Mewbourne School of Petroleum & Geological Engineering
The University of Oklahoma

Influence of Thermal Maturity on Organic Shale Microstructure

Mark E. Curtis

Oklahoma Shale Gas and Oil Workshop

November 20, 2013

100 nm

OU - IC³

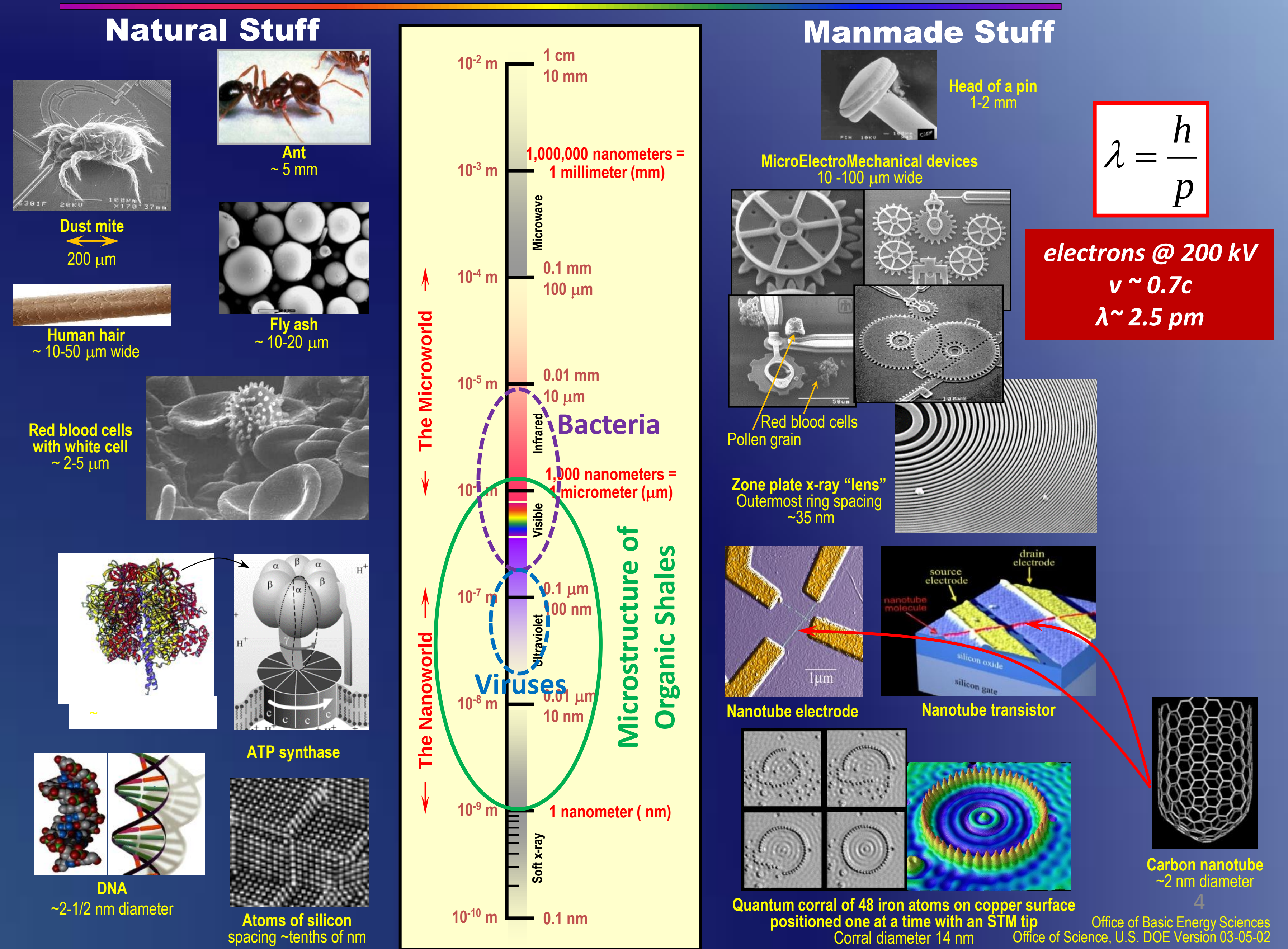
Outline

- Probing the Nanoscale.
- Microstructure of shales in the wet and dry gas windows.
- Microstructure of shales in the oil window
  - Woodford
  - Bakken
  - Avalon
- Conclusions

Driving Forces For Understanding Microstructure

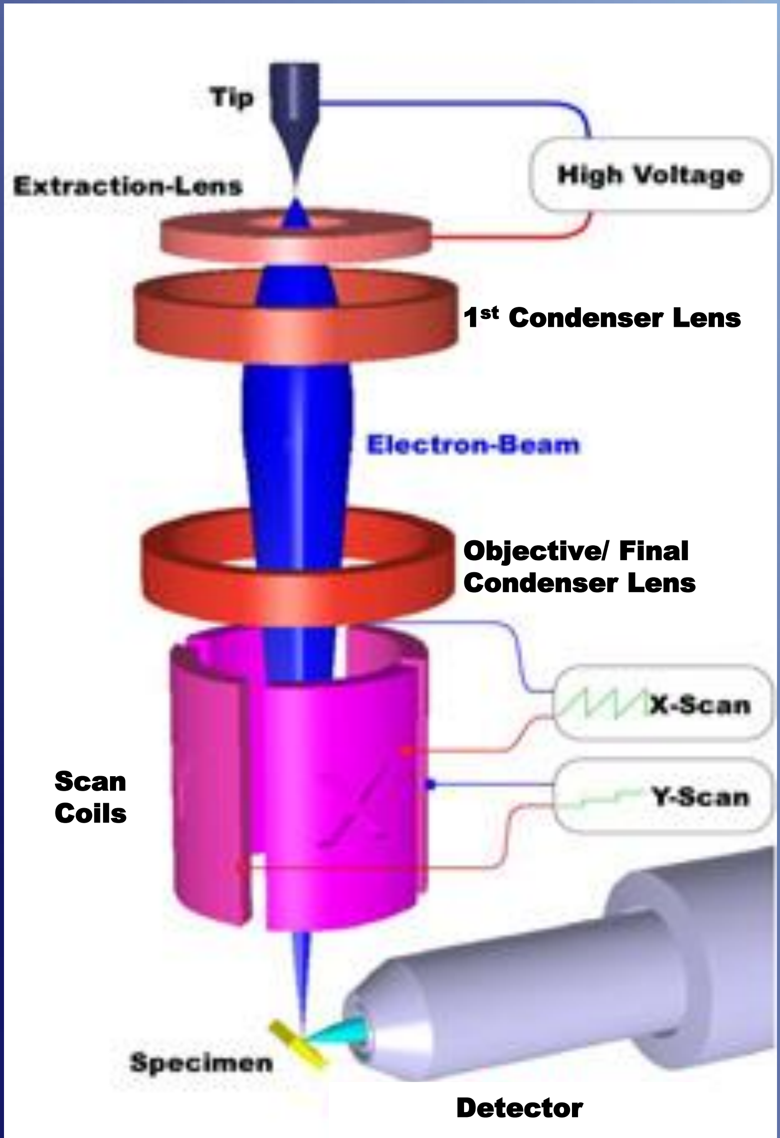
- Historically attention focused on gas shales but economic pressures have led to focus on liquids-rich plays.
- Microstructure of shale will control both storage and transport of hydrocarbons.
  - Pore sizes/shapes/number
  - Pore habits
  - Pore connectivity
- Thermal maturity tied to hydrocarbon generation and should have an influence on the structure of the organic matter.
- Want to know what are the ***key factors*** that control the microstructure and will this allow us to start to make ***predictions about storage and transport***.

Scale of Small Stuff



Scanning Electron Microscopy

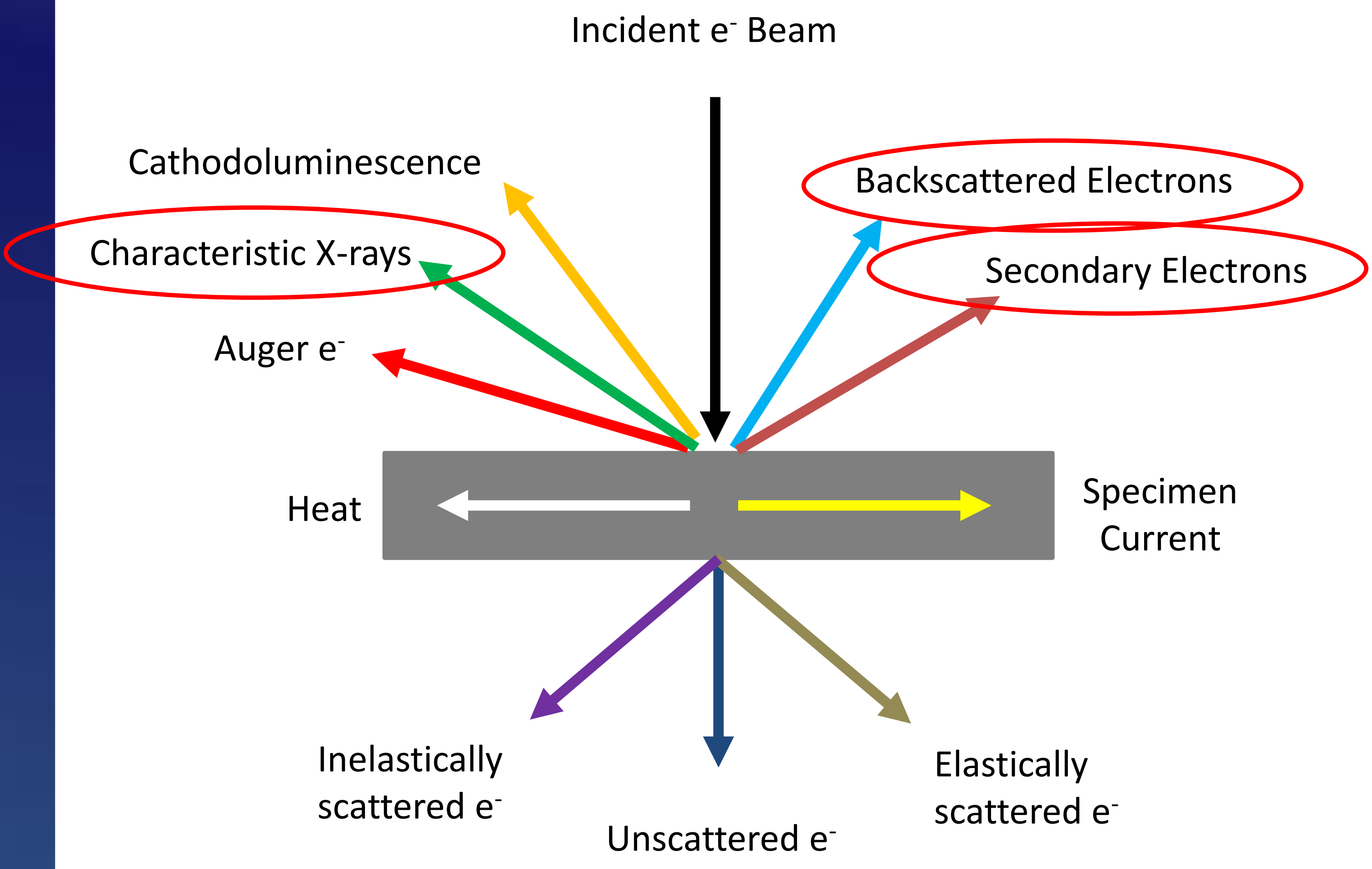
- ***Not*** a direct imaging technique (more akin to a scanning probe method).
- Focused beam of electrons is scanned over sample.
- Signal is generated and detected at each point along the scan.
- Magnification determined by raster area size.
- Sample must be conductive & under high vacuum.



