

# Hydrocarbon Geochemistry and Pore Characterization of Bakken Formation and Implication to Oil Migration and Oil Saturation\*

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## Abstract

The conventional model for determining petroleum expulsion efficiency is based solely on petroleum generation; it needs to be revised by combining hydrocarbon generation, pore characterization, and mineralogical/lithological characterization of organic-rich shales. In this study, 24 core samples from a single well which penetrated the intervals of Upper and Lower Bakken organic-rich shales and Middle Bakken dolomite/carbonate were used to characterize residual oil and gas geochemistry and to determine the porosity and pore size distribution (PSD).

Gas chemical compositions from the released gas of crushed rock samples provide important clues to fluid phase behavior in organic-rich source rocks and tight carbonate rocks. Gases in the Upper and Lower Bakken shales contain low levels of methane (0.34%) and ethane (6.4%), but high volumes of propane (47.5%), butane (33.7%) and pentane (12.1%). In contrast, gases in the Middle Bakken lower permeability dolomite-rich rocks contain high amounts of methane (53.8%) and ethane (16.4%), and relatively low levels of propane (12.6%), butane (10.4%) and pentane (6.5%). These differences in gas composition suggest that pores in the Upper and Lower Bakken are mainly filled with oil, and that gas is dissolved in oil rather than in a free gas phase.

Variations in oil saturation in the Upper and Lower Bakken shale intervals provide a basis for determining petroleum generation index (PGI). The middle sections of each of these shale intervals exhibit relatively constant residual oil saturation (12.8mg oil/g rock). By contrast, saturation values display a gradual decrease through a 3-5 ft interval near the contacts of these organic-rich shale source rocks and underlying and overlying carbonates, indicating that lithological stacking patterns greatly affect petroleum expulsion efficiency (PEE). More detailed study of SARA fractions of the residual oils is underway to refine our understanding of oil expulsion at the molecular compound level.

N<sub>2</sub> adsorption/desorption studies of PSD show that both the Upper and Lower Bakken are dominated by mesopores (2-32nm) and macropores (32nm - 270nm). About 60% of the total porosity (8%) in these rocks comes from mesopores. Middle Bakken carbonates, by contrast, have higher total porosity and greater pore volume of mesopores and macropores. Based on mass balance calculation, the residual oil in Middle Bakken carbonates only takes about 20% of total pore volumes.

### **References Cited**

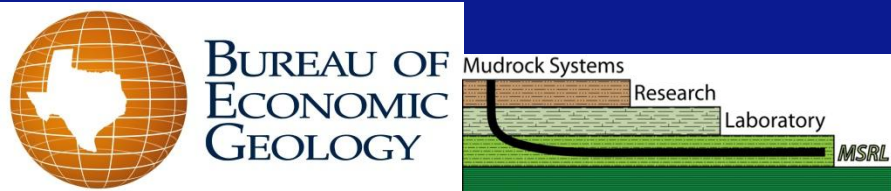
Kuhn, P.P., R. di Primio, R. Hill, J.R. Lawrence, and B. Horsfield, 2012, Three-dimensional modeling study of the low-permeability petroleum system of the Bakken Formation: AAPG Bulletin, v. 96, p. 1967-1897.

Kuhn, P.P., R. di Primio, and B. Horsfield, 2010, Bulk composition and phase behavior of petroleum sourced by the Bakken Formation of the Williston Basin: Proceedings of the 7th Petroleum Geology Conference, London, March 30–April 2, 2009, p. 1065–1077.

# Hydrocarbon Geochemistry and Pore Characterization of Bakken Formation and Implication to Oil Migration and Oil Saturation

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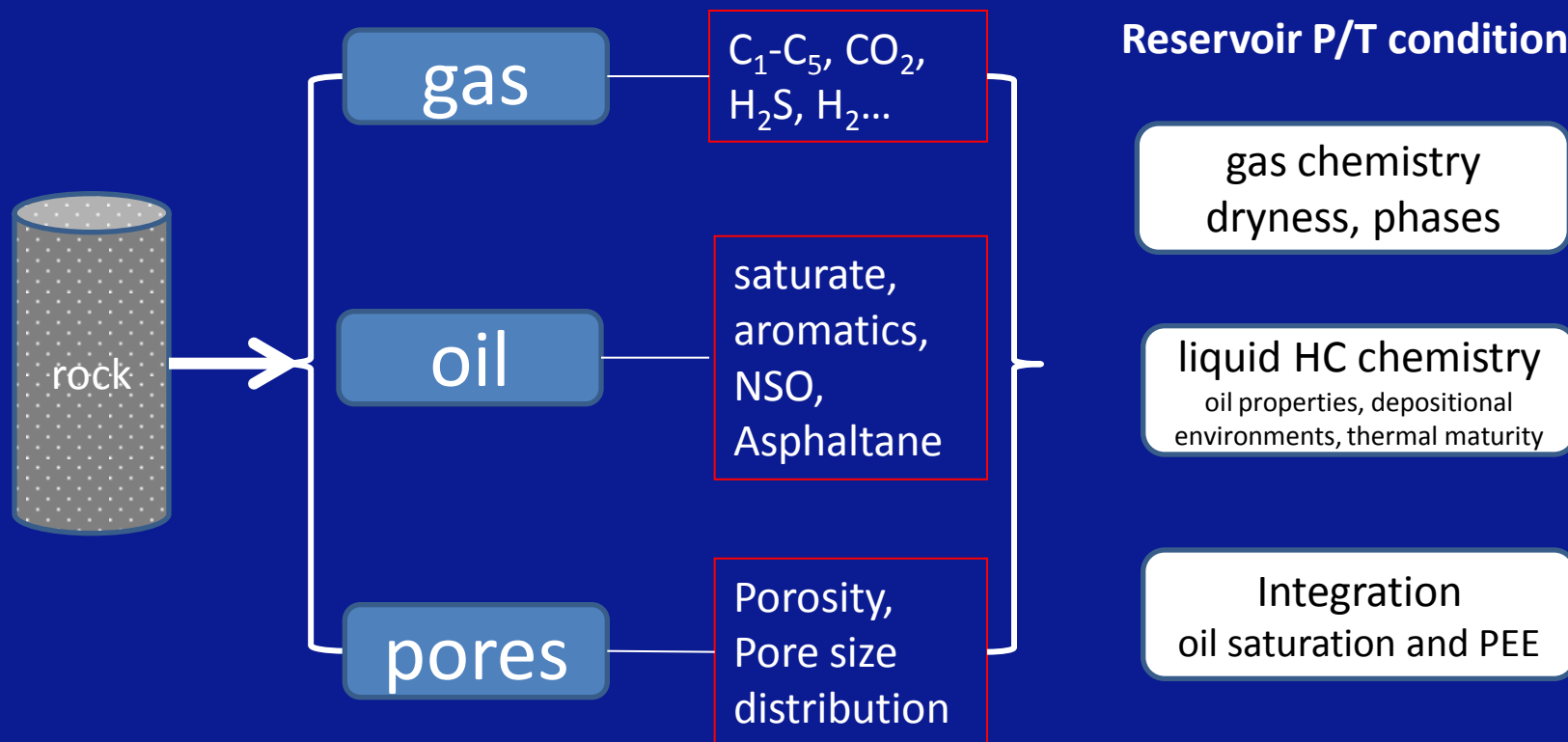
Bureau of Economic Geology, The University of Texas at Austin



# Objectives

- To revise the conventional model of petroleum expulsion efficiency (PEE) in organic-rich mudrocks based on both
  - petroleum generation
  - and lithology and pore characterization
- To characterize pores in the range of 0.38nm-300nm width with N<sub>2</sub> gas adsorption and desorption isotherms
  - some pores in mudrocks are too small to be detected by FE-SEM imaging
  - pore-size distribution (PSD), surface area and pore shapes with isotherms
- To define petroleum generation index and petroleum expulsion efficiency in the Bakken Formation
  - gas and liquid hydrocarbon characterization
  - PSD and porosity
  - residual oil saturation

# Fluid Studies in Source Rocks

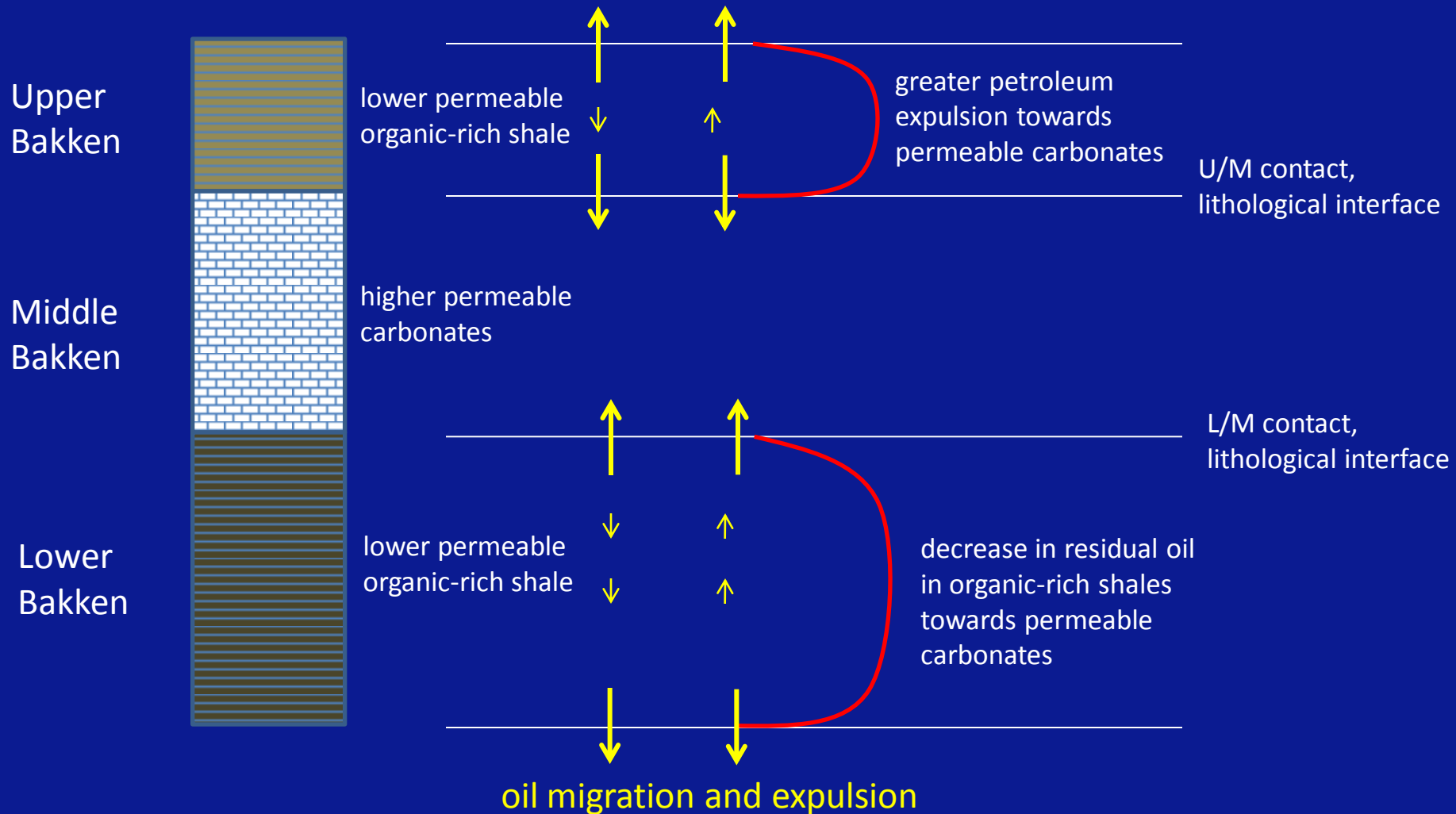


- chemical, physical processes on fluid chemistry in source rocks
- pore characterization of source rocks
- oil saturation, petroleum expulsion efficiency and fluid properties

