Investigating the Microstructure of Gas Shales by FIB/SEM Tomography & STEM Imaging

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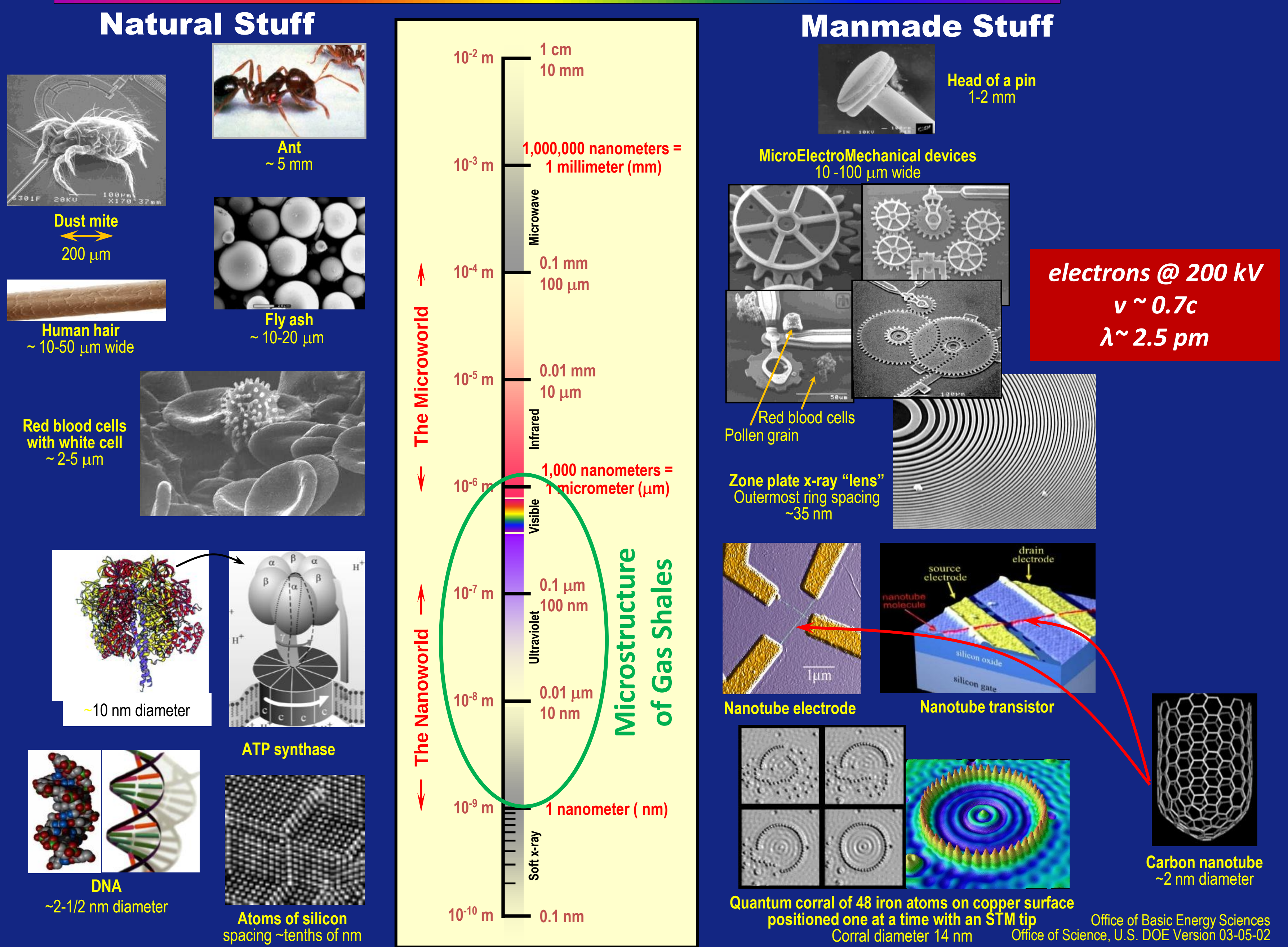
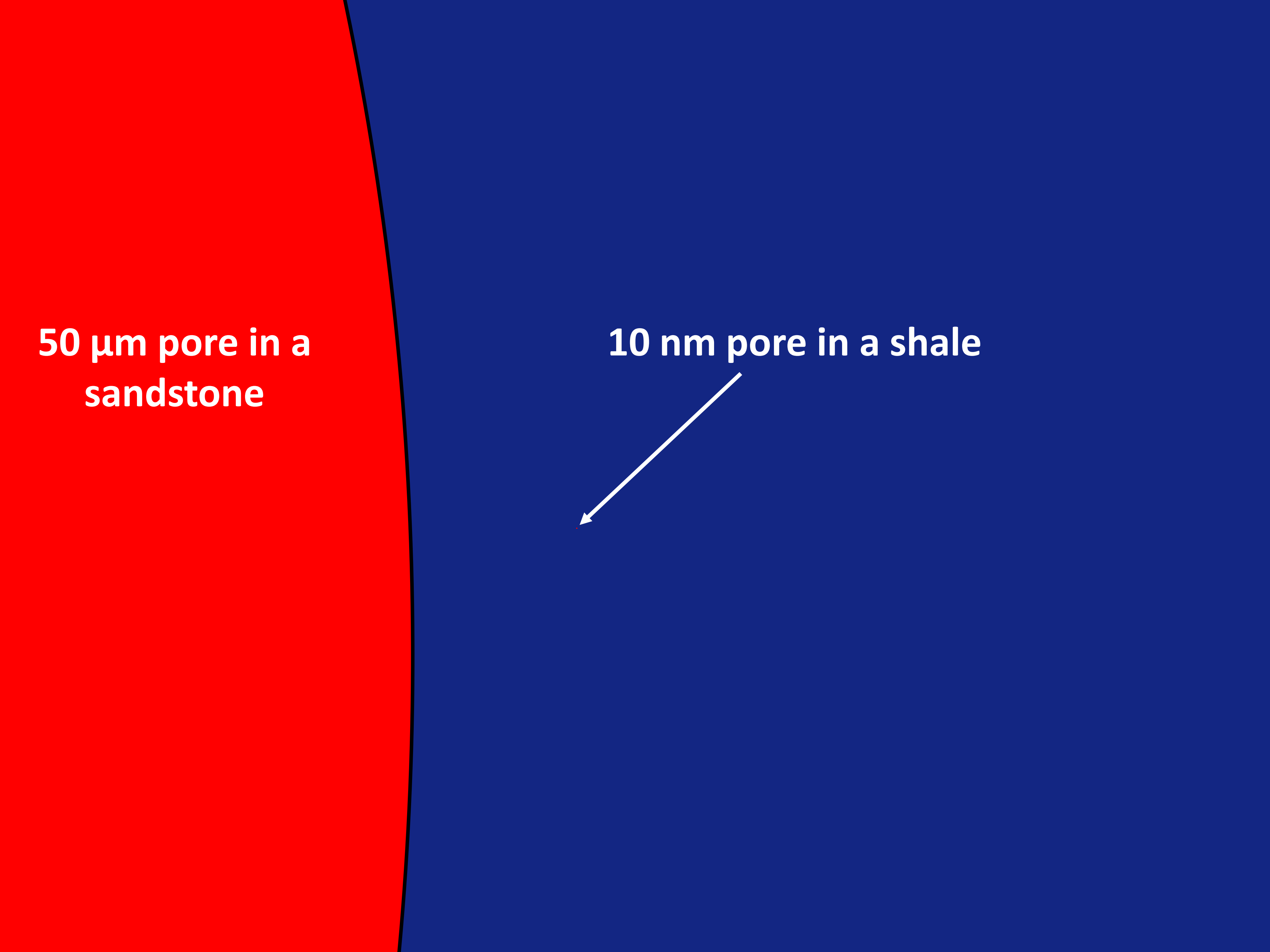
Overview

- Size perspective on gas shales.
- Preparing and imaging shale microstructure with a dual-beam FIB/SEM system.
- 2D and 3D SEM on gas shale microstructure.
- Scanning transmission electron microscopy (STEM) of shale microstructure.
- Summary

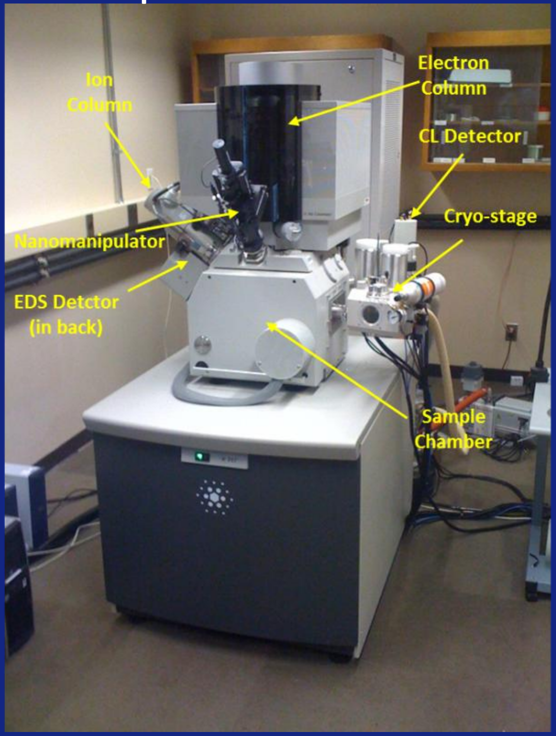
The Scale of Small Stuff



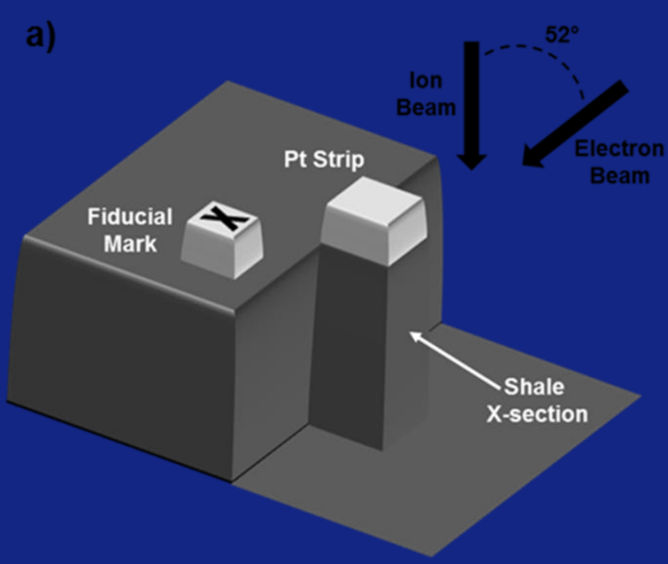

50 µm pore in a sandstone
10 nm pore in a shale

Imaging Shales with a Dual-Beam System

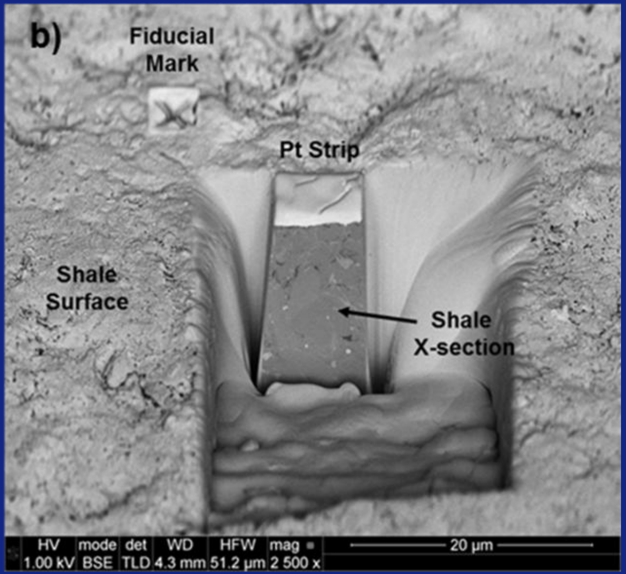
- Focused ion beam (FIB) and scanning electron microscope (SEM) integrated on same sample chamber.
- X-section shale surface via momentum transfer of high energy (30 kV) Ga^+.
- Image x-sectioned surface using backscattered electrons (BSE) for atomic number contrast.
- Can perform other analytical techniques in situ and ion-beam induced material deposition.



