# AV Black Shale Diagenesis: Insights from Integrated High-Definition Analyses of Post-Mature Marcellus Formation Rocks, Northeastern Pennsylvania*

**C. D. Laughrey[1], T. E. Ruble[1], H. Lemmens[2], J. Kostelnik[3], A. R. Butcher[2], G. Walker[1], and W. Knowles[1]**

Search and Discovery Article #110150 (2011)
Posted June 13, 2011

*Adapted from oral presentation at Session, U.S. Active and Emerging Plays--Paleozoic Basins and Cretaceous of Rockies, AAPG Annual Convention and Exhibition, Houston, Texas, USA, April 10-13, 2011

[1]Weatherford Laboratories, Golden, CO (christopher.laughrey@weatherford.com); Houston, TX; North Devon, UK
[2]FEI Company, Eindhoven, Netherlands; Queensland, Australia.
[3]Pennsylvania Geological Survey, Pittsburgh, PA.

## Abstract

Thermogenic shale-gas produced from the Marcellus Formation in northeastern Pennsylvania is post-mature. The reservoirs reached maximum burial temperatures characteristic of prehnite facies low-grade metamorphism. Although methane can be generated and remain stable under these conditions, this degree of burial diagenesis raises critical questions regarding metagenesis and reservoir quality. Late diagenesis implicates compaction, cementation, redox reactions involving formation fluids and transition metals, water loss, and dissolution/re-precipitation processes that may enhance or diminish reservoir potential.

Using a suite of high-resolution analytical techniques, we examined selected core samples from Sullivan County, Pennsylvania, to characterize the reservoir and develop a diagenetic history of the Marcellus Formation in the region. The organic-rich intervals in these samples comprise mostly quartz, illite, and calcite. Quartz occurs as detrital silt, authigenic overgrowths, cryptocrystalline replacement of allochems, pore-filling microquartz and megaquartz, and patchy sheets of silica platelets. Illite occurs as crenulated detrital platelets and authigenic clay. The mean illite crystallite thickness is 211Å, and the average Kübler index is 0.428, confirming the shales reached the low anchizone prehnite-pumpellyte metamorphic facies. Calcite occurs as crystalline spar replacing allochems and filling fossil molds, as crystals dispersed in clay and organic matrix, and as discontinuous parallel laminations of microspar. Additional minerals include anhydrite, plagioclase, illite-smectite, chlorite, pyrite, and graphite. Whole pattern fitting and Reitveld refinement quantify the abundance of graphite.

TOC ranges from 0.6 to 11 wt. percent. The original kerogen was mostly Type II.. Microscopy and 3D modeling show that pyrobitumen comprises a significant volume of the rocks. Most porosity in the Marcellus is associated with this graphitic pyrobitumen.

Early diagenesis of Marcellus sediments involved mechanical compaction and dewatering of muds during burial to approximately 500 m. Chemical compaction at greater burial depths was dominated by quartz cementation and clay mineral transformations. Organic porosity developed during late catagenesis and continued on into metagenesis at depths greater than 8 km, where storage capacity continued to evolve within a graphitic pyrobitumen matrix.

## Selected References


Abad, I., J.B. Murphy, F. Nieto, and G. Gutierrez-Alonso, 2010, Diagenesis to metamorphism transition in an episutural basin; the late Paleozoic St. Mary's Basin, Nova Scotia, Canada.: Canadian Journal of Earth Sciences, v. 47/2, p. 121-135.

Harrison, W.E., 1979, Levels of Graphitization of Kerogen as a potentially useful method of assessing paleotemperatures, *in* P.A. Scholle, and P.R. Schluger, (eds.), Aspects of Diagenesis: SEPM Special Publication, v. 26, p. 45-53. DOI:1032110/PEC.79.26.0045

Holzer, L., F. Indutnyi, PH. Gasser, B. Munch, and M. Wegmann, 2004, Three-dimensional analysis of porous $BaTiO_3$ ceramics using FIB nanotomography: Journal of Microscopy, v. 216/1, p. 84-95.

Houseknecht, D.W., and C. Spotl, 1993, Empirical observations regarding methane deadlines in deep basins and thrust belts, *in* D.G. Howell, (ed.), The future of energy gases: USGS Professional Paper 1570, p. 217-232.

Lash, G.G., and T. Engelder, 2011, Thickness trends and sequence stratigraphy of the Middle Devonian Marcellus Formation, Appalachian Basin; implications for Acadian foreland basin evolution: AAPG Bulletin, v. 95/1, p. 61-103.

Maynard, J.B., 1981, Carbon isotopes as indicators of dispersal patterns in Devonian-Mississippian shales of the Appalachian Basin: Geology, v. 9/6, p. 262-265.

Obermajer, M., L.D. Stasiuk, M.G. Fowler, and K.G. Osadetz, 1997, A comparative examination of organic geochemistry and petrology of Upper Devonian to Early Mississippian epicontinental black shales from Canada: AAPG Bulletin, v. 81/9, p. 1560-1561.

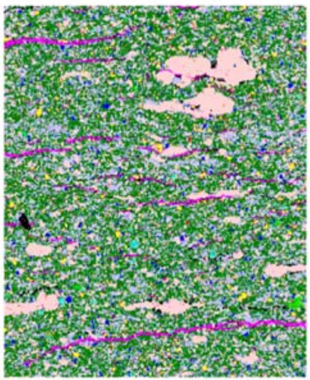
Schieber, J., D. Krinsley, and L. Riciputi, 2000, Diagenetic origin of quartz silt in mudstones and implications for silica cycling: Nature London, v. 406/6799, p. 981-985.

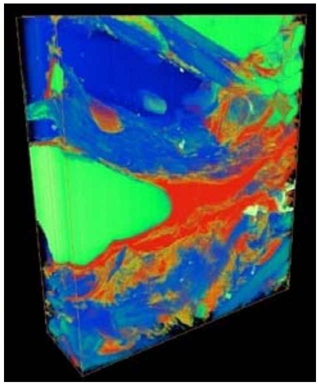
Scholle, P.A., 1979, A color illustrated guide to constituents, Textures, Cements, and Porosities of Sandstones and Associated Rocks: AAPG Memoir 28, 201 p.

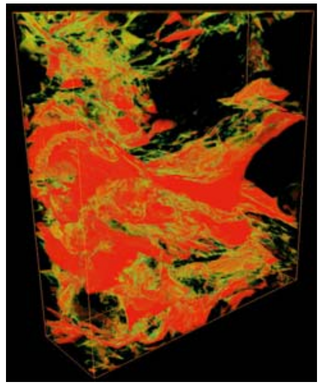
Sondergeld, C.H., R.J. Ambrose, C.S. Rai, and J. Moncrieff, 2010, Micro-Structural Studies of Gas Shales: SPE Paper 131771, SPE Unconventional Gas Conference, Pittsburg, Pa., 17 p, Web accessed 2 June 2011
http://www.onepetro.org/mslib/servlet/onepetropreview?id=SPE-131771-MS&soc=SPE

# BLACK SHALE DIAGENESIS:

## Insights from Integrated High-Definition Analyses of Post-Mature Marcellus Formation Rocks, Northeastern Pennsylvania







# Research Team

- Christopher D. Laughrey, Weatherford Laboratories, Golden, CO
- Tim E. Ruble, Weatherford Laboratories, Houston, TX
- Herman Lemmens, FEI Company, Eindhoven, The Netherlands
- Jaime Kostelnik, Pennsylvania Geological Survey, Pittsburgh, PA
- Alan R. Butcher, FEI Company, Queensland, Australia
- Greg Walker, Weatherford Laboratories, Houston, TX
- Wayne Knowles, Weatherford Laboratories, North Devon, UK

Weatherford LABORATORIES

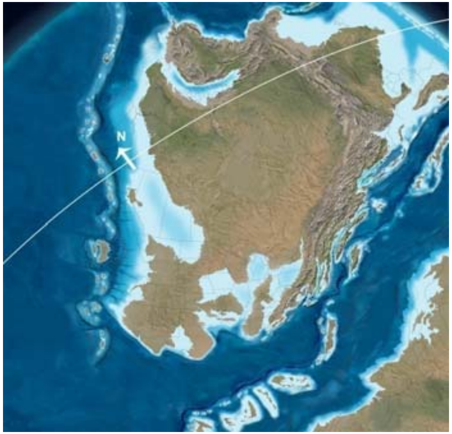
TOOLS FOR NANOTECH FEI

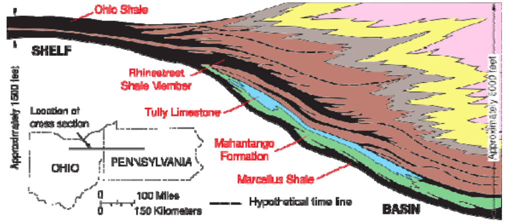
PENNSYLVANIA GEOLOGICAL SURVEY EST. 1836

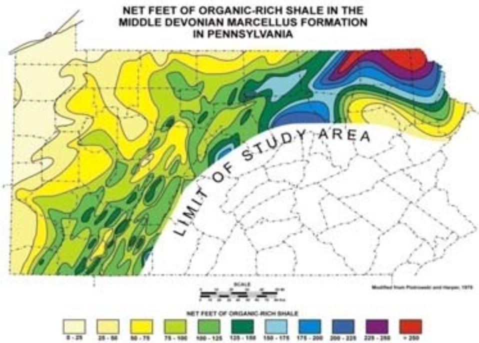
# Presentation

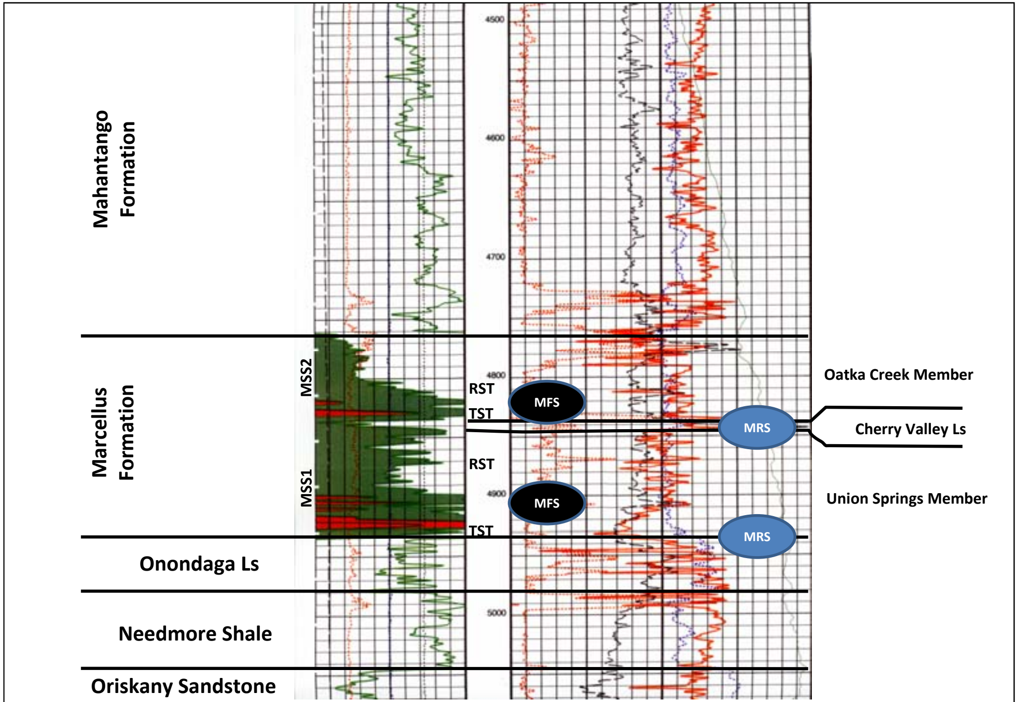
- Background:
  - Stratigraphy and drilling activity
  - Thermal maturity of Marcellus strata in northeast Pennsylvania
  - Critical elements for economic preservation of natural gas in highly mature strata
- Deep burial diagenesis of organic-rich shales and reservoir attributes
- Petroleum geochemistry and petrology of the Marcellus Formation in the northeast core region
- Discussion and conclusions

