 2015)



Dry sample

Saturated with DI water (H/D mixed)

Saturated with Decane (H/D mixed)



Inaccessible pores

DI water (H/D mixed)

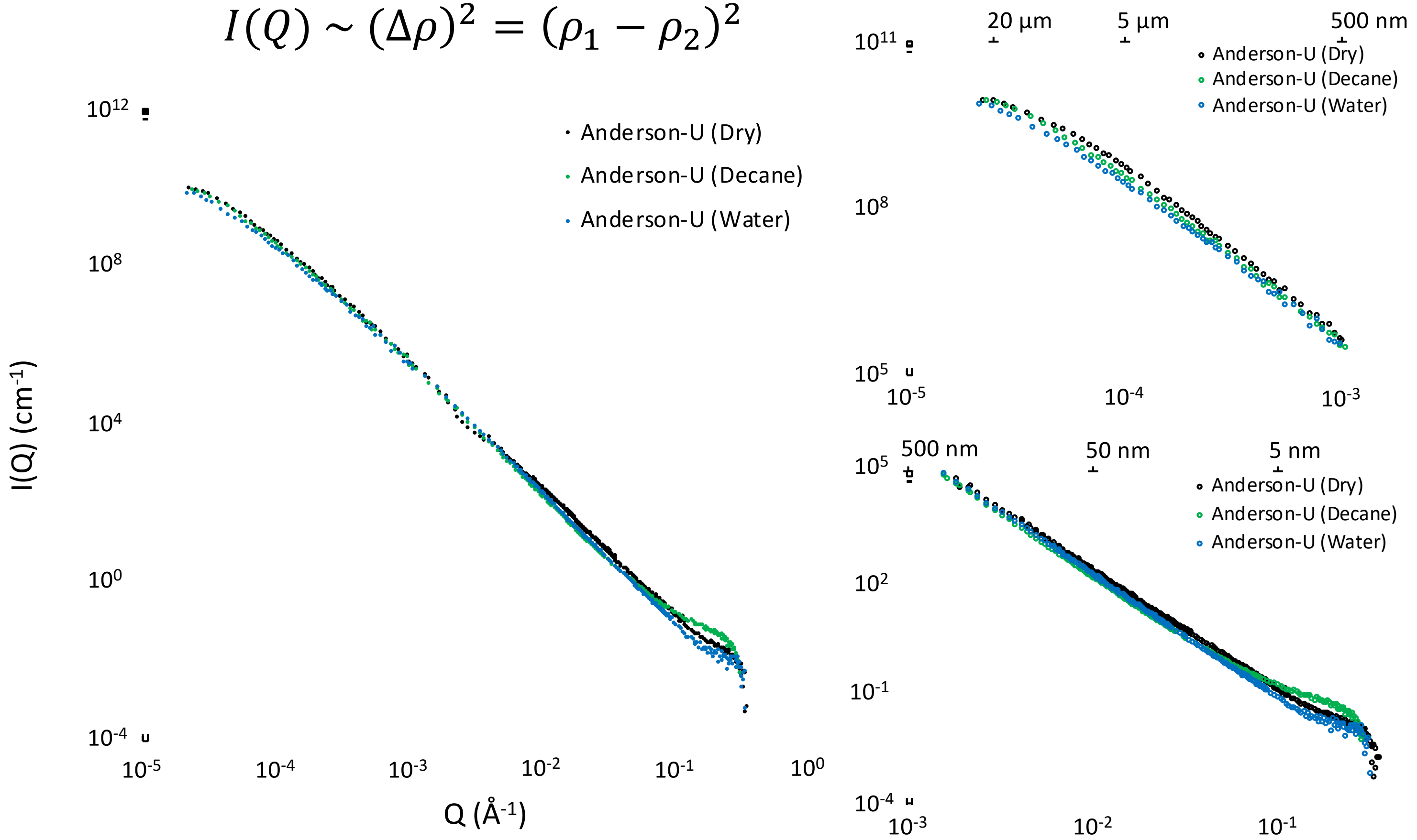
Decane (H/D mixed)

Results - Hydrophobic & Hydrophilic Porosity - Upper Bakken

Sample	Total porosity
Dry	14.21%
Decane (H/D mixed)	10.77%
Water (H/D mixed)	9.13%