Dual-beam FIB/SEM.



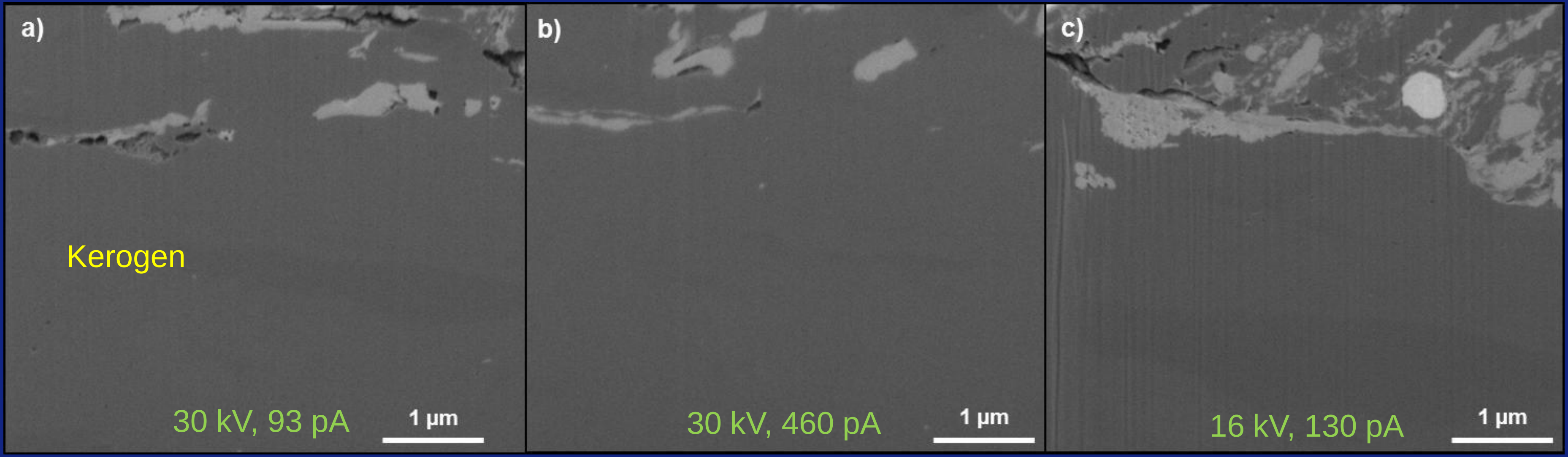
Curtis et al., *submitted*, 2010



a) schematic of dual beam site preparation using FIB and imaging using SEM. b) BSE image of x-sectioned shale.

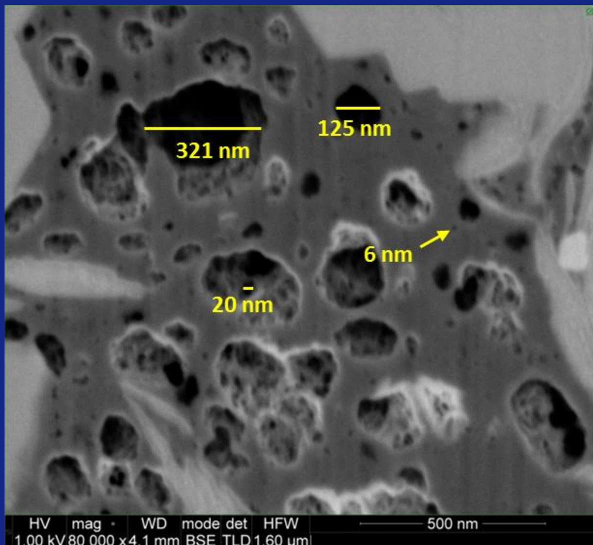
FIB Damage Test

- Tested effect of different ion energies and currents on kerogen.
- Experimented on kerogen-rich Kimmeridge shale sample.
- Little kerogen porosity visible and no significant changes in microstructure.
- More curtaining seen at lower energies.
- FIB can be used to section delicate biological specimens.

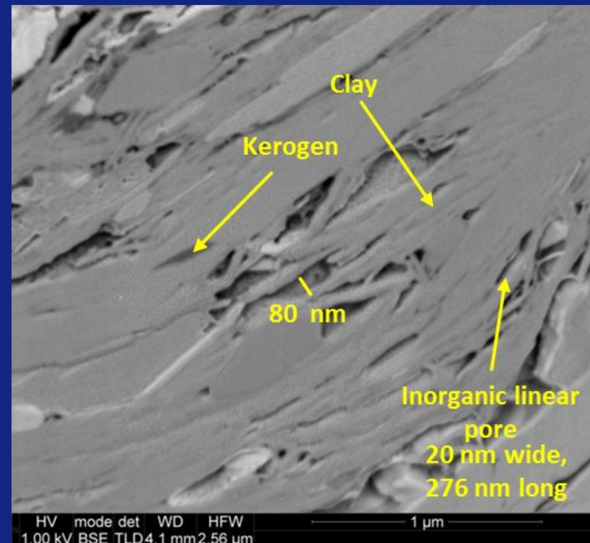


BSE images of Kimmeridge shale milled with the FIB using different ion energies and currents.

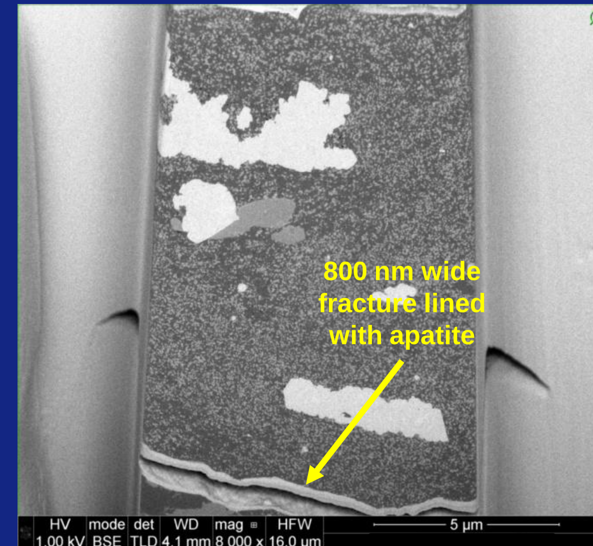
Porosity: Size, Shape, Amount, and Location