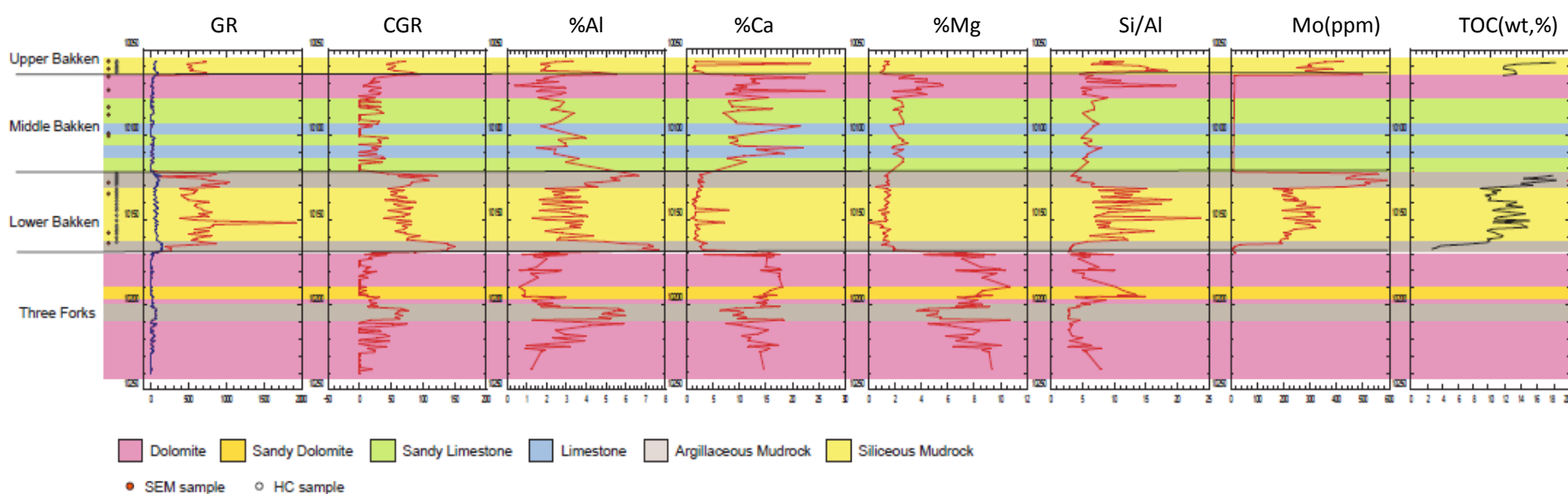
# Approaches

- Chemical composition of the released gases from crushed rocks  
(Agilent 7890GC modified by Wasson-ECE)
- Residual oil extraction and quantification  
(FOSS Soxlet 2043 extraction unit)
- Saturate, aromatic, resin and asphaltene (SARA) separation and quantification  
(small-scale silica-gel column)
- Identification and quantification of saturates and aromatics fractions  
(Shimadzu GCMS )
- PSD, BET surface area and porosity measurement  
(Quantachrome autosorb pore analyzer)

# Conceptual Model For Oil Migration in Organic-rich Thick Layers



# Facies and Chemistry of Bakken Fm. in the Investigated Well

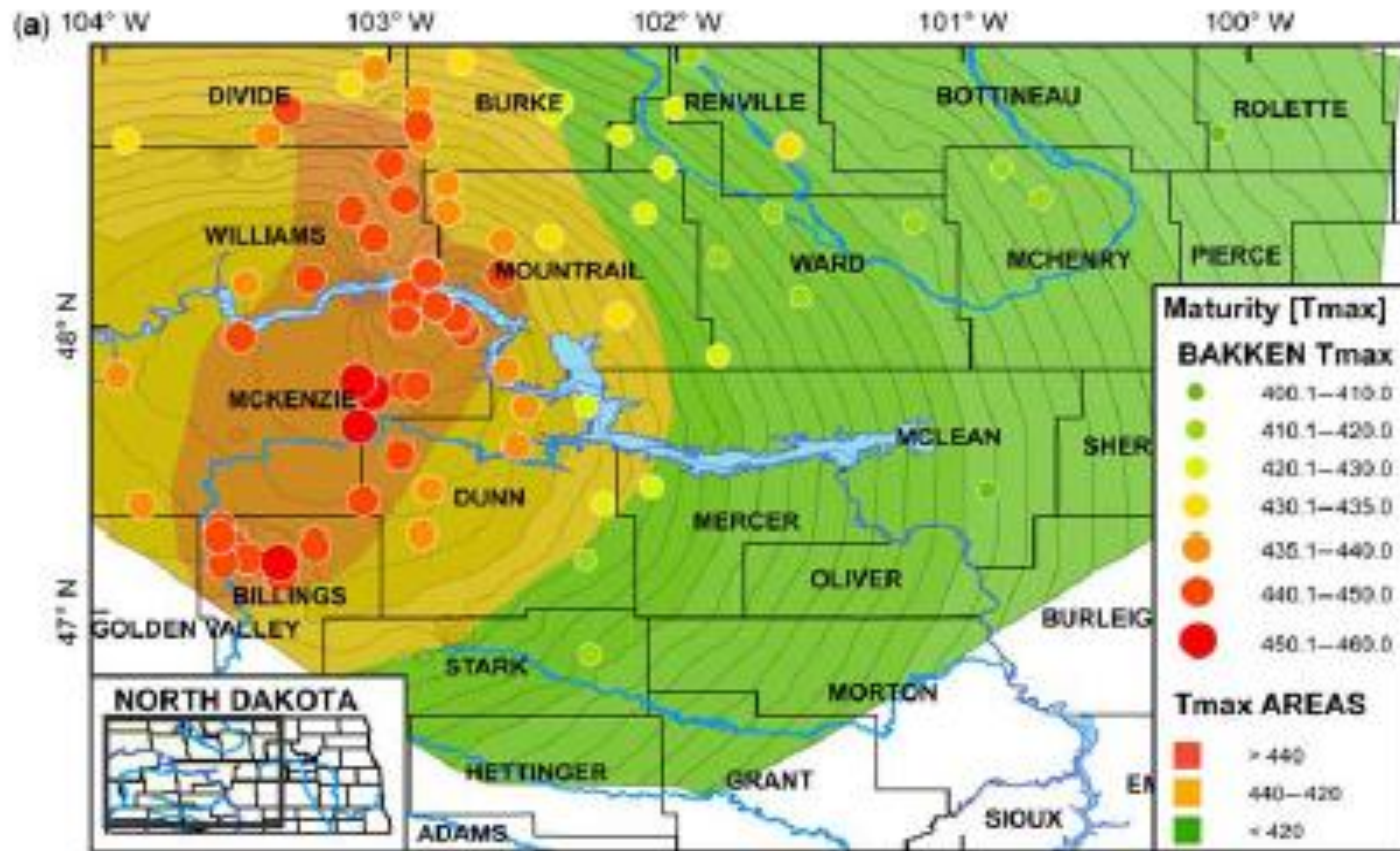


- Examine the gas and oil chemistry within organic-rich Upper and Lower Bakken shales
- Determine petroleum expulsion efficiency related to lithology variation
- Understand chemical and physical processes to affect liquid hydrocarbons properties



# Thermal Maturity Map of the Bakken Formation, the Williston Basin

- Tmax as thermal maturity indicator is positively correlated with current burial depth, and the highest Tmax value of the Bakken Formation is around 450°C.
- The investigated well is located in Mountrail County, North Dakota



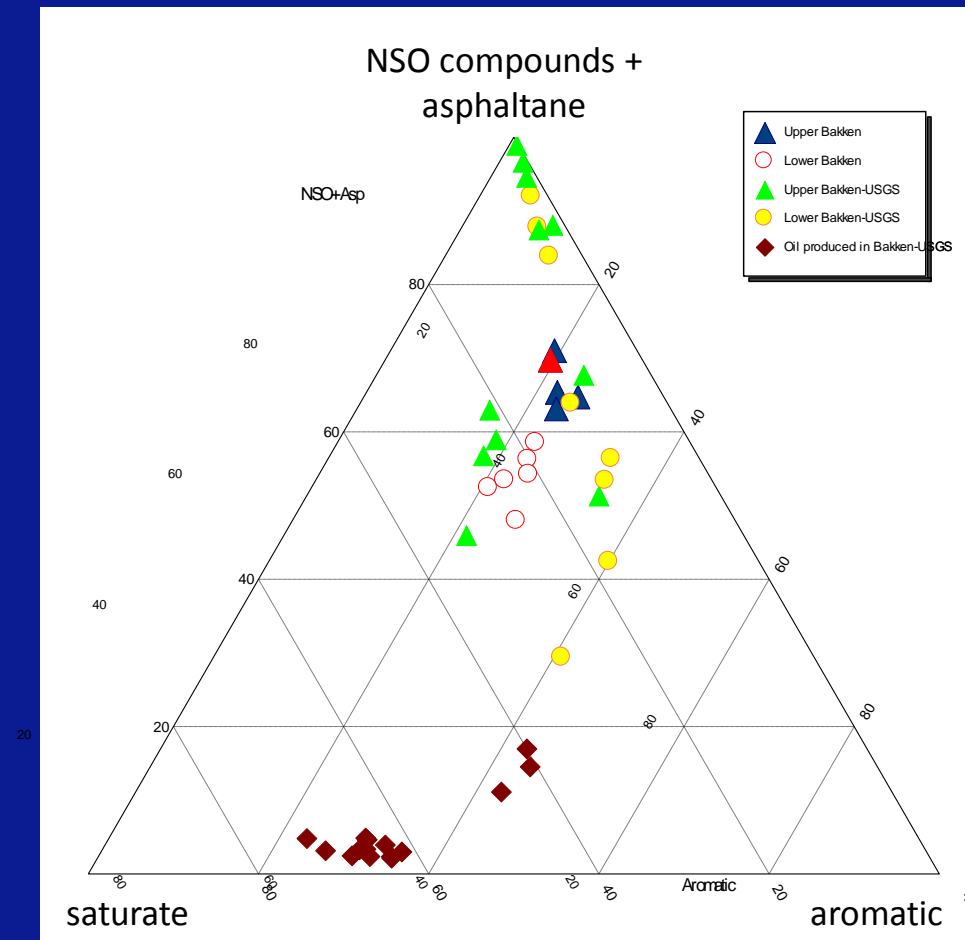
(Kuhn et al., 2010, 2012)