Hydrophobic Porosity (oil-wet)	**3.44%**
Hydrophilic Porosity (water-wet)	**5.08%**
Accessible porosity	**8.52%**
Inaccessible porosity	**5.69%**

$$I(Q) \sim (\Delta\rho)^2 = (\rho_1 - \rho_2)^2$$

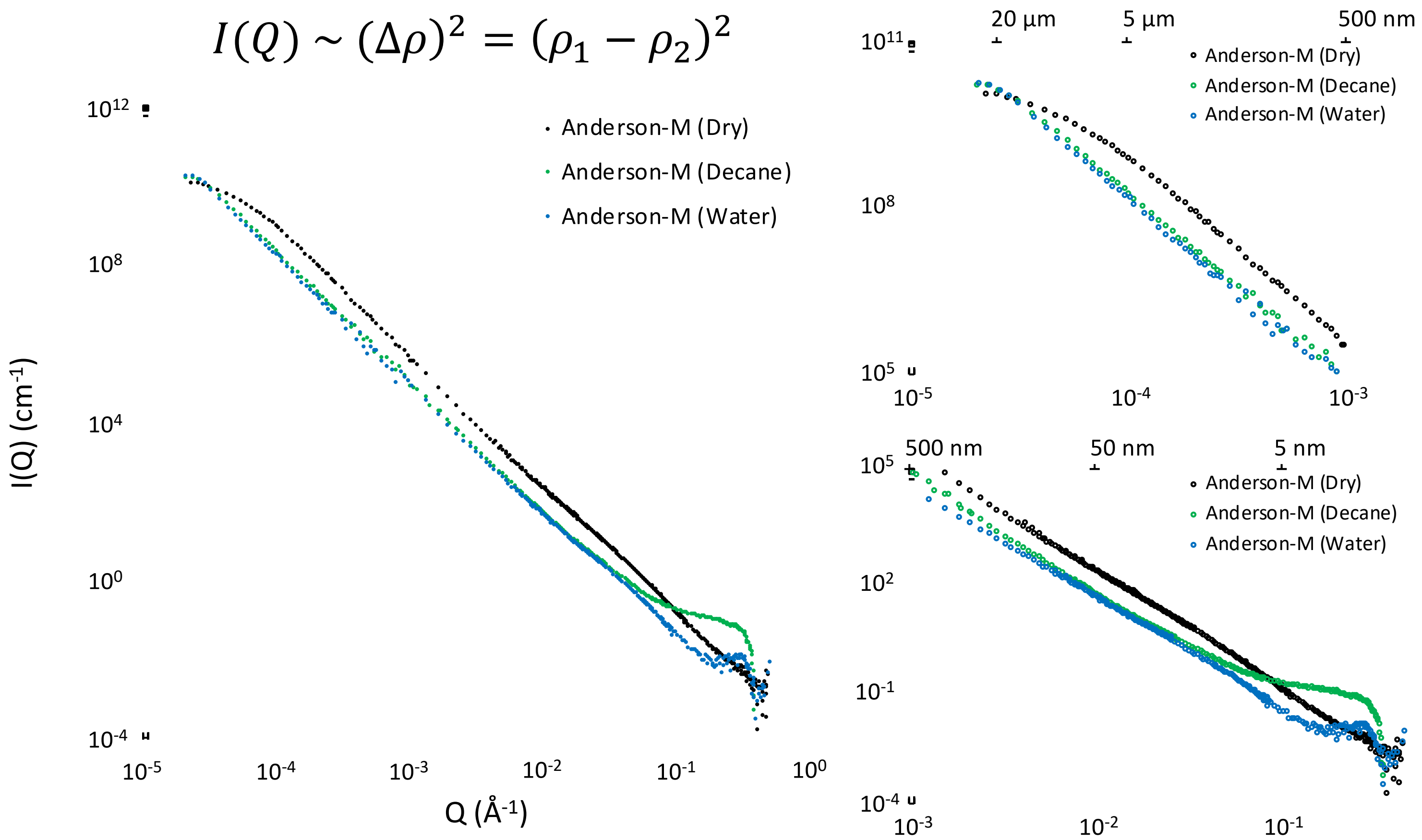


Results - Hydrophobic & Hydrophilic Porosity - Middle Bakken

Sample	Total porosity
Dry	7.20%
Decane (H/D mixed)	5.08%
Water (H/D mixed)	2.12%

Hydrophobic Porosity (oil-wet)	2.12%
Hydrophilic Porosity (water-wet)	5.08%
Accessible porosity	**7.20%**
Inaccessible porosity	**0**

