Characterization of Gas Shales for Enhanced Natural Gas Recovery and Carbon Storage Applications

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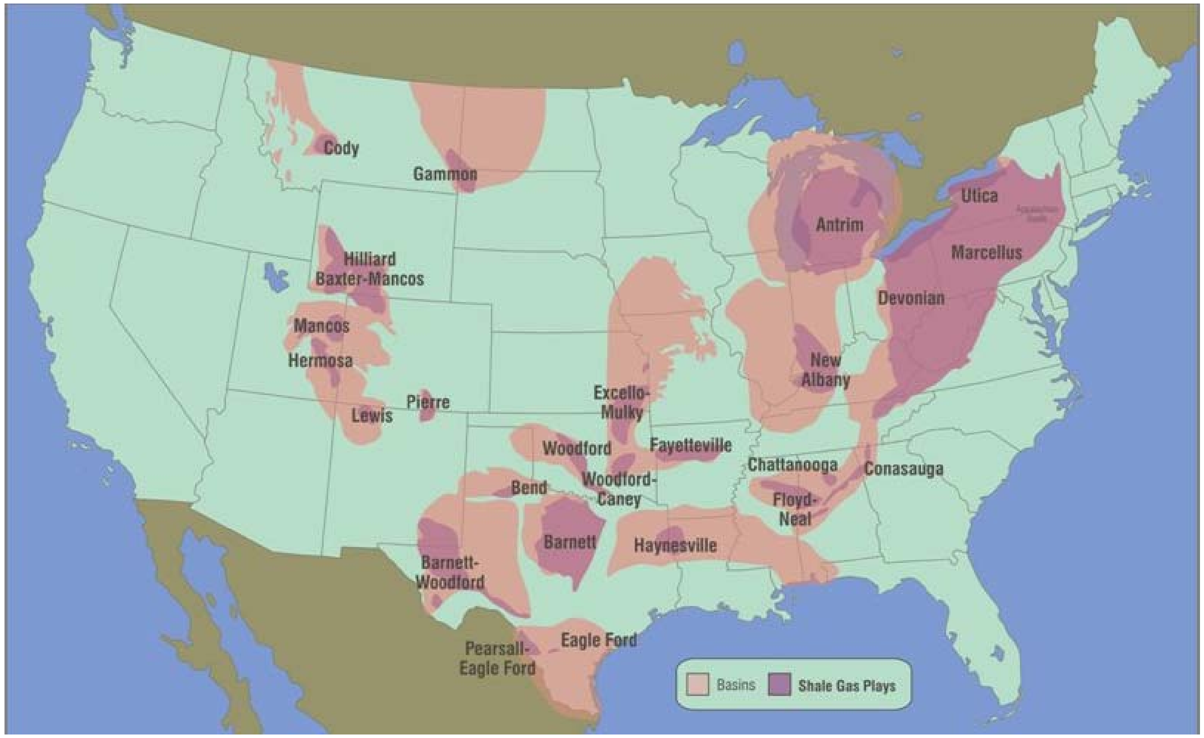
Overview

Overarching Goal: characterize chemistry and morphology of shale to determine gas storage potential and mechanism of enhanced natural gas recovery through experiments and modeling

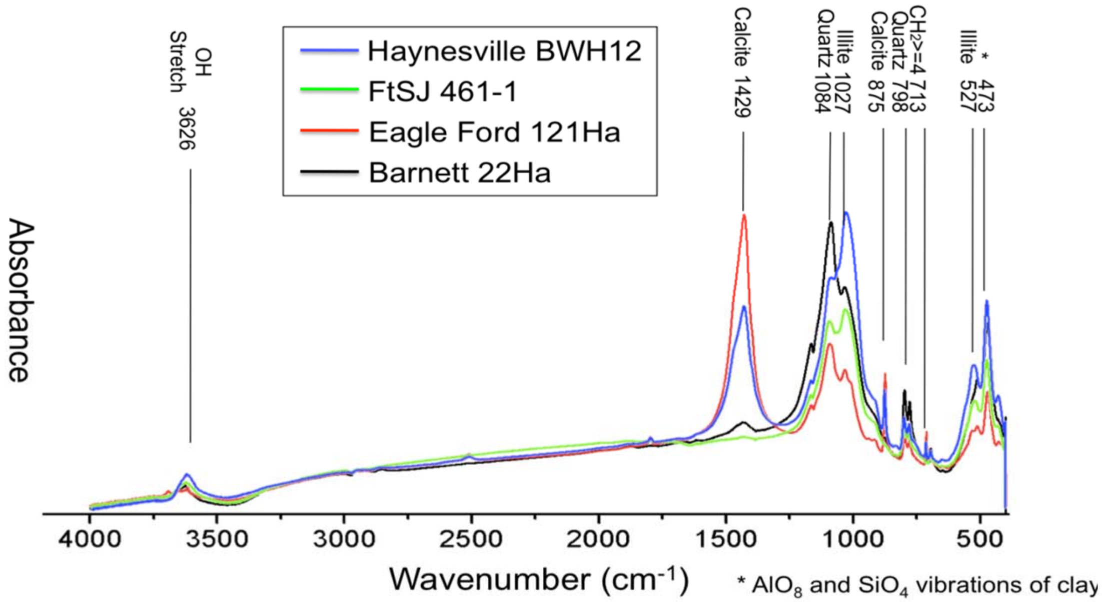
- Shale mineralogy
  - Shales are complex!
  - Role of kerogen versus clay
- Pore volume and pore size distribution
  - Outgassing procedure
  - Synthetic vs real shale samples
- High pressure and temperature isotherms indicative of realistic subsurface conditions
- Importance of realistic models
  - Adsorption isotherm simulations (storage) – GCMC
  - Enhanced recovery properties (wettability) - MD

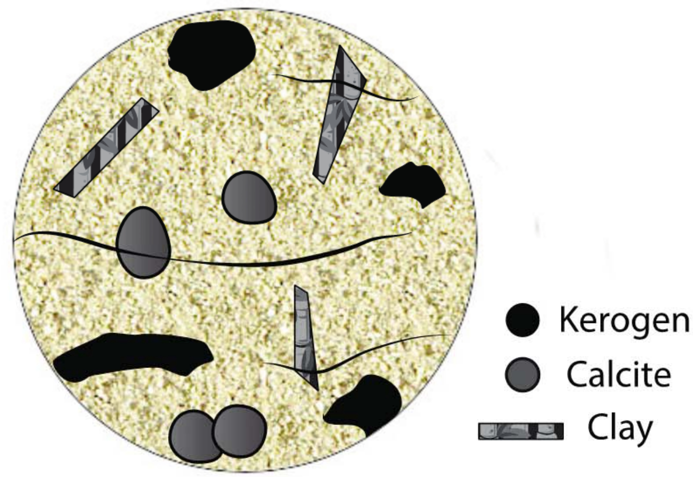
Shale Deposits in the United States



Shale	Barnett	Haynesville	Fayetteville	Marcellus
Depth (m)	1950-2550	3150-4050	300-2100	1200-2550
T (˚C)	68.5-86.5	104.5-131.5	19-73	46-86.5
P (MPa)	20-25	30-40	3-20	12-25

