Application of Neutron Scattering to Earth Science – the Legacy of David Mildner

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Earth Science and Neutron Scattering

Neutron diffraction – mineral structure, element site specificity, order-disorder, phase transition kinetics, textural analysis, water and solute structure

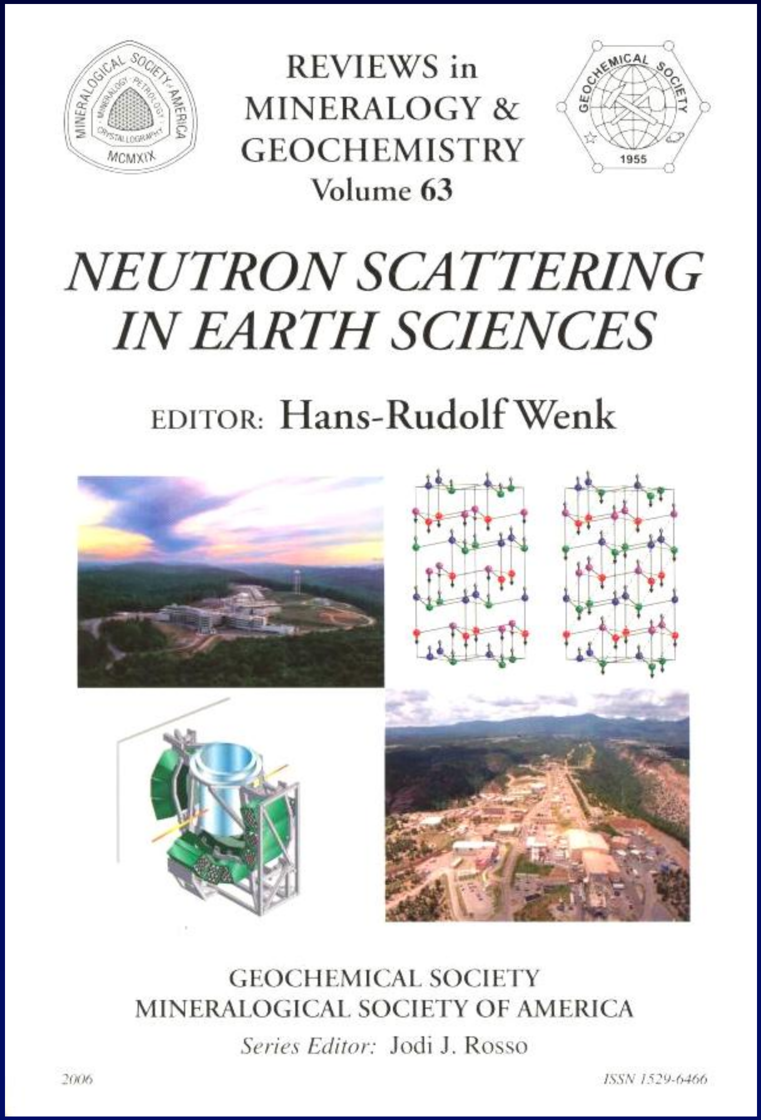
Inelastic neutron scattering – phono excitations, electron-phono coupling, hydrogen vibrational density of states