# Hydrocarbon Geochemistry

- Residual oil abundance and SARA fractions
- Gas chemistry as fingerprints to petroleum expulsion

# SARA Fractions of Produced Oil and Extracts of Rocks from Bakken Formation

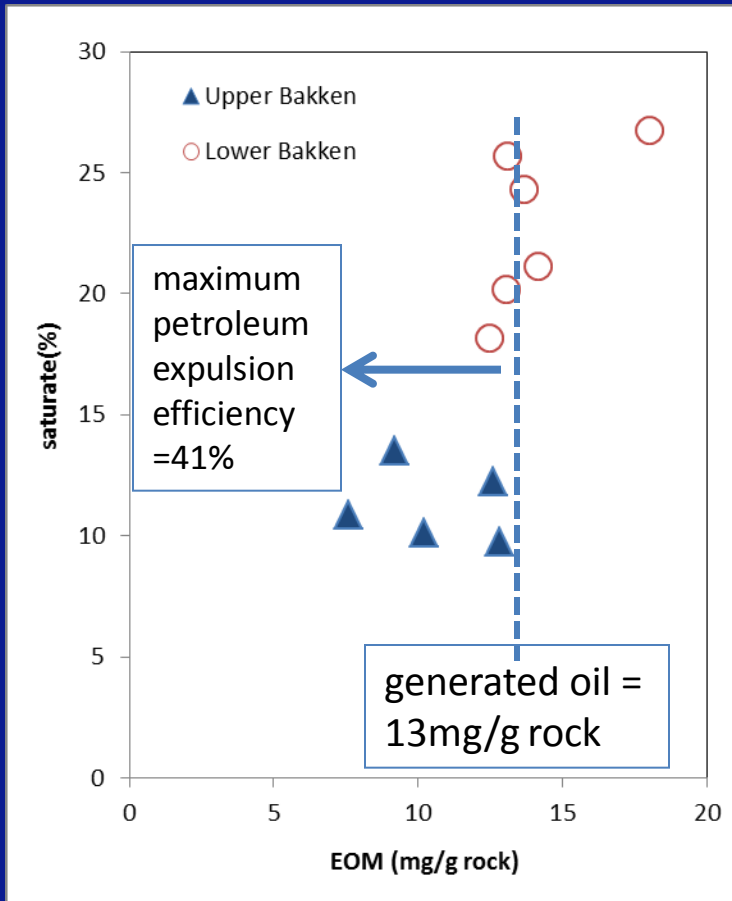
- The produced oil is mainly composed of saturates and aromatics
- NSO-compounds and asphaltene fractions are major components of the residual oil in the Upper and Lower Bakken intervals
- The great polarity and large molecular mass of NSO-compounds and asphaltene leads to a strong retardation in petroleum expulsion.



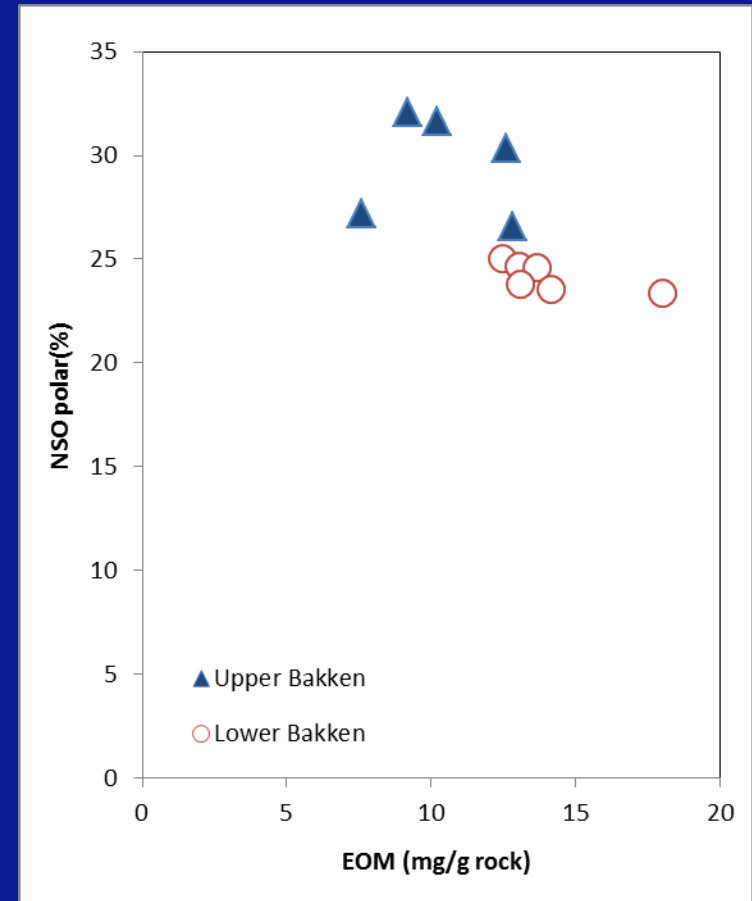
Data from USGS Energy Database and BEG Geochemistry Lab.