Shale Mineralogy

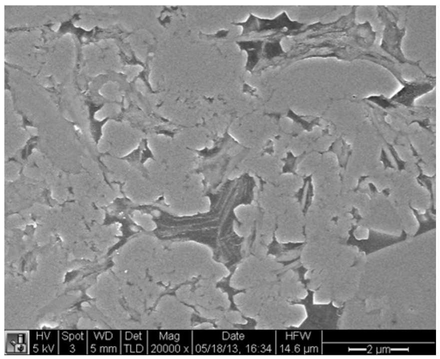


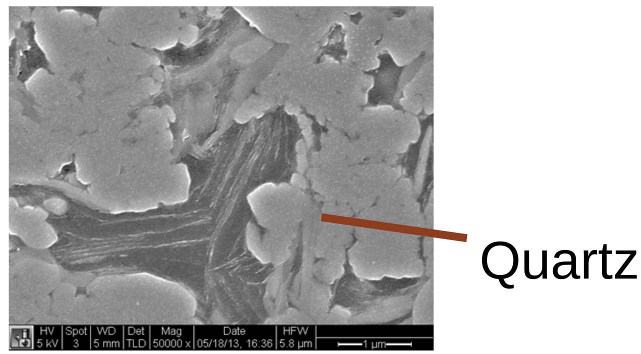


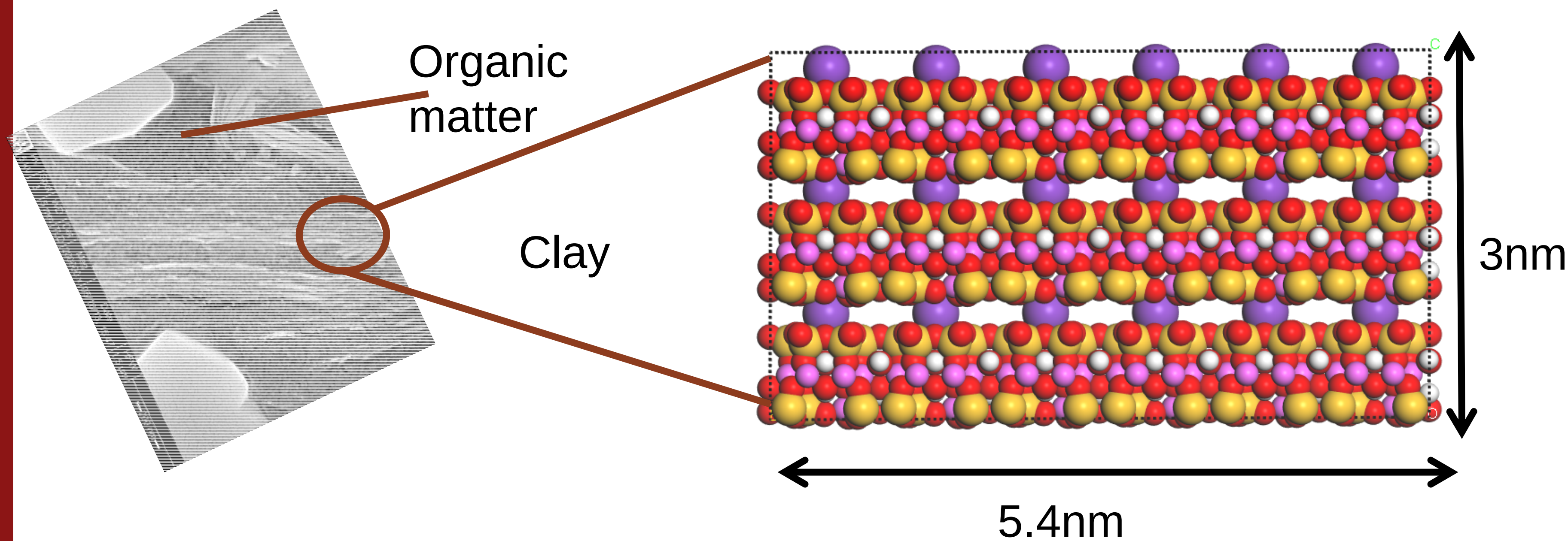
XRD Compositional Data(wt%)			
Component	**Formula**	**Barnett**	**Eagle Ford**
Quartz	SiO_2	38%	21.2%
Feldspar	$KAlSi_3O_8 - NaAlSi_3O_8 - CaAl_2Si_2O_8$	3.8%	0%
Calcite	$CaCO_3$	0.9%	54.2%
Pyrite	FeS_2	1.8%	3.6%
Clay	Illite	**39%**	**15.8%**
TOC		**16%**	**4.97%**