# Stratigraphic Setting



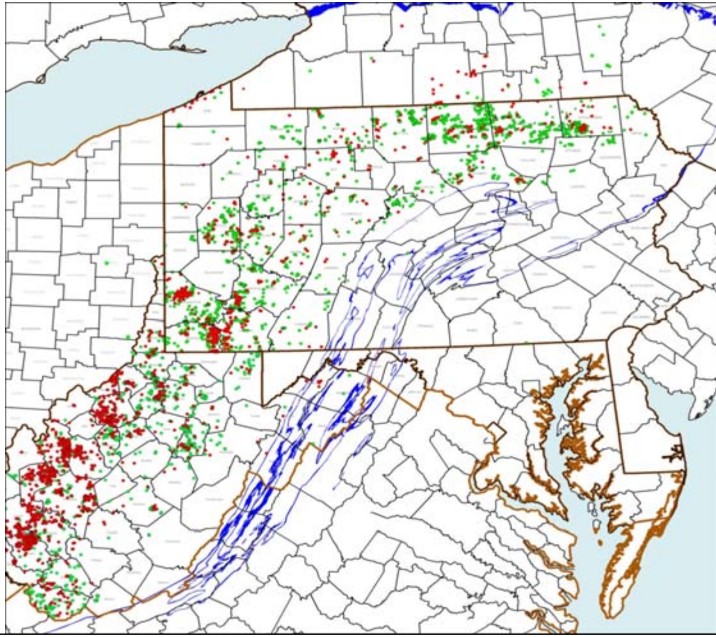






Sequence stratigraphy parameters of Lash and Engelder, 2011

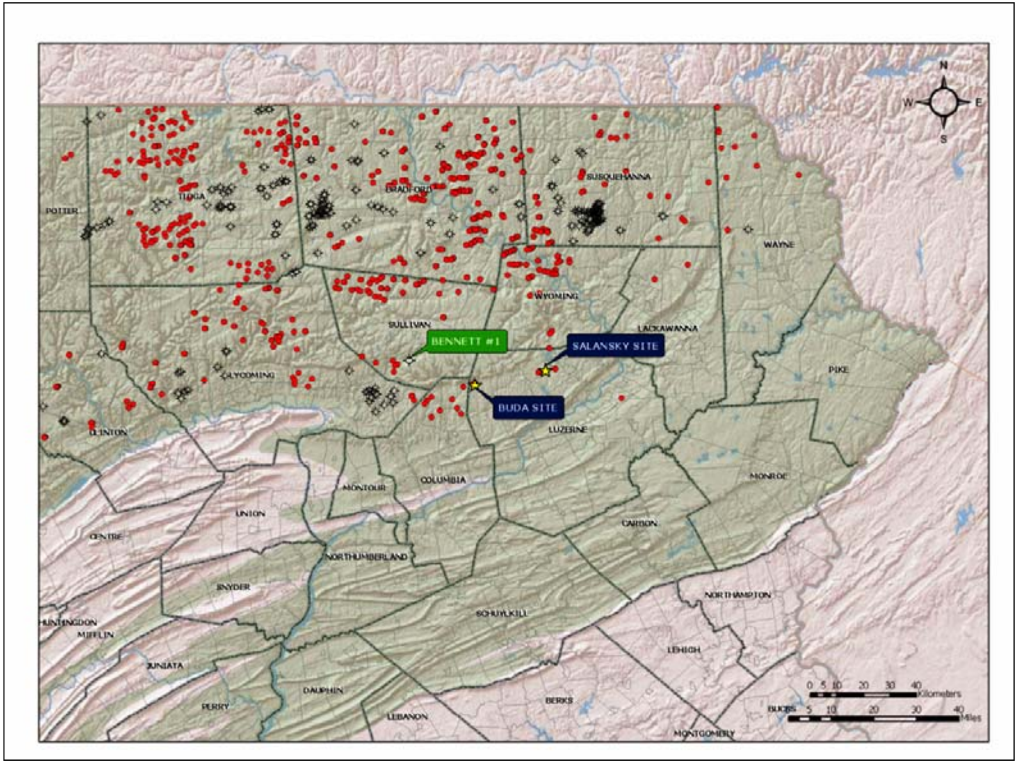
# Marcellus Activity Map, 2010



Drilled Marcellus well

Permitted Marcellus well

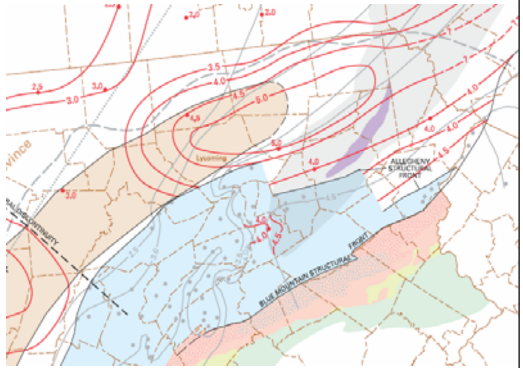
*Courtesy G. Wrightstone, 2010*
*Texas Keystone Oil and Gas*



N
W
E
S
POTTER
TIOGA
BRADFORD
SUSQUEHANNA
WAYNE
WYOMING
SULLIVAN
LACKAWANNA
BENNETT #1
SALANSKY SITE
LYCOMING
PIKE
BUDA SITE
CLINTON
LUZERNE
MONTOUR
COLUMBIA
MONROE
UNION
CARBON
CENTRE
NORTHUMBERLAND
SNYDER
NORTHAMPTON
SCHUYLKILL
HUNTINGDON
MIFFLIN
LEHIGH
JUNIATA
DAUPHIN
PERRY
BERKS
LEBANON
BUCKS
MONTGOMERY
0 5 10 20 30 40 Kilometers
5 10 20 30 40 Miles

# Marcellus Formation, NE Pennsylvania: Prehnite Facies Low-Grade Metamorphism

- Mapped %$VR_o$ = 2 to >3
- Mapped CAI = 4 to 5
- Mapped illite crystallinity > 0.13
- Fluid inclusion trapping temperatures:
  - 195˚ - 245˚C (Pennsylvanian strata)
  - 180˚ -230˚C (Ordovician – Devonian strata)
- Crenulated to slaty cleavage
- Early metamorphic mineral assemblages:
  - *Albite + quartz + prehnite + pumpellyte + chlorite + sphene*
  - *Zeolites*



# Critical elements for the economic preservation of natural gas in highly mature ($R_o$ > 3%) strata:

1. **Generation, migration, and accumulation of $CH_4$ and nonhydrocarbon gases ($CO_2$, $N_2$, $H_2S$) during late catagenesis and metagenesis. Hydrocarbon destruction (TSR etc.).**
2. **Effectiveness and longevity of seals exposed to deep burial, high temperatures, and tectonic deformation.**
3. ***Diagenesis of rocks exposed to deep burial and high temperatures.***

**- Houseknecht and Spötl, 1993, *Empirical observations regarding methane deadlines in deep basins and thrust belts*, USGS PP 1570, p. 217 – 231.**

# Deep Burial Diagenesis of Organic-Rich Shales

- Compaction
- Mineral dissolution/re-precipitation reactions
- Cementation
- Redox reactions involving hydrocarbons, transition metals, and water
- Water loss
- Organic metamorphism

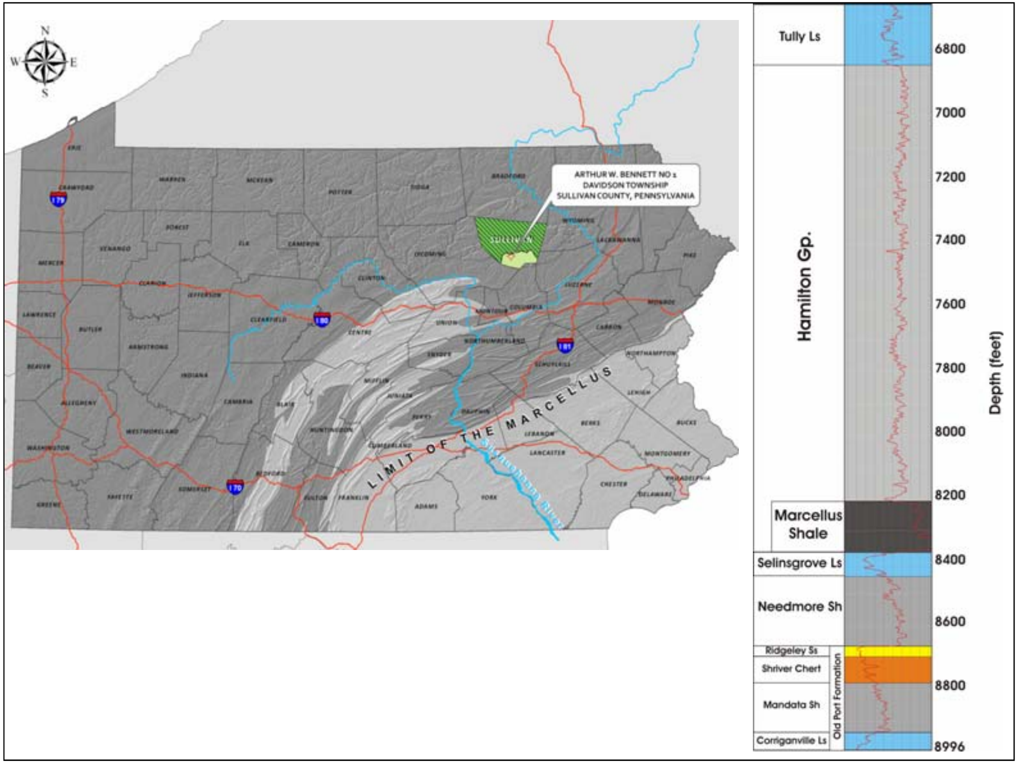
- Basic Shale Reservoir Attributes:
  - *Rock composition (bulk and grain density)*
  - *Total organic carbon*
  - *Porosity and permeability*
  - *Free and sorbed gas*
  - *Water saturations*
  - *Thermal maturity*



***Presenter's Notes***: All of these processes may enhance or diminish reservoir potential by retaining or releasing gas from the system at high thermal maturities and by diagenetically altering shale reservoir properties.