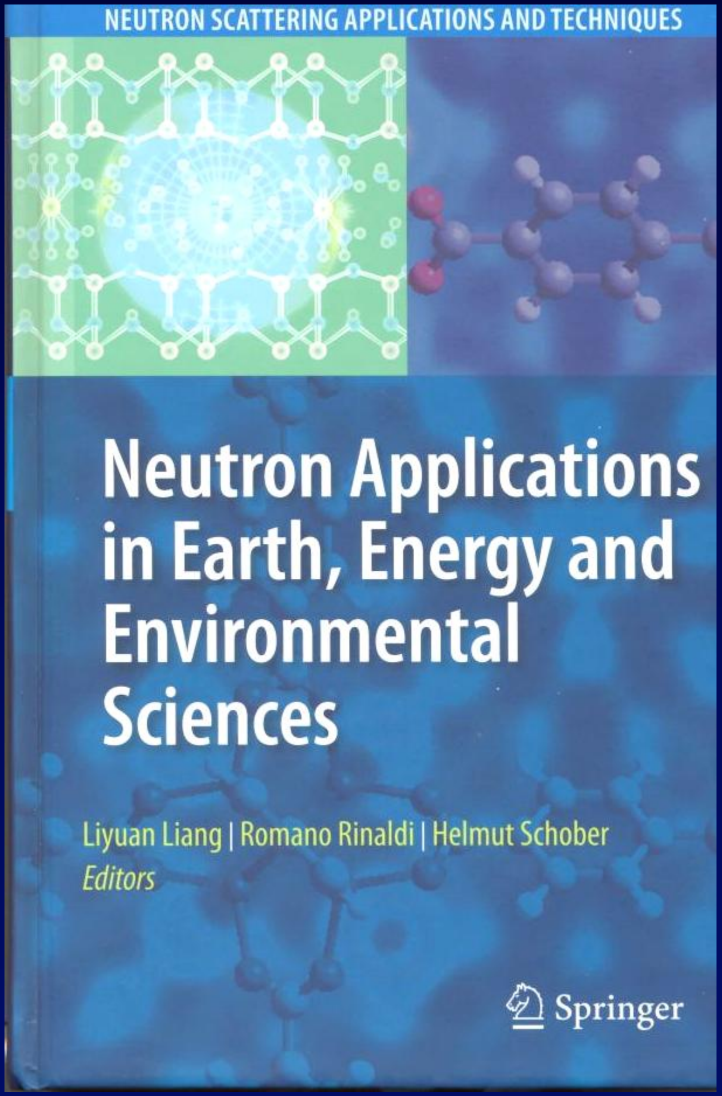
Quasielastic neutron scattering – hydrogen diffusive motion and relaxation, collective excitations in condensed matter

Neutron reflectivity – mineral surface structure, sorbates on surfaces, diffusion in near surface layer

Small/ultra small angle NS -– pore features (e.g., pore size, volume, surface area, fractality), sorbed fluid behavior

Earth Science and Neutron Scattering





Motivation

Pores and pore network control the flow of fluids in the subsurface and reactions with host rock

What do pore structures look like in reservoir and seals or caprocks?

How do we quantify their size, distribution and connectivity?

Is pore mineralogy different than the bulk?

How do complex fluids wet them?

How do pores change during reaction?

Why is the nano- to microscale important?

Transport– large pores or fractures may control flow but total accessible surface area may be at these scales

Pore Throats – on the micron scale or smaller

Fluid Confinement – reduced dimensionality (interfaces, nanopores) impacts thermophysical, dynamics and transport properties (e.g., sorption)