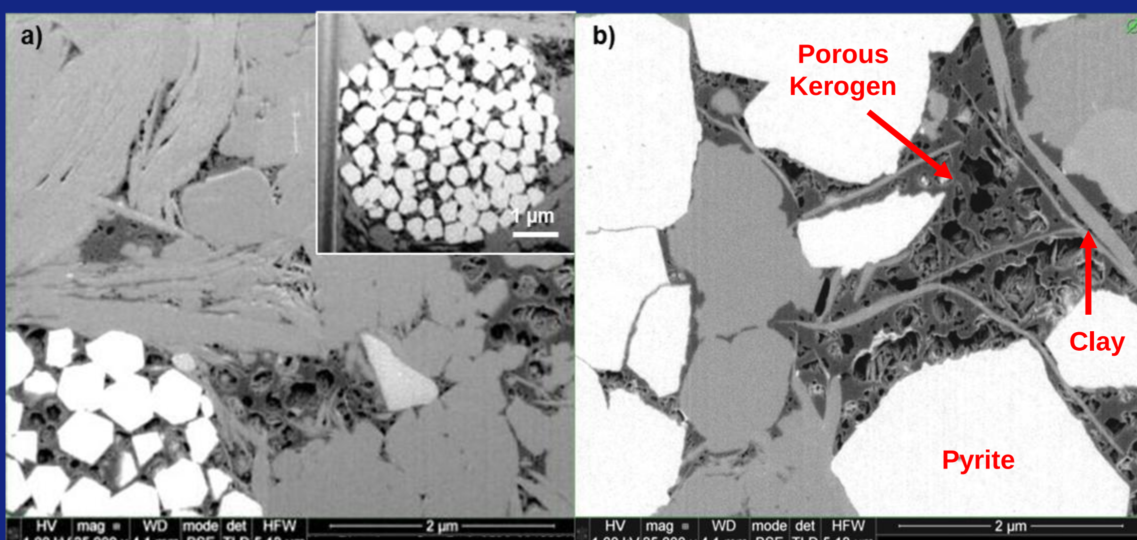
Organic Porosity



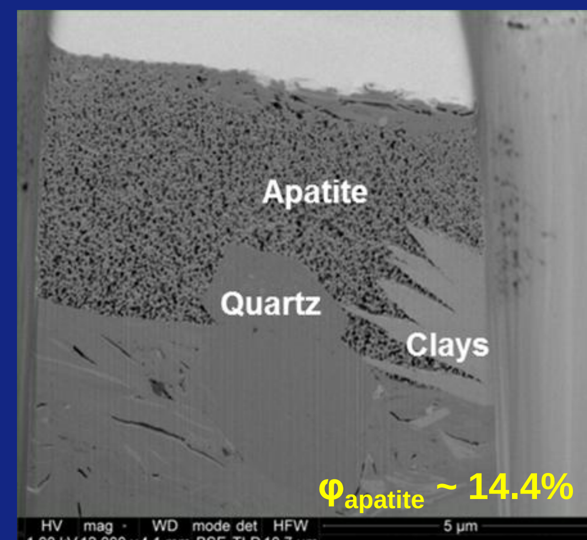
Phyllosilicate Porosity



Cracks and Fractures



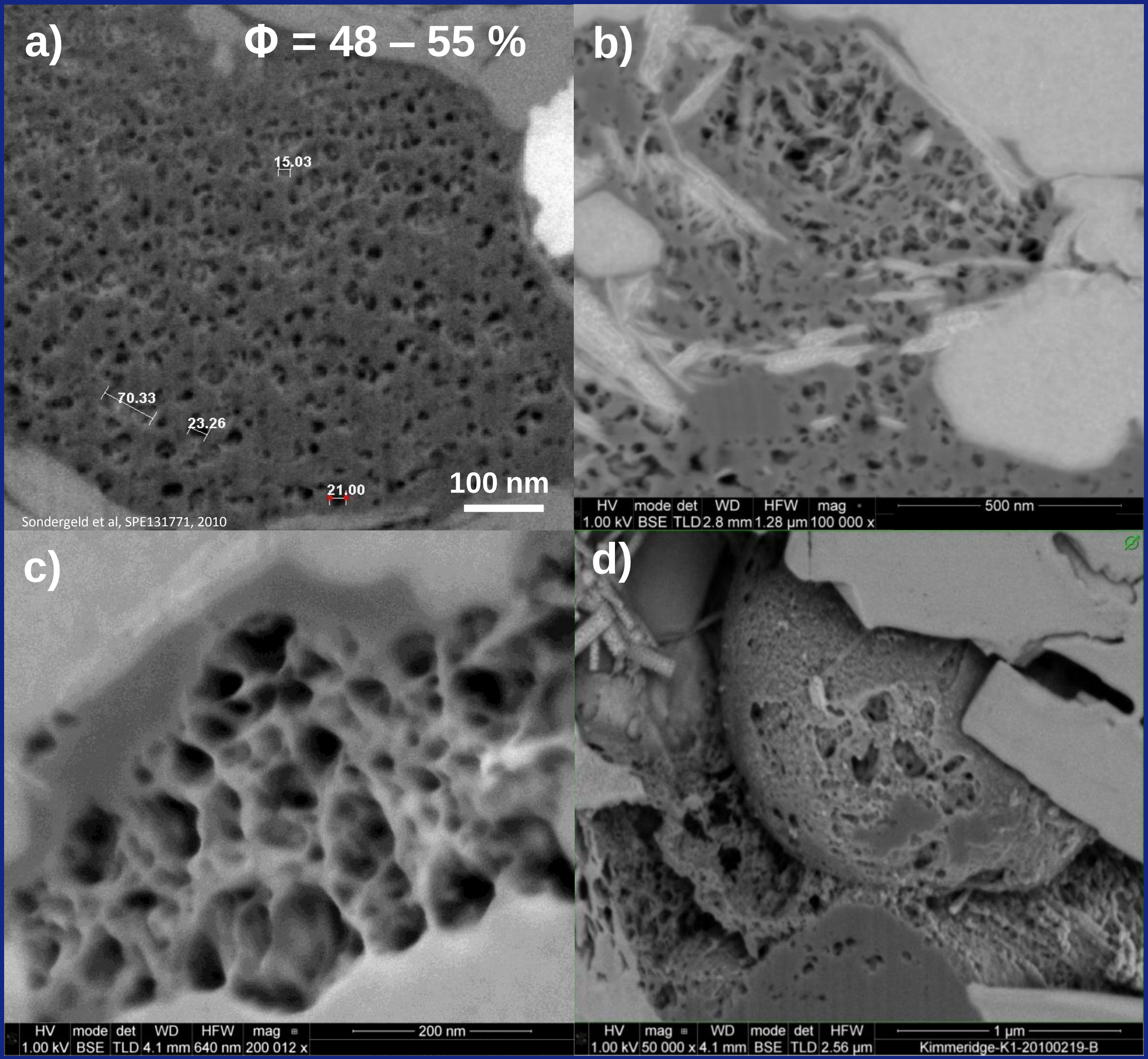
Porosity Associated with Pyrite



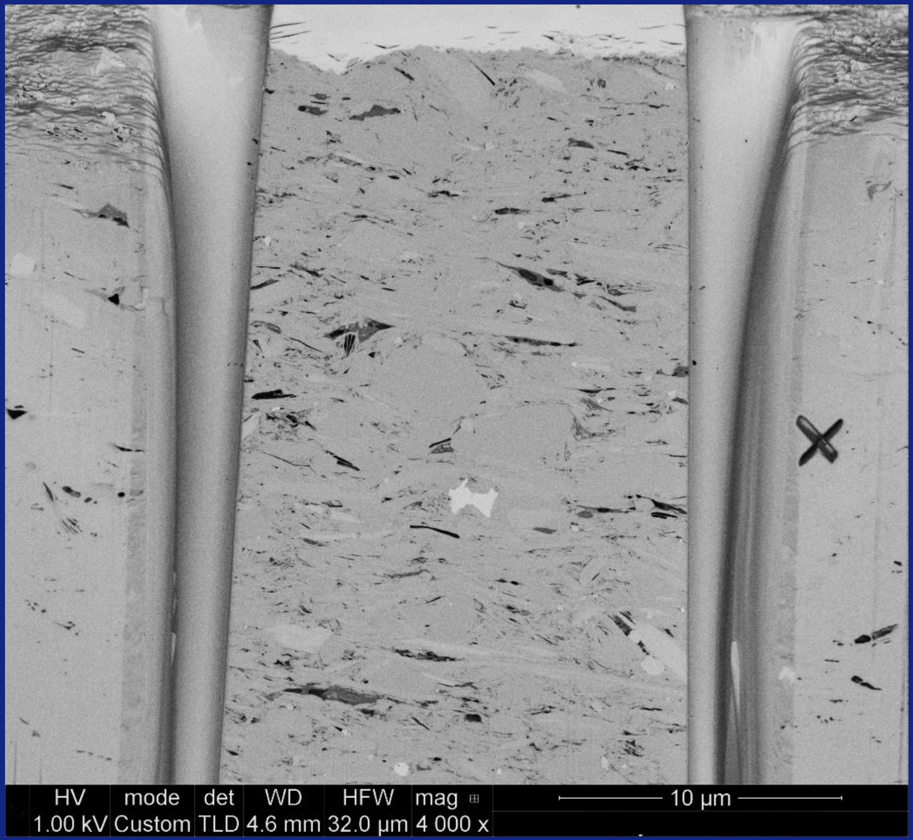
Porosity Associated with Apatite

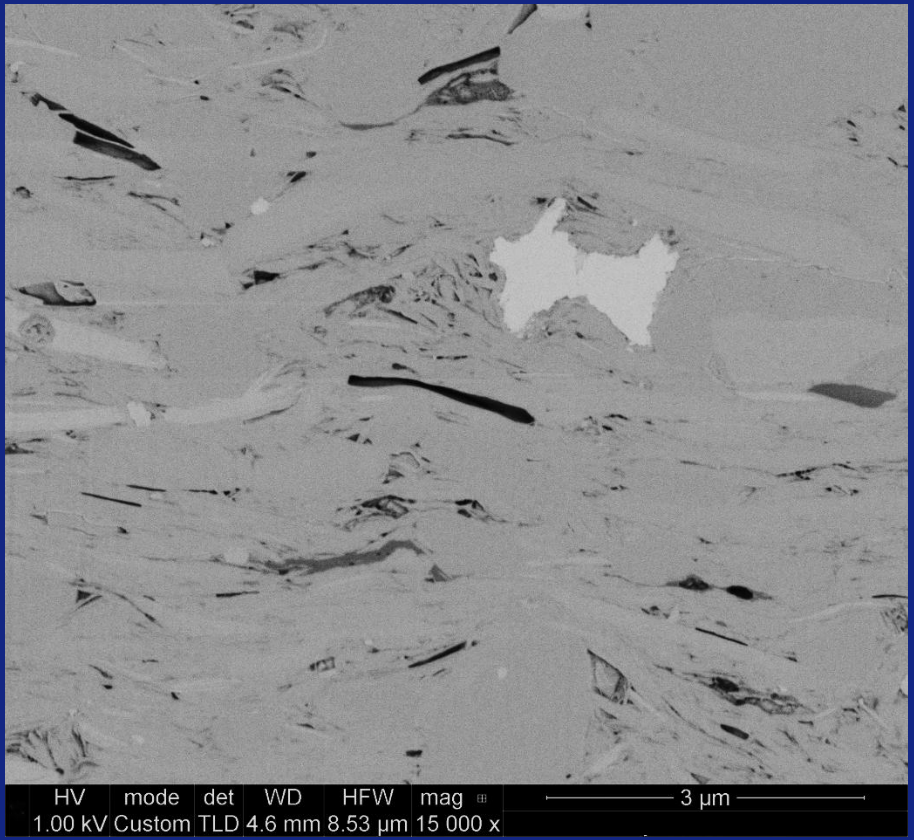
Organic Porosity

- Shape tends to be round.
- Provides volume for storage and increased surface area for adsorption.
- Porosities upwards of 50% observed in kerogen.
- 2D images suggest connectivity.

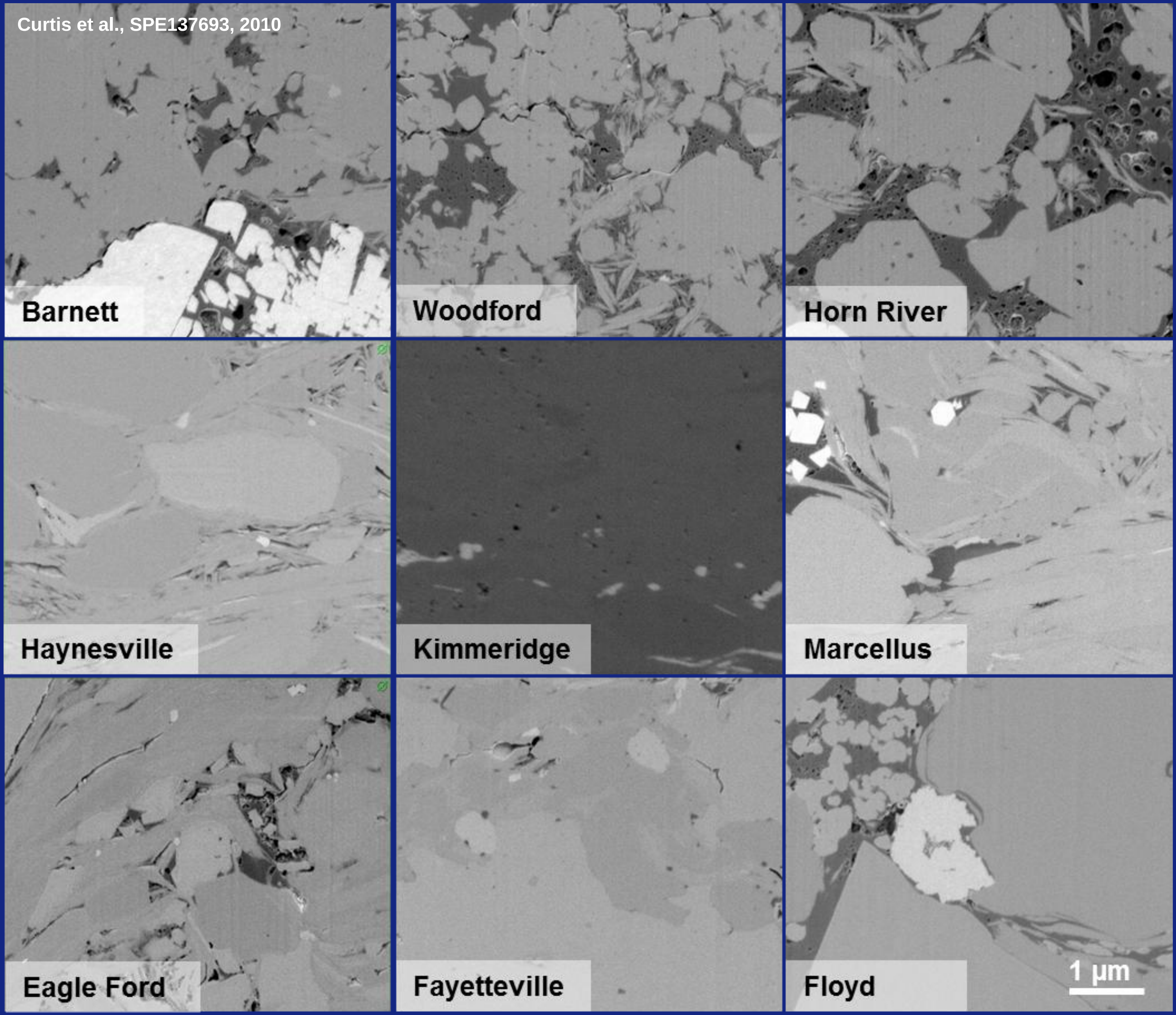


Phyllosilicate Porosity - Haynesville



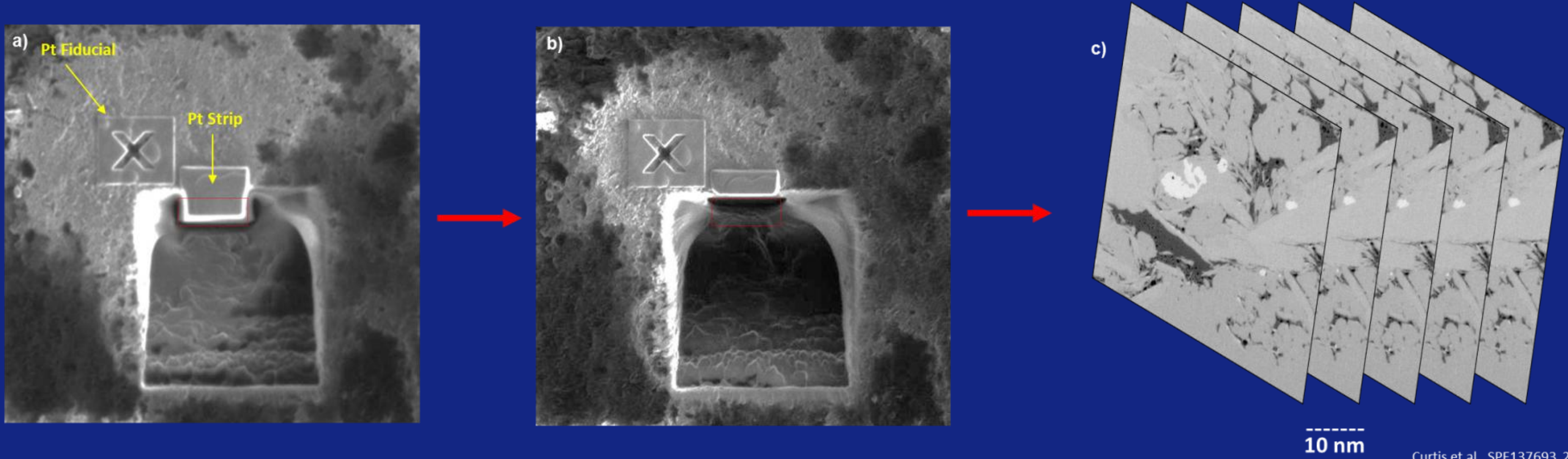


- Porosity between clay platelets.
- Lenticular, slit-like in geometry.
- Should have different wettability than the organophyllic porosity.
- Structural integrity of pores questionable due to pressure of overlying rock as gas is drawn out of the pores.