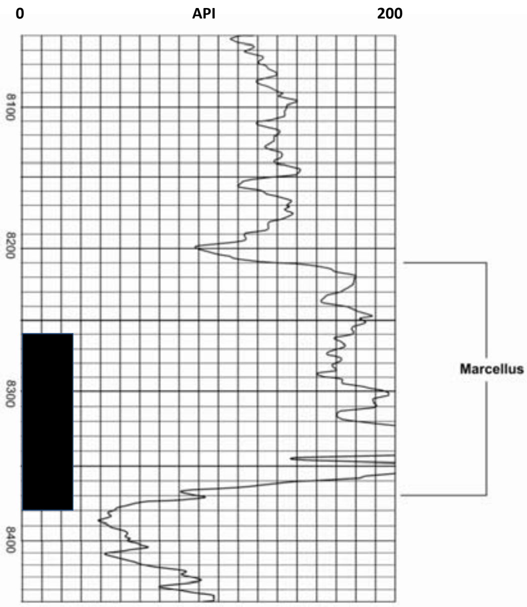
# Petroleum Geochemistry and Petrology of the Marcellus Formation in the Northeast Core Region

- Quantity, quality, and thermal maturity of organic matter
- Quantitative mineralogy
- Construct a 3D model of mineral, organic matter, and porosity distribution in the rock
- Describe and classify porosity
- Interpret the diagenetic history of the shale-gas reservoir
- Define the key reservoir attributes of post-mature Marcellus Formation rocks in the northeast core region
- Compare these attributes in productive and unproductive areas


N
W
E
S
ARTHUR W. BENNETT NO 1
DAVIDSON TOWNSHIP
SULLIVAN COUNTY, PENNSYLVANIA
LIMIT OF THE MARCELLUS
Tully Ls
Hamilton Gp.
Marcellus Shale
Selinsgrove Ls
Needmore Sh
Ridgeley Ss
Shriver Chert
Mandata Sh
Corriganville Ls
Old Port Formation
6800
7000
7200
7400
7600
7800
8000
8200
8400
8600
8800
8996
Depth (feet)

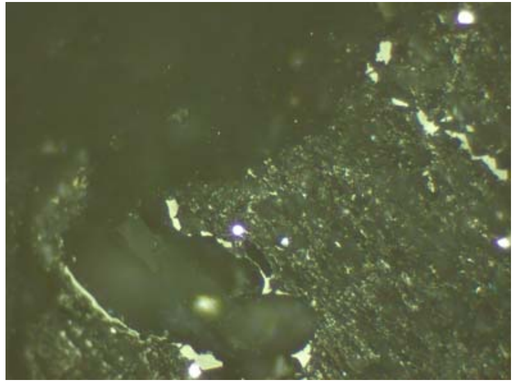
# Bennett #1 well Marcellus Formation organic-rich intervals:

*Laminated to thinly bedded or bioturbated fossiliferous, calcareous, quartzose mudstone and mudshale*

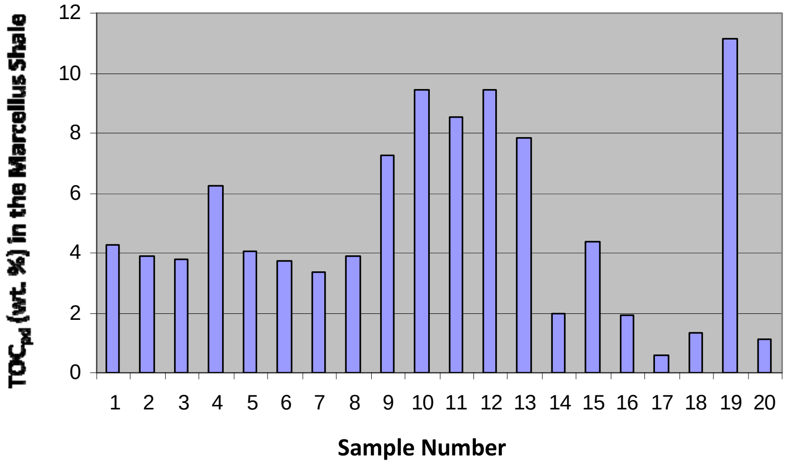


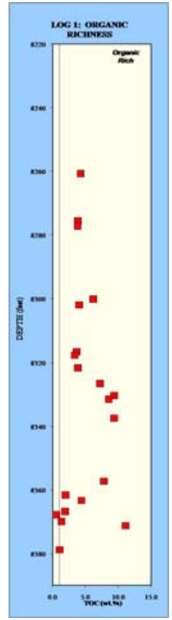

# Petroleum Geochemistry

- Leco TOC
- Rock-Eval and SRA pyrolysis
- Organic petrography:
  - Organic matter type
  - Vitrinite reflectance
  - Solid hydrocarbon reflectance
- Micropaleontology
  - CAI



# Total Organic Matter

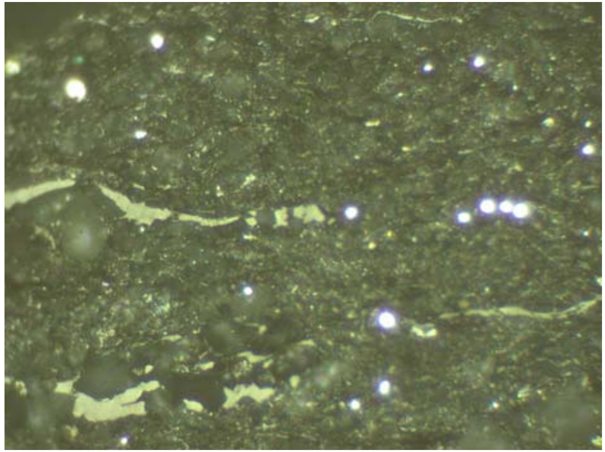



***Presenter's Notes:*** TOC ranges from 0.58 – 11 wt. % with most of the cored interval TOCpd = 2 – 4 wt%.

# Kerogens Types

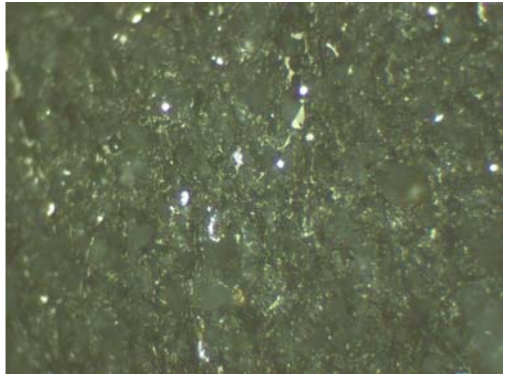
- **Inertinite**
- **Solid hydrocarbons (SHC)/pyrobitumen**
- **Vitrinite**
- **Alginite**
- **Amorphous**



**Bennett #1, 8371.2 ft.**

# Whole Rock vs. Mineral Corrected Kerogen Percentages

- **Mean whole rock:**
  - **Minerals: 49**
  - **Inertinite: 43.6**
    - **Semifusinite: 0.27**
  - **Solid hydrocarbons/pyrobitumen: 2.6**
  - **Framboidal pyrite: 2**
  - **Vitrinite: 1.8**
  - **Alginite: 1.4**
  - **AOM: 0.9**
- **Mean mineral corrected kerogen:**
  - **Inertinite: 84**
    - **Semifusinite: 0.6**
  - **Solid hydrocarbons/pyrobitumen: 5.7**
  - **Framboidal pyrite: 4.5**
  - **Vitrinite: 1.2**
  - **Alginite: 2.2**
  - **AOM: 1.9**

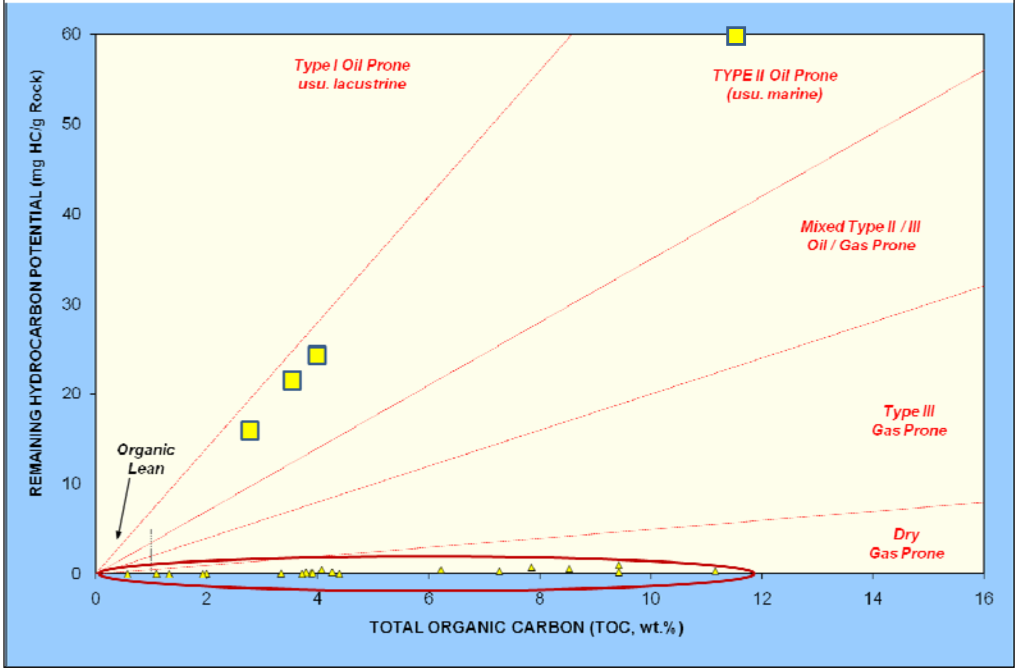


***Presenter's Notes:*** Framboidal pyrite: Microscopic aggregate of pyrite grains (spheroidal clusters resemble a raspberry; Sulfide crystals fill chambers or cells in bacteria/algae.