Schematic of an SEM.

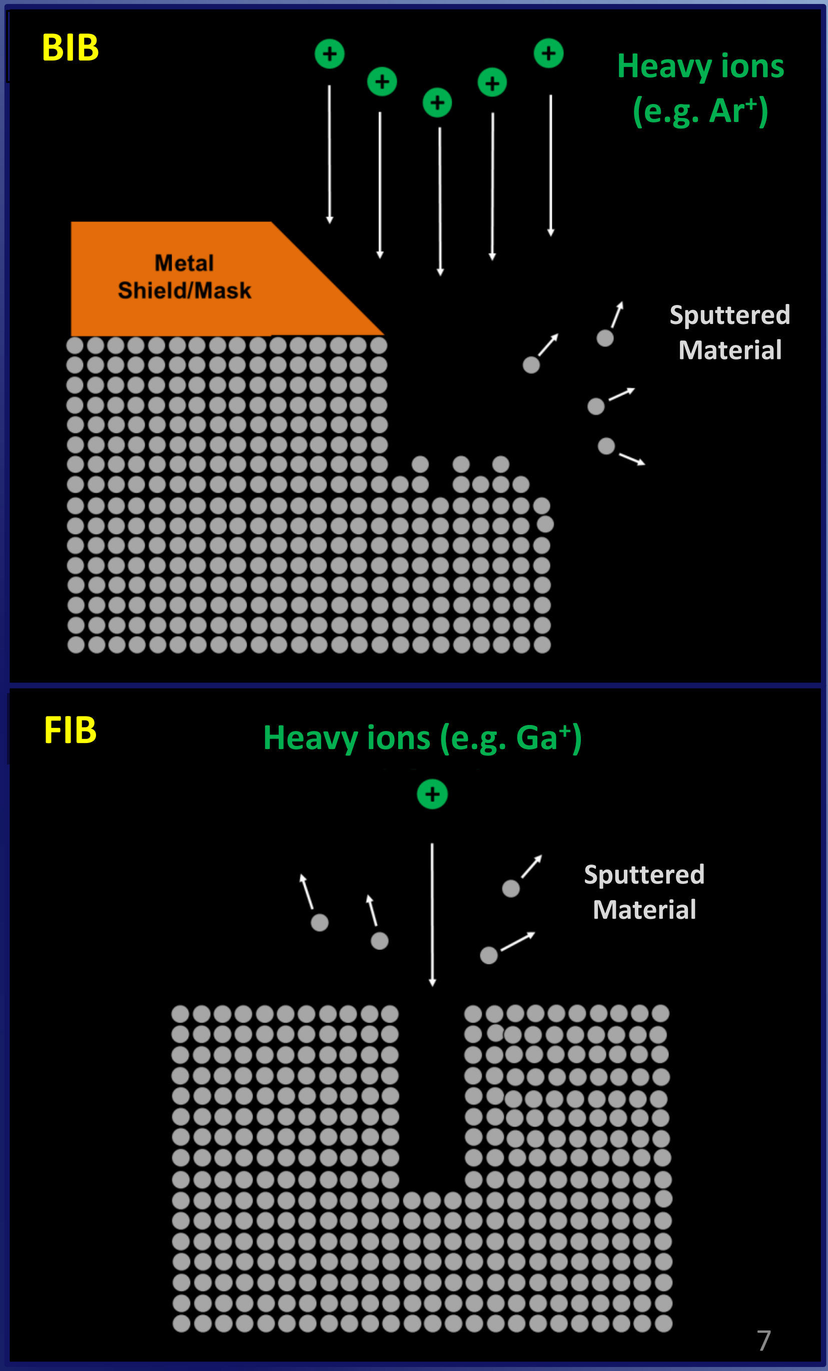
Modified from http://www.microstructure.ethz.ch/?node_ID=229

Electron Beam Signals

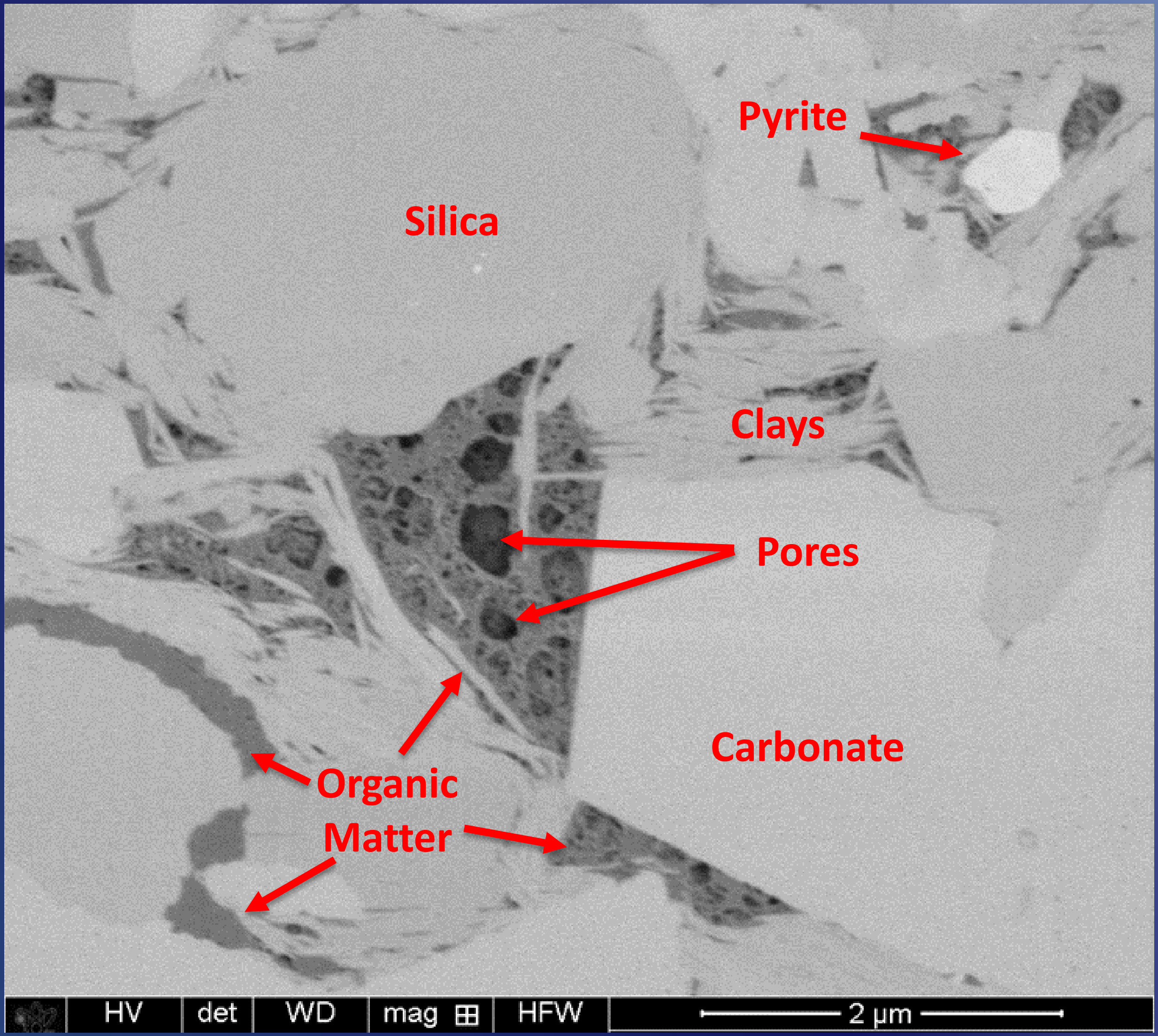


Sample Preparation

- Want surface with minimal artifacts.
- Broken surfaces very useful for 3D info but can have ambiguities.
- Mechanical polishing leaves many artifacts on sample surface.
- Ion milling is typically the best method.
  - **Broad Ion Beam (BIB) milling** (i.e. Ar^+ milling).
  - **Focused Ion Beam (FIB) milling** (i.e. Ga^+ milling).
- Need to be aware of the artifacts involved in your preparation process.



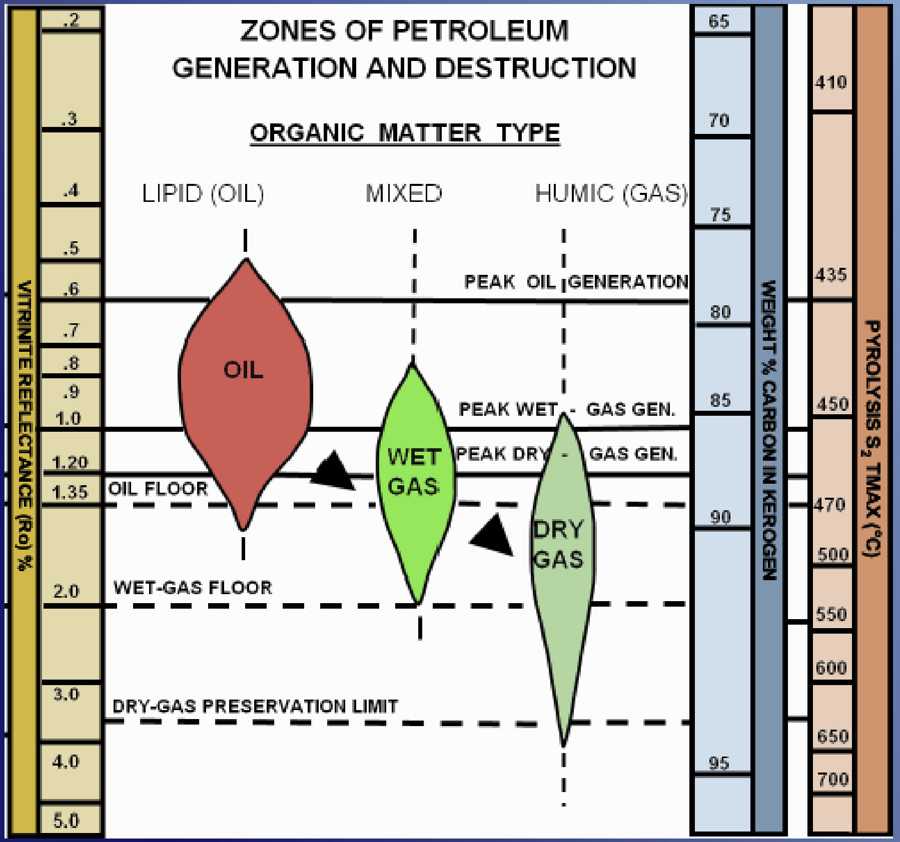
Shale Microstructure



Backscattered electron (BSE) image of an FIB milled shale surface.