Microscopic to Nano-scale

Clay in organic matter of Barnett shale







SEM images courtesy of Cindy Ross

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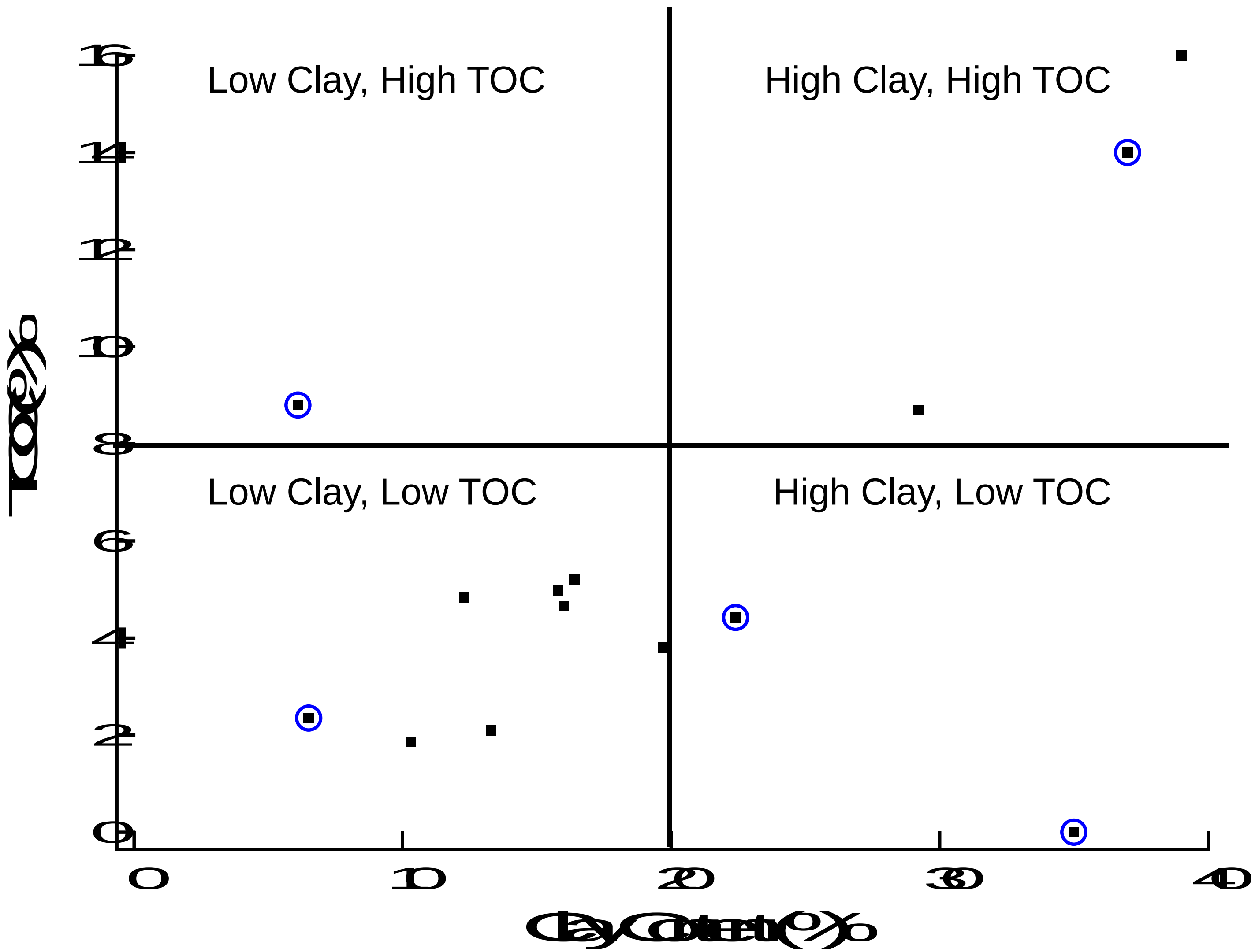
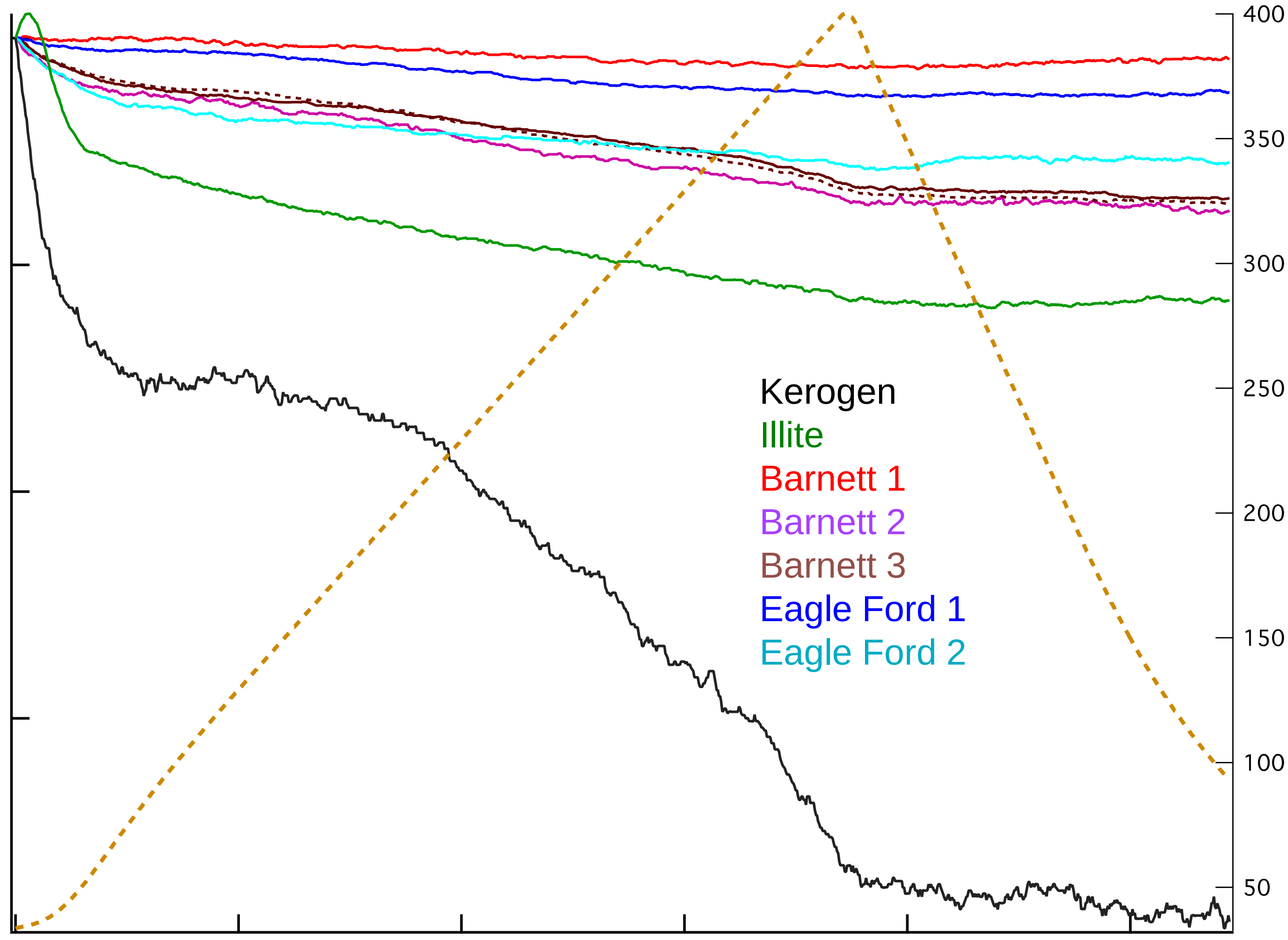
Shale Samples

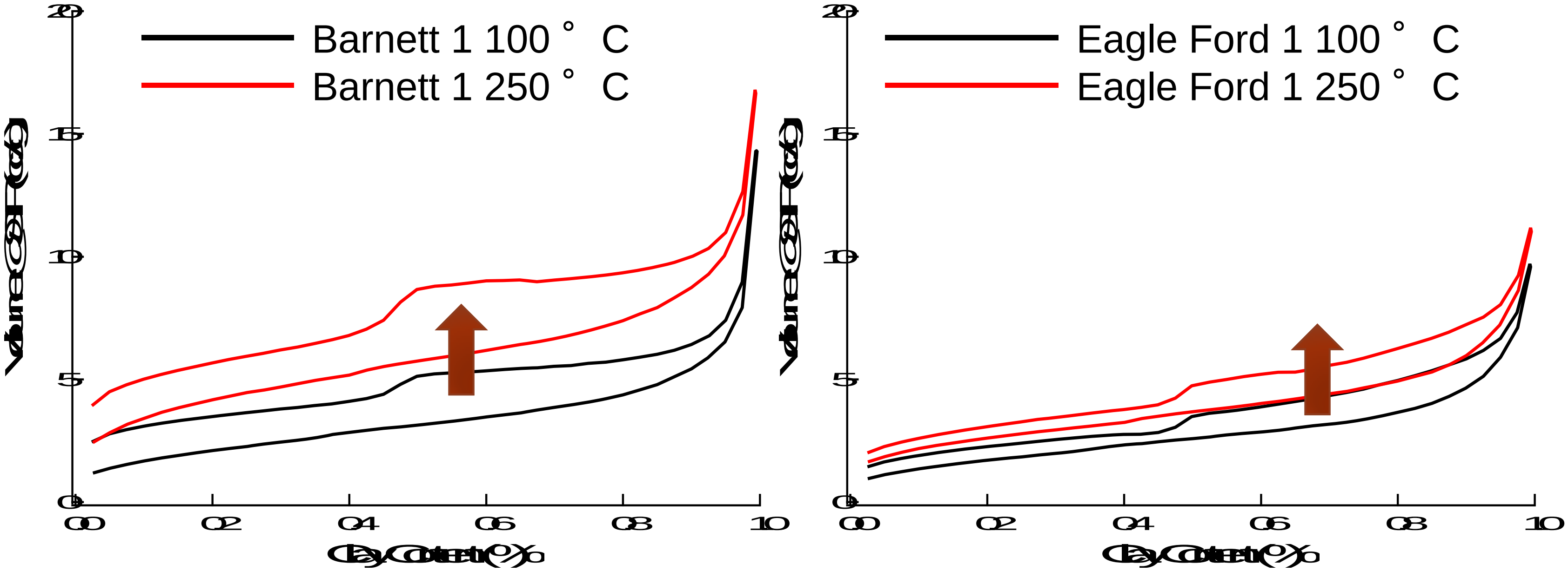


TGA Graphical Results



Netzsch STA 449 F3 Jupiter Simultaneous Thermal Analyzer and Differential Scanning Calorimeter

V = f(Outgas Temperature)