# Original Composition

- **Kerogen quality:**
  - Type II mean % = 95.5
  - Type I mean % = 2.7
  - Type III: mean % = 1.2
  - Type IV mean % = 0.6
  - Mean % oil-prone: 98.2
  - Mean % gas-prone: 1.3
  - Original organic matter mean percentage of whole rock: 46.6
  - Mean AOM conversion = 97.9 % (ratio inert OM/ total OM)

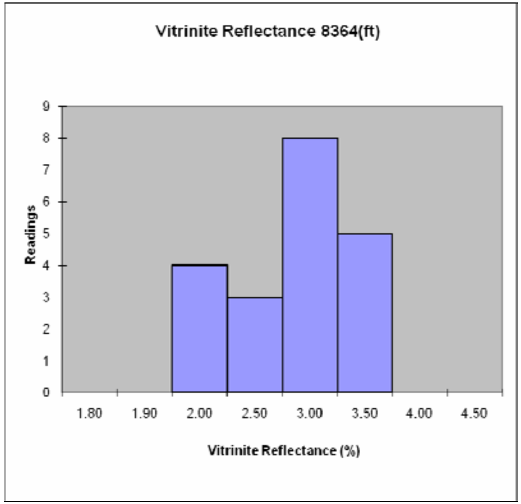
# Generation Potential (S2) versus Organic Richness




***Presenter's Notes:*** Large yellow squares are early mature Marcellus from southwestern Ontario (Obermajer and others, 1997)

# Thermal Maturity

- **Thermally post mature:**
  - **Mean %$VR_o$ = 2.99**
  - **CAI = 4.5 - 5**
  - **$T_{max}$:**
    - **348° - 377°C (ltS2p)**
    - **464.8°C (high-temperature pyrolysis)**
      - **$T_{max}$ $S_{py}$: 724°C**
  - **PI: 0.54 – 0.87**

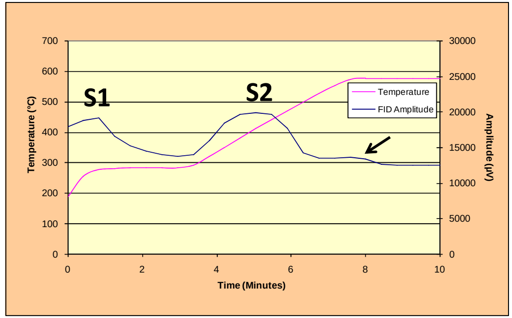


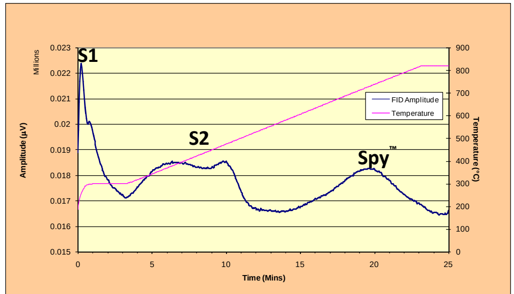



***Presenter's Notes:*** Metagenesis: semi-anthracite to anthracite coal rank.

# Post-Mature Marcellus, 8371.2 feet

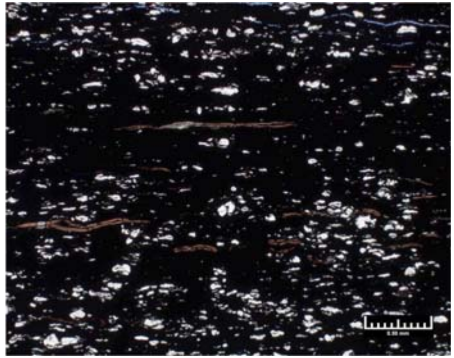
- **Programmed pyrolysis data:**
  - **TOC = 8 wt. percent**
  - **S1 = 0.22 mg HC/g**
  - **S2 = 0.36 mg HC/g**
  - **$T_{max}$ = 395.9˚C**
  - **PI = 0.38**
  - **S3 = 1.36 mg/g**
  - **HI = 4 mg HC/g TOC**
  - **OI = 16 mg $CO_2$/g TOC**
  - ***$S_{py}$ peak resolved***



# Quantitative Mineralogy

- Automated quantitative mineralogy (QEMSCAN)
- Thin-section analyses
- X-ray diffraction
- SEM (SE and BE) with EDS



***Presenter's Notes:*** Detrital and authigenic silt-size quartz, carbonate allochems, clay, organic matrix, and minor to trace components – daunting to approach the petrography of such fine-grained material.

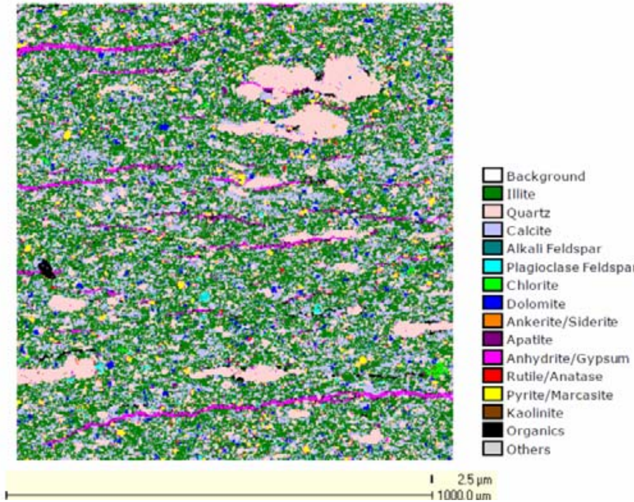
# Marcellus shale QEMSCAN mineralogy


31mm, EDX every 10 microns

***Presenter's Notes:*** QEMSCAN image of the Marcellus Shale (8365 feet) analyzed at 10-µm spacing.
Area analyzed: 31 × 14 mm (sample size is 70 × 20 mm).

# Rocks are dominated by quartz, illite, and calcite

| *Mineral* | *QEMSCAN Mass %* |
|---|---|
| Illite/Smectite | 19.8 |
| Quartz | 47.9 |
| Calcite | 11.4 |
| Alkali Feldspar | 0.2 |
| Plagioclase | 1.3 |
| Chlorite | 1.5 |
| Dolomite | 3.3 |
| Ankerite/Siderite | 0.4 |
| Apatite | 0.4 |
| Anhydrite/Gypsum | 2.5 |
| Rutile/Anatase | 0.7 |
| Pyrite/Marcasite | 7.6 |
| Kaolinite | 1.3 |
| Organics | 0.0 |
| Others | 1.6 |
| Total | 100.0 |






***Presenter's Notes:*** Detailed view of a small area (1 × 1 mm) mapped at 2.5-µm spacing.

# Quartz

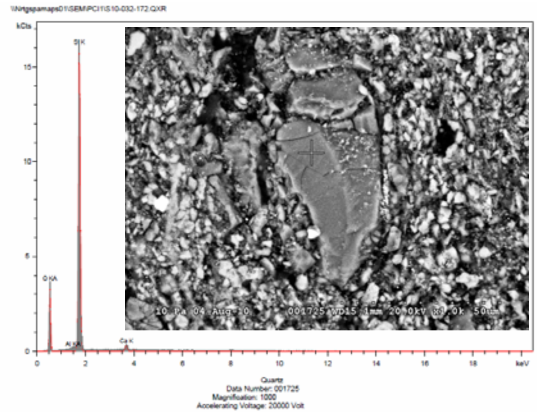
- Detrital silt and associated authigenic silica overgrowths
- Diagenetic quartz silt: cryptocrystalline quartz replaces fossil allochems and fills algal cysts : *accounts for >90% of silt-sized quartz*!
- Pore-filling microquartz and megaquartz cements
- Patchy sheets of quartz cement platelets



***Presenter's Notes:*** Bullets in approximate order of diagenetic sequence.

# Detrital Silt

- Medium/coarse silt-size
- Low-sphericity, angular grains with sharp corners
- Conchoidal fracture
- Surface textures
- Polymodal
- Strong luminescence
- Authigenic silica overgrowths

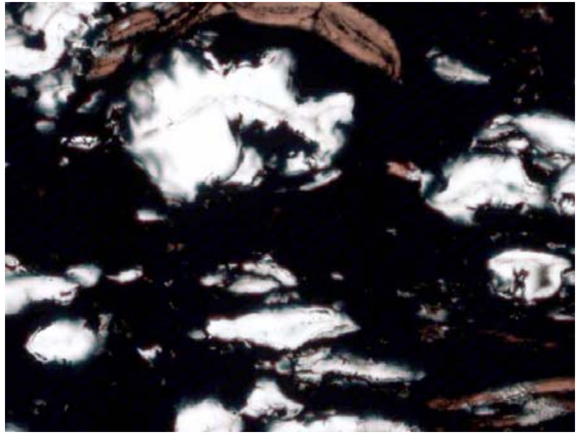


*Diagnostic criteria of Schieber, Krinsley, and Riciputi, 2000*

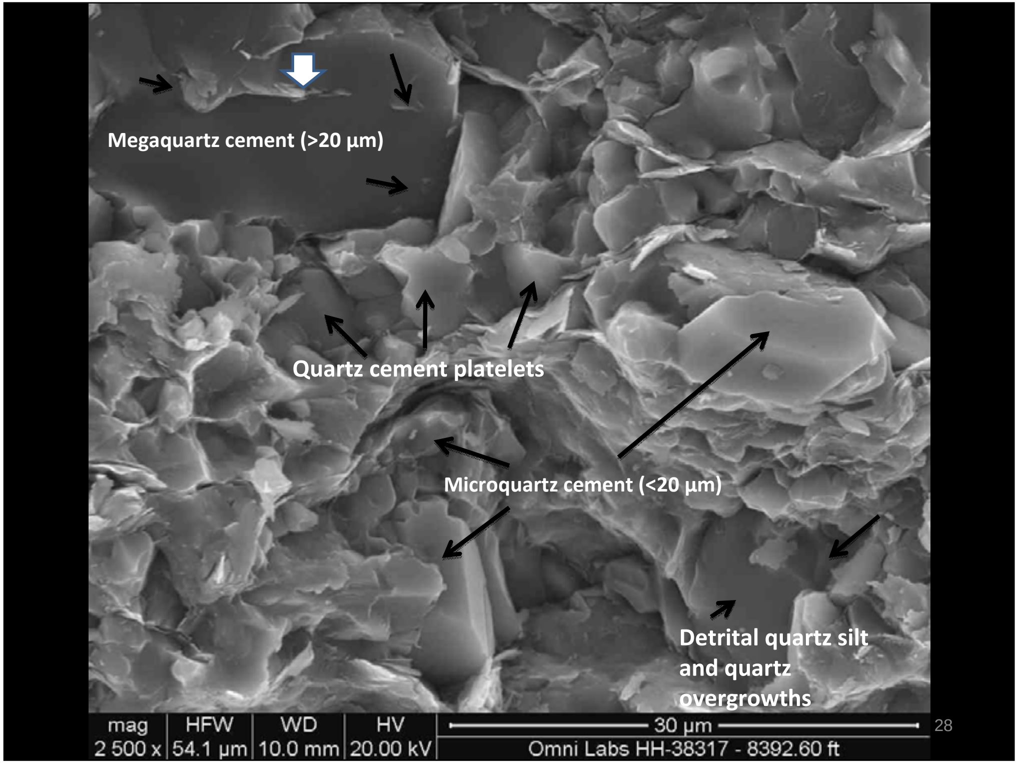
***Presenter's Notes:*** Detrital quartz – coarse silt, low-sphericity, polymodal, angular grains with sharp corners, conchoidal fracture, surface textures, and strong luminescence.