Organic Matter, Thermal Maturity, & Microstructure

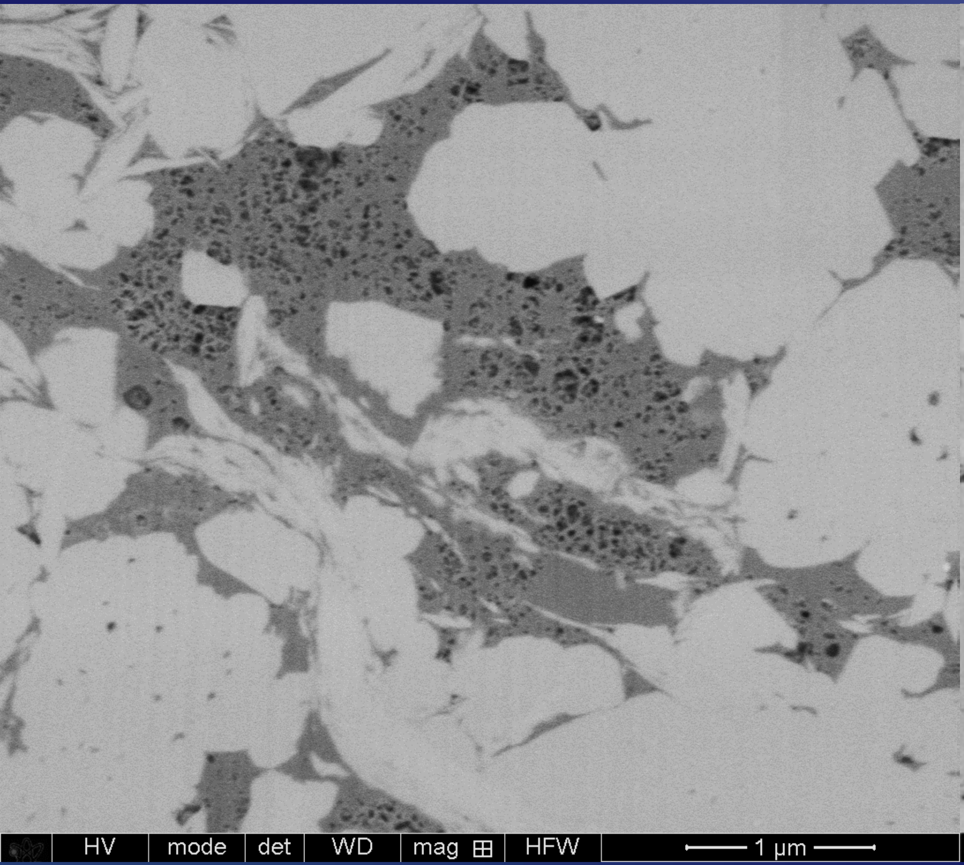
- Different types of kerogen (Type I-IV) are prone to produce different hydrocarbons with increasing thermal maturity.
- Thermal maturity determined using several methods.
  - Vitrinite Reflectance (%Ro)
  - Pyrolysis (Tmax, Transformation Ratio)
- All of the thermal maturity indices have intrinsic shortcomings.
- Need a robust index of thermal maturity across all thermogenic windows.
- Also dealing with presence of bitumen and not just kerogen in shales.
- Influence of clay and metal catalysts, sulfur, & water in hydrocarbon generation and microstructure transformation.



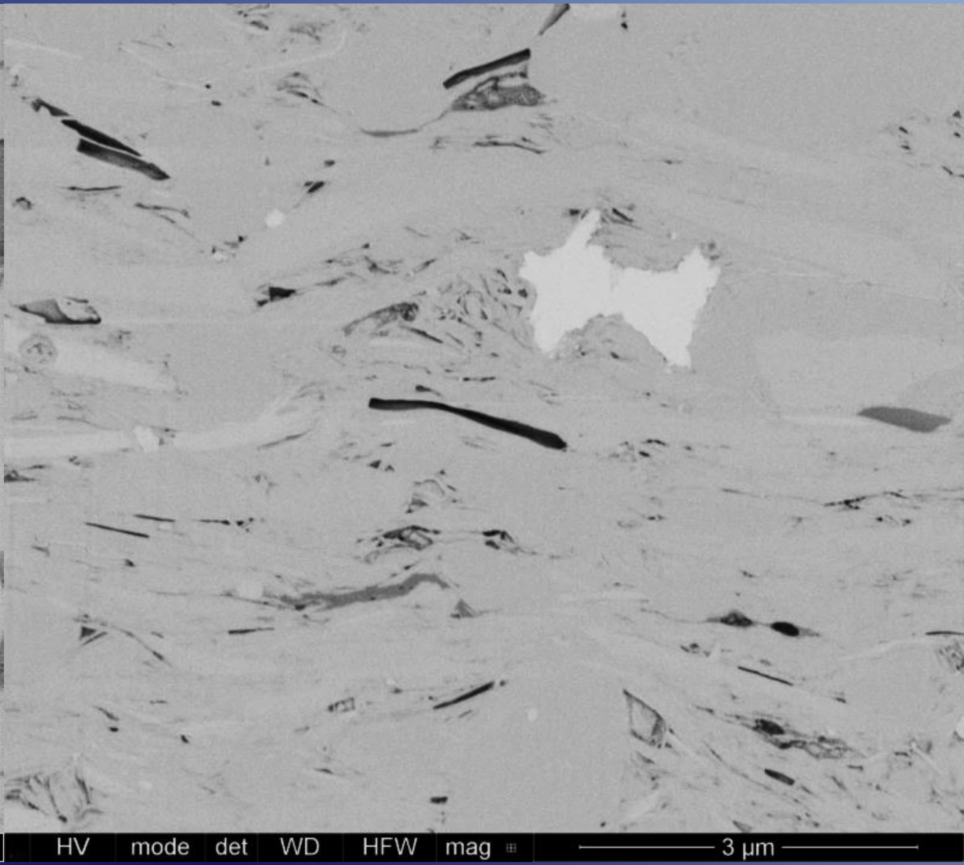
Thermogenic oil & gas windows and thermal maturation indices.

Modified from Dow, W.G., *Journal of Geochemical Exploration*, 1977.

Types of Porosity Observed



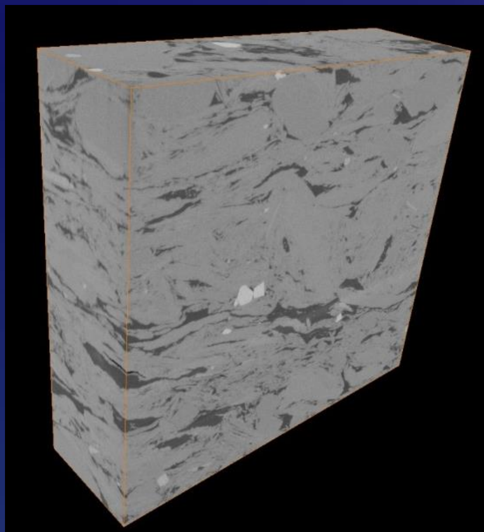
Organic Porosity



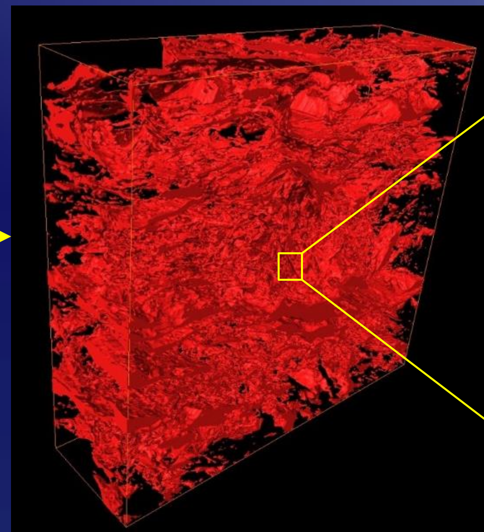
Phyllosilicate Porosity

- Shales can show a dominance of one pore system or a combination of both.
- Differences in wettability of the pore systems due to host materials.
- Difference in pore morphology suggests different reactions to stress.

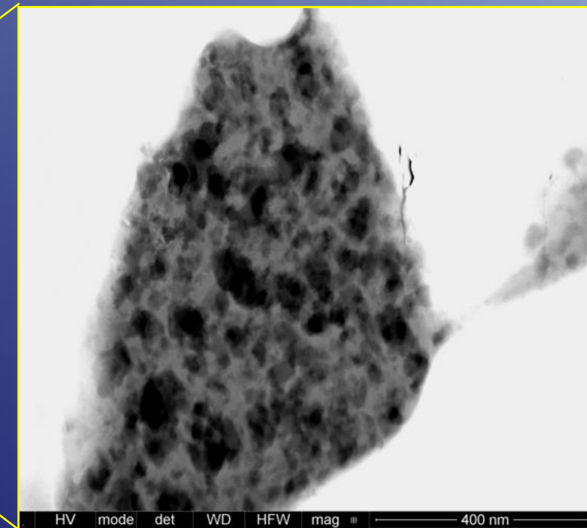
Importance of Organic Porosity



3D reconstruction of shale microstructure



Organic network: 93.6% is a single connected network

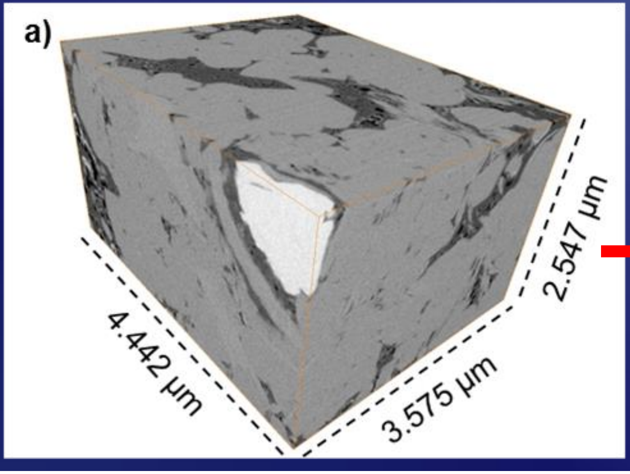


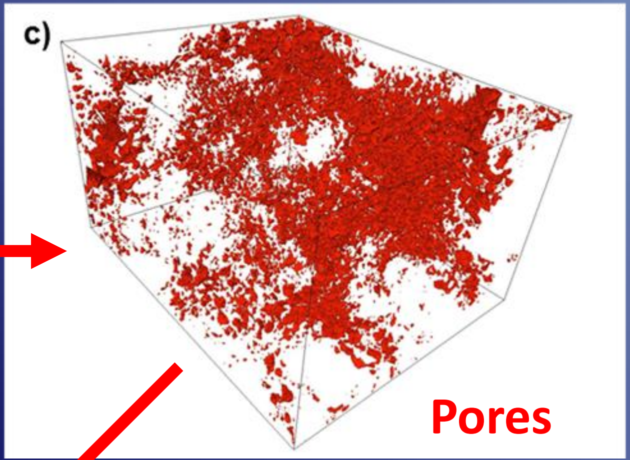
ADF STEM image of organic matter in shale