Porosity – nanopore volume may be non-trivial

Fluid Separation – chromatographic effects

Rock Strength – fracture initiation, pore collapse

Natural Systems at the Nano- to Microscale

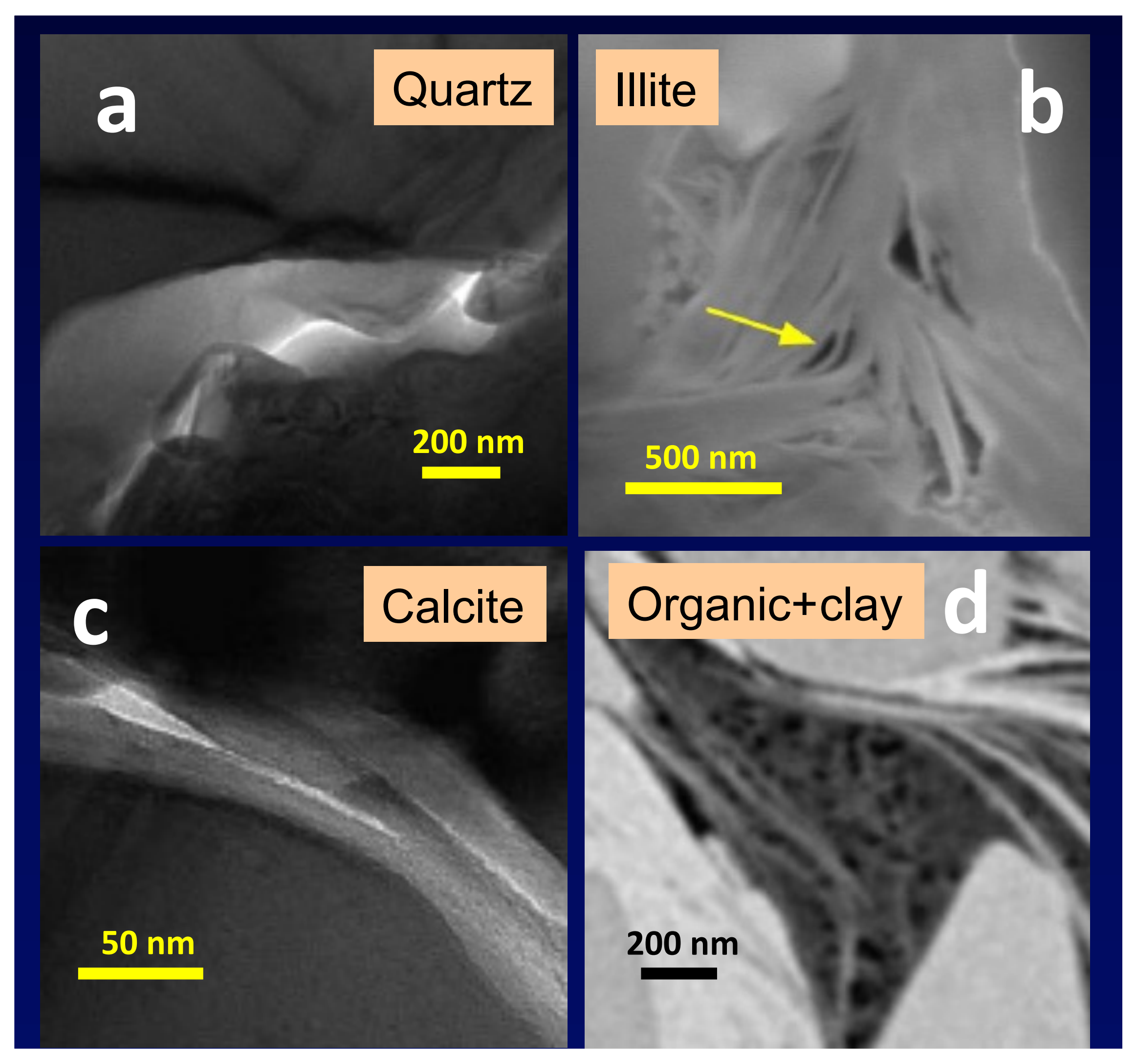
Standard Petrophysics: MICP plus BET

SANS/USANS coupled with SEM/BSE, TEM, dual-beam FIB/SEM, µXCT

Pore sizes: 10^8 orders of magnitude; non-trivial % are below 100 nm

May comprise a significant fraction of RSA

These host hydrocarbons, volatiles, aqueous soln'

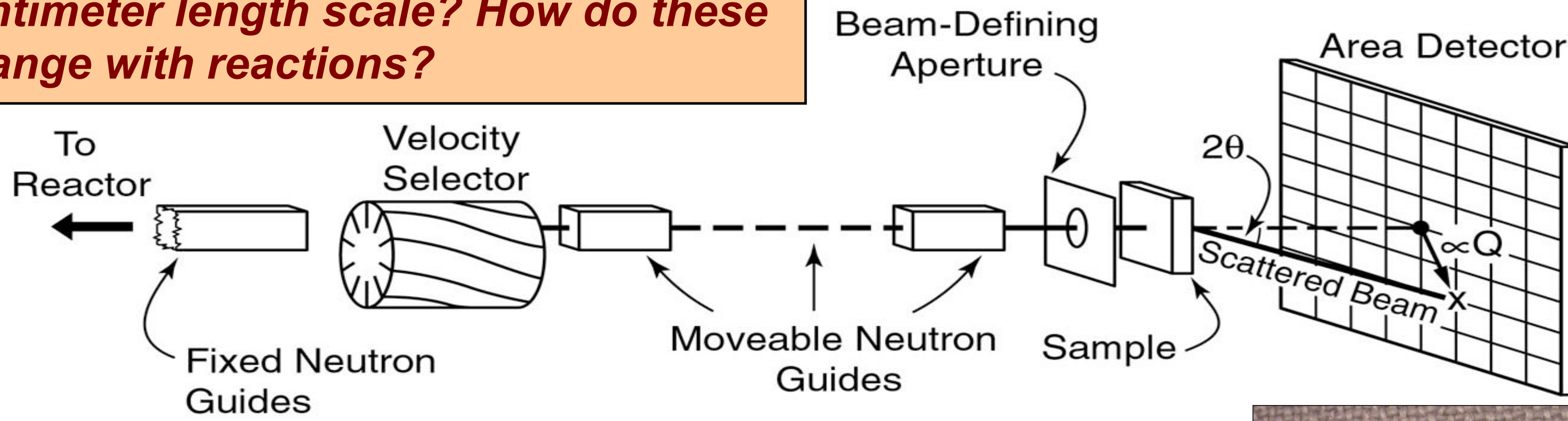


Anovitz et al. 2009, 2013, 2015 GCA; Arthur and Cole 2014, Elements; Swift et al., 2014; Anovitz and Cole, 2015, MSA RiMG