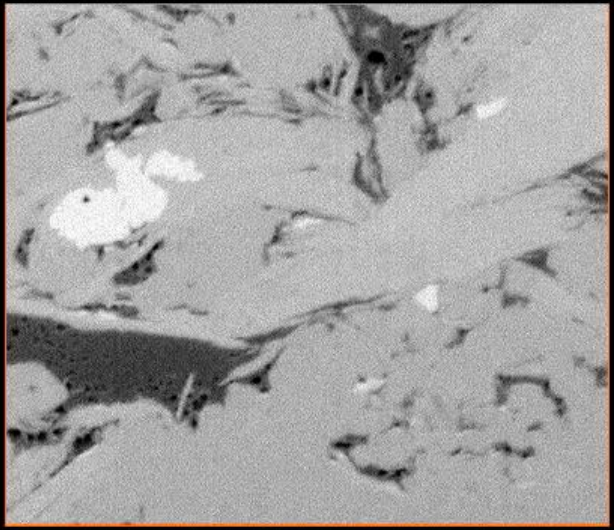

Curtis et al., SPE137693, 2010
Barnett
Woodford
Horn River
Haynesville
Kimmeridge
Marcellus
Eagle Ford
Fayetteville
Floyd
1 µm

Serial Sectioning of Gas Shale Microstructure

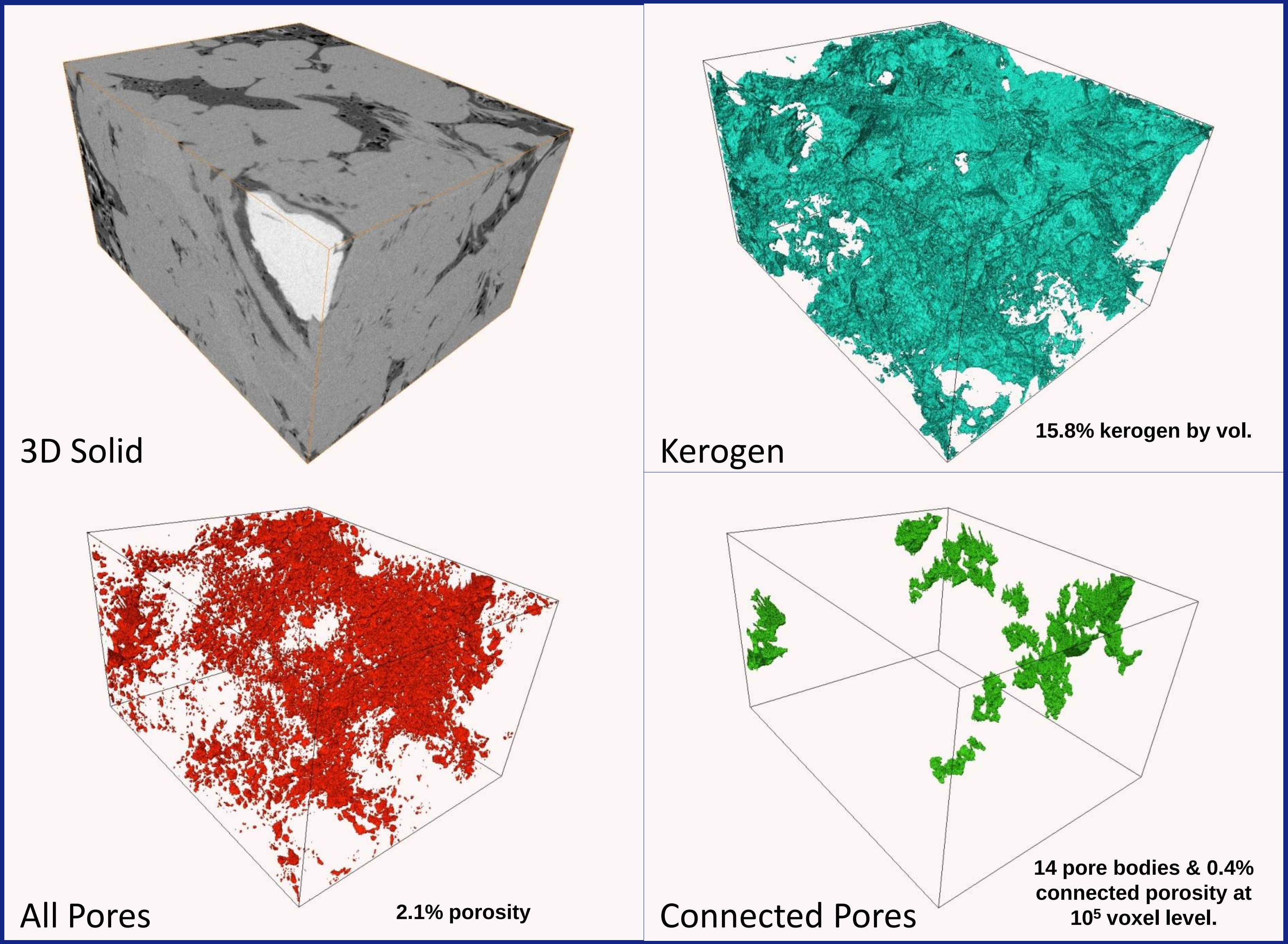
- Want to investigate pore connectivity and kerogen distribution in 3D.
- Prepare site using Pt deposition and FIB milling.
- Image FIB x-sectioned shale face.
- Use FIB to remove a 10 nm thick layer off x-section face.
- Image x-section face and repeat procedure ~500-600 times.
- Now have a 3D data set of shale microstructure.



Curtis et al., SPE137693, 2010



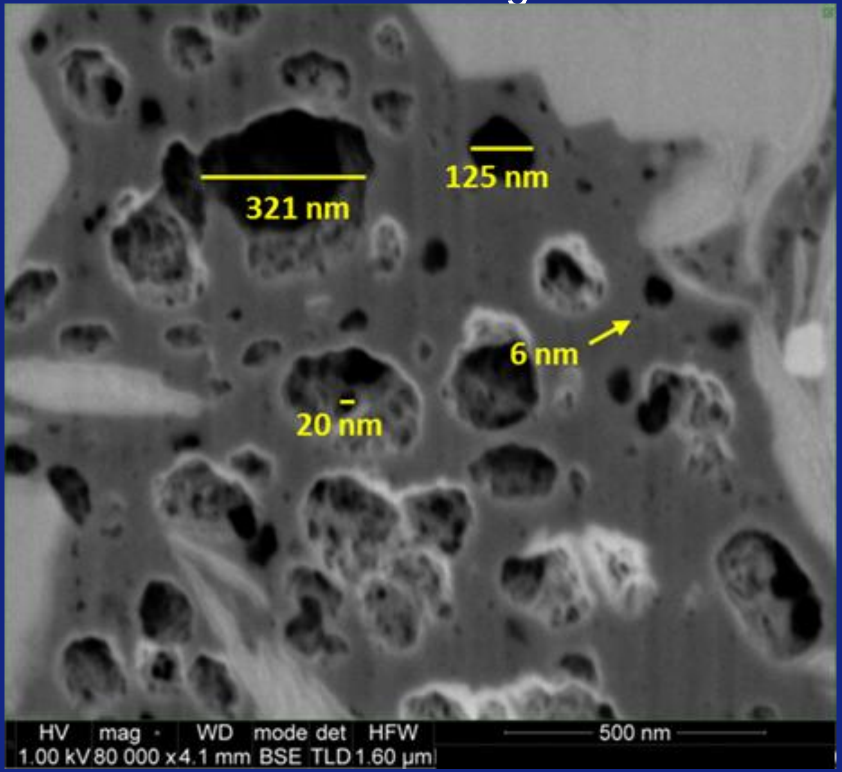
3D Shale Microstructure



Estimates of Porosity & Kerogen Contents

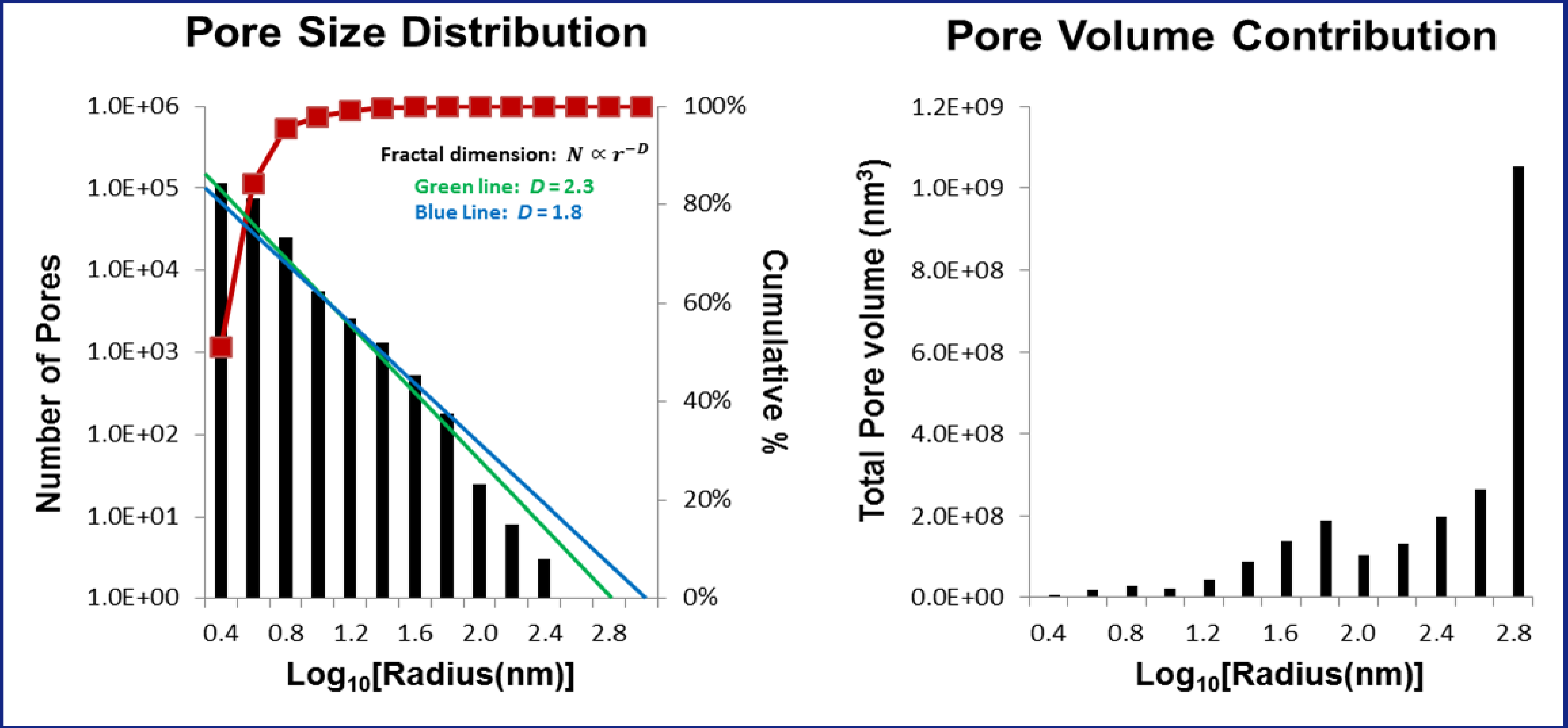
- Threshold gray scale to draw surfaces enclosing gray scale values.
- Estimate porosity & kerogen content based on volume enclosed by surface.
  - Reservoirs large compared to volumes sampled. (scaling issue)
  - Setting thresholds is subjective.
  - Can underestimate large pores due to efficient collection of BSE off inner walls of large pores.
  - Can overestimate small pores by setting threshold maximum too high.