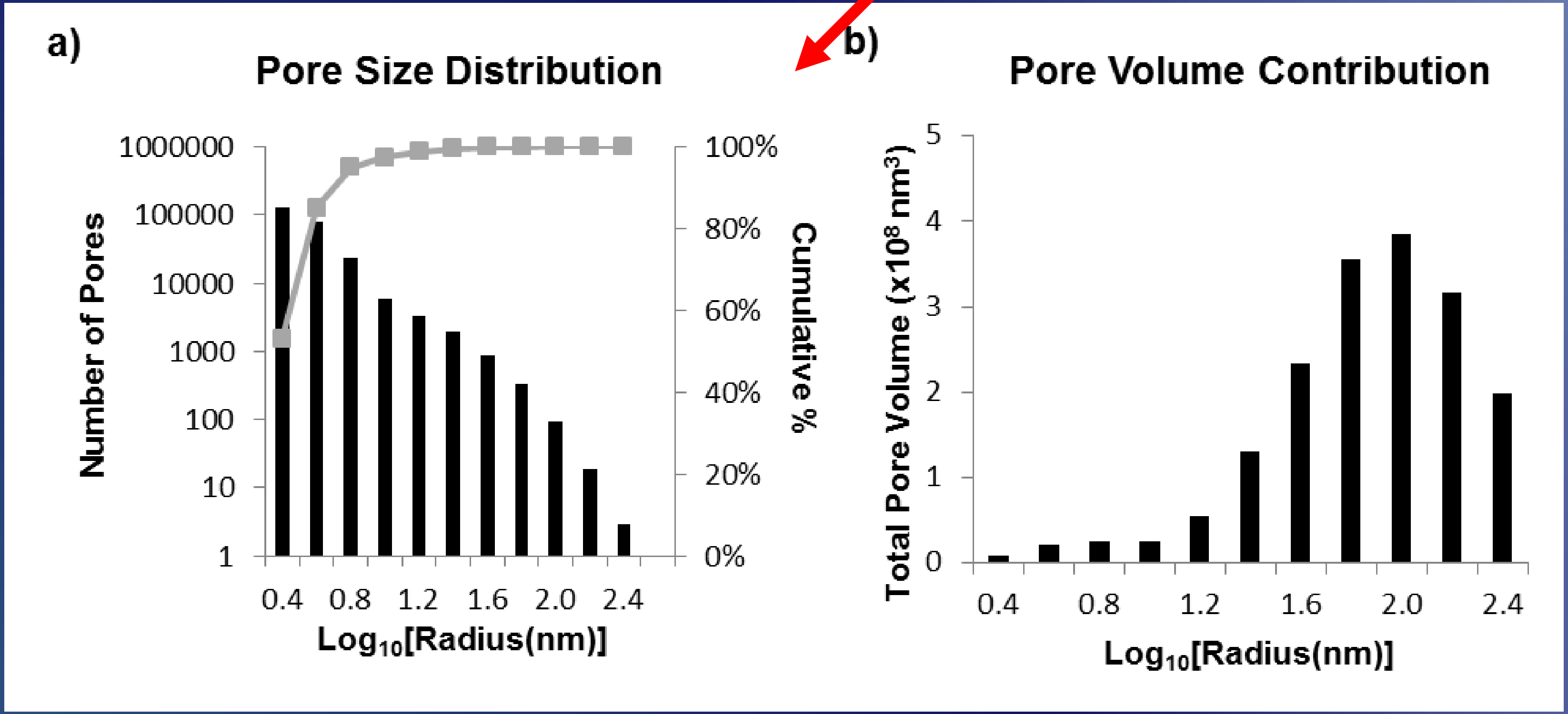
- STEM imaging of organic matter shows it to have a nebulous structure.
- Organic networks show high degree of connectivity in 3D FIB/SEM tomography.
- Together these raise the possibility of connected pathway for flow through the organic matter.
- Eventually must connect up to a fracture.
- In systems with both organic porosity and inorganic matrix porosity, need to determine whether flow is predominantly in series or parallel.

Curtis et al., *SPE144391*, 2011

3D Pore Size Distributions



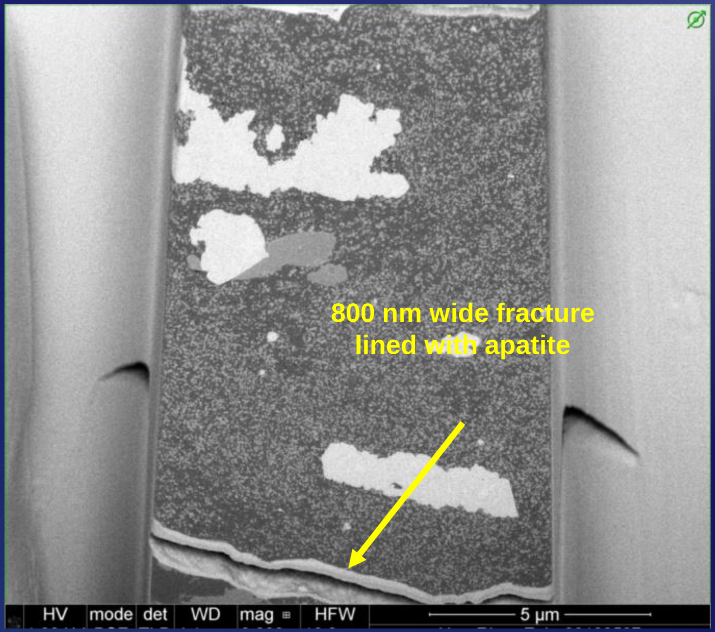


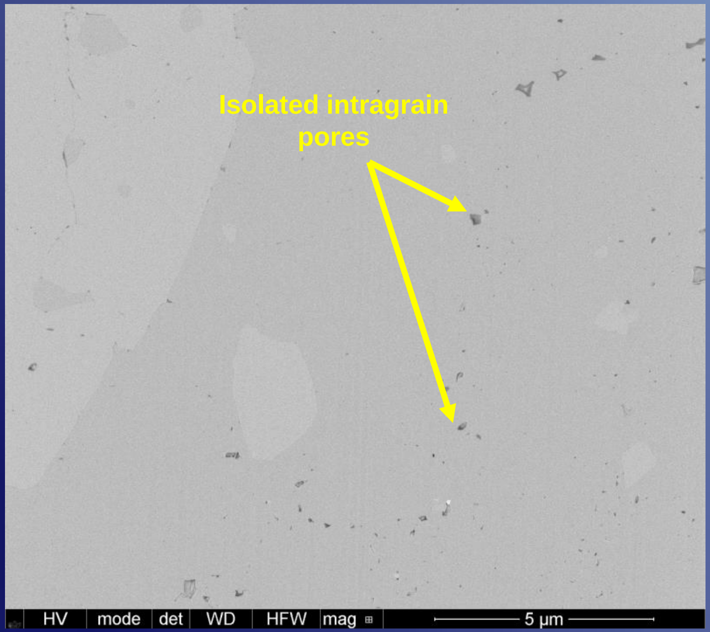


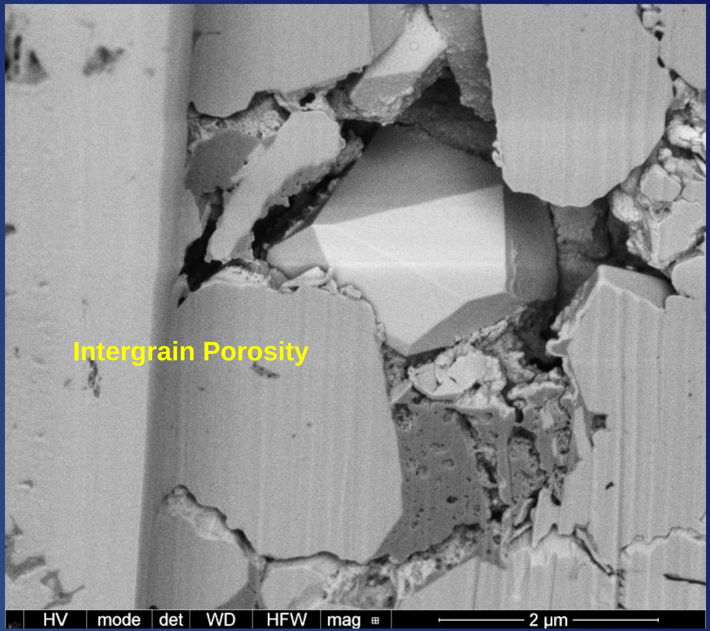
Large pores dominate the volume but the small pores may limit the radius of connected pathways!

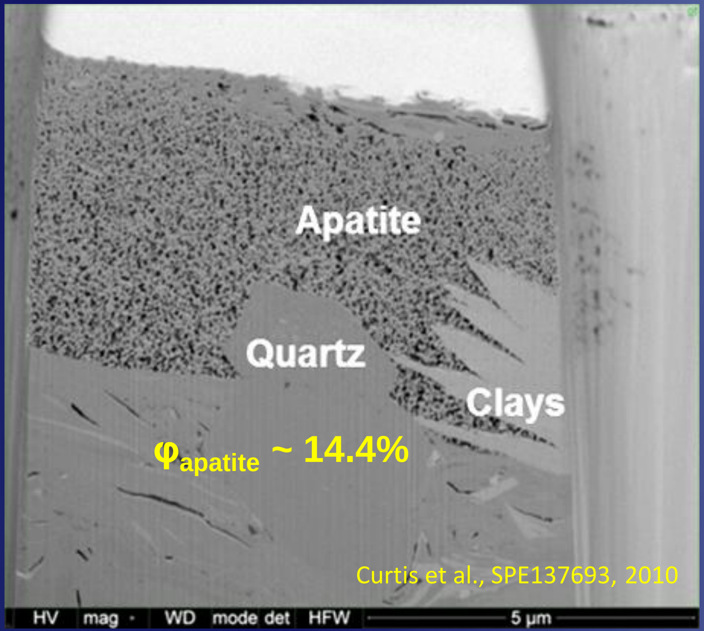
Curtis, M.E. et al., *AAPG Bulletin*, 2012.