# Diagenetic Quartz Silt

- Embayments
- Lobate to pointed projections
- Unimodal quartz
  - Internal zoning visible with CL
- Non-luminescent to low luminescence
- Algal wall fragments



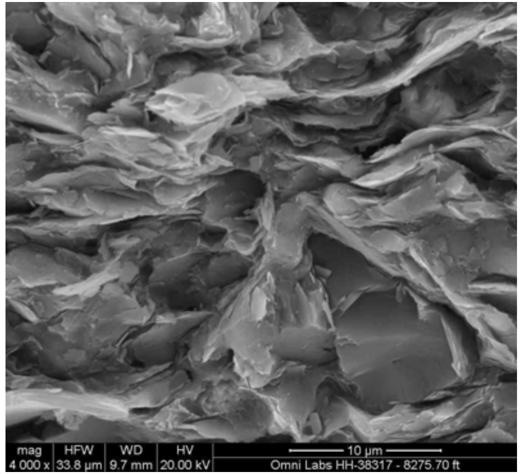
*Diagnostic criteria of Schieber, Krinsley, and Riciputi, 2000*

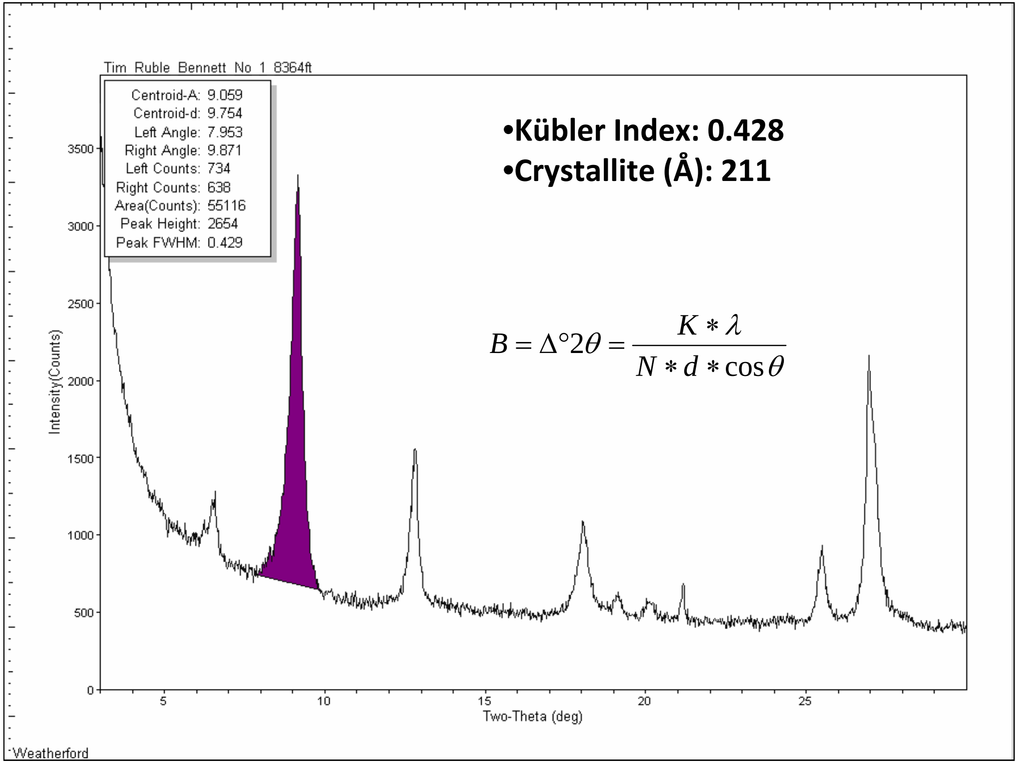



***Presenter's Notes:*** Megaquartz/microquartz cutoff = 20 µm (Scholle, 1979).

# Illite

- *2M* polytype
- Crenulated ($S_o$), flake-like detrital platelets
- Thin flakes and filaments of pore-filling authigenic clay
- Mean illite crystallite thickness is 211 Å.
- Average Kübler index is 0.428





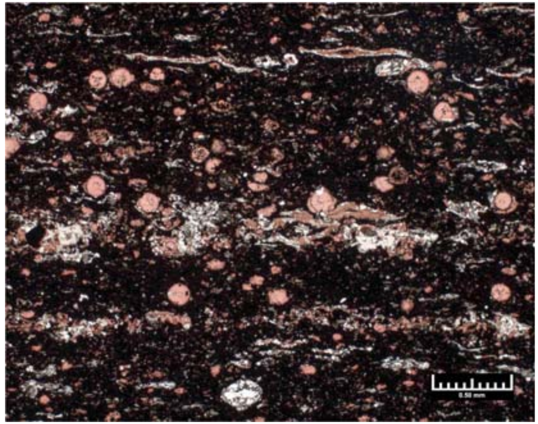

***Presenter's Notes:*** Relationship between the sharpness of the illite 10 A diffraction peak and the degree of low-temperature metamorphism in argillaceous rocks. Sharpness of the 10 A illite basal reflection peak width at half the maximum height. B = angular width at half maximum (in 2 theta).

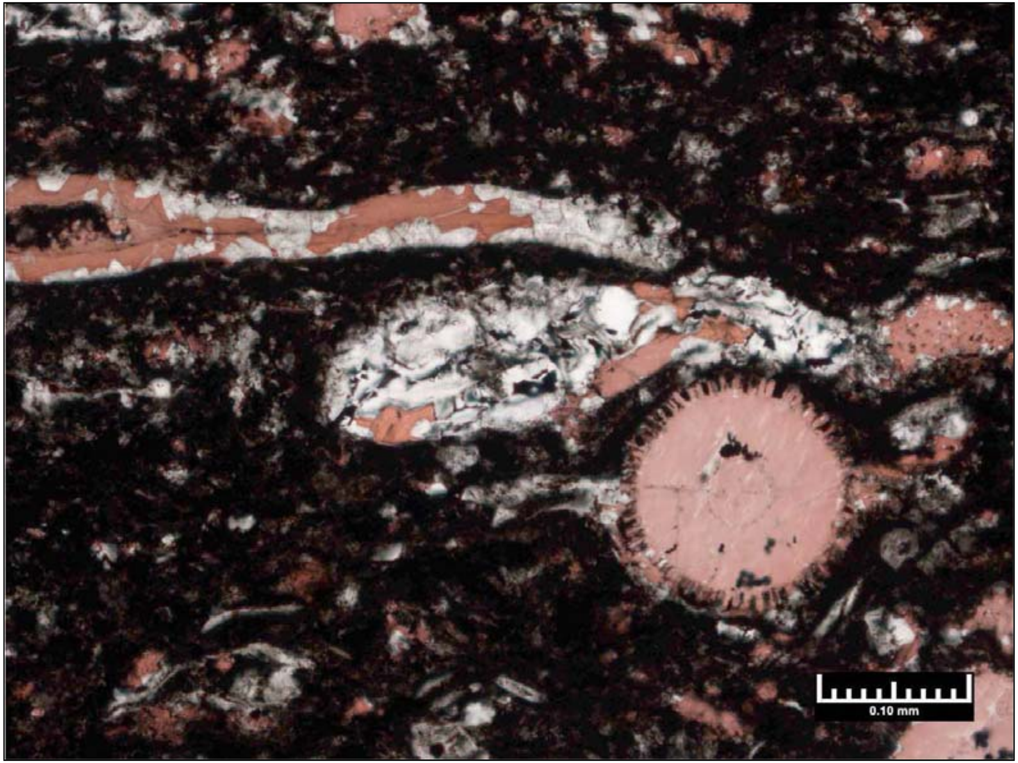
# Correlation of metamorphic facies, fluid zones, maturation stages, and organic maturity indices (Isabel Abad, 2010)

| Metapelitic zone (depth, km) | Temperature (°C) | KI(Δ°2θ) | % Illite in I/S | TEM mean illite crystallite thickness (Å) | Illite-muscovite polytype | Typical pelitic lithologies | Characteristic microfabrics | Metamorphic facies | Fluid zone | Maturation stages | Vitrinite reflectance Rr% | Conodont alteration index (CAI) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Shallow diagenetic zone | | | | | | | | | | Diagenesis | | 1 |
| 3.5-4 | ~100 | ~1.00 | 60-80 | | $1M_d$ (1M?) | shale/ mudstone | | zeolite | HHC | | 0.5 | |
| Deep diagenetic zone | | | | | | | bedding-parallel ($S_0$) | | | Catagenesis | 1.35 | 2<br>3 |
| 6.5-8 | ~200 | 0.42 | ~90 | 200 | | | | | | | 2.00 | |
| Low anchizone | | | | | $2M_1$ (3T) | slate | crenulated($S_0$)<br>slaty | prehnite- pumpellyte | ($CH_4$) | Metagenesis | | 4 |
| | | 0.30 | 95 | 400 | | | | | | | 3.00 | |
| High anchizone | | | | | | | cleavage ($S_1$) | | | | 4.00 | 5 |
| 10-12 | ~300 | 0.25 | >99 | 500 | | | | | | | | 5.5 |
| Epizone | | | | | $2M_1$ (3T) | slate (phyllite) | ($S_{1+}$) | greenschist | ($H_2O$) | | | |