Sample	Kerogen (Vol.) %	Porosity %
Barnett	5.3	2.3
Eagle Ford	2.4	0.4
Fayetteville	0	0.3
Floyd	16.7	0.8
Haynesville	3.8	2.0
Horn River	15.6	2.0
Kimmeridge	90.0	0.3
Marcellus	5.0	0.2
Woodford	17.9	0.4



Curtis et al., SPE137693, 2010

Pore Size Distributions

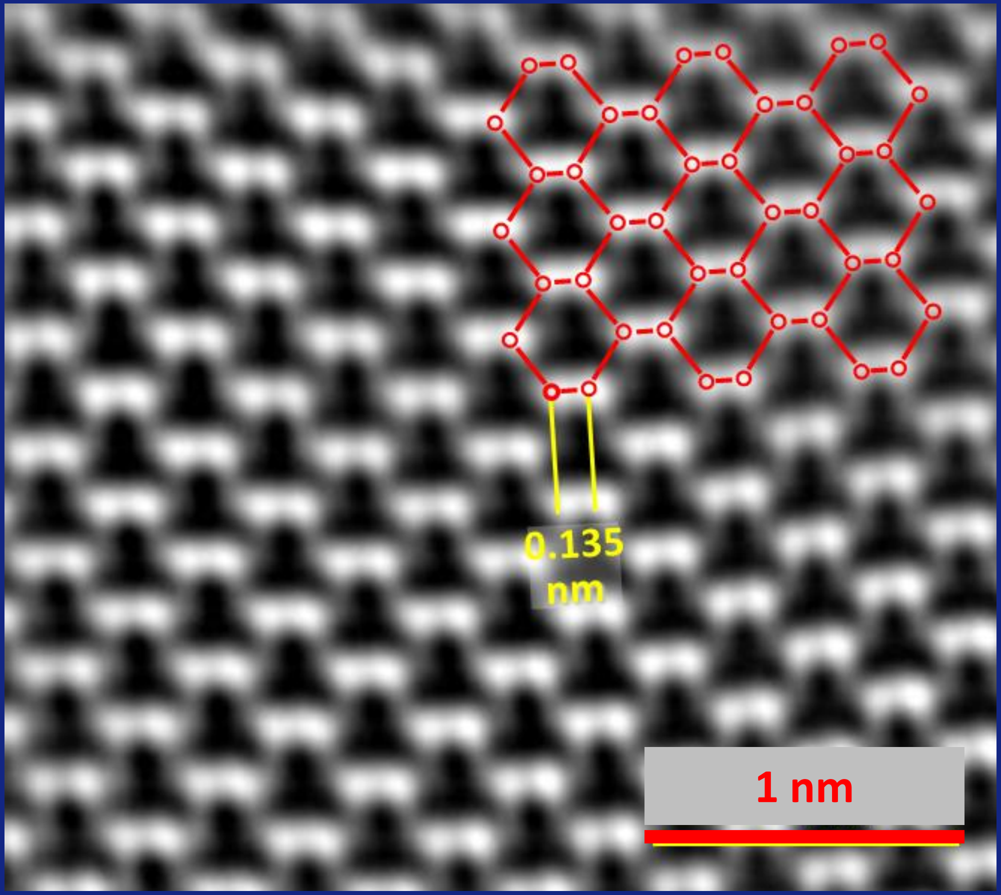


- Estimate distribution of pore body radii (assume spherical pores) in rendered volume.
- Small pores tend to dominate in number but large pores dominate volume contribution.
- Thresholding gray scale can cause overestimation of small pores and underestimation of large pores.

Curtis et al., SPE137693, 2010

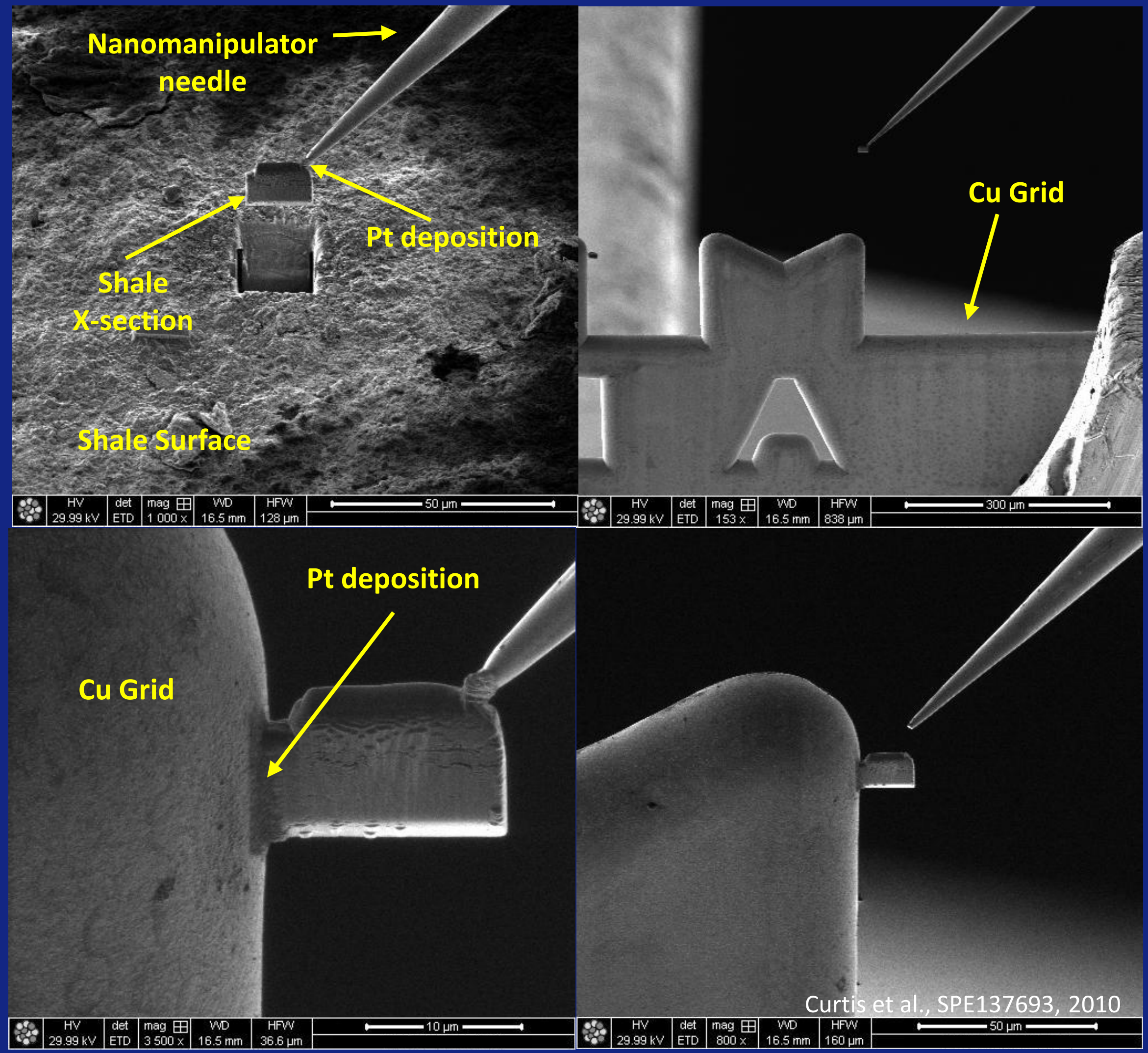
STEM Imaging

- Scanning Transmission Electron Microscopy.
- Transmit electrons through a thin (< 100 nm) sample.
- Higher resolution (~ 50 pm for best scopes).
- STEM allows correlation of spatial position with EDS map for high-resolution elemental analysis.
- Can image in several modes:
  - Bright field (BF).
  - Annular dark field (ADF)
  - High angle annular dark field (HAADF).

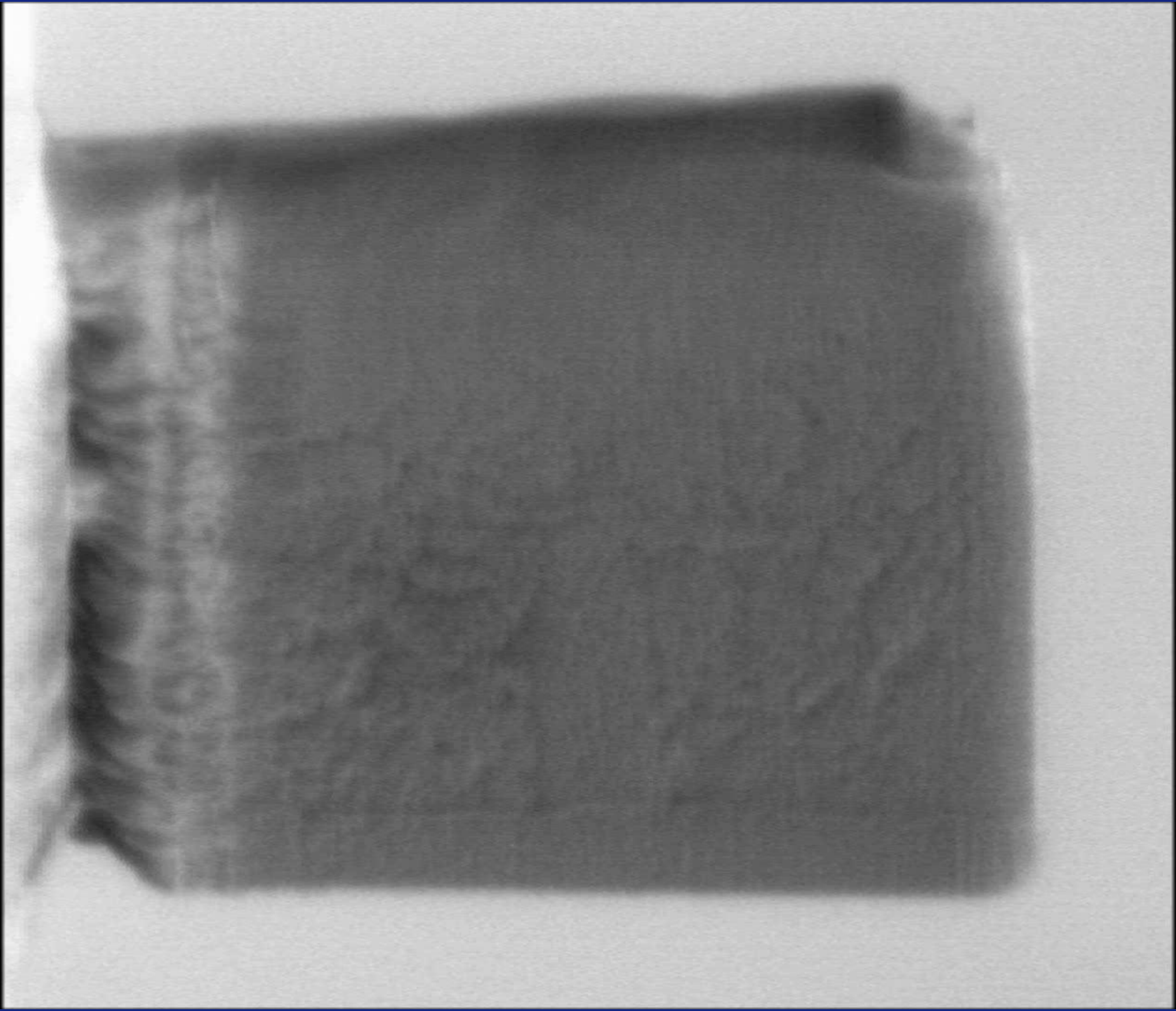


High angle annular dark field (HAADF) STEM image of silicon [110] showing 1.35 Å resolution. Individual dots represent columns of Si atoms. Image take at OU on JEOL 2010F.