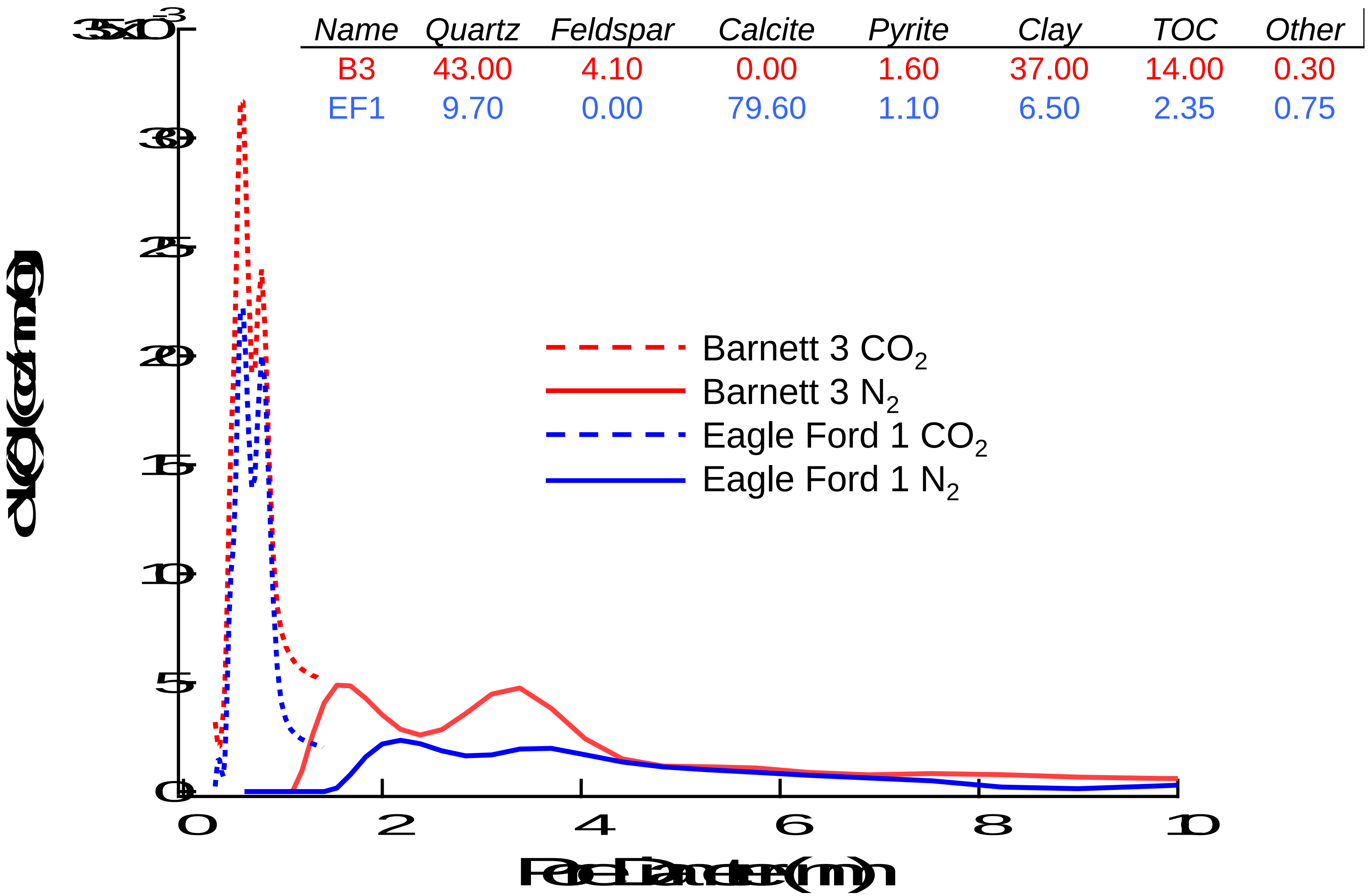


Increased temperatures during outgassing increase observed pore volume, primarily in micropores

Autosorb iQ_2 (Quantachrome) low-pressure gas sorption analyzer

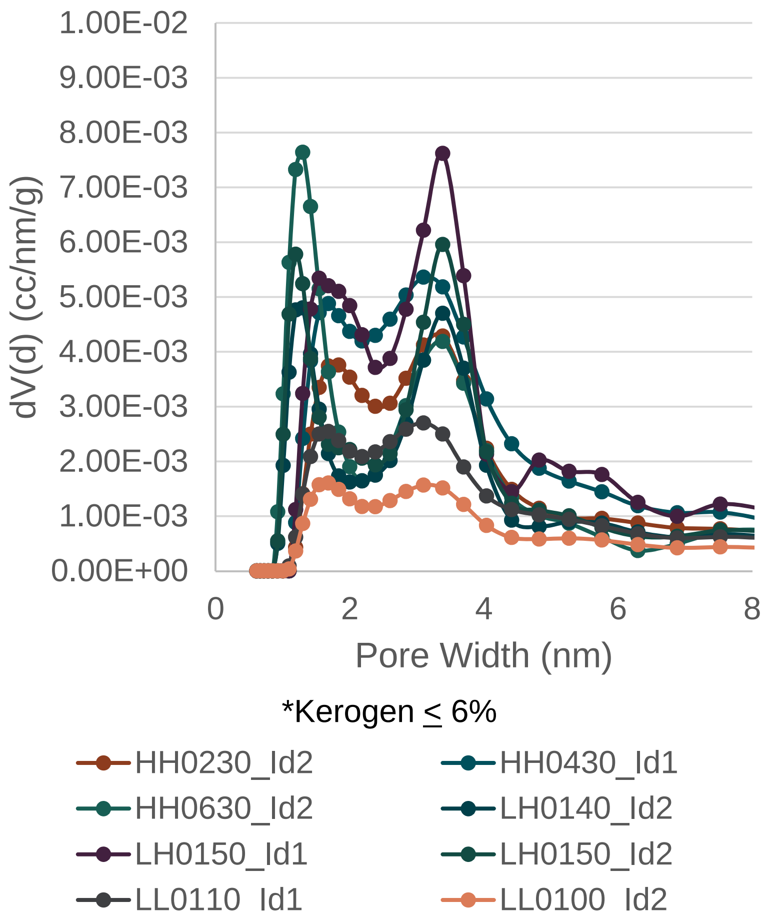
Comparison Between CO_2 and N_2

Name	Quartz	Feldspar	Calcite	Pyrite	Clay	TOC	Other
B3	43.00	4.10	0.00	1.60	37.00	14.00	0.30
EF1	9.70	0.00	79.60	1.10	6.50	2.35	0.75