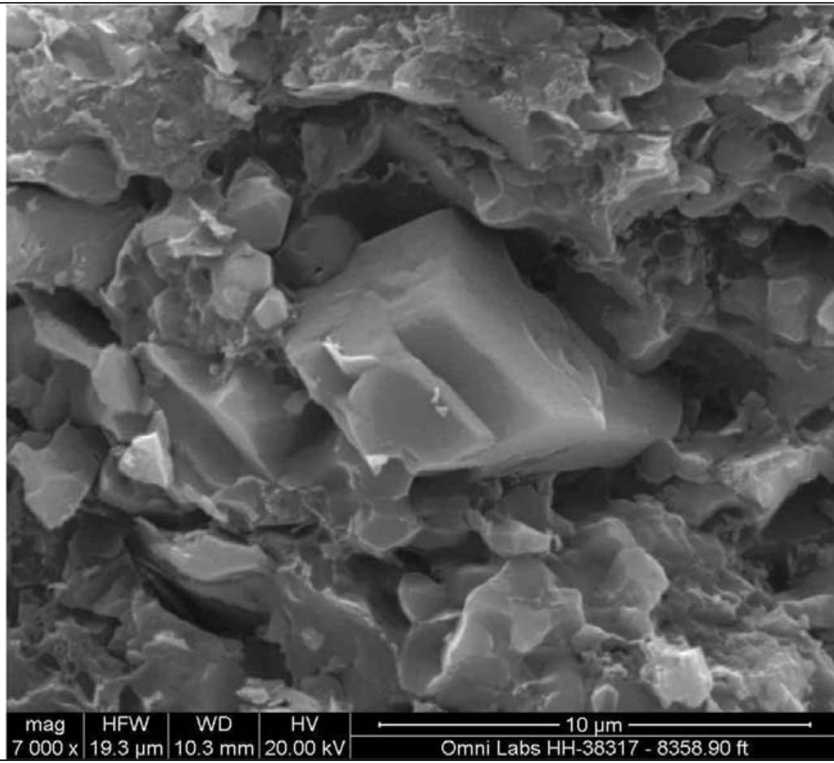
# Calcite

- **Finely crystalline equant spar replacing allochems and filling fossil molds**
- **Micron- and decimicron-sized crystals dispersed in clay and organic matrix**
- **Discontinuous parallel laminations of microspar and pseudospar:**
  - **Associated with minor amounts (trace to 2.5%) of anhydrite**





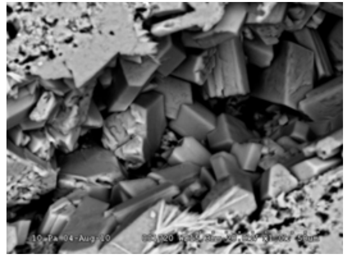

***Presenter's Notes:*** 8361.7 feet, TOC = 2.0 wt. %.

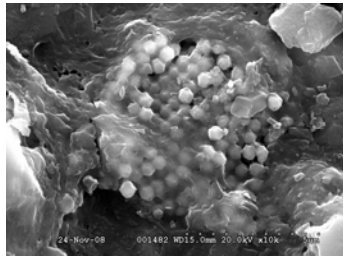

mag
7 000 x
HFW
19.3 µm
WD
10.3 mm
HV
20.00 kV
10 µm
Omni Labs HH-38317 - 8358.90 ft

# Additional Minerals (mean %)

- **Authigenic albite (9%)**
- **Authigenic pyrite (4%)**
- **Authigenic chlorite (4%)**
- **Authigenic dolomite, apatite, kaolinite**

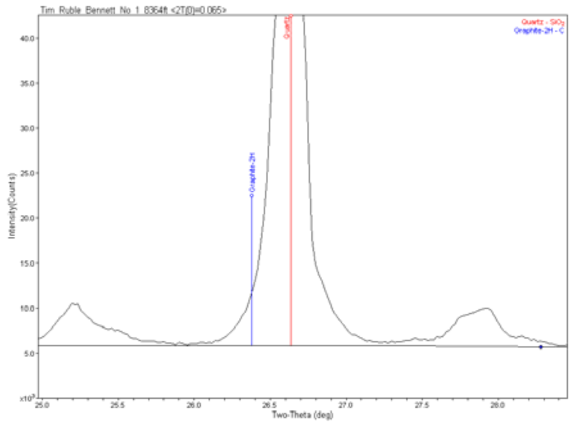
  **and zeolites (1% each)**
- **Trace amounts of ankerite, siderite, k- feldspar, muscovite, rutile, and anatase**
- ***“Graphite”***





# Actually a carbonaceous, graphite-like residue

- **3 wt. % of sample from 8364 ft.**
- **Graphite-like atomic arrangement developed in kerogen and pyrobitumen as a function of high burial temperatures:**
  - **Increased aromaticity**
  - **Highly condensed ring systems**
  - **Increased dimensions of aromatic clusters:**
    - **aromatic layers ordered enough to develop a graphite-like structure.**

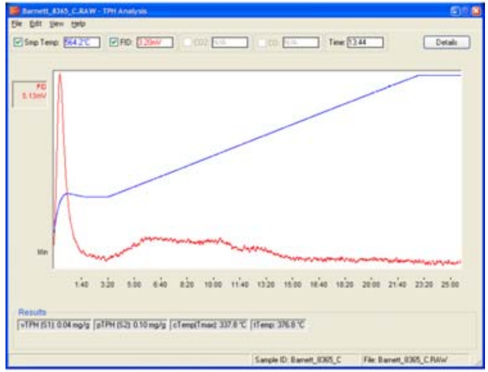



***See Harrison, 1979 SEPM Special Publication 26, p. 45 – 53.***

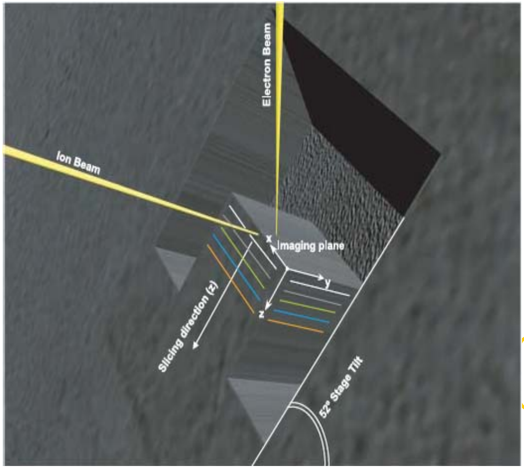
***Presenter's Notes:*** 3 wt % of sample from 8364 ft = graphite from x-ray diffraction using whole-pattern fitting and Reitveld refinement: Quantitative phase analysis using calculated full patterns as a method of refining crystal structures using neutron powder diffraction data. Minimize the sum of the weighted squared differences between observed and calculated intensities.

# Graphitic Marcellus Sample

- TOC = 4.39 wt.%
- Abundant pyrobitumen
- High-temperature pyrolysis shows no response in the 600˚ – 800˚C region of the pyrogram where pyrobitumen is typically detected.
- Undetected by the FID due to highly aromatic graphitic nature?



# Dual Beam FIB/SEM 3D Model




L. HOLZER, et al., *Journal of Microscopy*
*Vol. 216, Pt 1 October 2004, pp. 84–95*

Acquire images

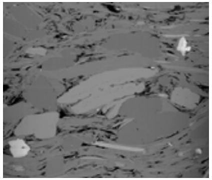
Set of images

Align image stack

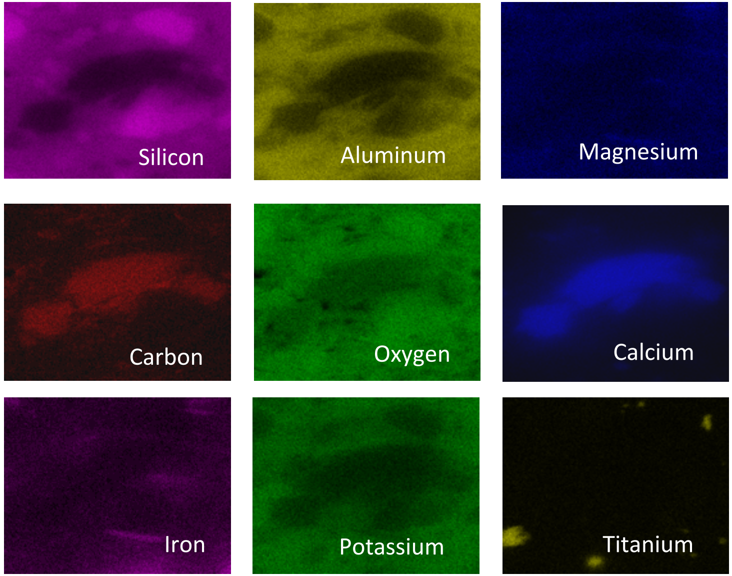
Reconstruct 3D Volume

3D model

# Marcellus Sample 20 keV EDS Maps

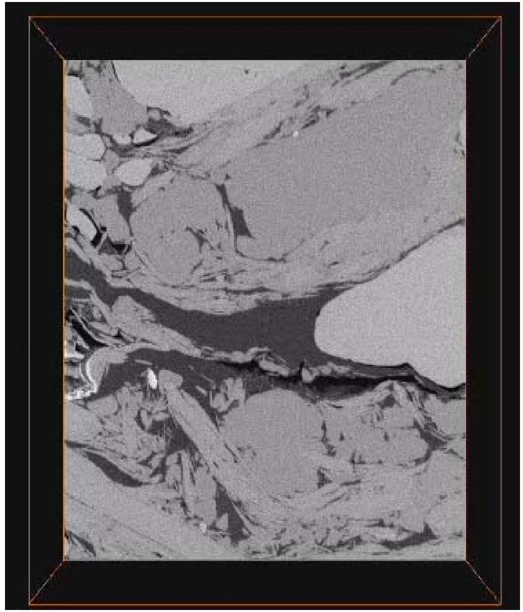


20 keV EDS
At 2.7 nA



# Marcellus 3D Model (8363 ft.)

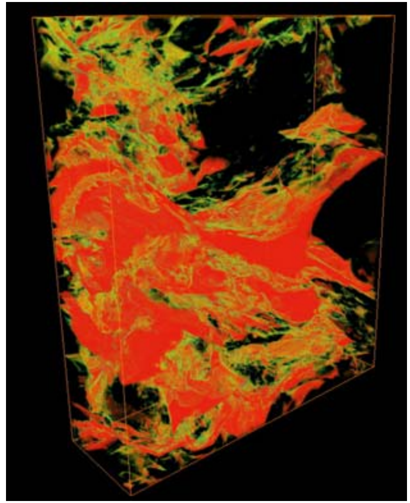
- TOC = 4.39 wt. percent
- Porosity = 4.97 percent
- Data set
  - 1 keV; 340 pA Backscatter Electrons
  - Image Resolution of 4096 x 3536 pixels
    - Pixel Dimensions (2 nm X 2.5 nm X 10 nm)
  - Horizontal Field Width of 8 µm
  - Number of Slices 220
  - Slice Thickness: 10 nm
  - Voxel Size: 50 $nm^3$
    - Image) s resolution times slice thickness (2 nm X 2.5 nm X 15 nm)