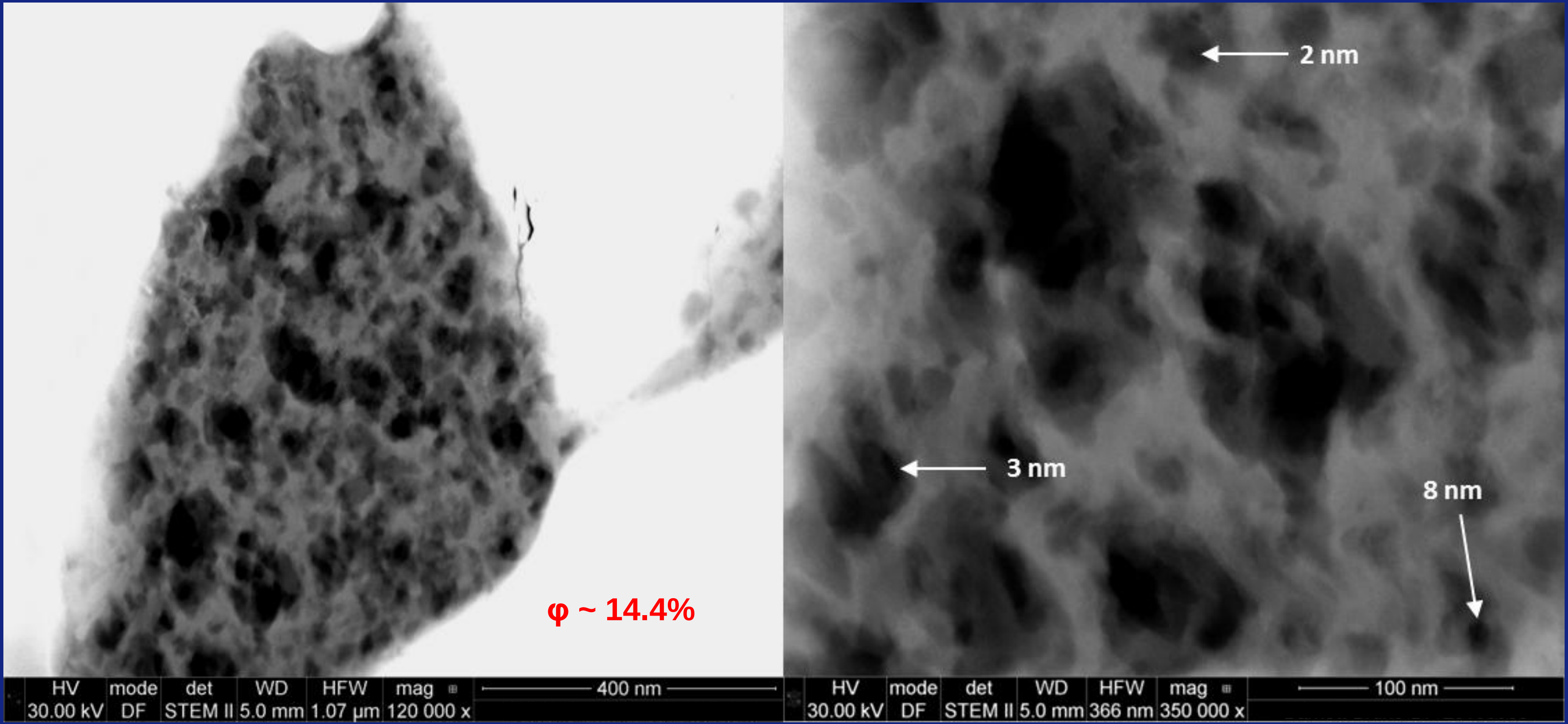
STEM Sample Preparation



Curtis et al., SPE144391, 2011



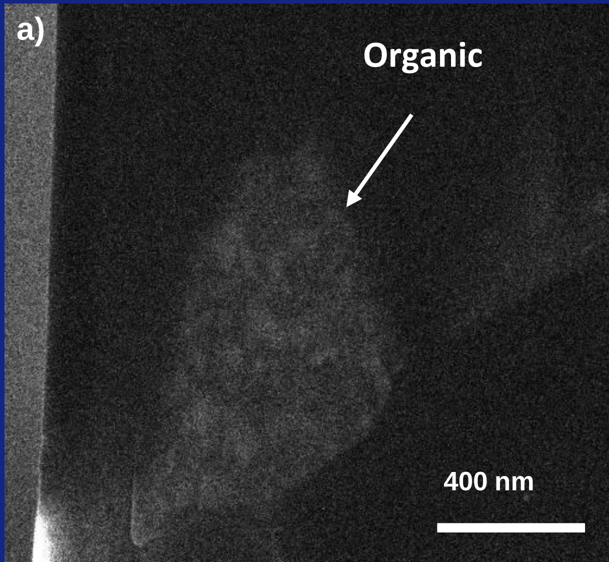
STEM Imaging of Barnett Shale

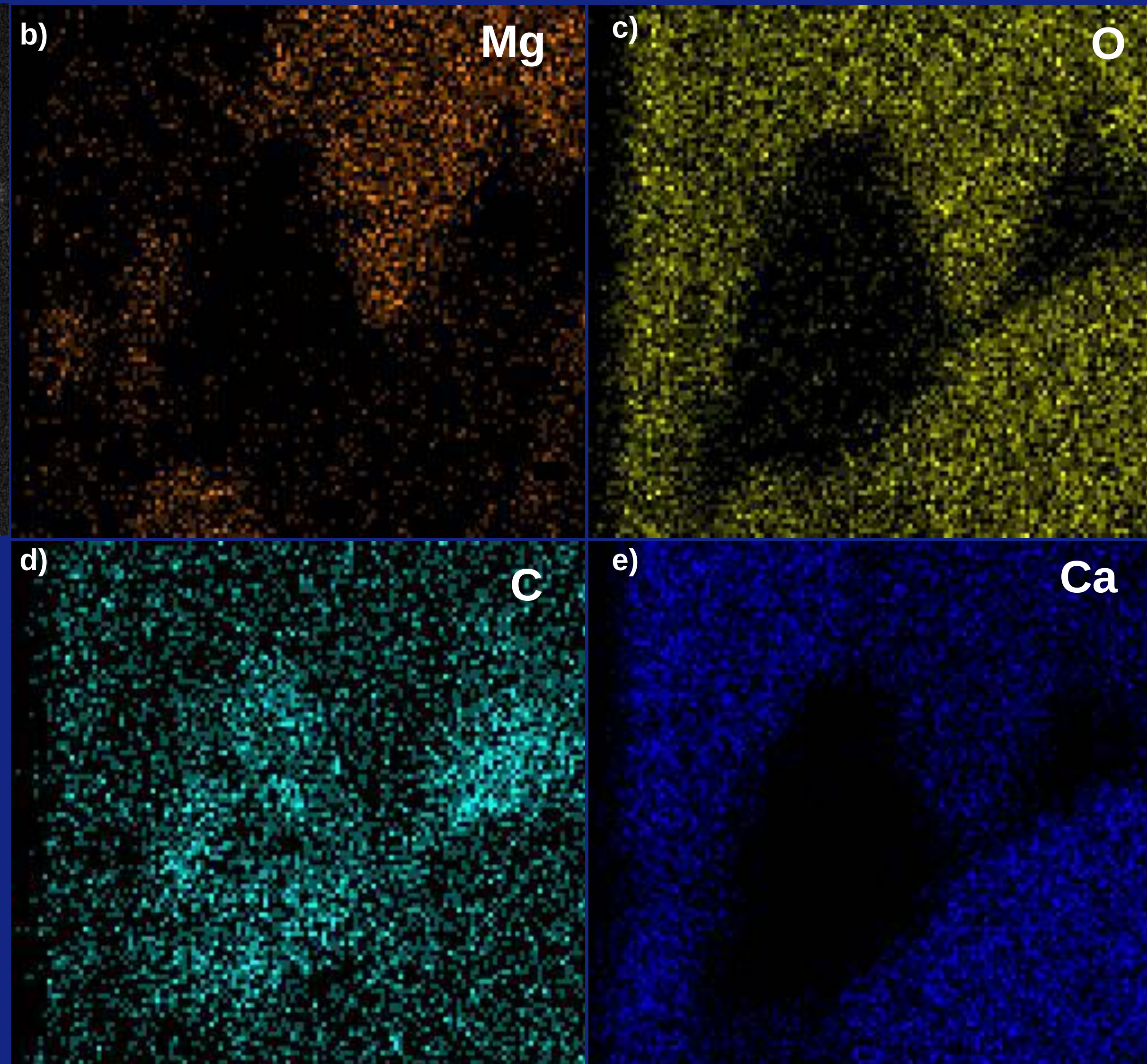


ADF STEM images of organic porosity in Barnett shale.

Curtis et al., SPE144391, 2011

EDS of Barnett Shale in STEM mode





Thinner Samples

↓

Reduced Electron Interaction Volume

↓

Improved Resolution

EDS map of the organic region. a) SEM image of kerogen region. b) – e) Elemental maps of magnesium, oxygen, carbon, and calcium, respectively.

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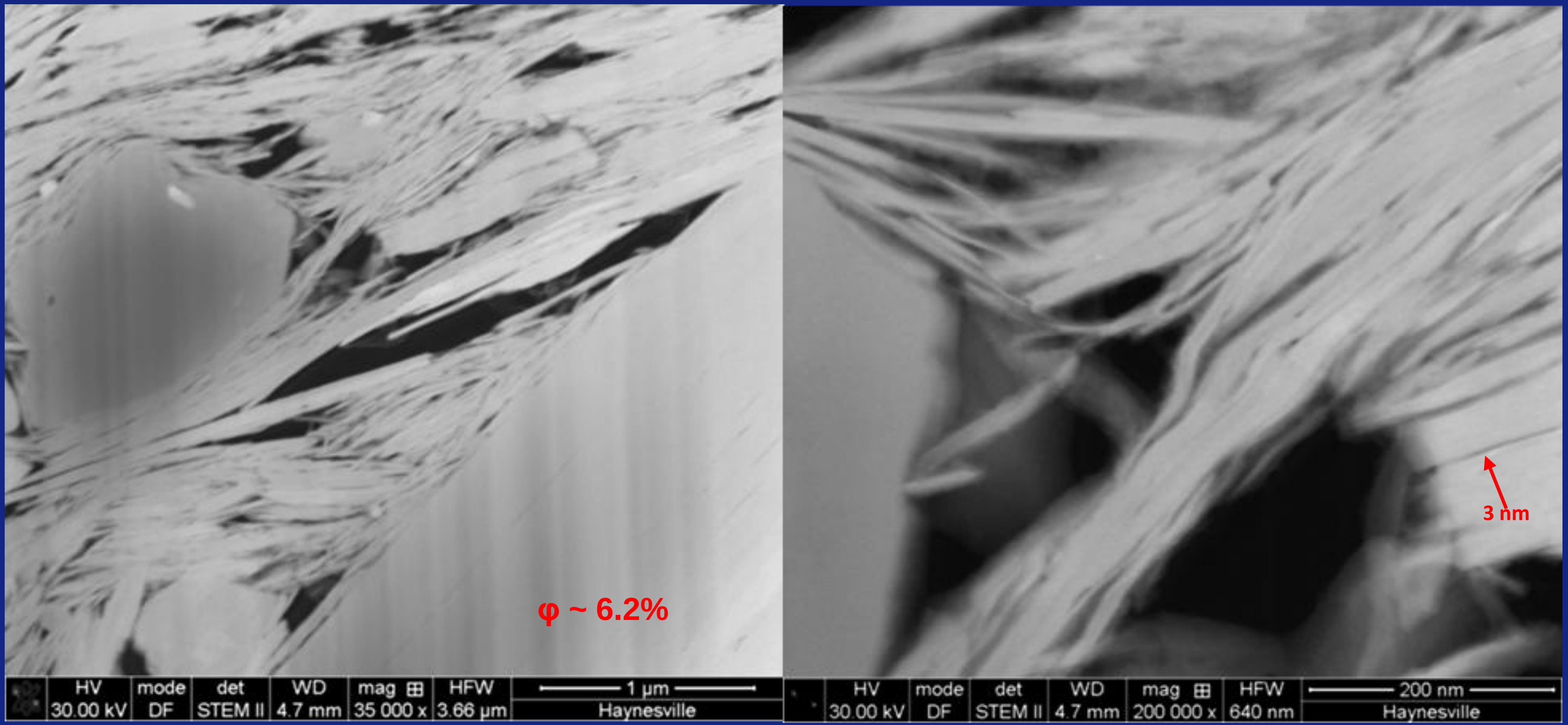
Curtis et al., SPE144391, 2011