# Both Thermal Maturation and Petroleum Migration Affect Liquid Hydrocarbon Property

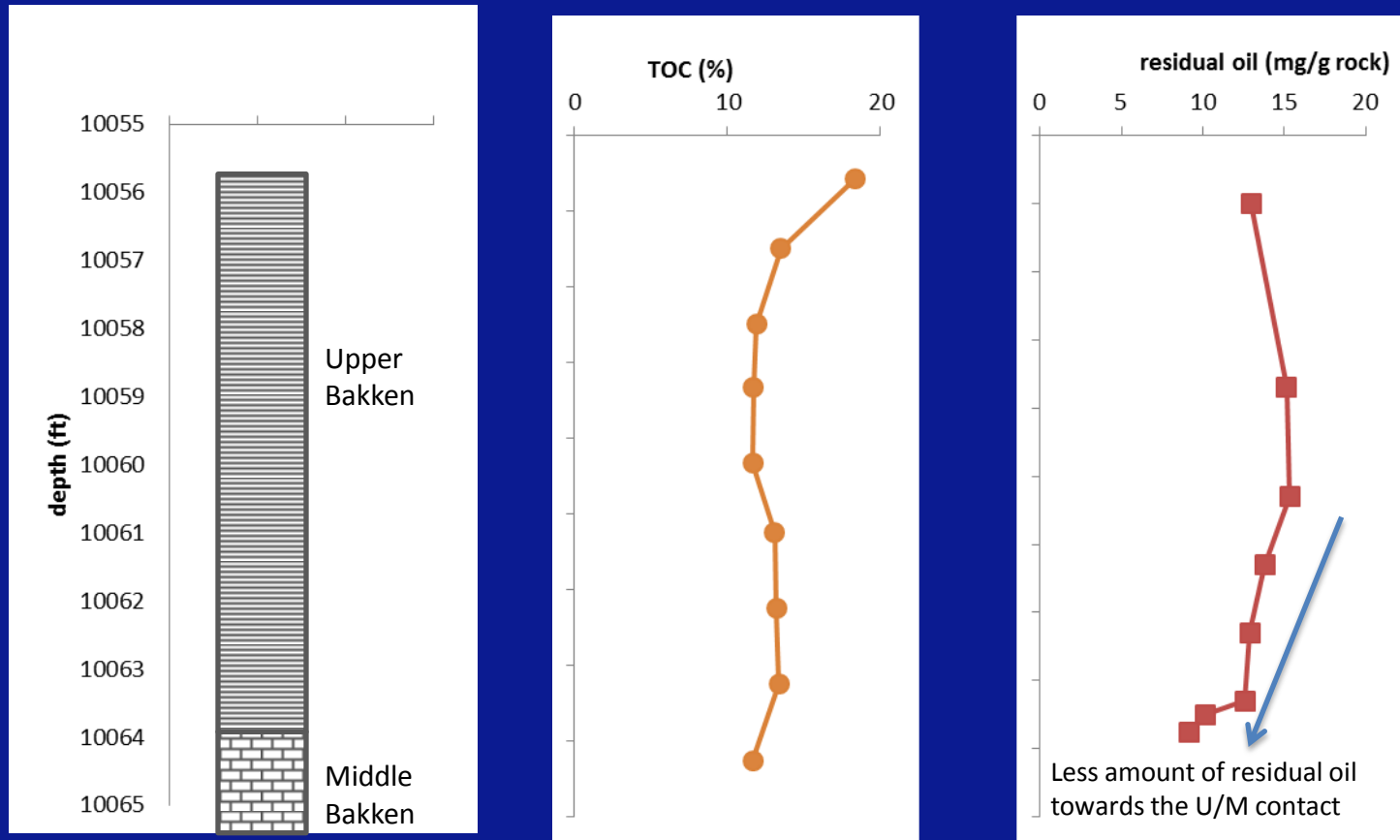
Saturate fraction in U/L Bakken



NSO polar compounds retain in rocks in petroleum expulsion

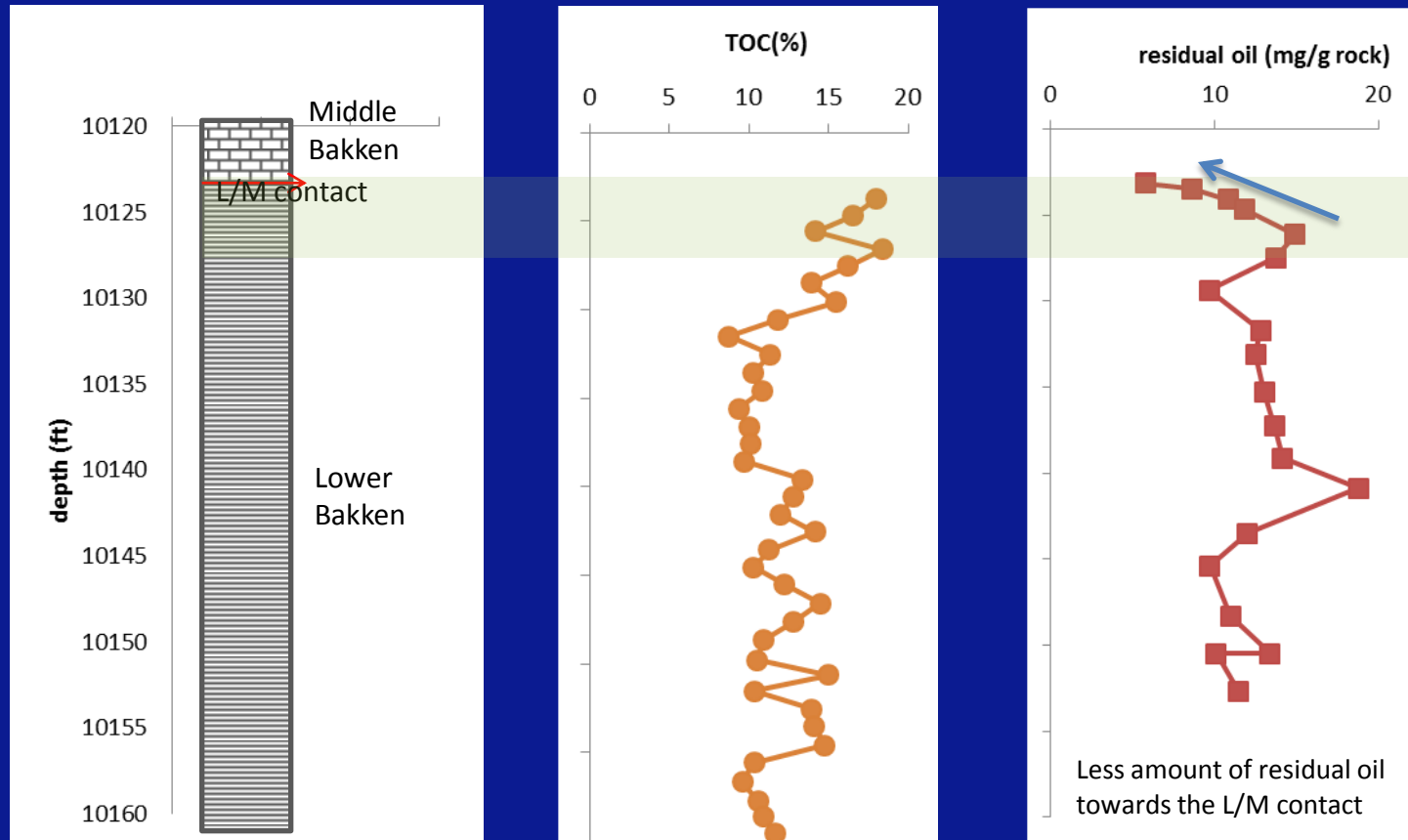


# Lithology Variation Greatly Affects Petroleum Expulsion Efficiency in Upper Bakken Shale



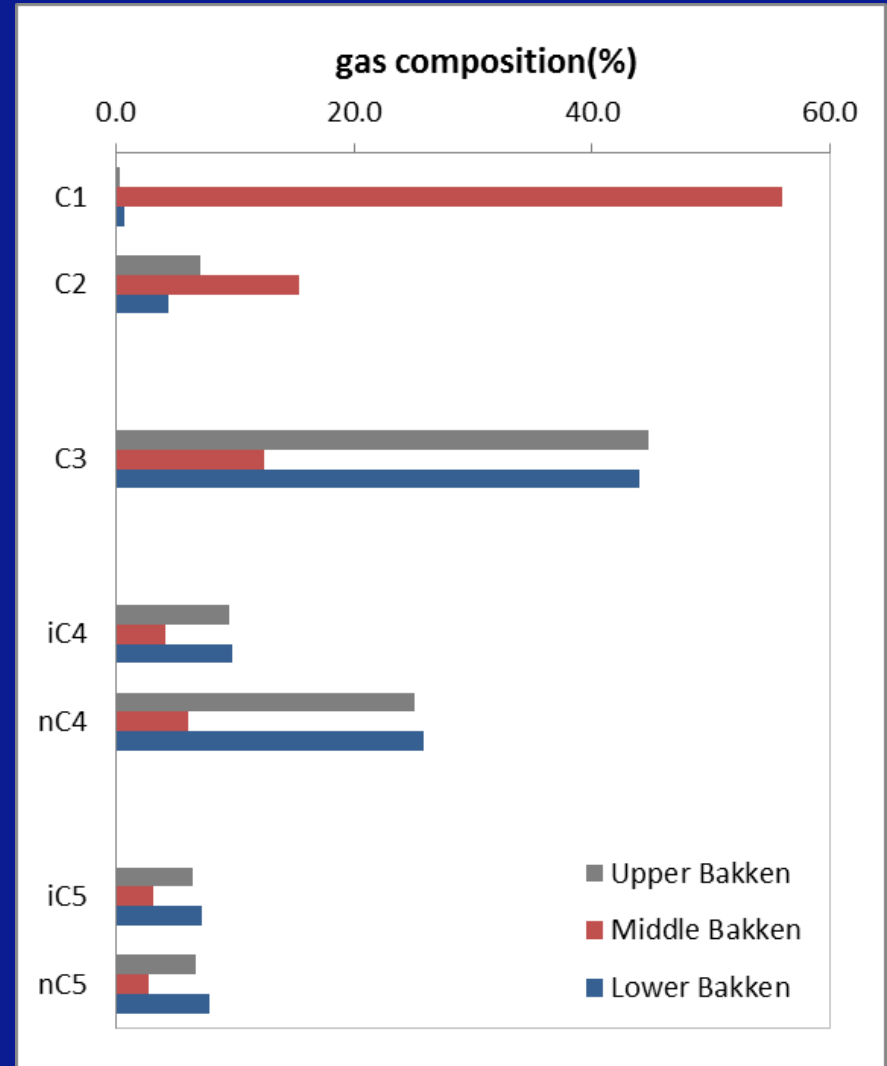
A gradual decrease in the amount of residual oil through a 3-5ft interval near U/M lithological contact suggests that petroleum expulsion efficiency (PEE) is determined by lithology.

# Similar Petroleum Expulsion Pattern is Observed in Lower Bakken Siliceous Mudrocks



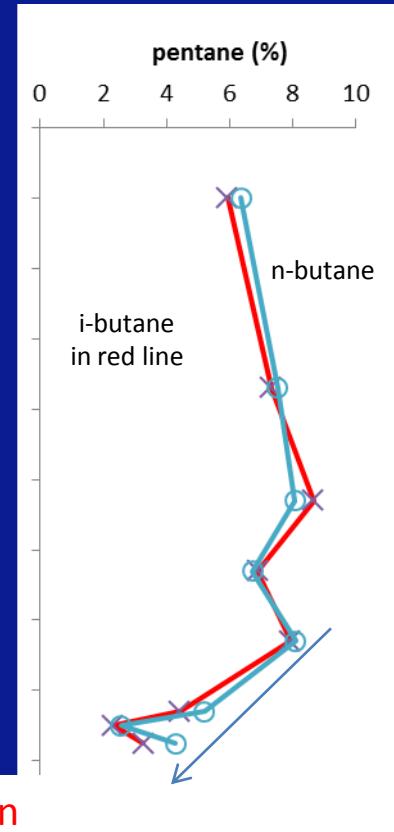
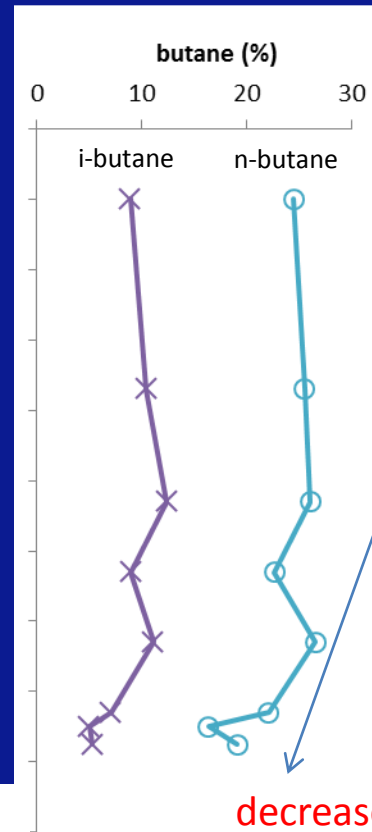
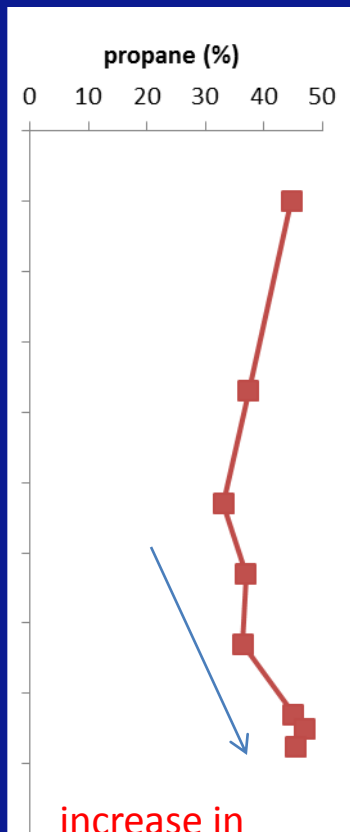
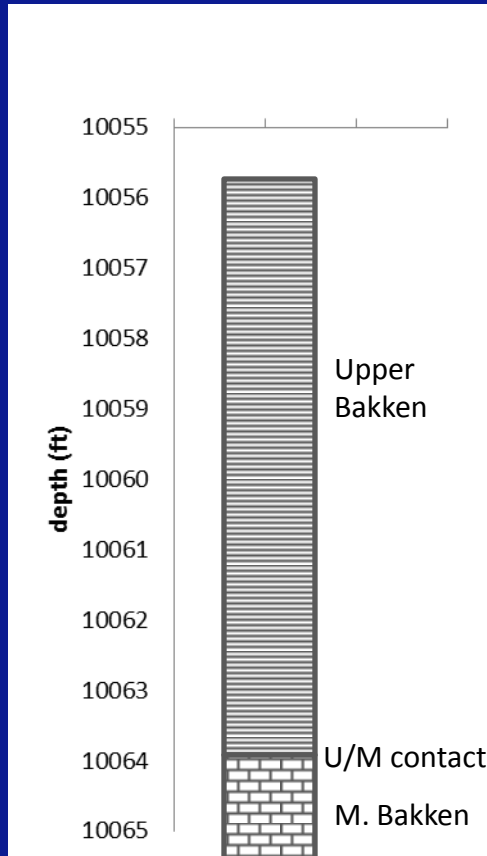
A gradual decrease in the amount of residual oil through a 3ft interval near L/M lithological contact is indicative of the change of petroleum expulsion efficiency (PEE) with lithology.