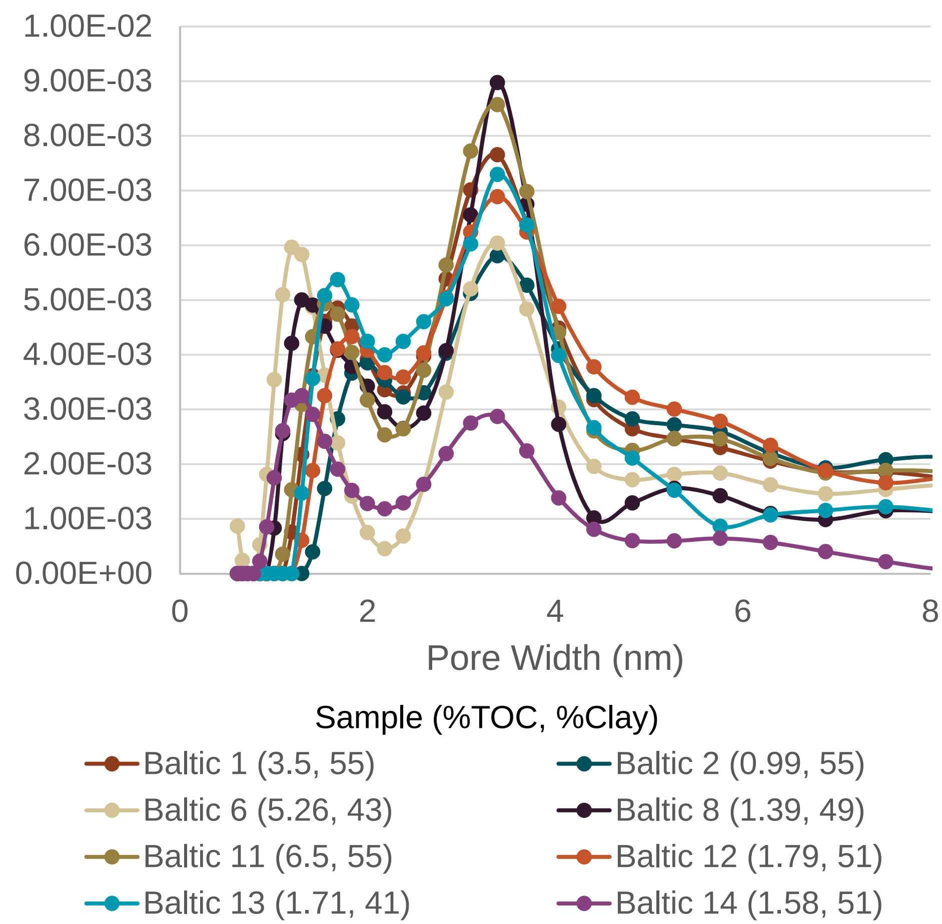


Pore Size Distributions General Trend

Idealized Shales
Kerogen ≤ 6%, Clay 30-50%



Validation Shales
TOC ≤ 6.5%, Clay 41-55%



Model: QSDFT N_2-carbon slit-pore equilibrium model

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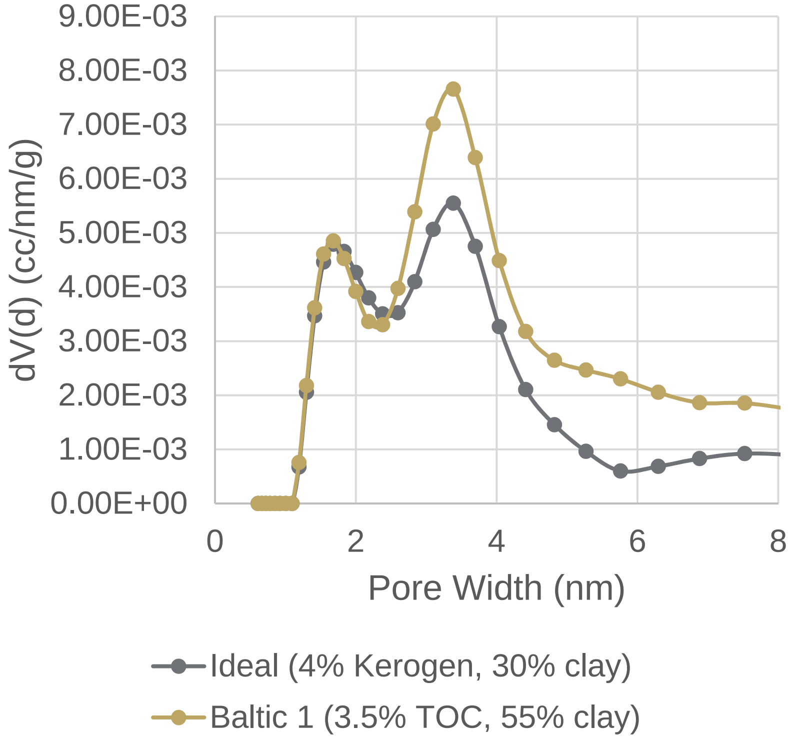
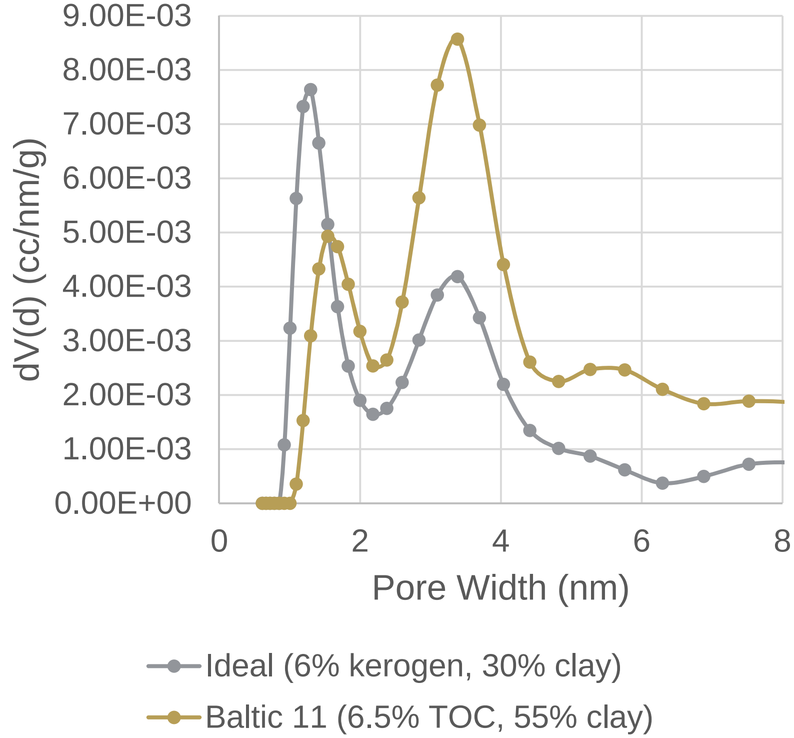
QSDFT Pore Size Distributions