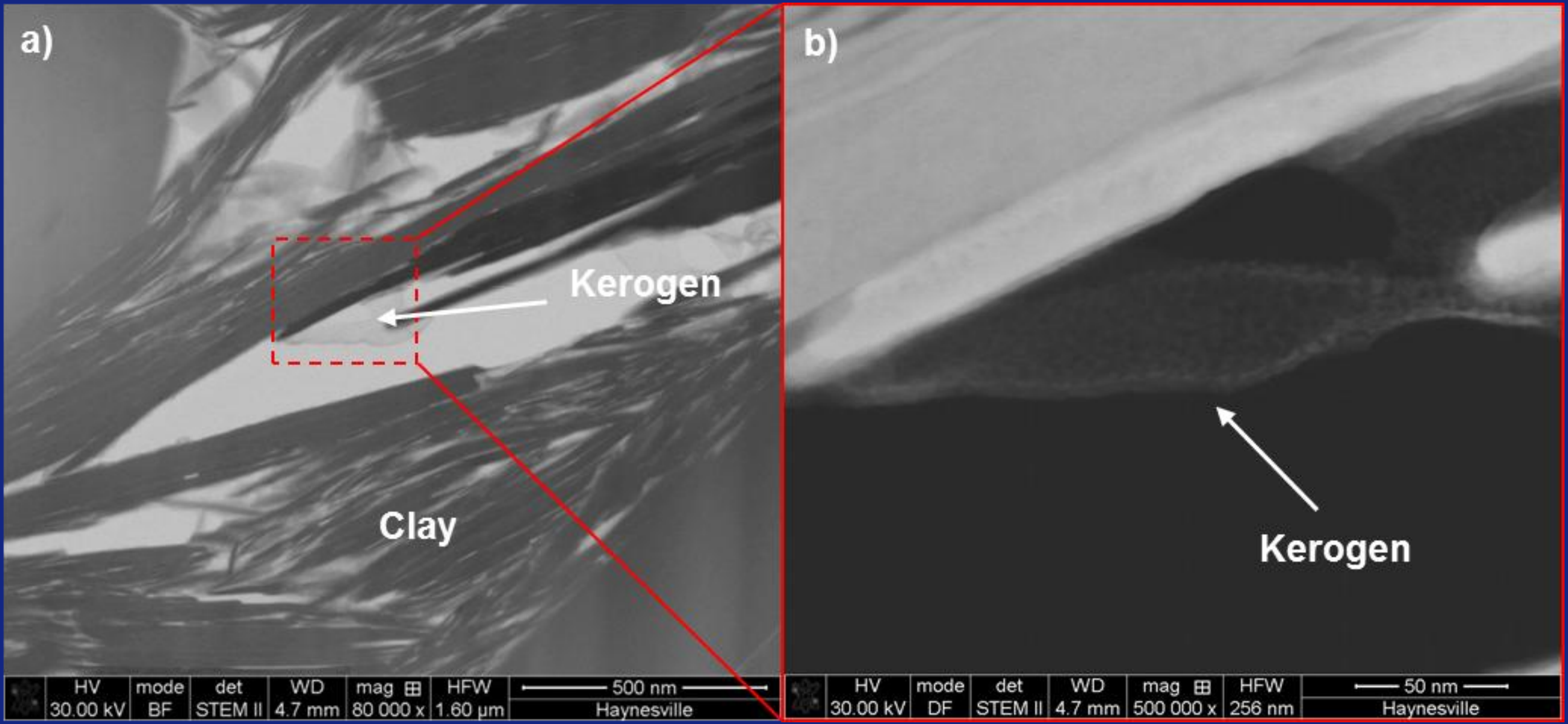
STEM Imaging of Haynesville Shale



ADF STEM images of phyllosilicate porosity in the Haynesville

Curtis et al., SPE144391, 2011

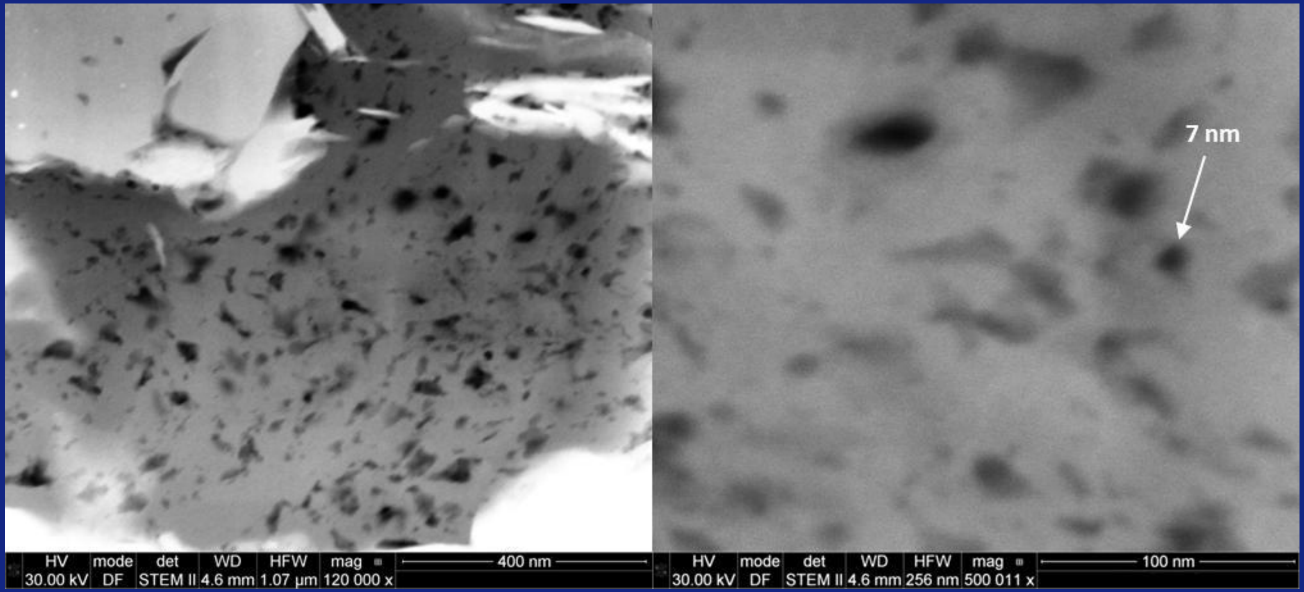
STEM Imaging of Haynesville Shale



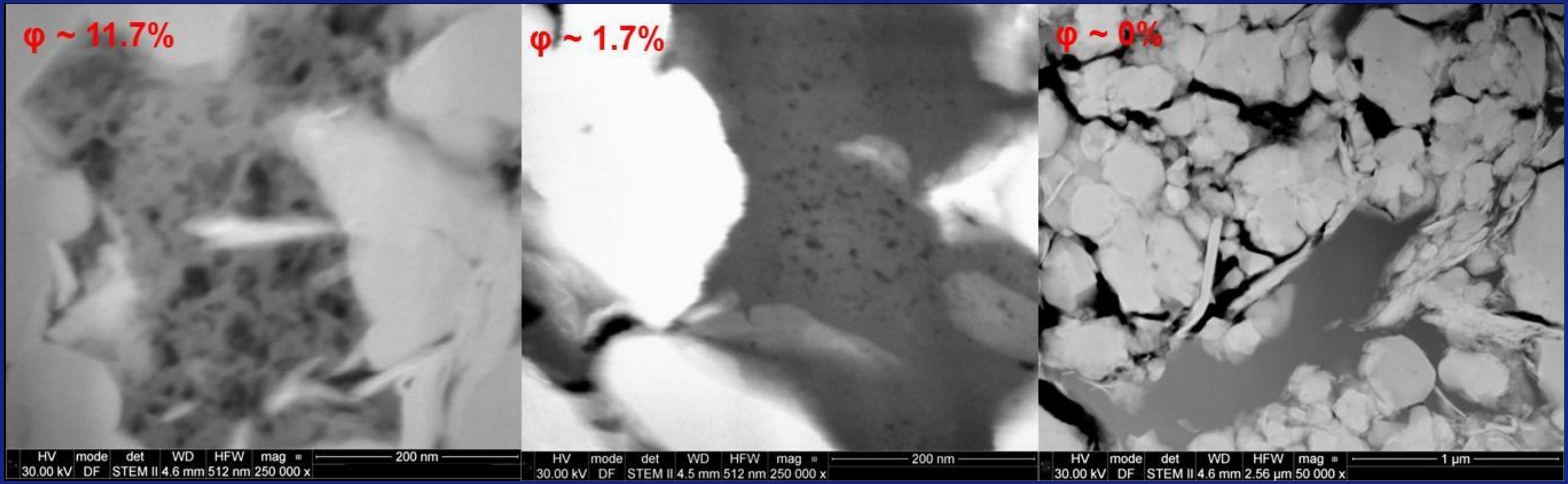
Bright-field STEM image of Haynesville shale.

Dark-field STEM image of kerogen in Haynesville shale.

STEM Imaging of Horn River & Woodford



ADF STEM images of Horn River Shale



ADF STEM images of Woodford Shale

Curtis et al., SPE144391, 2011

Thermal Maturity

- Thought that porosity is produced as oil/gas are expelled from organics due to heating.
- Whether oil or gas is produced is dependent upon temperature (thermal maturity).
- Thermal maturity estimated using vitrinite reflection.
- Not all organics show similar porosity despite having the same thermal history. *Indicates different types of kerogen may be present in the same shale!*

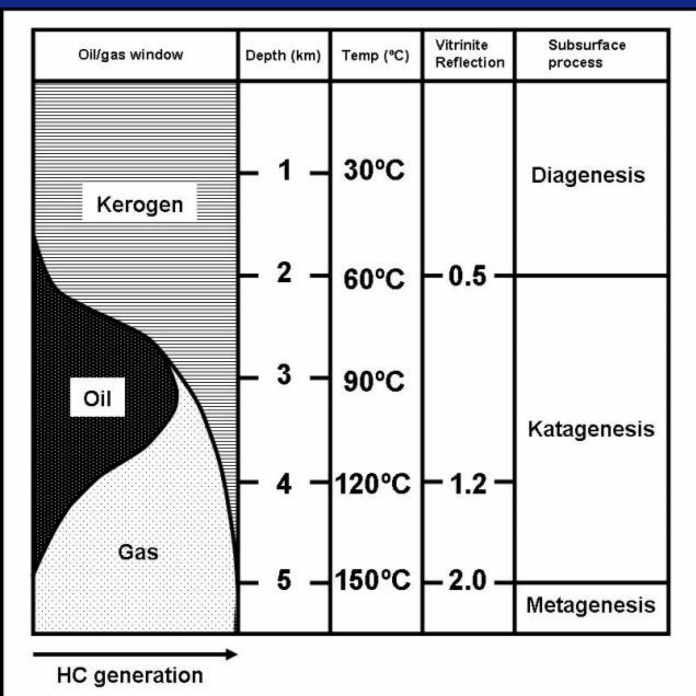
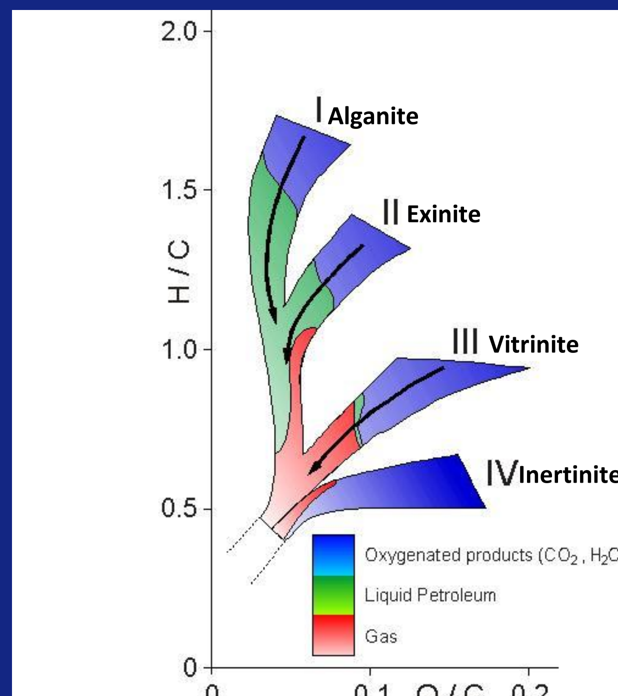