**The Difference in Gas composition suggests that pores in the Upper and Lower Bakken are mainly filled with oil, and that gas is dissolved in oil rather than in a free gas phase, and the dissolved gas may greatly reduce oil density, and increase oil mobility.**



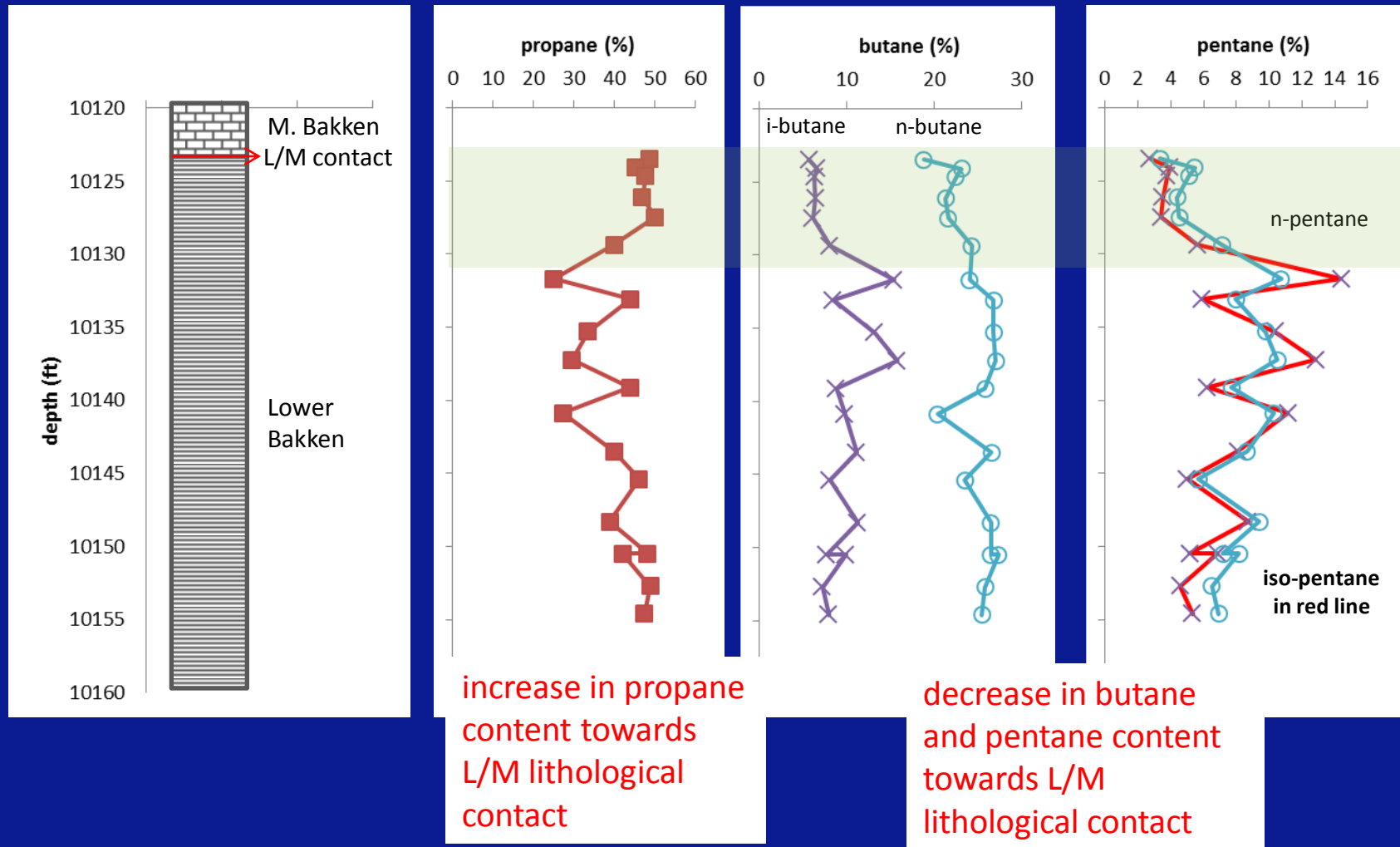
	C <sub>1</sub> (%)	C <sub>2</sub> (%)	C <sub>3</sub> (%)	iC <sub>4</sub> (%)	nC <sub>4</sub> (%)	iC <sub>5</sub> (%)	nC <sub>5</sub> (%)
U/L B	0.3/0.8	7.1/4.4	44.8/43.9	9.5/9.7	25/25.9	6.4/7.2	6.7/7.9
MB	56	15.4	12.4	4.2	6.1	3.1	2.8

# Vertical Variation of Gas Compositions within the Upper Bakken Provides Consistent Evidence That Petroleum Expulsion Was Affected by Lithology