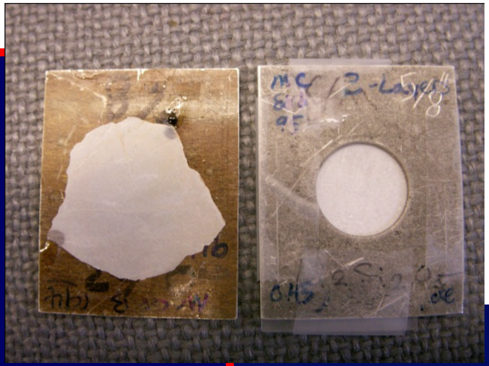
Small Angle Neutron Scattering

What is the pore size, pore distribution, pore connectivity at the nanometer to centimeter length scale? How do these change with reactions?

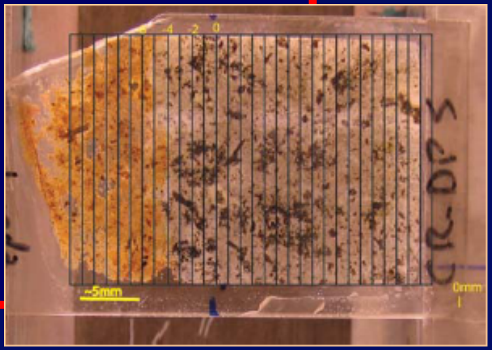
Complements BET; Hg porosimetry



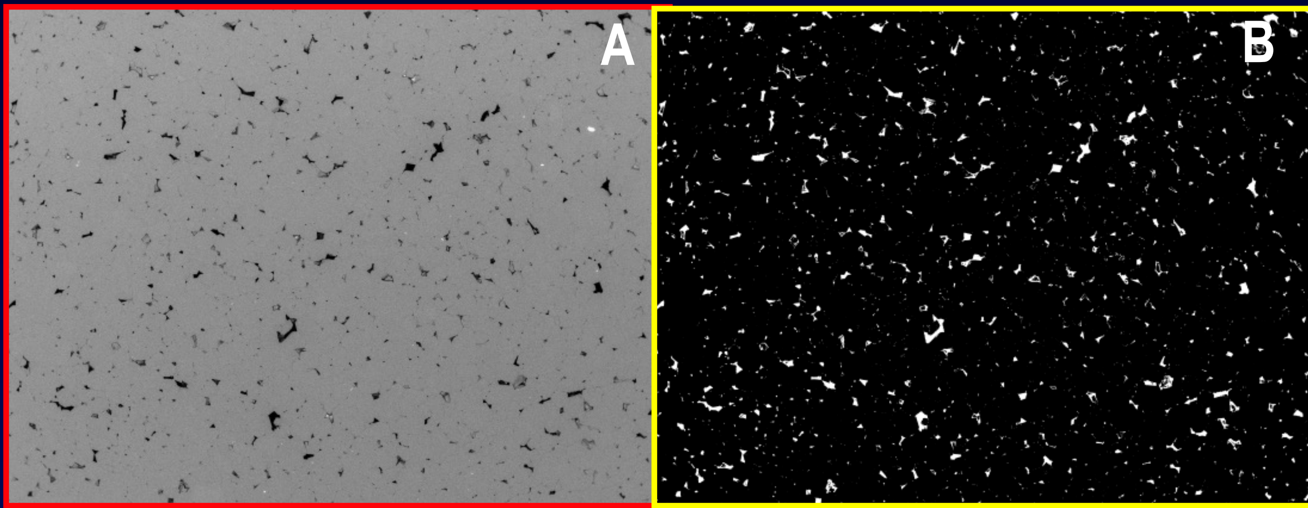
- SANS: structures on length scales 5 – 2000 Å (micro- & mesoscopic)
- Combination with WANS, USANS, BSE, SALS: lengths 1 Å – ~1 cm
- High penetration depth, H/D contrast variation (assess connected vs unconnected pores); *scattering length density differences*
- Pore features quantified:
  - Porosity
  - Pore size distribution
  - Pore surface area/volume
  - Pore connectivity
  - Surface & mass fractal nature of pores