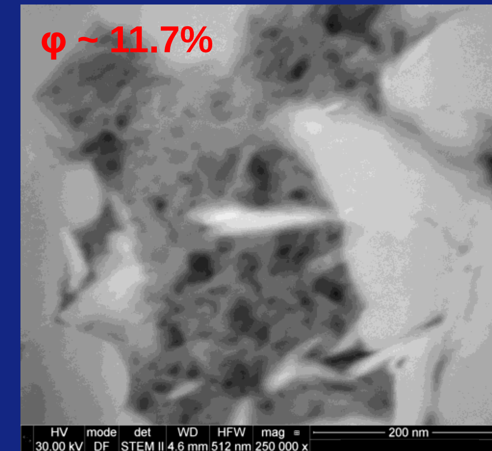
Diagram of thermogenic oil/gas windows

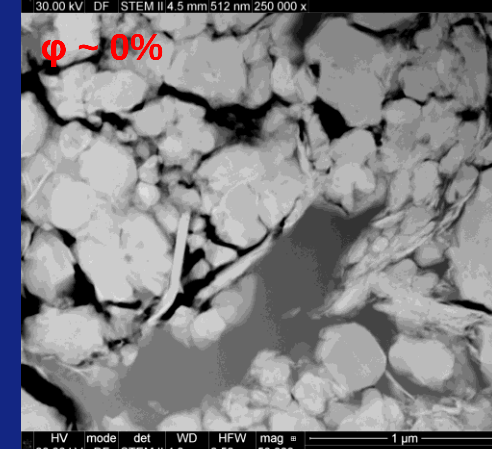
http://oilandgasgeology.com/



Van Krevelen diagram showing different kerogen types

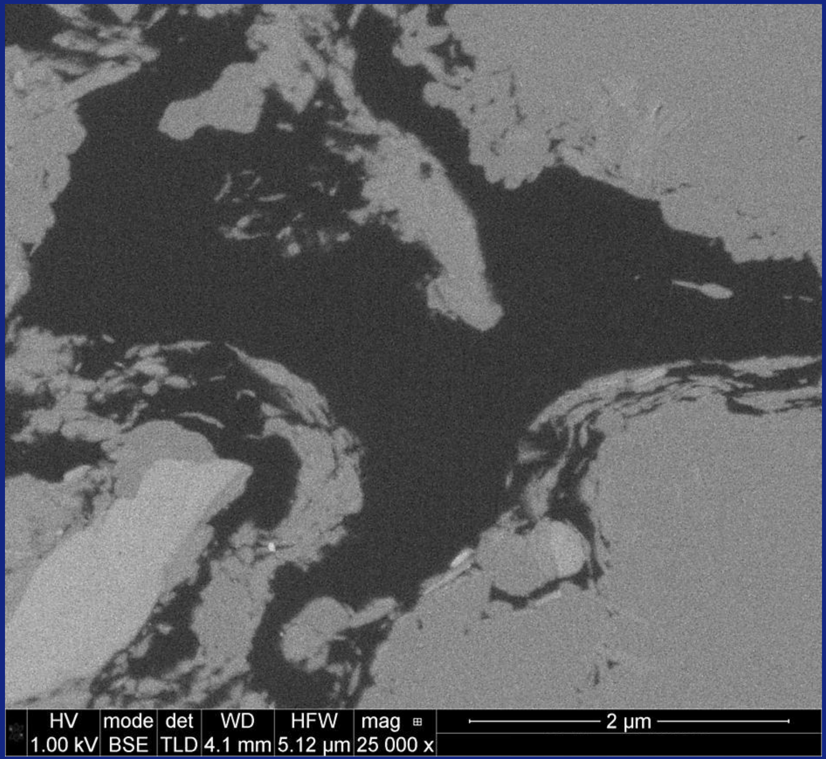
(http://www.geosci.monash.edu.au/heatflow/chapter5.html)



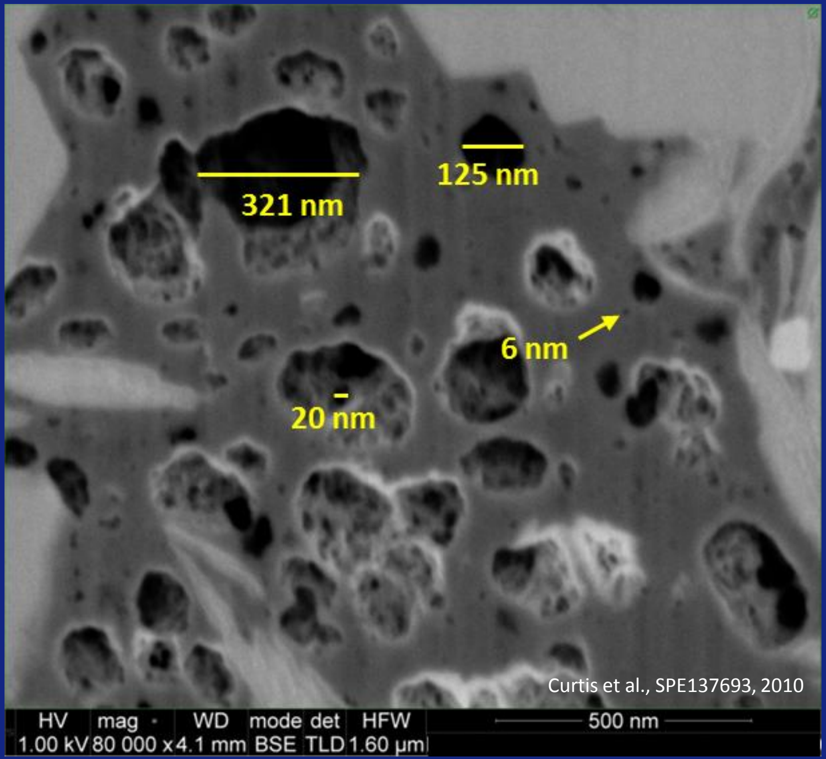


Curtis et al., SPE144370, 2011

When Does This Transition Occur?????



Oil Window

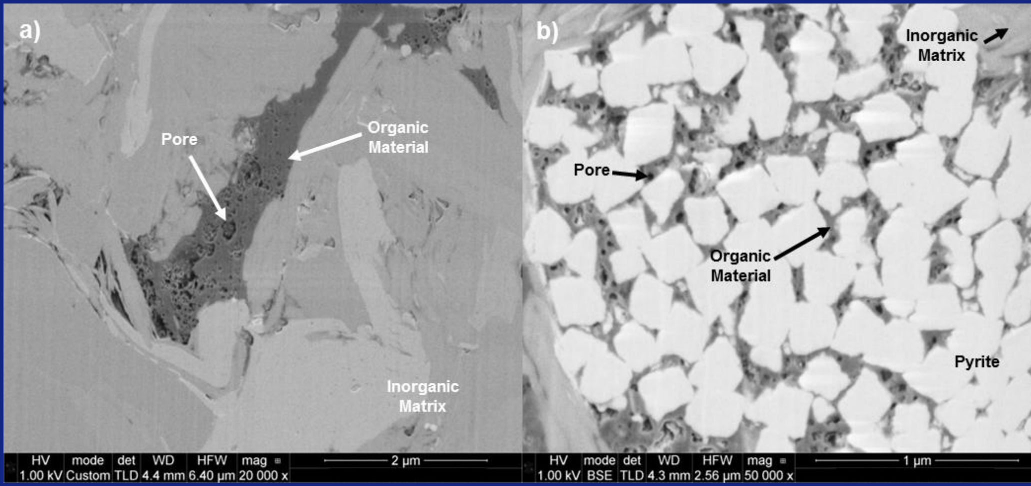


Gas Window

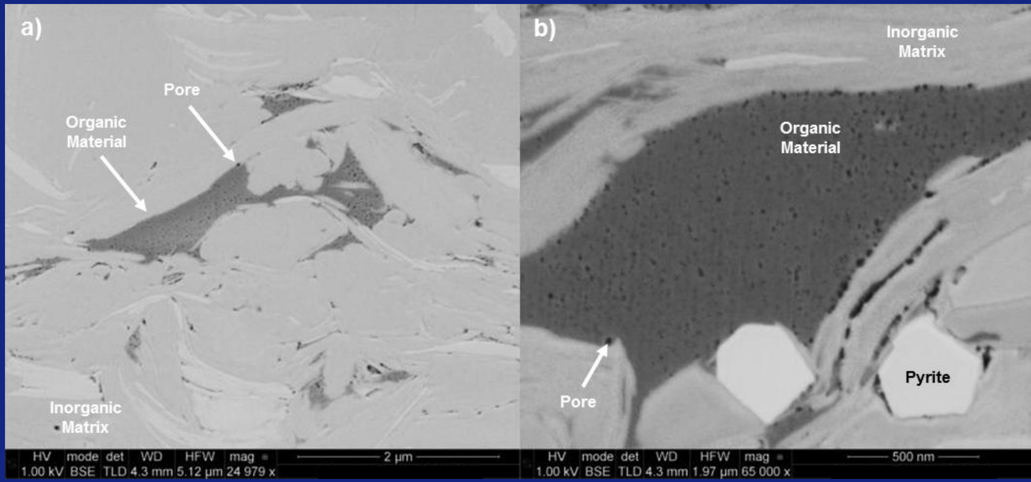
Curtis et al., SPE144370, 2011

SEM Results of Marcellus Thermal Maturity

- 2 Marcellus shale samples with R_o = 1.1%+ and >> 3.1% milled and imaged.
- Round porosity seen within the organic matter in the shale.
- R_o = 1.1%+
  - Pore diameters: 10 -140 nm.
  - Organic porosity: a) 18.5%, b) 12.1%.
- R_o = >> 3.1%
  - Pore diameters: 5-20 nm.
  - Organic porosity: a) 15.4%, b) 6.1%.



Backscattered electron images of Marcellus shale R_o = 1.1%+



Backscattered electron images of Marcellus shale R_o = >>3.1%.

Summary

- Pore sizes observed by SEM and STEM are on the same scale as those seen with MICP & NMR.
- Observations of different shales shows that not all shales are the same therefore should not be expected to behave the same.
- Using FIB/SEM in combination we can begin to quantify the microstructure of shales in 3D.
- STEM images of some organics in shale show a sponge-like internal structure with a high degree of surface area.
- STEM images of Haynesville shale show increased phyllosilicate porosity at a smaller scale than with SEM.
- Significant differences in organic porosities observed by STEM raises questions about the role of organic matter type in organic pore formation.

Acknowledgements

- We would like to thank Devon Energy for their generous support of this project.
- We would also like to thank Dr. Terry Engelder of The Pennsylvania State University for providing the Marcellus shale samples.