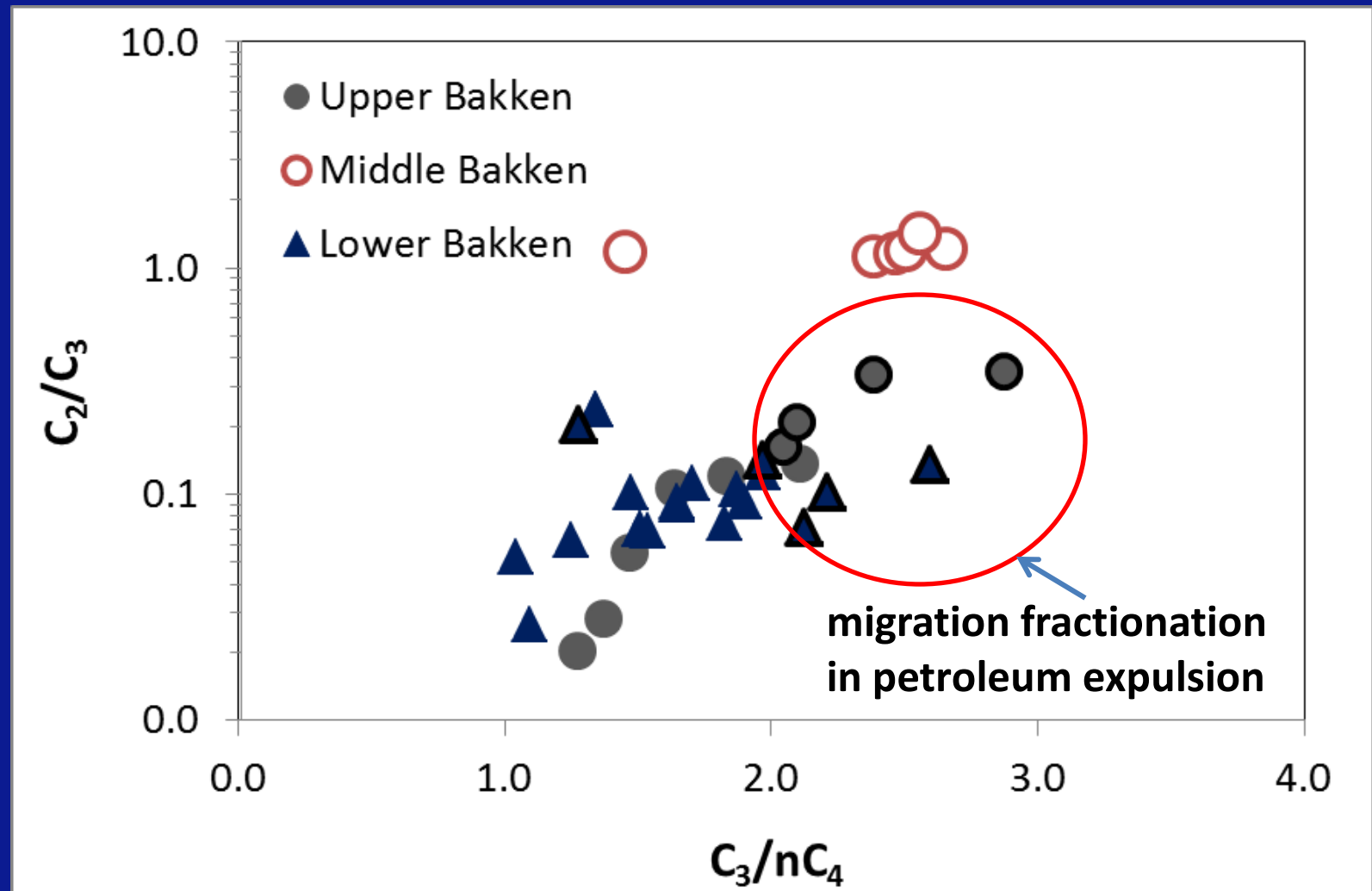




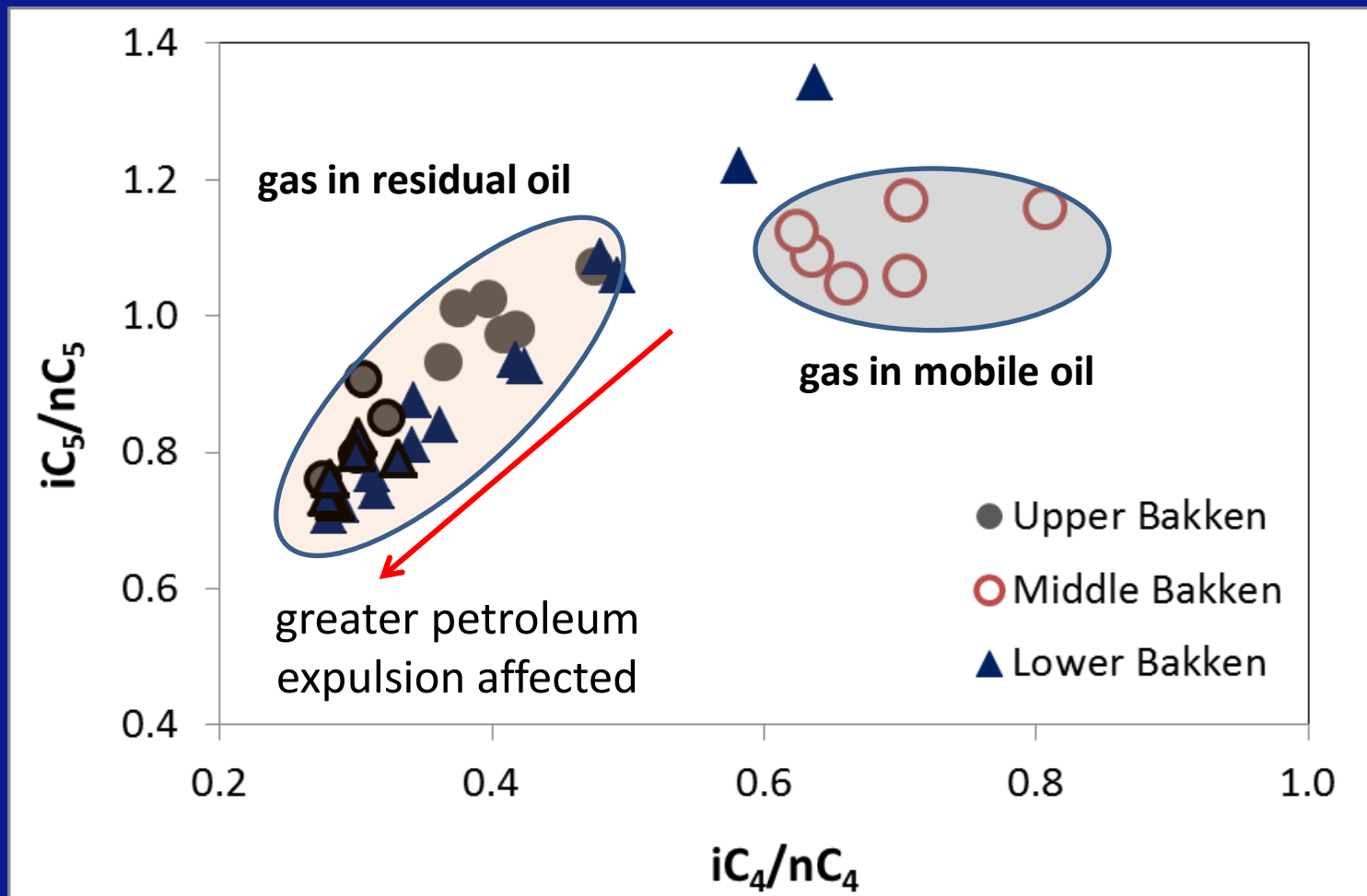
# Similar Variation in Gas Compositions Caused from Petroleum Expulsion is Observed in the Lower Bakken Siliceous Mudrocks



# Plot of $C_2/C_3$ vs. $C_3/nC_4$ Indicates A Preferential Migration of Low-mass Gas Molecules In Petroleum Expulsion



# Extent of Petroleum Expulsion within Thick Organic-Rich Shales Can Be Evaluated with A Plot of $iC_4/nC_4$ vs. $iC_5/nC_5$

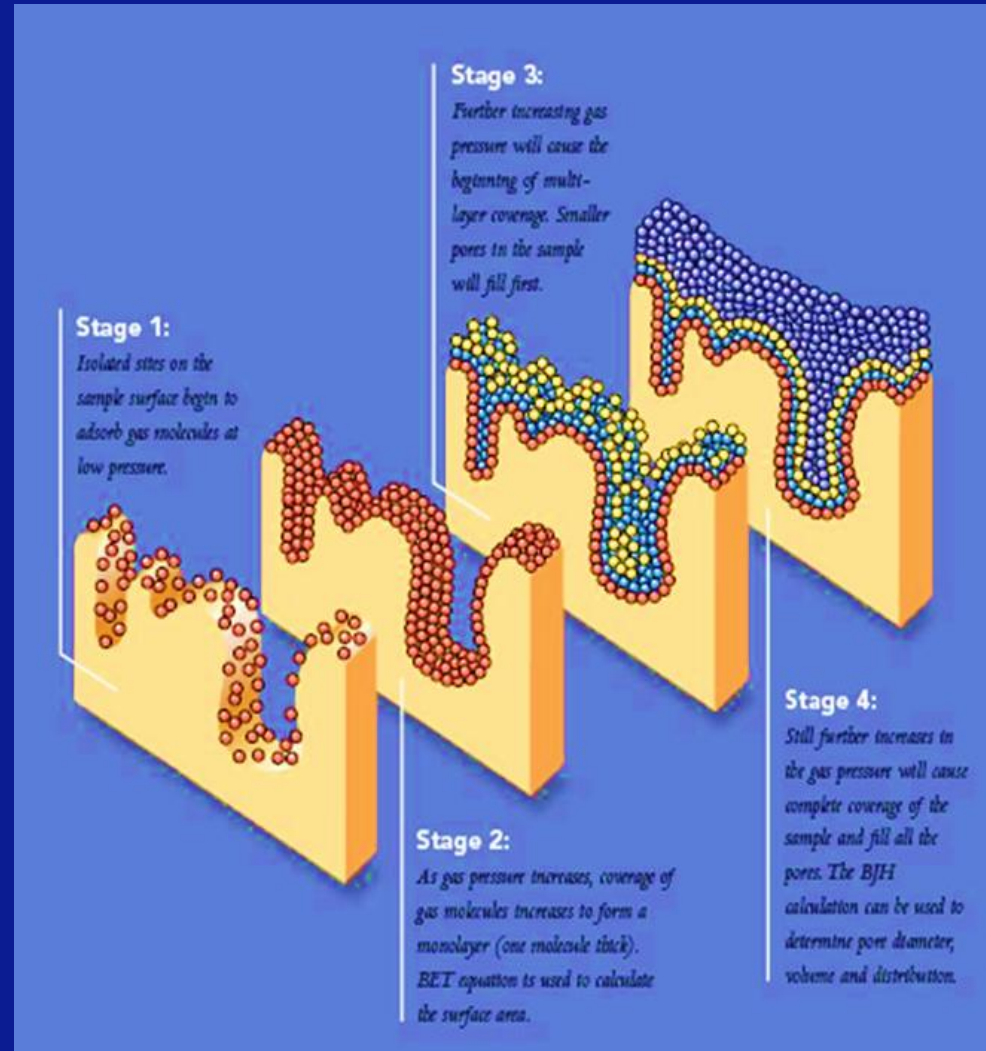


# Pore Characterization

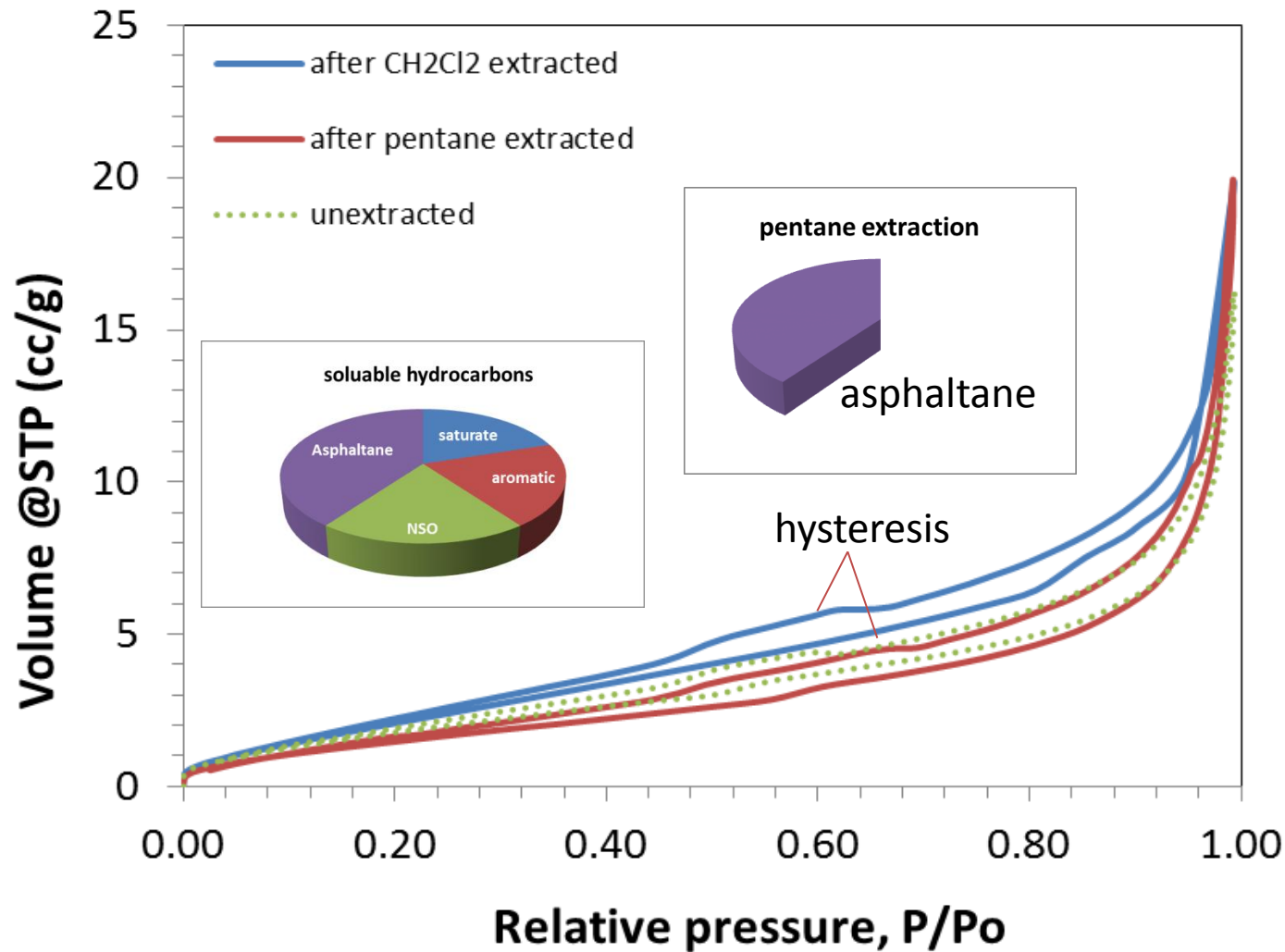
- $\text{N}_2$  gas adsorption and desorption isotherms
- 0.38nm ~ 300nm pore size distribution
- Pore volume, BET surface area and pore shape