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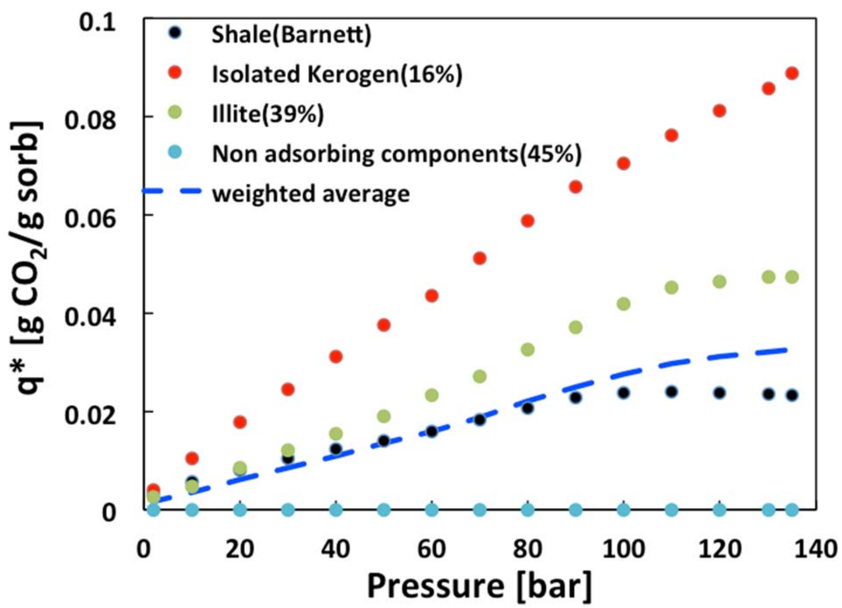
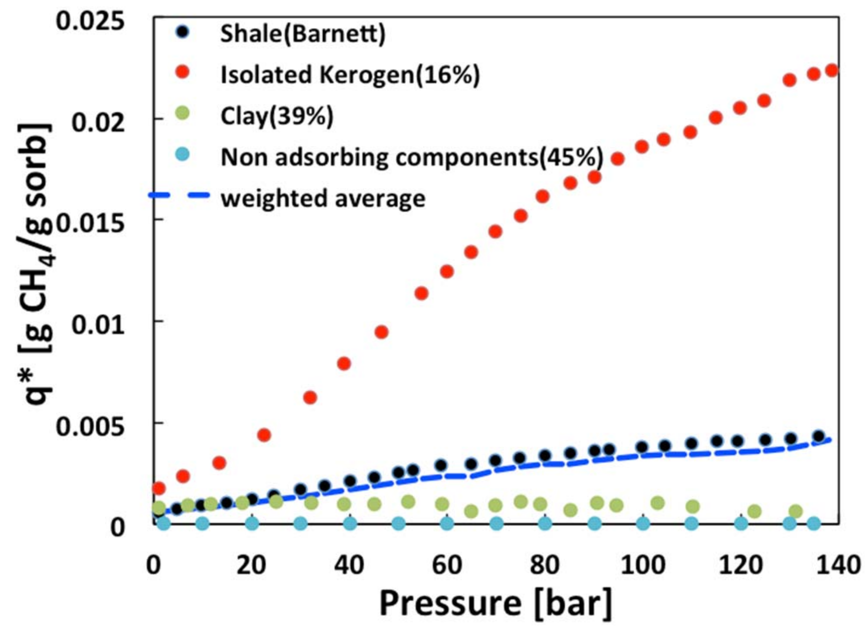
CO_2 and CH_4 Isotherms

CO_2 isotherm



CH_4 isotherm



Enhanced uptake of CO_2 over CH_4 at subsurface conditions, e.g., 80 ° C

Rubotherm Magnetic Suspension Balance

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Atomistic Models of Illite

General formula - $Ca_{0.059}$, $K_{0.655}(Si_{3.597}, Al_{0.403})(Fe_{0.628}, Al_{0.969}, Mg_{0.428})$ per $O_{10}(OH)_2$

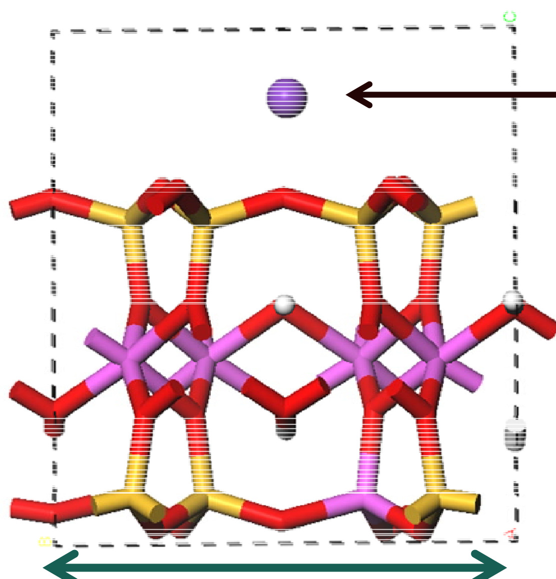
Oxygen
Silicon
Potassium
Aluminium
Hydrogen