Other Types of Porosity



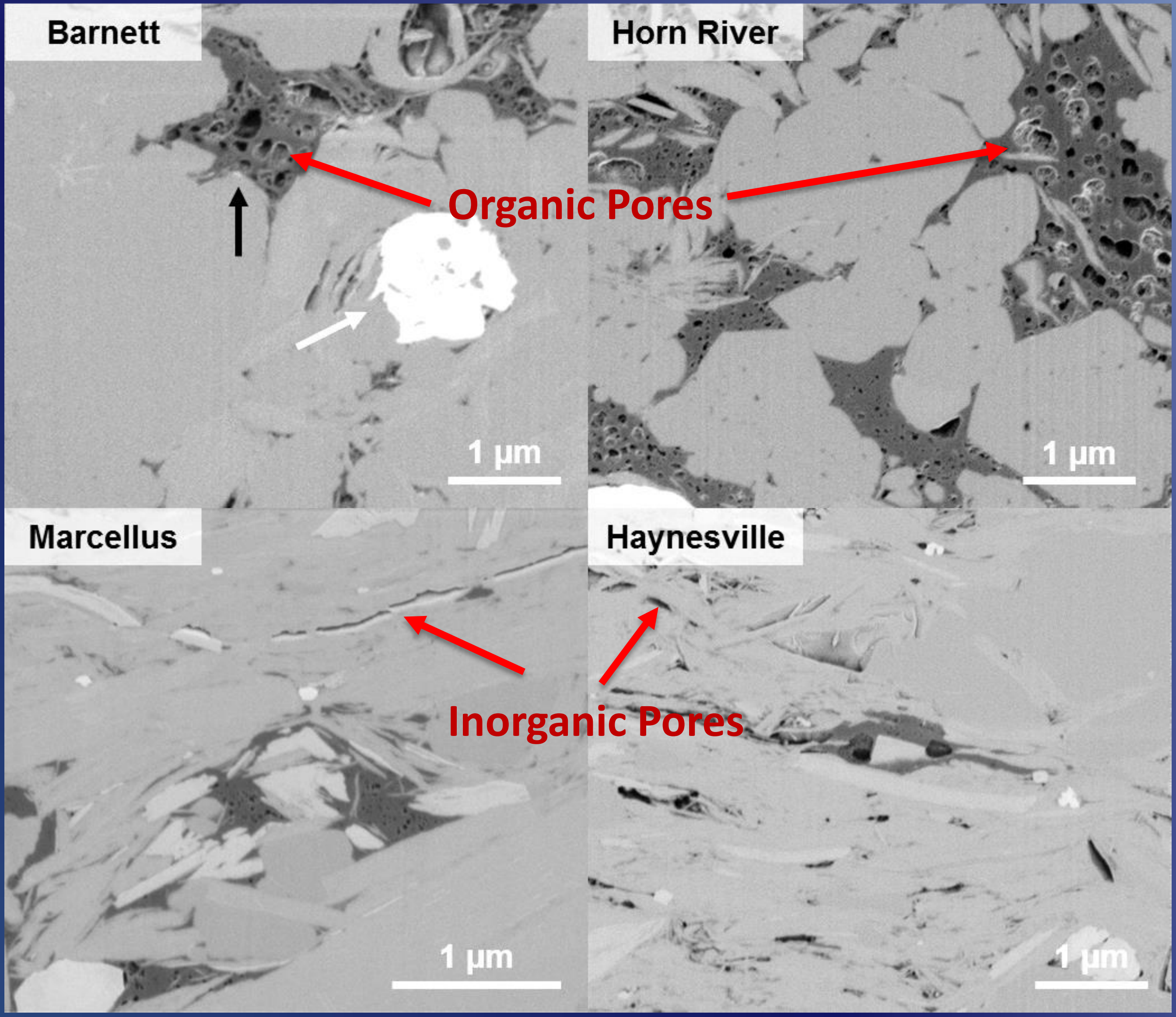






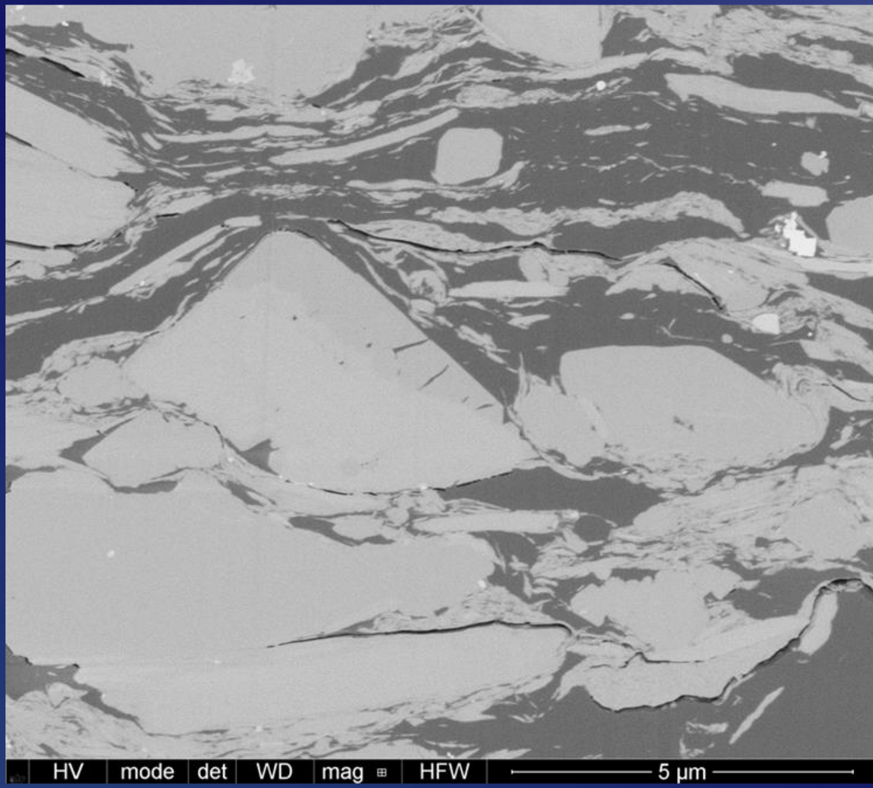
Curtis et al., SPE137693, 2010

Microstructure in Wet & Dry Gas Windows

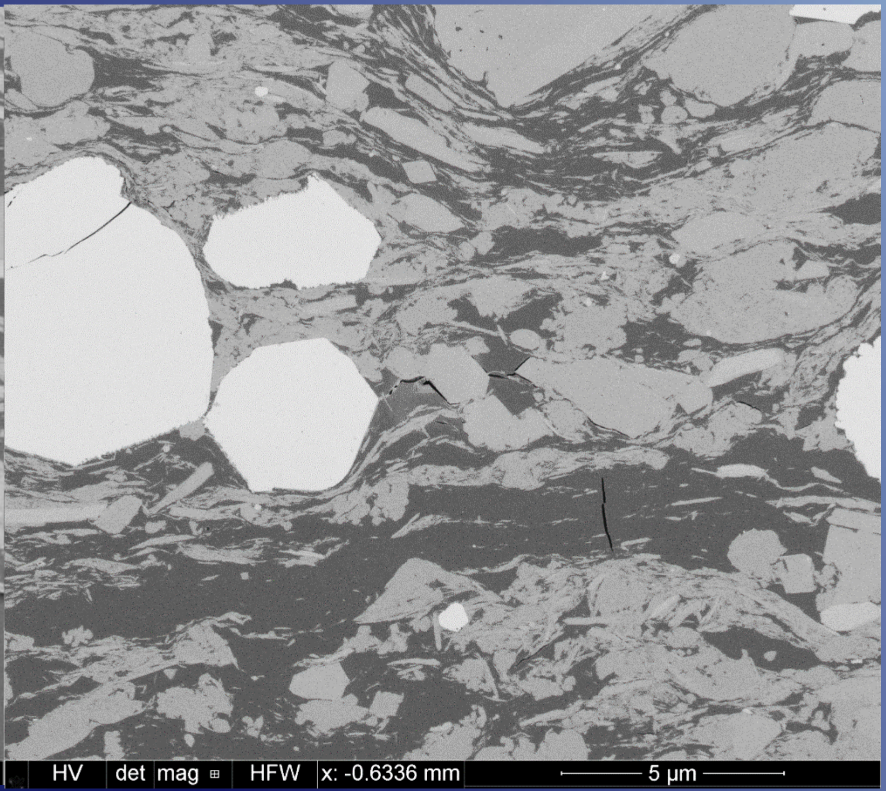


Curtis, M.E. et al., *URTeC*, 2013.

Microstructure in the Oil Window



Woodford Shale



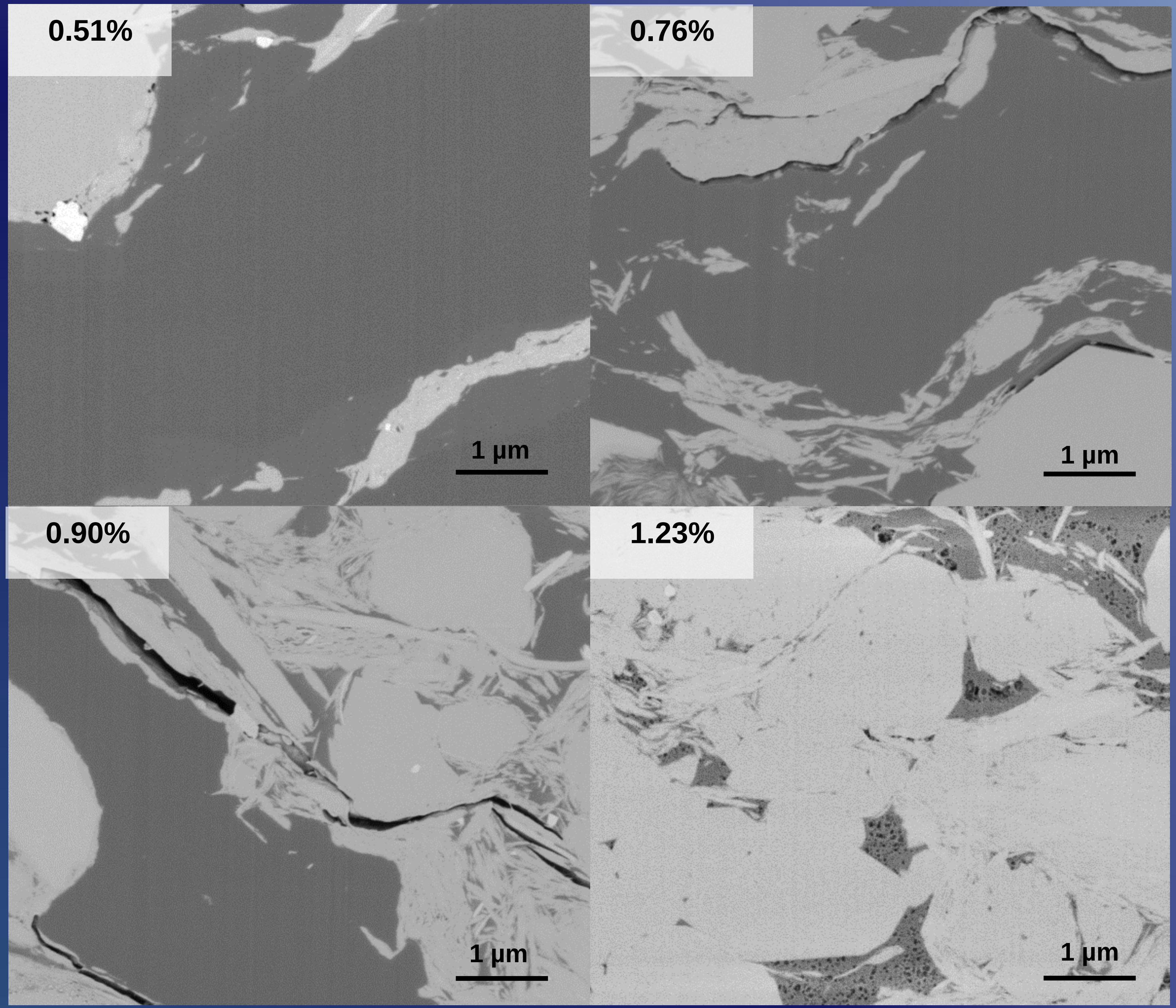
Bakken Shale

Note the complete lack of porosity in the organic matter. Some cracks can be seen on the edge of the organic matter between it the inorganic grains.

Possible that pores destroyed due to further compaction.