# Physisorption of Gases and Pore Characterization

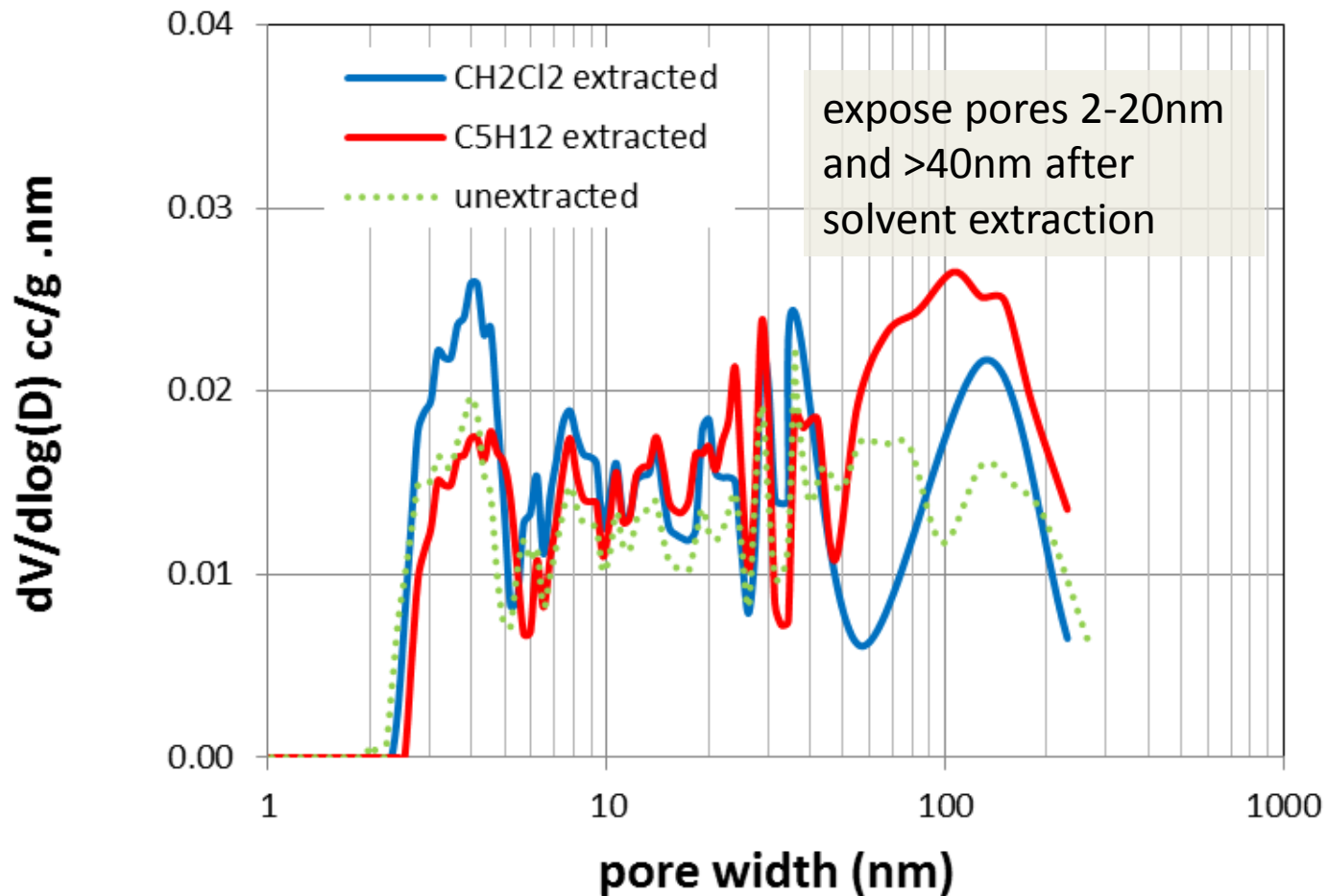
- Expose a solid sample to the gas (adsorptive) in an evacuated tube, hold at low temperature (77 K for  $N_2$ ) to a series of pressures, ranging from  $P/P_0 < 1 \times 10^{-7}$  to 0.999
- As the pressure increases, the amount of gas adsorbed onto the surface of the sample increases.
- During this process the micropores are filled first (at very low pressures). Finally, the larger pores are filled.
- Similarly, for the desorption process, the pressure is systematically reduced to release the adsorbed molecules from the surface.
- Adsorption/Desorption Isotherms are one of the best methods for monitoring network effects and connectivity



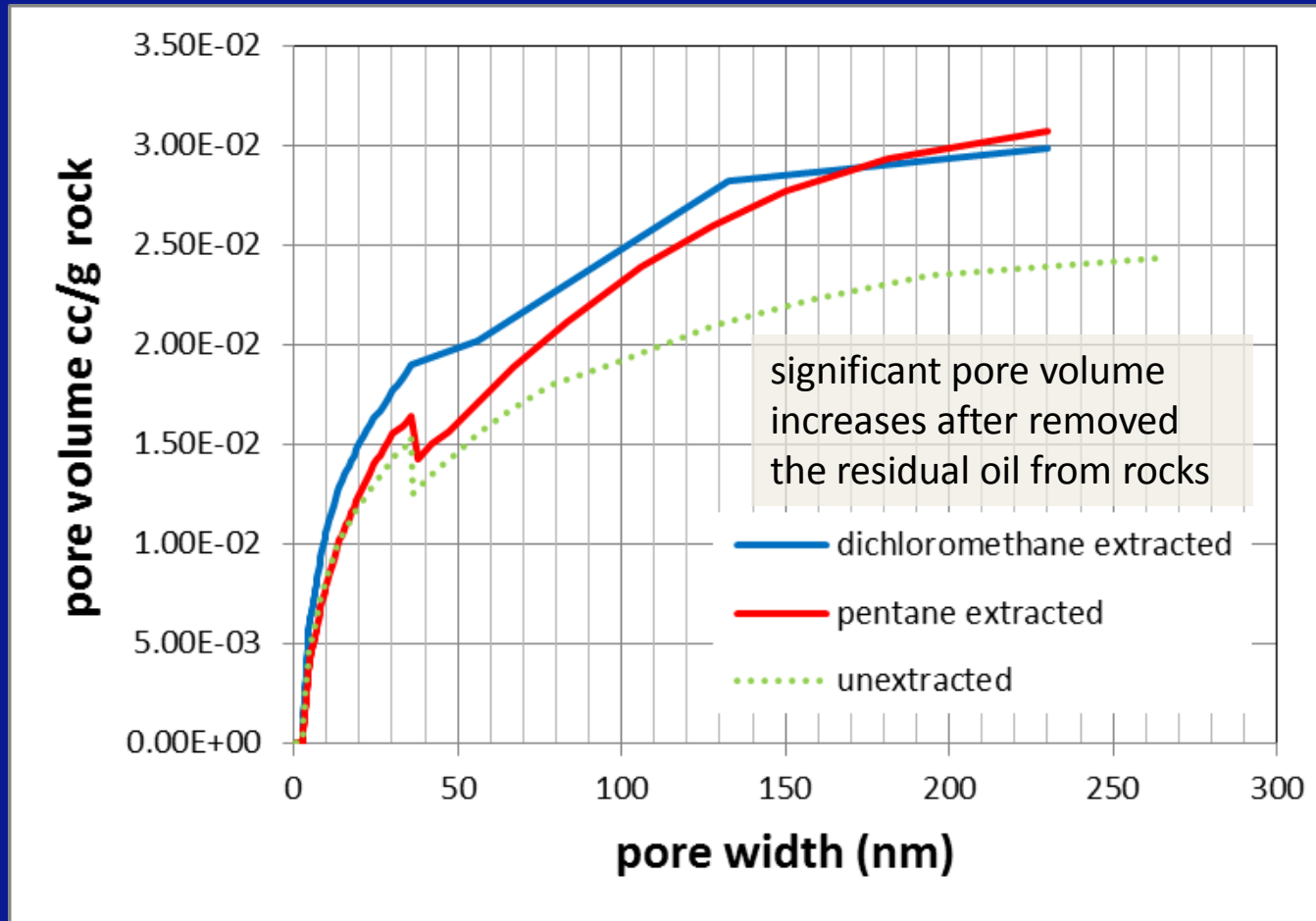
# N<sub>2</sub> Gas Adsorption and Desorption Isotherms of Lower Bakken Sample at 77K