1M

Interlayer cation

$Ca_{0.059}$, $K_{0.655}$

$(Si_{3.597}, Al_{0.403})$



$(Fe_{0.628}, Al_{0.969}, Mg_{0.428})$ per $O_{10}(OH)_2$

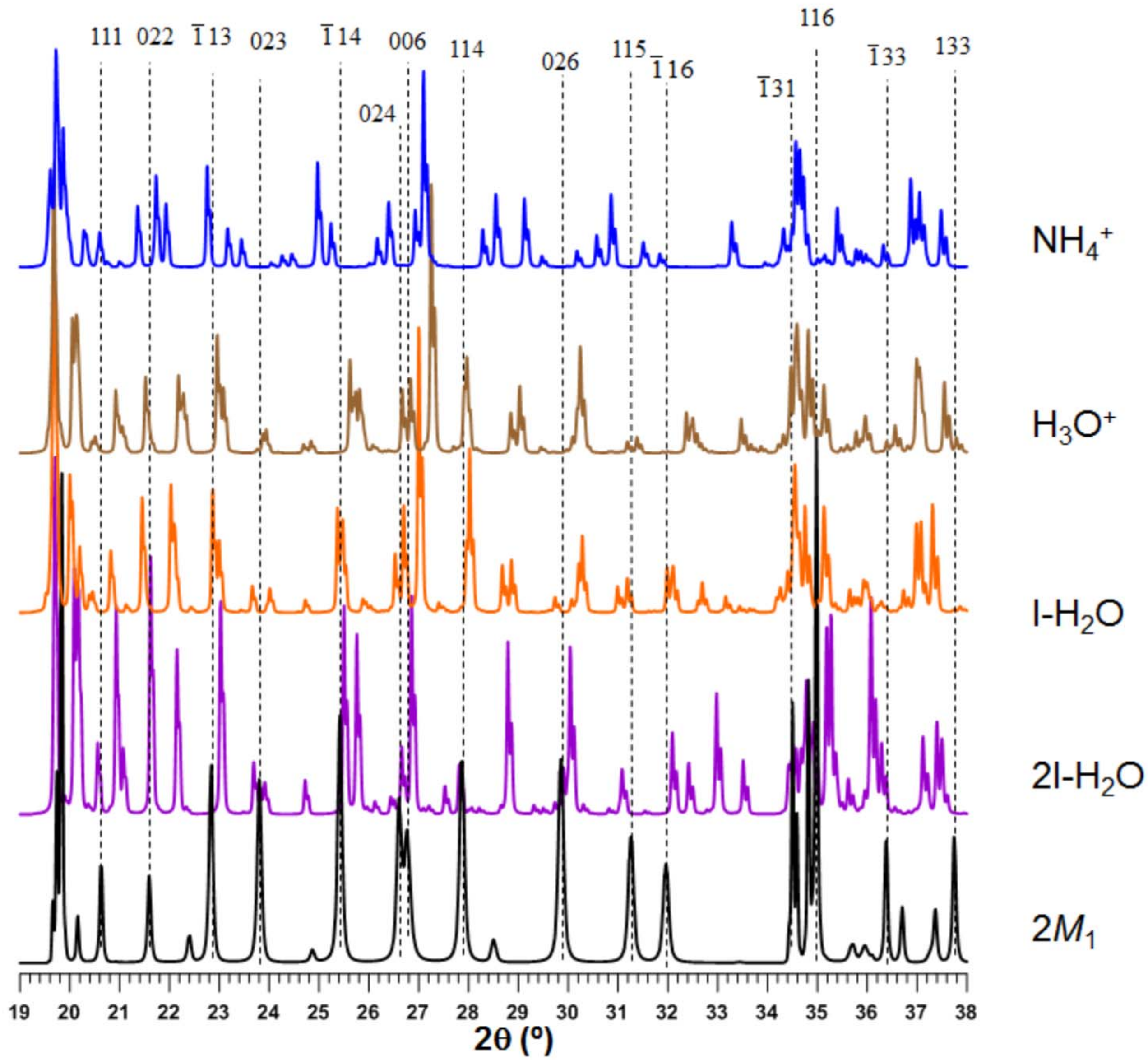
10Å

Substitution of Al for Si in tetrahedral sheets

Substitution of Fe/Mg for Al in octahedral sheet

D Geatches, J Wilcox, 2014, Eur. J. Mineral. (26), 127-144

XRD



Courtesty of Douglas McCarty, Chevron

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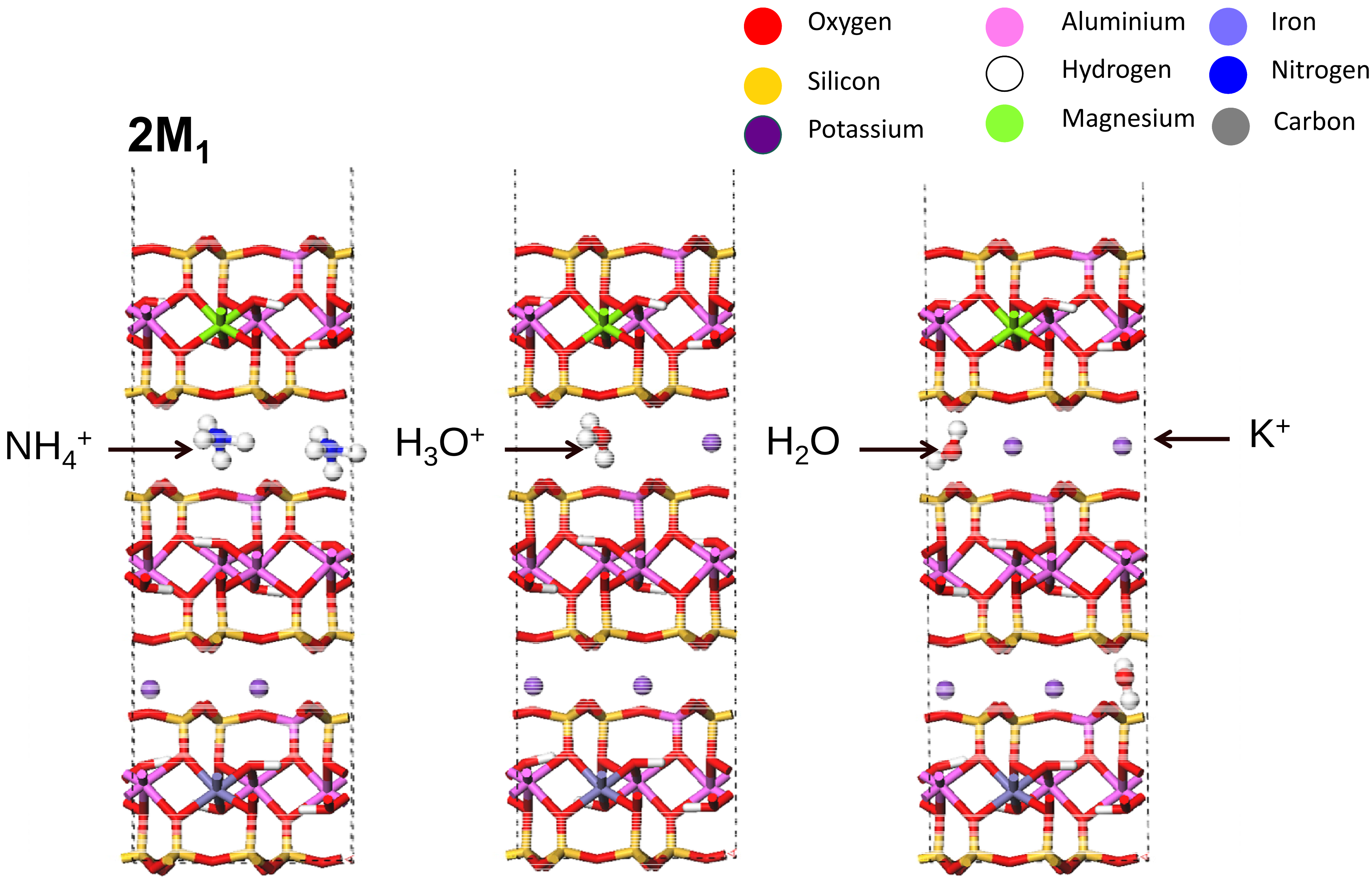
Atomistic Models of Illite



D Geatches, D McCarty, J Wilcox, 2014, Am. Min., (99)1962-1972.

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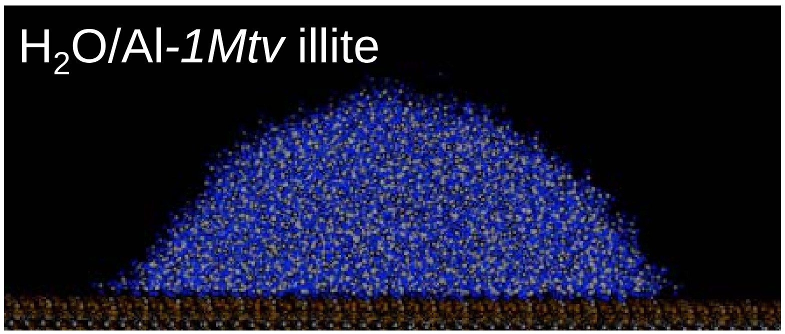
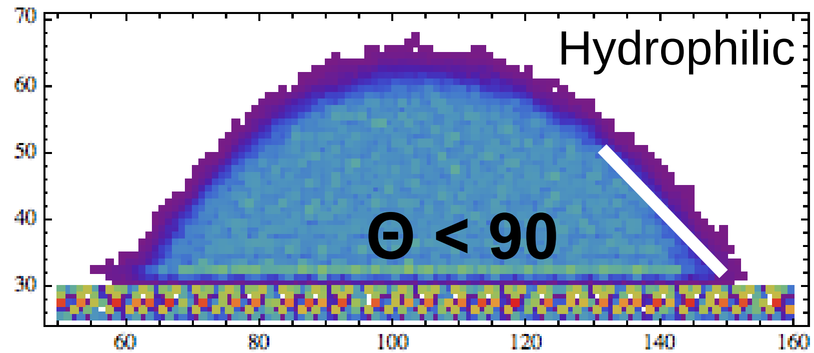
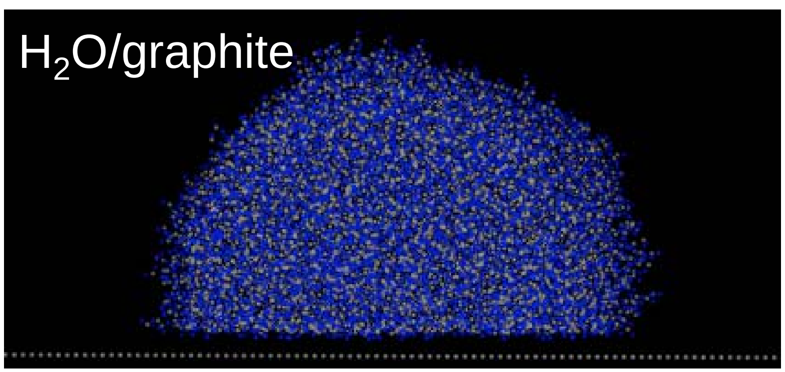
Measuring Wettability with Contact Angles