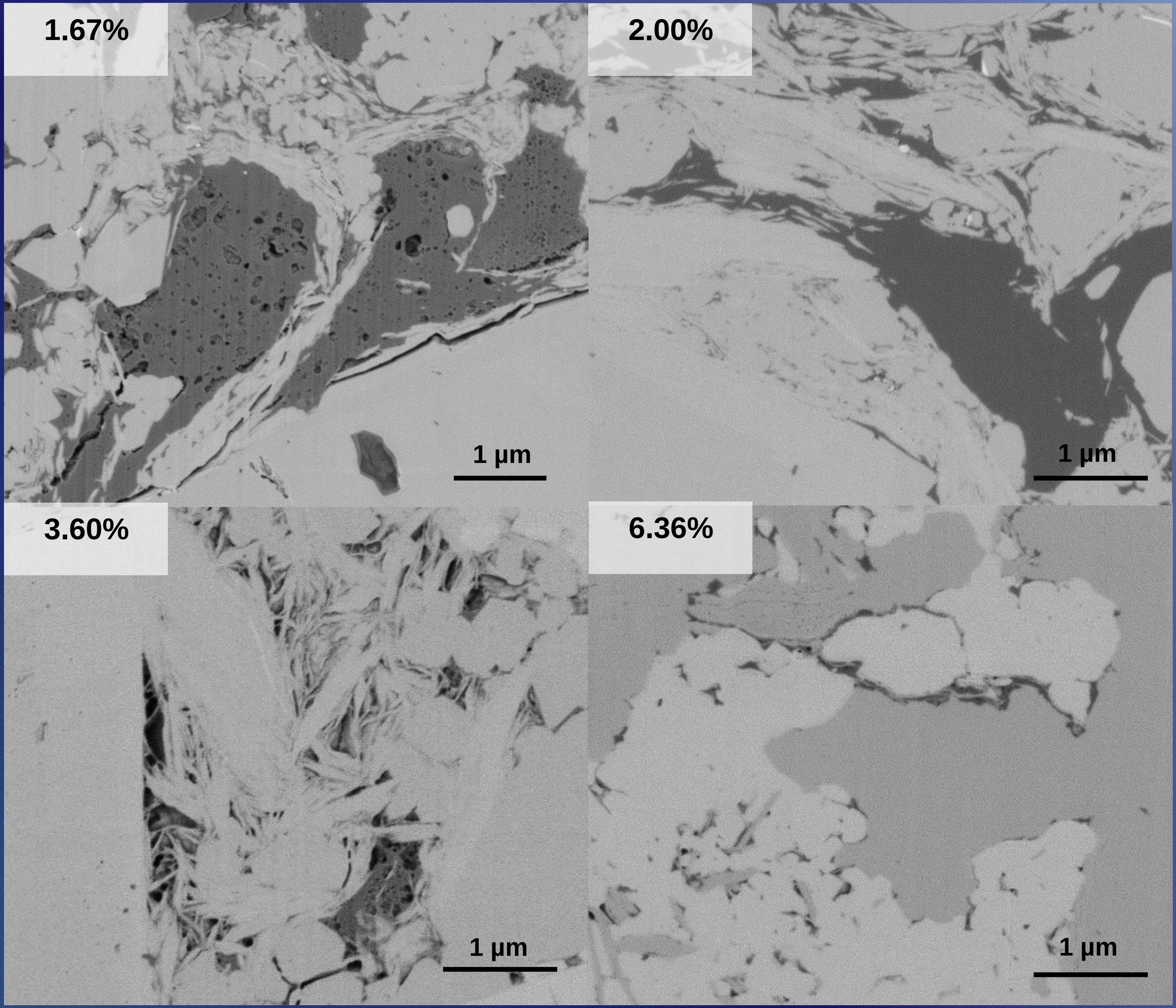
Curtis et al., *SPE164540*, 2013
Curtis, M.E. et al., *International Journal of Coal Geology*, 2012.

$\phi_{Organic}$ vs Thermal Maturity in Woodford



Curtis, M.E. et al., *International Journal of Coal Geology*, 2012.

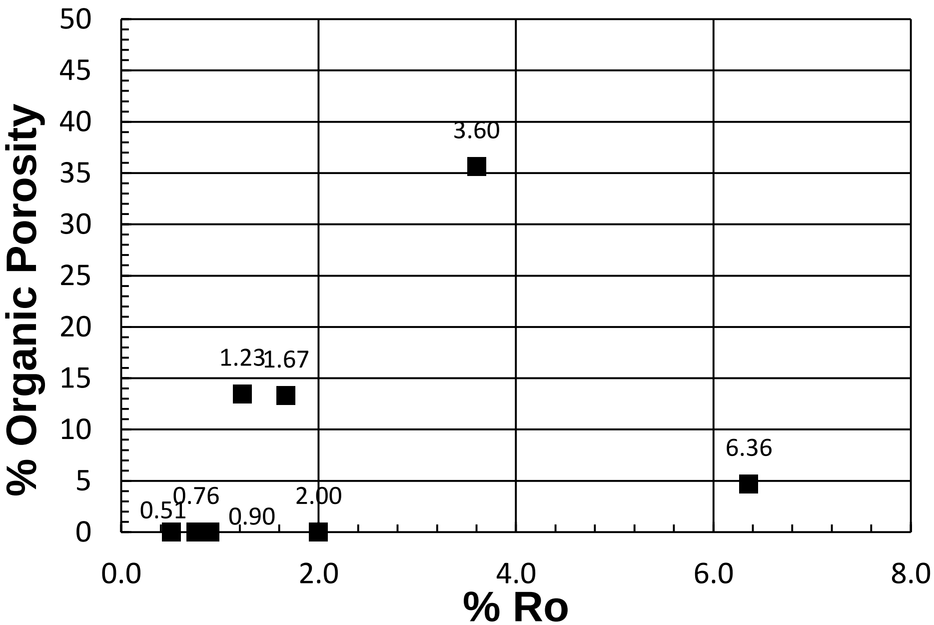
$\phi_{Organic}$ vs Thermal Maturity in Woodford



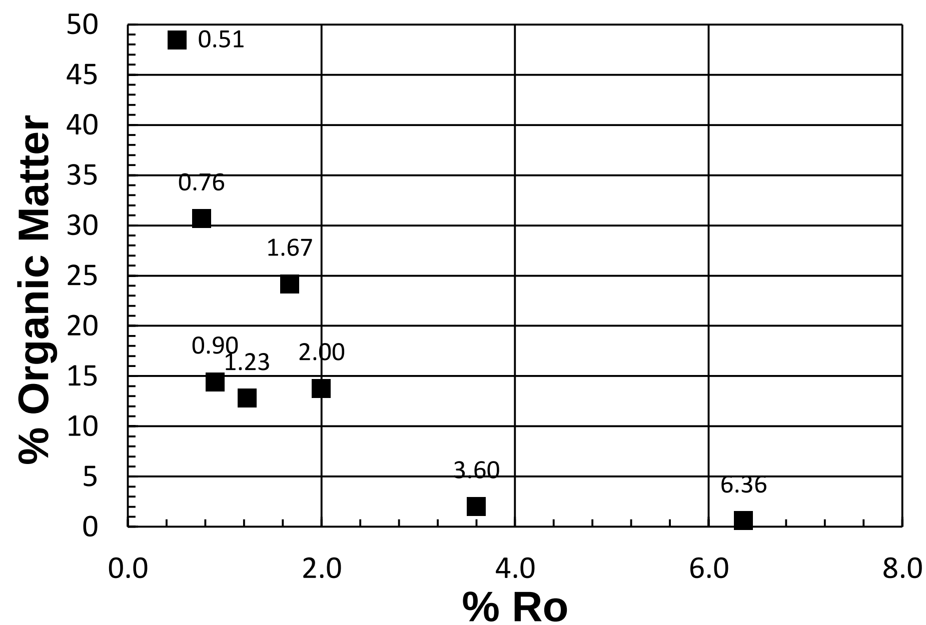
Curtis, M.E. et al., *International Journal of Coal Geology*, 2012.

%Ro vs Organic Porosity and % Organic Matter

- % organic matter and % organic porosity estimated by setting thresholds on grayscales of images.
- No trend was observed in % organic porosity with changing %Ro.
- This has been previously observed in the Marcellus shale (Curtis et al., 2011).
- % organic matter observed to decrease with increasing %Ro.



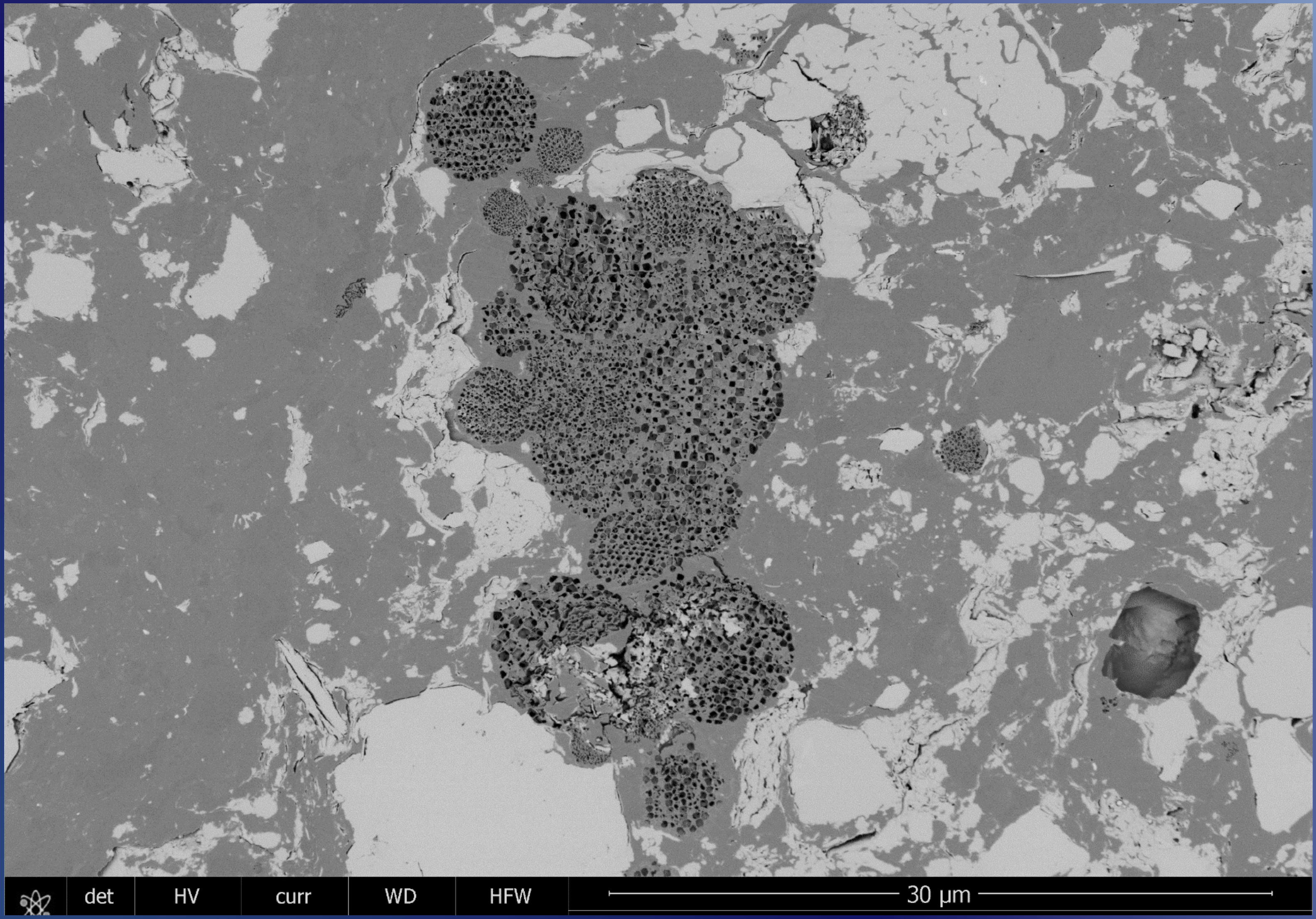
% organic porosity vs %Ro



% organic matter vs %Ro

Curtis, M.E. et al., *International Journal of Coal Geology*, 2012.