# More Pores Can Be Exposed After Solvent Extraction



# Oil Is Mainly Stored in Pores with Width Larger Than 20nm

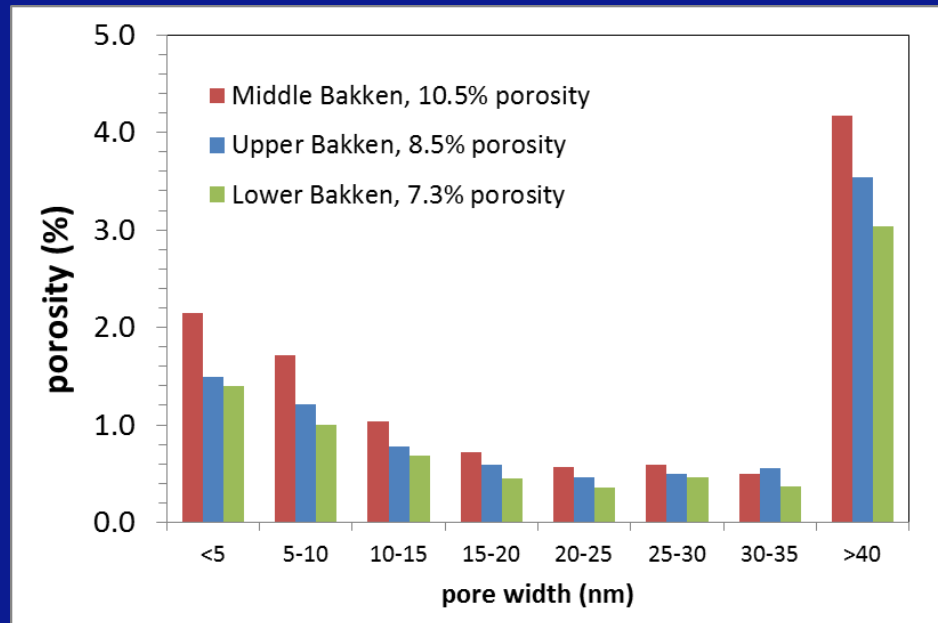
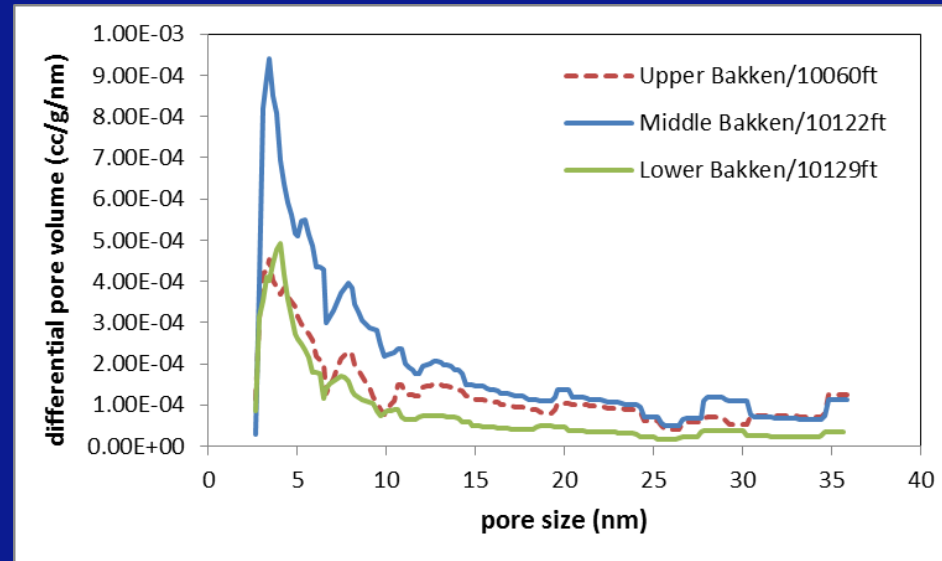




# Pore Size Distribution in Bakken Formation

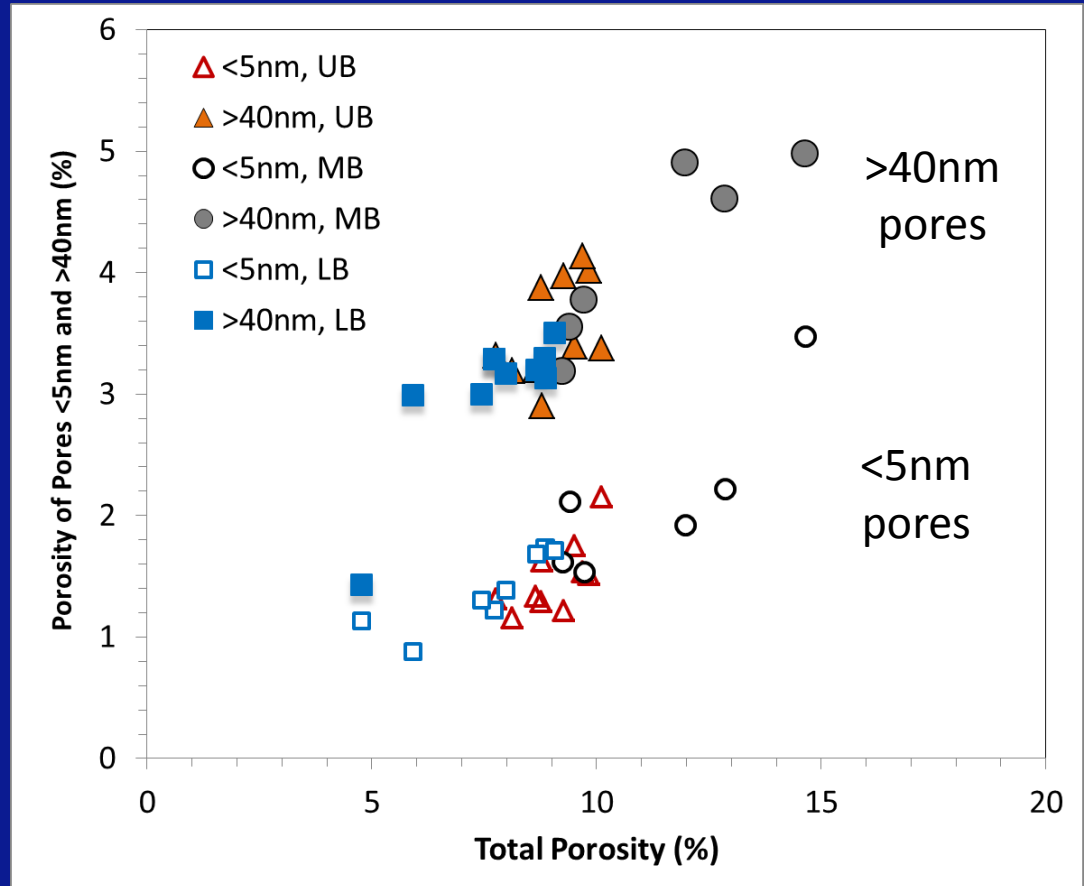
- No micropores (<2nm) develops.
- Both the Upper Bakken and Lower Bakken are dominated by mesopores (2-32nm) and macropores.
- Middle Bakken has higher porosity.
- About 60% of the total porosity comes from mesopores.

Pore Size Distribution

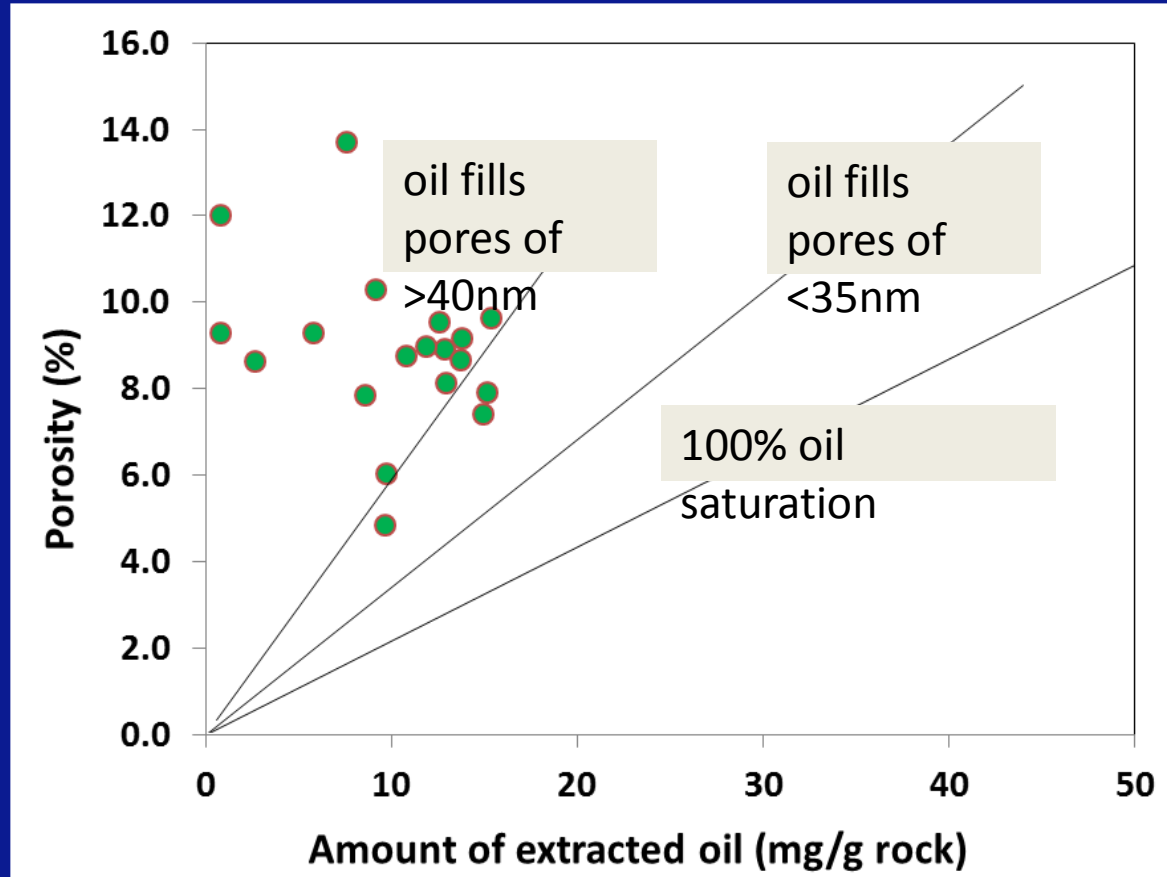


# Controls to Porosity Variation in Bakken Fm. are Complicated

- The porosity varies significantly within three Bakken units.
- Middle Bakken, sandy limestone/dolomite, has higher porosity than the Upper and Lower Bakken siliceous mudstone.
- The lower Bakken generally has the low value porosity.
- The difference in lithology and compaction plays an important role to porosity variation.



# Residual Oil in the Upper and Lower Bakken Occupies about 40% Total Pore Volume



Based on the mass balance calculation, the residual oil saturation in the Upper and Lower Bakken is about 40%, and oil possibly mainly fills the pores larger than 40nm

# Summary (1)

- Oil SARA fractions can be significantly affected by petroleum expulsion and oil migration.
- Petroleum expulsion efficiency is determined by lithology; maximum expulsion efficiency is about 41% and occurs near the contacts of the Upper and Lower Bakken with the Middle Bakken.
- No significant petroleum expulsion is observed in the middle of the Upper and Lower Bakken.
- Residual oil is mainly stored in pores larger than 20 nm in width.

# Summary (2)

- Gas is mainly dissolved in residual oil in the Upper and Lower Bakken rather than in free gas phase, and gas dissolved in oil increases oil mobility.
- Gas chemistry is an indicator for identifying gas in mobile oil, gas in residual oil, and the extent of petroleum expulsion.
- Adsorption and desorption isotherms are powerful tools for monitoring pore size distribution, porosity, and pore networks.
- Integrated pore studies with SEM pore imaging are required to adequately define the genetic relationships between pore sizes and pore types.