~150 μm thick section
30-40 mm^3



Extension to low-Q: SEM/BSE

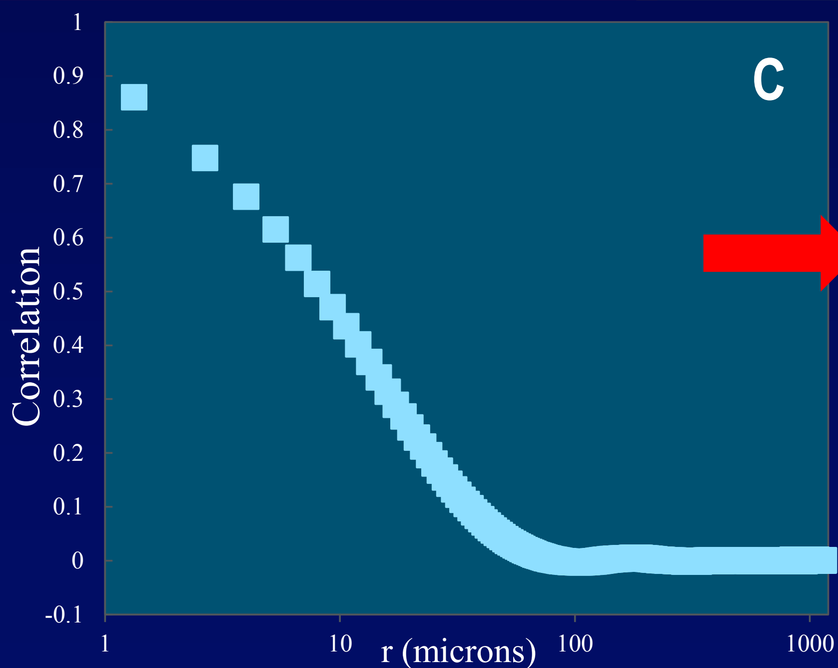


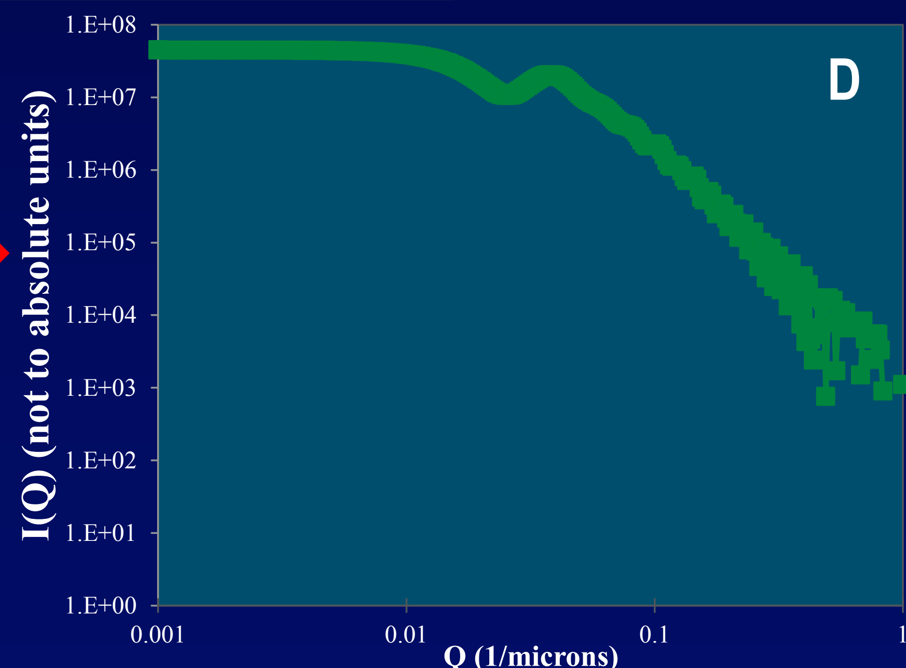
A) Original BSE Image 12.5 mm across