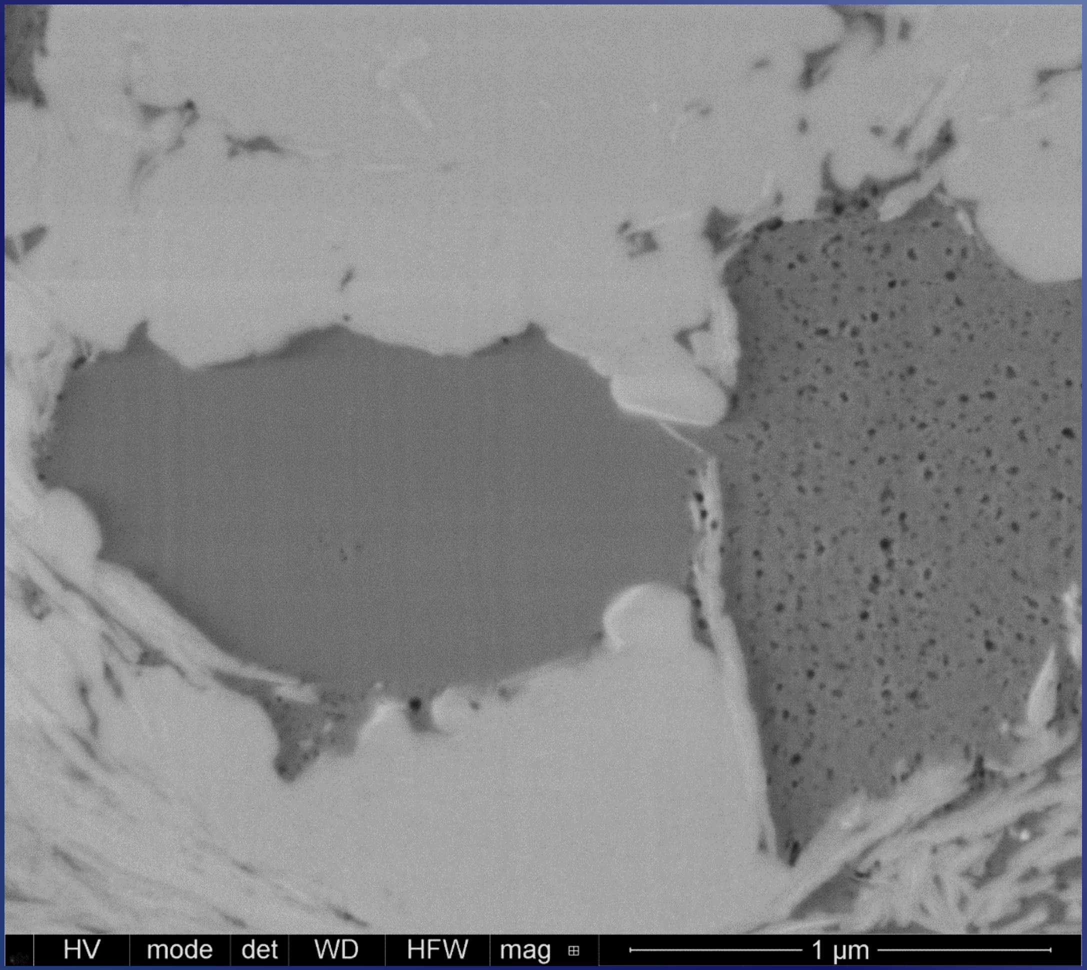
Primary Porosity in Shale



Woodford shale at 0.53% Ro showing primary porosity in the organic matter not caused by thermal maturation.

Curtis, M.E. et al., *URTeC*, 2013.

Incomplete Porosity Formation



Woodford shale at 1.4 %Ro showing non-uniform porosity formation in the organic matter. This suggests that something in addition to thermal maturity (e.g. type of organic matter) is controlling organic pore formation.

Curtis, M.E. et al., *International Journal of Coal Geology*, 2012.

Shales in the Oil Window

- Oil window samples show a general lack of porosity in the organic matter.
- Fits idea that secondary organic matter nanoporosity is a result of gas generation (Bernard et al., 2012; Loucks et al., 2009; Schieber, 2010).
- Lack of porosity presents a problem for storage and transport in the shales known to produce oil.
  - In the case of Bakken, oil is stored in middle porous dolomite layer.
  - Need to focus attention on porosity in inorganic matrix which could have significant storage.
  - Possibility that there are thinly stacked layers of source & storage in shales below the log scale.
  - Question still remains how does oil get to these layers.
  - Are there pores below the resolution of the microscope and how significant is this population?

Avalon Shale Microstructure

2 Wells ~ 1 mile apart

***Samples courtesy the Mewbourne Oil Company**

Sample Properties

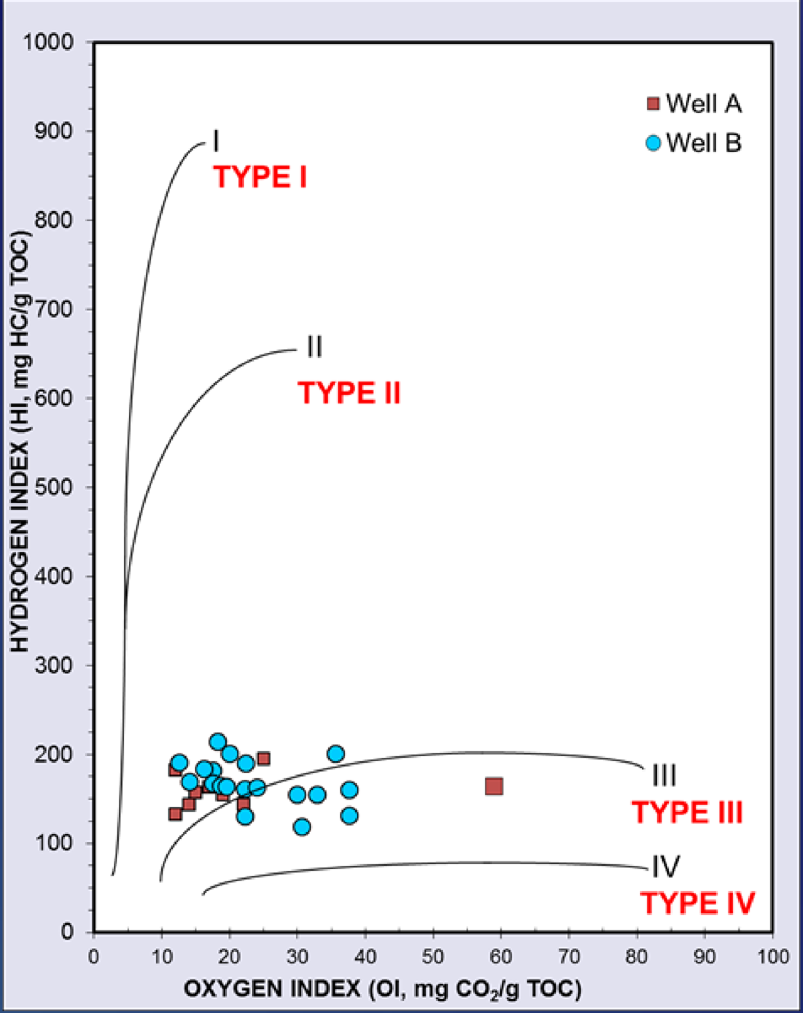
Well/Depth (ft)	TOC (wt %)	Mineralogy			
		% Quartz	%Carbonate	% Clay	% Other
A 8764	9.57	35	4	44	17
A 9180	5.62	38	13	43	6
A 9300	3.08	48	1	44	7
B 8890	5.92	60	11	18	11
B 9210	5.28	38	7	43	12
B 9330	5.41	40	13	38	9

Two wells labeled A and B
3 samples from each well

Samples mostly quartz and clays with good organic content.

Curtis et al., *SPE164540*, 2013

Pyrolysis Results

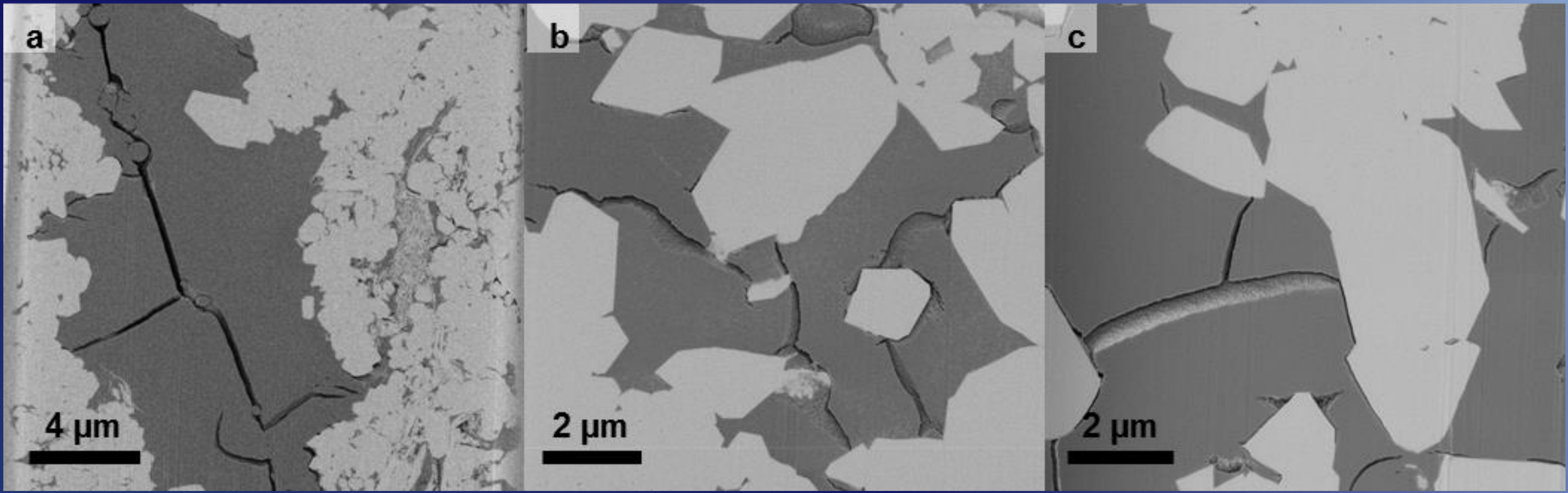


Well	No. of Samples	Depth range (ft)	Ave.Tmax (°C)	% Ro equiv.	S1/(S1+S2)
A	10	8840-9334	435 ± 3	0.67	0.21
B	20	8640-9440	439 ± 4	0.75	0.26

Pyrolysis indicates that the kerogen is type III. Indicates thermal maturity of well B is slightly greater than A, but unfortunately the error bars overlap. May explore FTIR to better determine the thermal maturity of each well.