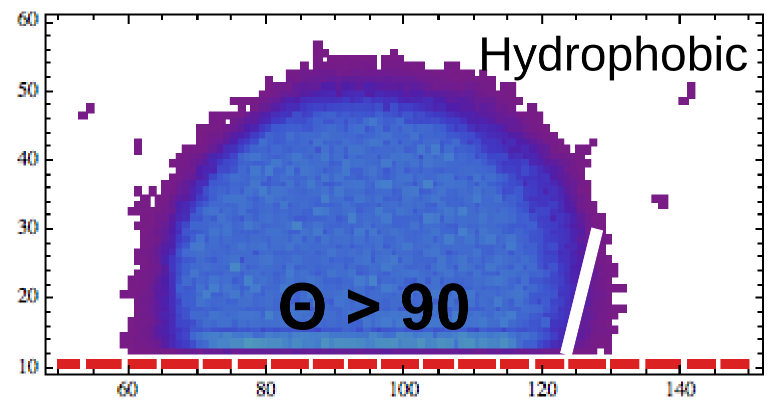
Graphite versus illite clay

Density plot



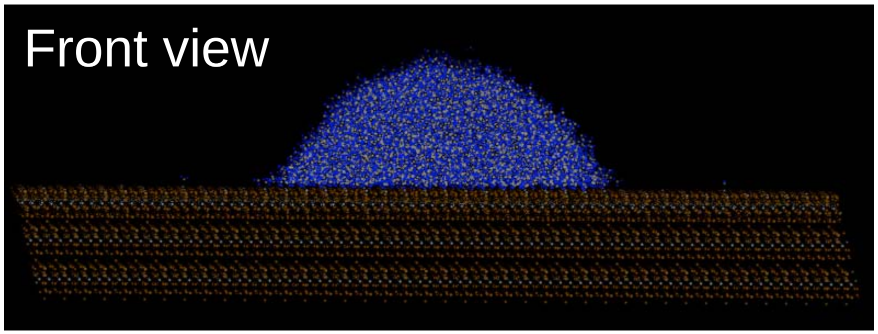


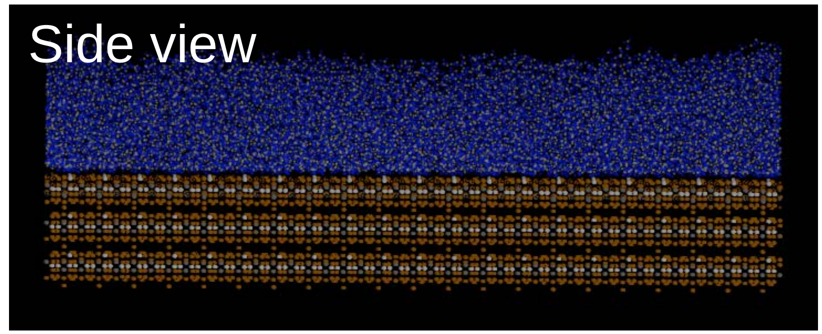


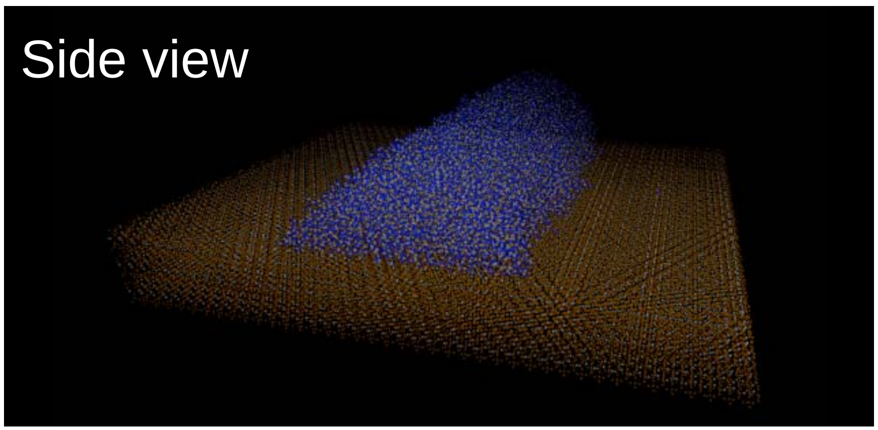


H_2O Wettability on Illite

MD simulation using LAMMPS package
The surface dimension: 215Å x 190Å x 3 layers with 11154 H_2O
Periodic boundary conditions are applied in x and y directions





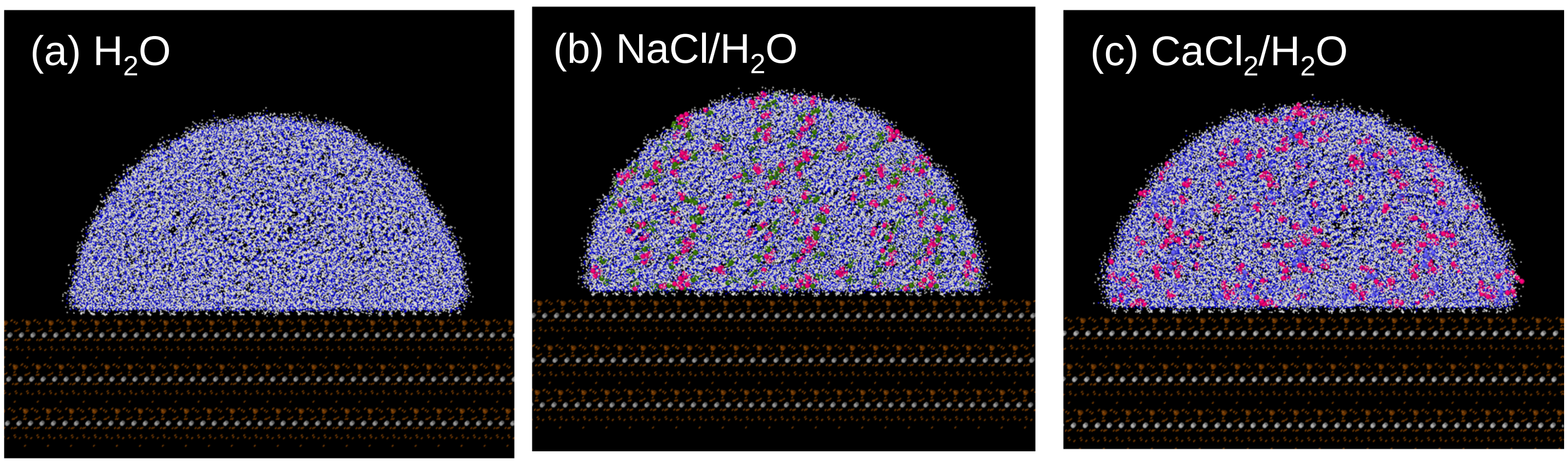


Al-1Mtv $K(Si_7Al)\ Al_4O_{20}(OH)_4$ +
SPC/Fw H_2O (at 300 K)

Clay unit cell from Geatches, Wilcox, Eur. J. Mineral. 26 (2014) 127

Influence of Exchangeable Cations on the Wettability

- Surface properties of clay minerals, and the water film adsorbed on the surface, can be modified by introducing various exchangeable cations, which affect these properties by changing the hydration state of the surface



MD simulations of (a) water and (b) 0.75 M NaCl (c) 0.25 M $CaCl_2$ cylindrical droplet on *Al-1Mtv* illite surface. (in early simulation stage)

In Summary

- Shales are complex systems
  - Pore shape – slit and cylindrical
    - Depends upon clay versus carbon content
  - Pore size – micro and mesoporous
  - Pore chemistry – clay and kerogen (carbon)

- Realistic models can lead to accurate estimates
  - Storage potential (CO_2)
  - Available natural gas – more accurate estimates
  - Enhanced uptake using CO_2 displacement


Questions?
Clean Energy Conversions Website:
http://cec-lab.stanford.edu