$$I(Q) \sim (\Delta\rho)^2 = (\rho_1 - \rho_2)^2$$

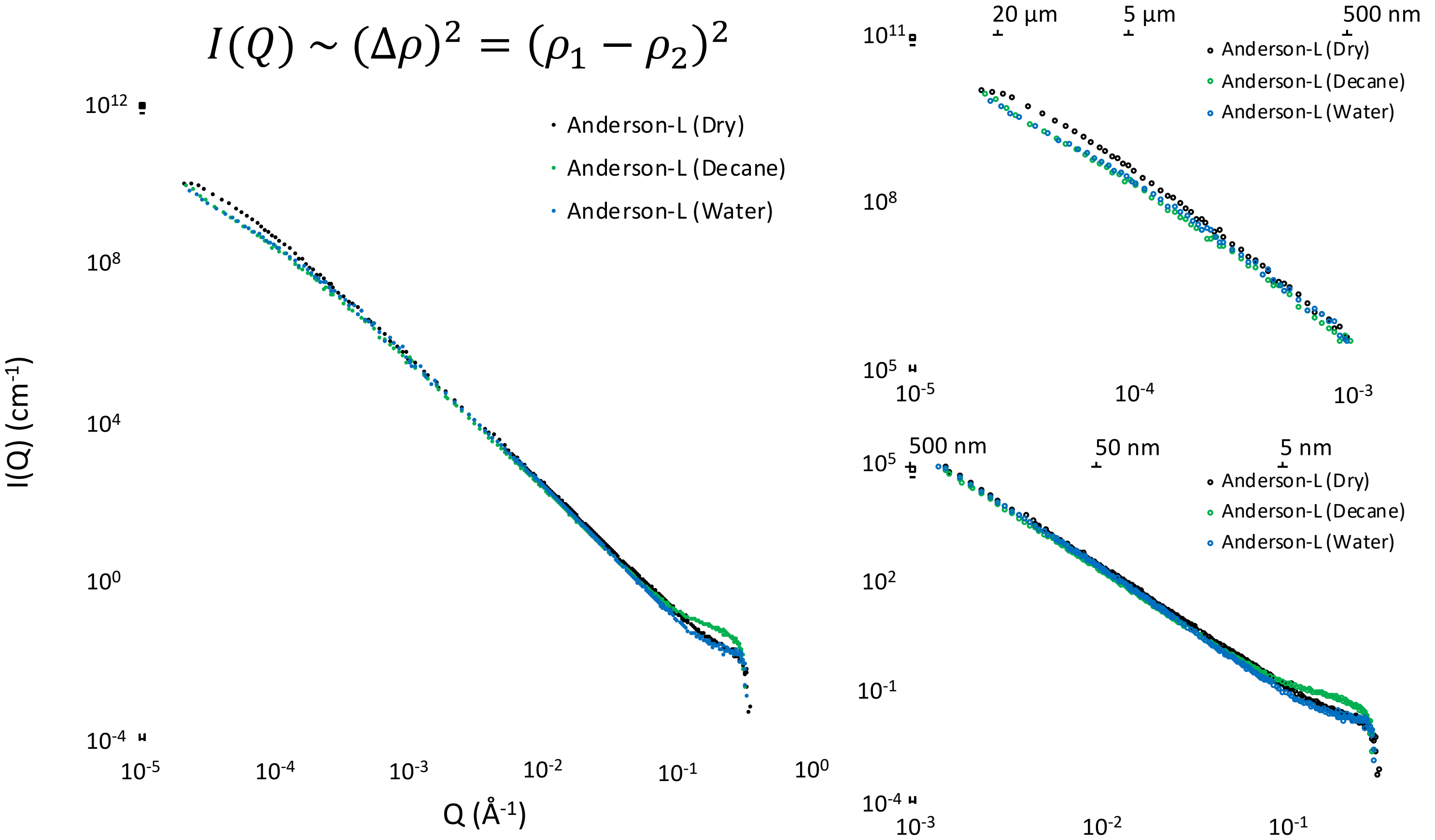


Results - Hydrophobic & Hydrophilic Porosity - Lower Bakken

Sample	Total porosity
Dry	11.10%
Decane (H/D mixed)	8.99%
Water (H/D mixed)	8.89%

Hydrophobic Porosity (oil-wet)	**2.11%**
Hydrophilic Porosity (water-wet)	**2.21%**
Accessible porosity	**4.32%**
Inaccessible porosity	**6.78%**

$$I(Q) \sim (\Delta\rho)^2 = (\rho_1 - \rho_2)^2$$



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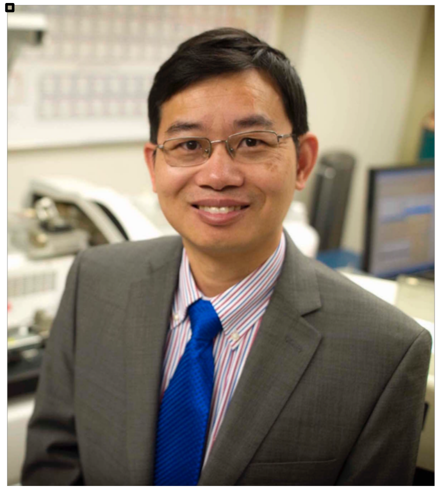

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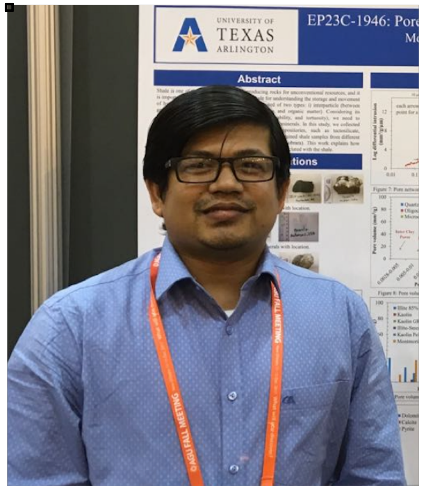

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