Curtis et al., *SPE164540*, 2013

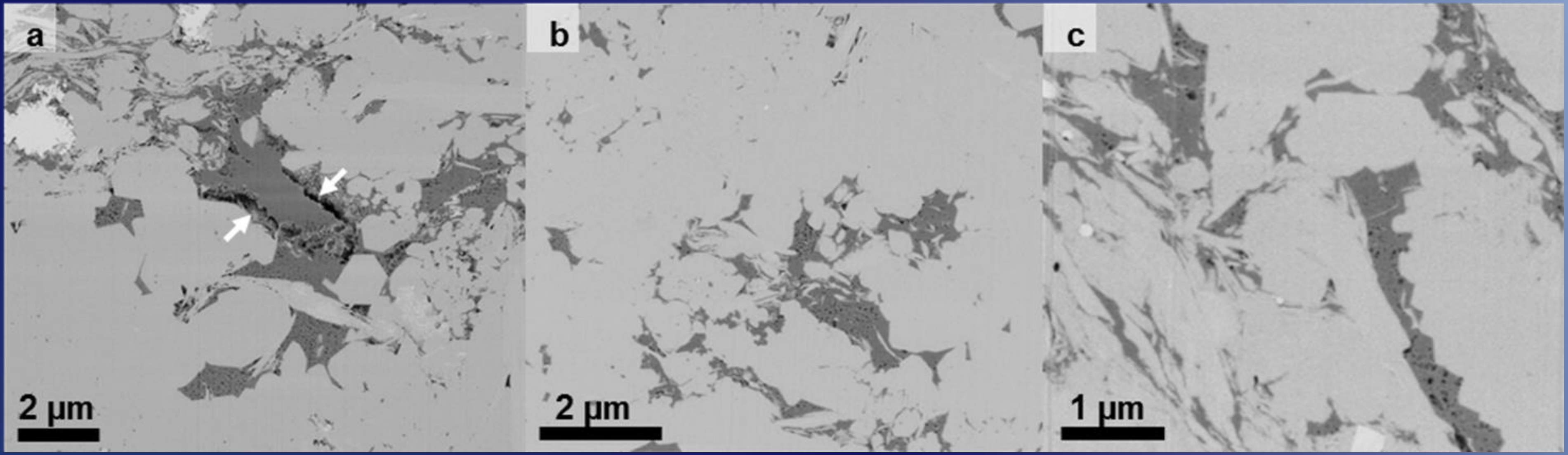
Well A: Tmax = 435 ± 3 °C (0.67 %Ro equiv.)



- **Organic microstructure in well A dominated by fractures contained wholly within the organic regions.**
- **This is a marked difference from the previous oil window samples.**
- **These fractures are possibly due to hydraulic fracturing during oil generation by the excess volume created by the oil (Curtis et al.; Dahl et al., 2012).**

Curtis et al., *SPE164540*, 2013

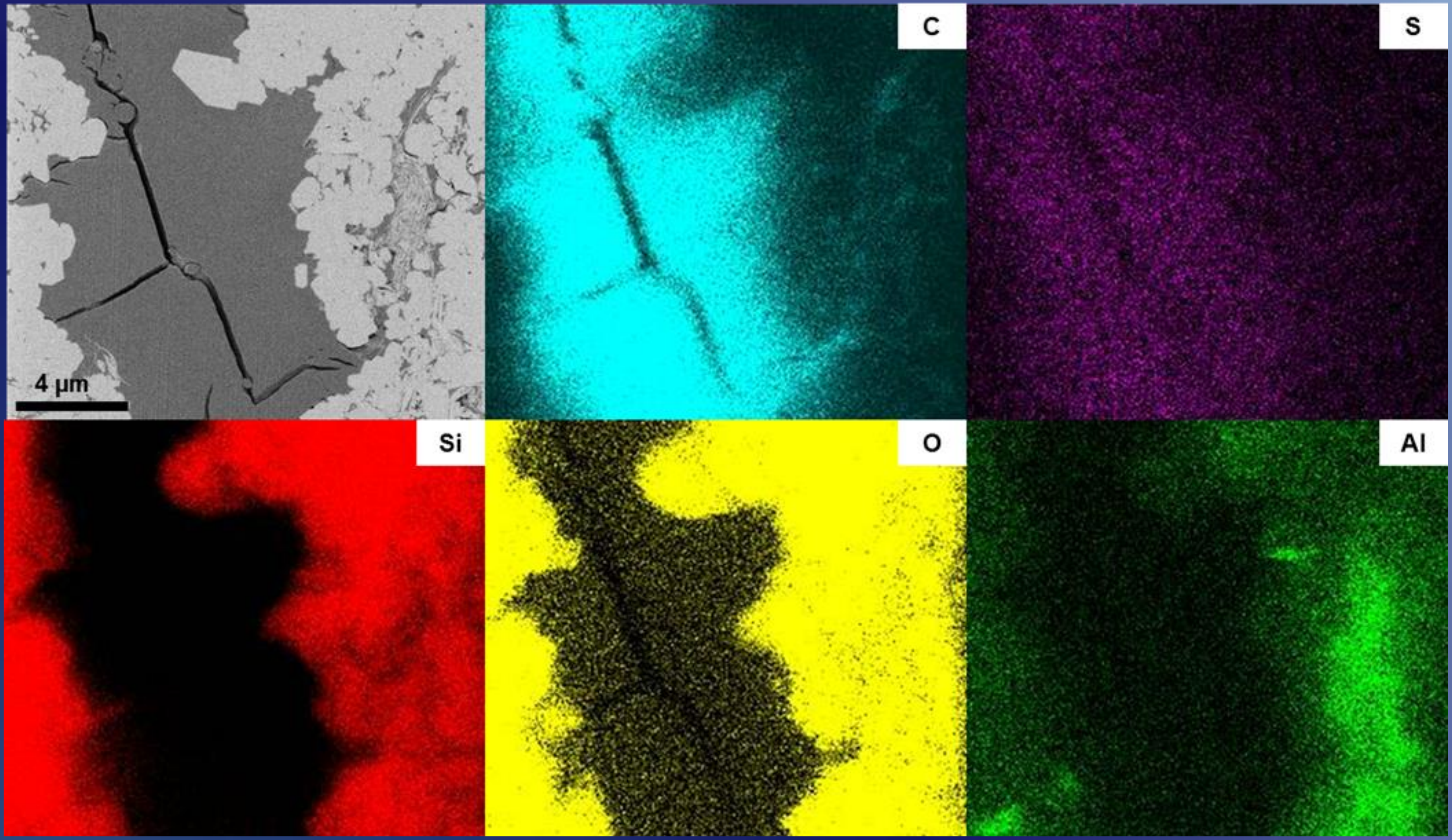
Well B: Tmax = 439 ± 4 °C (0.75 %Ro equiv.)



- Porosity dominated by round pores in the organic matter. Some vestiges of fractures may be present. This is different not only from well A in the Avalon but also from the other oil window shales previously imaged.
- Oil window samples may be sensitive to slight changes in thermal maturity resulting in different microstructures.
- Reed et al., 2012 also report secondary organic pore formation ~ 0.8% Ro.

Curtis et al., *SPE164540*, 2013

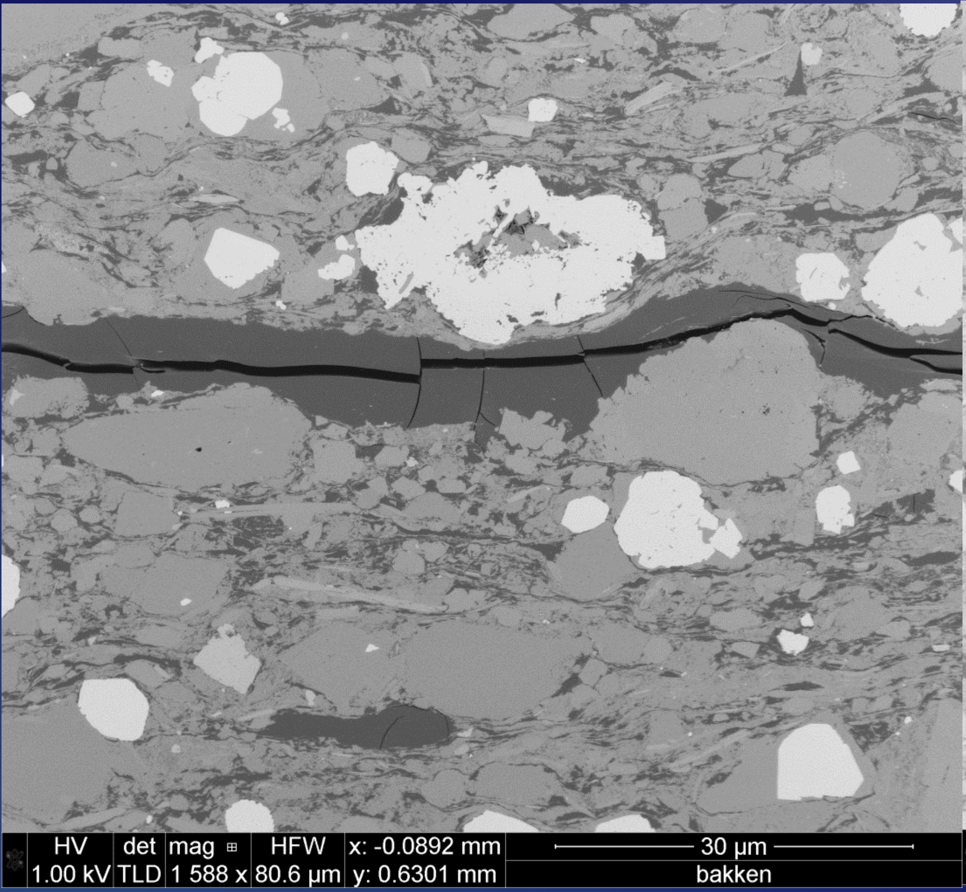
EDS of Organic Matter



Organic region from well A found to contain sulfur. The organic regions from other samples investigated showed no sulfur content.

Curtis et al., *SPE164540*, 2013

Bakken Organic Matter Fractures



Bakken shale in the oil window showing fractures in the organic matter similar to that in the Avalon.

Conclusions

- Wet and dry gas window samples have organic matter dominated by nanoporosity. Few exceptions have been found.
- Not all organic matter regions within a shale show the same microstructure at a given thermal maturity suggesting other factors (e.g. organic matter type) complicate porosity development.
- Oil window samples exhibit a complex microstructure in the organic matter that is as of yet hard to predict.
  - Many oil window samples have no form of porosity in the organic matter. Need to look for storage areas in the inorganic matrix.
  - Fractures dominate the structure of organic matter of oil window samples from an Avalon shale well whereas ~ 1 mile away round pores in the organic matter dominate.
  - Differences in microstructure of organic matter between the two Avalon may be due to slight differences in thermal maturity but results are inconclusive.

Acknowledgements

- Thanks to Dr. Carl Sondergeld & Chandra Rai (University of Oklahoma).
- Thanks to Gary Stowe & Jeremy Jernigen (University of Oklahoma).
- Thanks to Brian Cardott at the OGS for providing some of the Woodford samples and performing some of the vitrinite reflectance measurements.