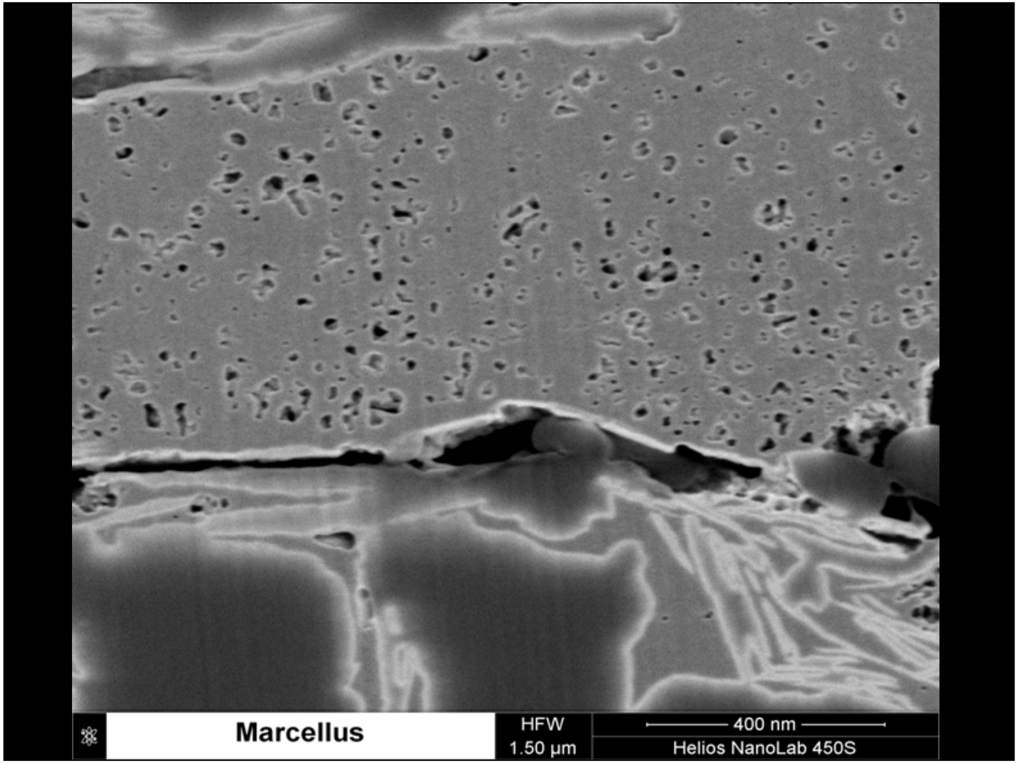
***Presenter's Notes:*** 8 µm – 10 µm (image dimensions) is the size of fine to medium silt between 1/64 – 1/128 mm or 7 – 6 phi).

# Porosity in the Marcellus Formation

- As received porosity:
  - 2.44 – 16.6 % of BV
- Organic porosity:
  - Interconnected nanopore- to micropore-scale voids in pyrobitumen and kerogen
- Carbonate pore textures:
  - Moldic
  - Intercrystalline
- Intercrystalline porosity in clay matrix



***Presenter's Notes:*** 8363 feet: porosity = 4.97%; TOC = 4.39 wt.%.

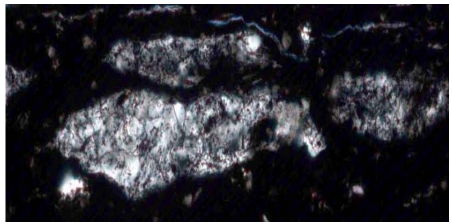

Marcellus
HFW
1.50 μm
400 nm
Helios NanoLab 450S

# Diagenetic History

- Deposition and early diagenesis
- Mechanical compaction and dewatering
- Chemical compaction
- Organic catagenesis and metagenesis
- Low anchizone metamorphism
- Porosity loss and development
- Fate of hydrocarbons

# Deposition and Early Diagenesis

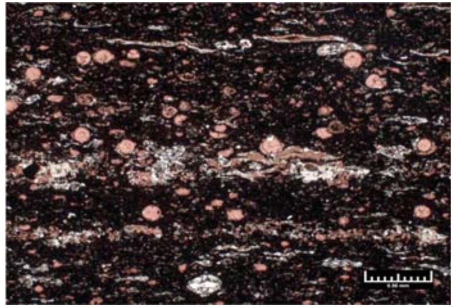
- Organic aggregates of planktonic tests, radiolarians, fecal pellets, and clay descend through the water column (“*marine snow*”)
- Microbial degradation and micro-anoxic environment within the snow particles in shallow-water column and bottom sediments
- Rapid episodic suspension settling after phytoplankton blooms (episodic anoxia?)
- Deposition beneath an oxic/sub-oxic to seasonally anoxic, density-stratified shallow-marine water column
- Hypersaline bottom conditions with restricted benthos; anoxic sediment within cm’s of the sediment/water interface.

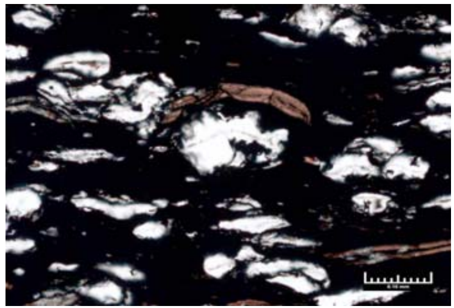


*See Macquaker, 2010 and 2011 AGC*

# Deposition and Early Diagenesis

- Dissolved oxygen depleted from pore waters a few tens of cm beneath the sediment/water interface:
  - Sulfate reduction and iron sulfide, siderite, ankerite cementation
  - Carbonate precipitation
- ***Biogenic silica dissolution and redistribution – development of major diagenetic silt***
- Muds contain 70% to 90% water by volume, but expulsion of excess pore water accelerates as burial compaction increases.





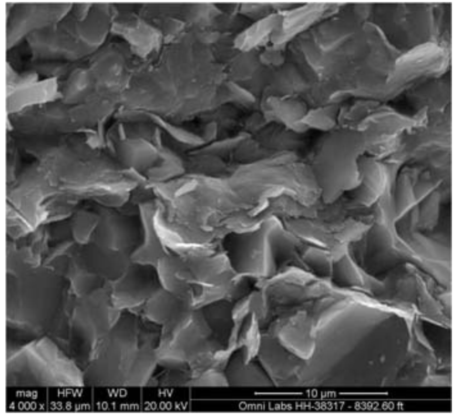
***Presenter's Notes:*** Diagenesis dominated by redox processes involving organic matter and the products of organic-matter decomposition.

# Mechanical Compaction and Dewatering

- Compaction reduces thickness of deposited sediment
- At 1 – 1.5 km burial mudrocks still retain ~ 30% water mostly in the lattice of clay minerals and adsorbed onto the clays
- Early catagenesis and petroleum generation at burial temperatures ~ 60˚ - 70˚ C

# Chemical Compaction and Organic Catagenesis

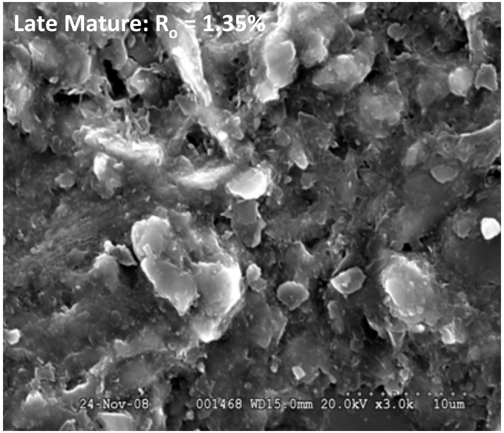
- **Burial depths 4 to 7 km and temperatures to 180˚C:**
  - **Dehydration of clays**
  - **Increasing crystallinity of illite**
  - **Quartz cementation and rock hardening (porosity loss)**
- ***Smectite + $Al^{+3}$ + $K^{+5}$ = illite + chlorite + quartz***
- ***Peak oil through wet gas generation and expulsion***

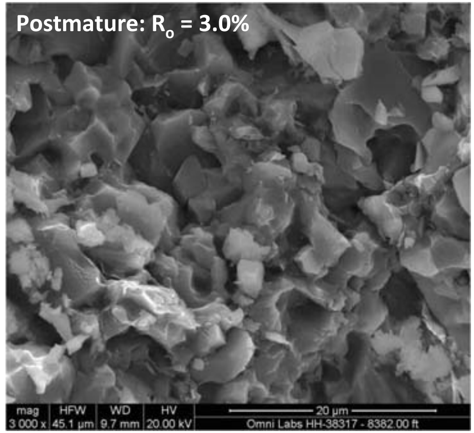


# Organic Metagenesis

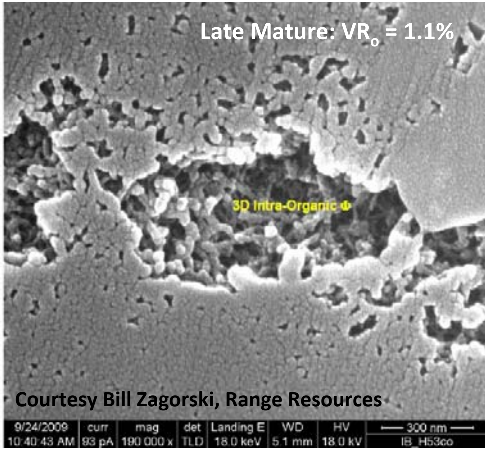
- **Maximum burial depth > 8 km and temperatures ~ 200˚ - 250˚C**
- **Residual bitumen and petroleum crack to $CH_4$; aromatization (graphitization)**
- **Evolution of organic porosity**
- ***Late-stage methane?***
  - $C_{20}H_4 = 19C + CH_4$
  - $C_{20}H_4 + 2H_2O = 17C + 2CH_4 + CO_2$
  - $C + 2H_2O + 4Fe_3O_4 = 3Fe_2O_3 + CH_4$
- ***Hydrocarbon destruction?***
- ***Uplift; overpressure?***

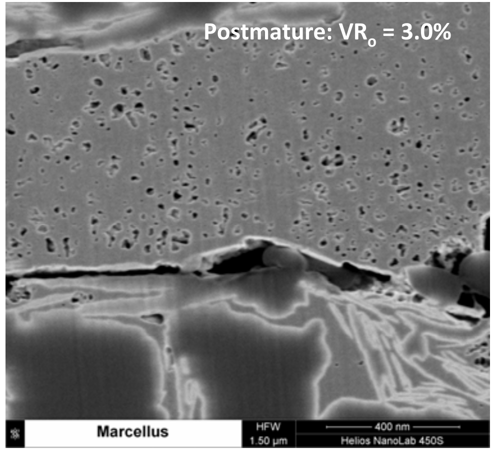
# Porosity loss: mechanical and chemical compaction



# Organic porosity development and changes



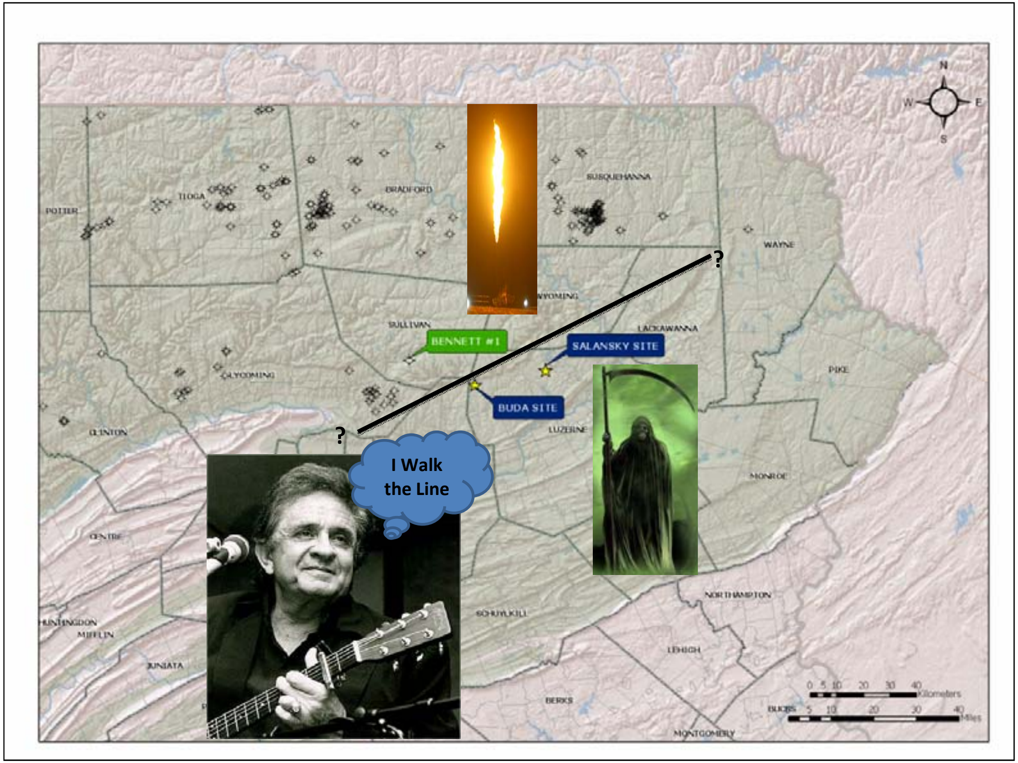

***Presenter's Notes:*** RANGE: Marcellus – 2-4 percent organic porosity.

## Several Key Marcellus Formation Reservoir Attributes In The Bennett #1 Well Core Yield Desired Results:

- **Mean rock composition:**
  - **33% quartz:**
    - **≥ 90% biogenic ("authigenic silt")**
  - **20% carbonate:**
    - **19% calcite; 1% dolomite**
  - **32% clay**
    - **Essentially no expandability**
- **$TOC_{pd}$:**
  - **O.58 to 11 wt. percent**
  - **Mean $TOC_{pd}$ = 4.91 wt. percent**
- **Thermal maturity:**
  - **Dry gas window**
    - **$\%R_o$ = 2.54 to 3.22 (2.99 mean)**
    - **Thermogenic dry gas**
- **Porosity and permeability:**
  - **Porosity: 2.44 to 16.6% of BV**
  - **Permeability (pressure-decay): 0.000047 to 0.000217 md**
- **Free versus sorbed GIP?**

***Parameters from Sondergeld and others, 2010***

***Presenter's Notes:*** Quartz: 8 – 46 %; mean = 33%.



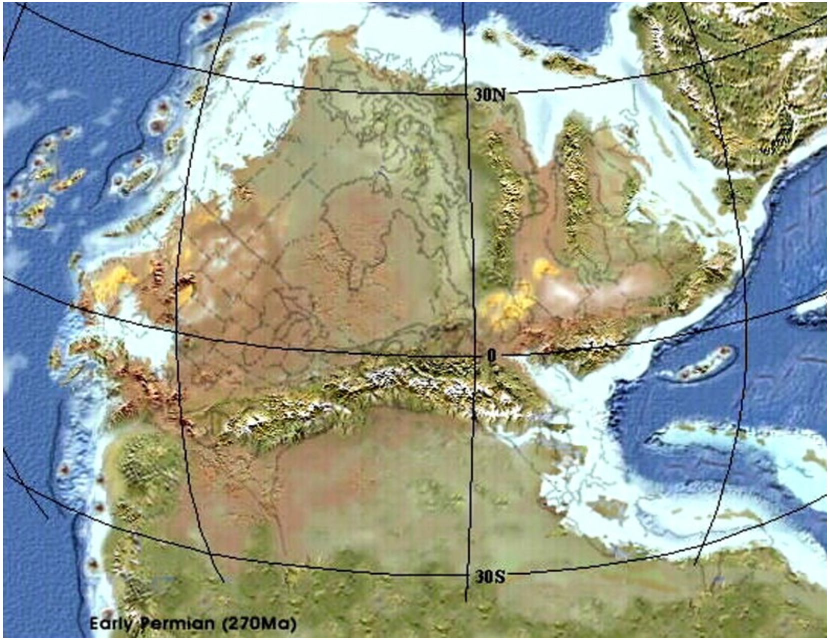
N
W
E
S
POTTER
TIOGA
BRADFORD
SUSQUEHANNA
WAYNE
SULLIVAN
BENNETT #1
SALANSKY SITE
LACKAWANNA
LYCOMING
BUDA SITE
PIKE
CLINTON
LUZERNE
?
?
I Walk the Line
MONROE
CENTRE
NORTHAMPTON
SCHUYLKILL
HUNTINGDON
MIFFLIN
JUNIATA
LEHIGH
BERKS
BUCKS
MONTGOMERY
0 5 10 20 30 40 Kilometers
0 5 10 20 30 40 Miles

# Critical elements for the economic preservation of natural gas in highly mature ($R_o$ > 3%) strata:

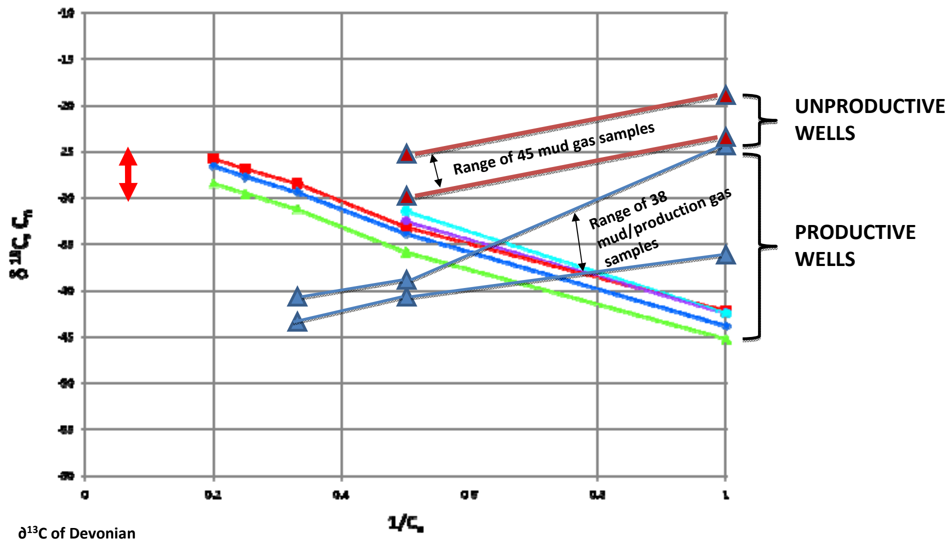
1. ***Generation, migration, and accumulation of $CH_4$ and nonhydrocarbon gases ($CO_2$, $N_2$, $H_2S$) during late catagenesis and metagenesis. Hydrocarbon destruction (TSR etc.).***
2. ***Effectiveness and longevity of seals exposed to deep burial, high temperatures, and tectonic deformation.***
3. **Diagenesis of rocks exposed to deep burial and high temperatures.**

**- Houseknecht and Spötl, 1993, *Empirical observations regarding methane deadlines in deep basins and thrust belts*, USGS PP 1570, p. 217 – 231.**

# Fate of the Hydrocarbons?



# Marcellus Gas Isotopes, Southwestern versus Northeastern Pennsylvania

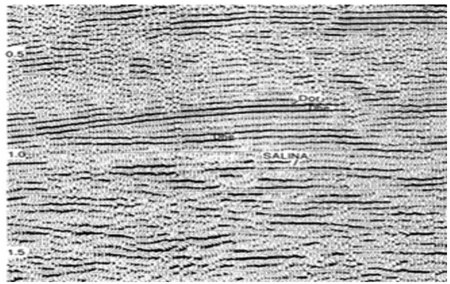



$\partial^{13}C$ of Devonian Organic Matter (Maynard, 1981)

# Effectiveness and Longevity of Seals?

- Elevated temperatures
- Abnormal fluid pressures
- High confining or tectonic pressures accompanying deep burial in sedimentary basins and thrust belts

*Courtesy Duff Gold, Pennsylvania State University*




Houseknecht and Spötl, 1993

# Conclusions

- Integrated high-resolution petrologic techniques and organic geochemistry provide a powerful approach to investigating the diagenesis and reservoir characteristics of post-mature shale-gas prospects.
- The data obtained by such an approach address several key attributes of thermogenic shale-gas reservoir properties in the Marcellus Formation of northeastern PA that were subjected to deep burial and high temperatures:
  - Rock composition
  - TOC
  - Thermal maturity
  - Porosity and permeability
  - Free and sorbed gas?

# Conclusions

- **Although post-mature, early metamorphic Marcellus Formation rocks may still exhibit desirable shale-gas reservoir characteristics, several critical elements remain ambiguous:**
  - ***Permeability to gas with increasing aromaticity of organic matter***
  - ***Graphitization of kerogen and $R_t$?***
  - ***Methane stability in the metagenetic zone***
  - ***Geologic structure and integrity of reservoir seals***


Courtesy Duff Gold, Pennsylvania State University
?