B) Binary Image

C) Calculated autocorrelation function

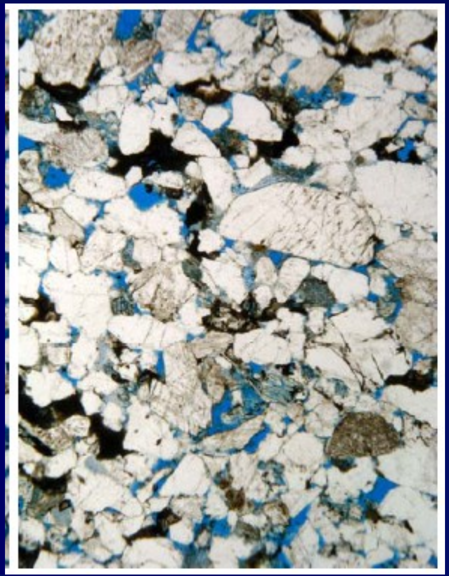
D) Calculated low-Q scattering curve



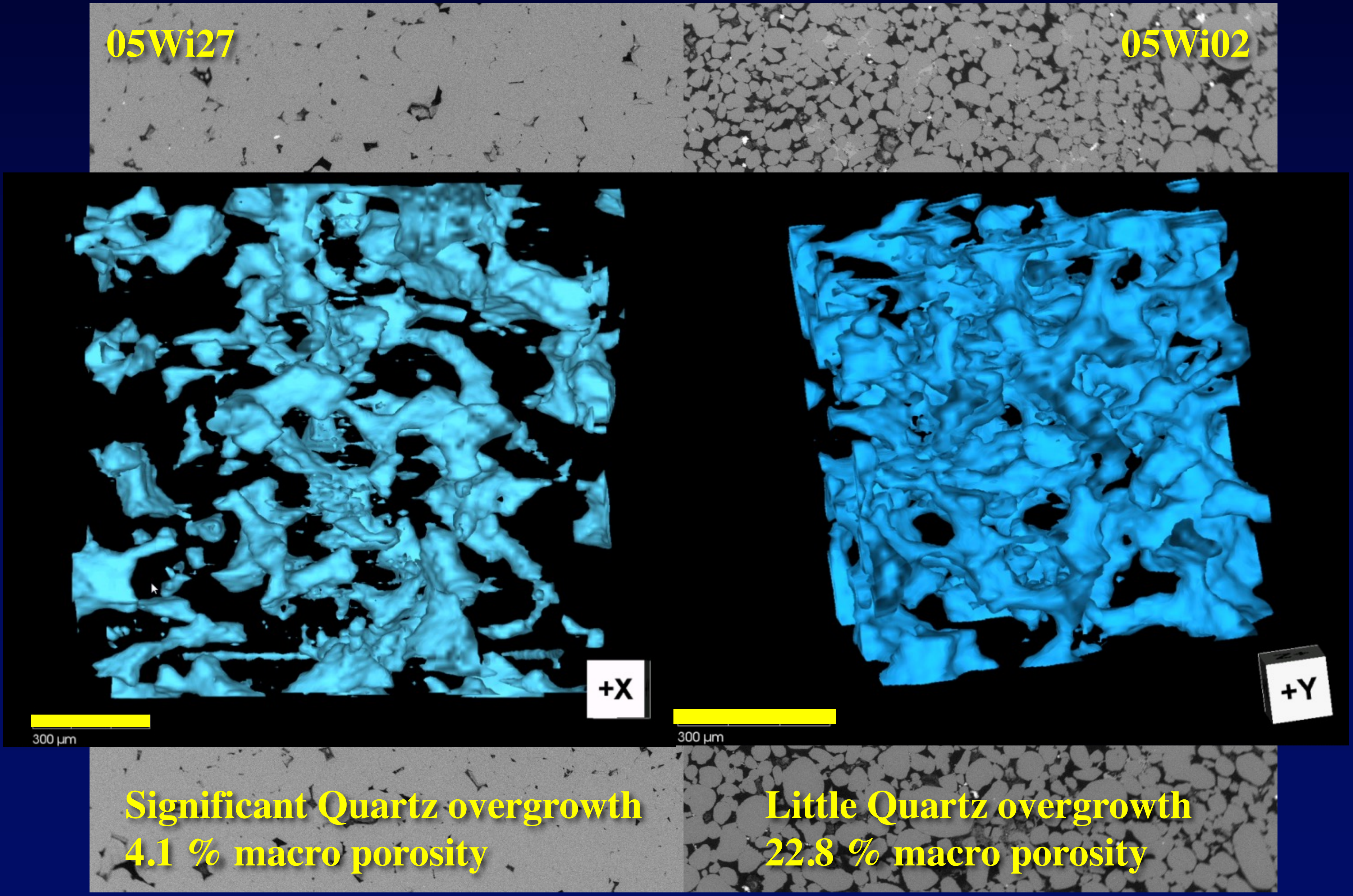


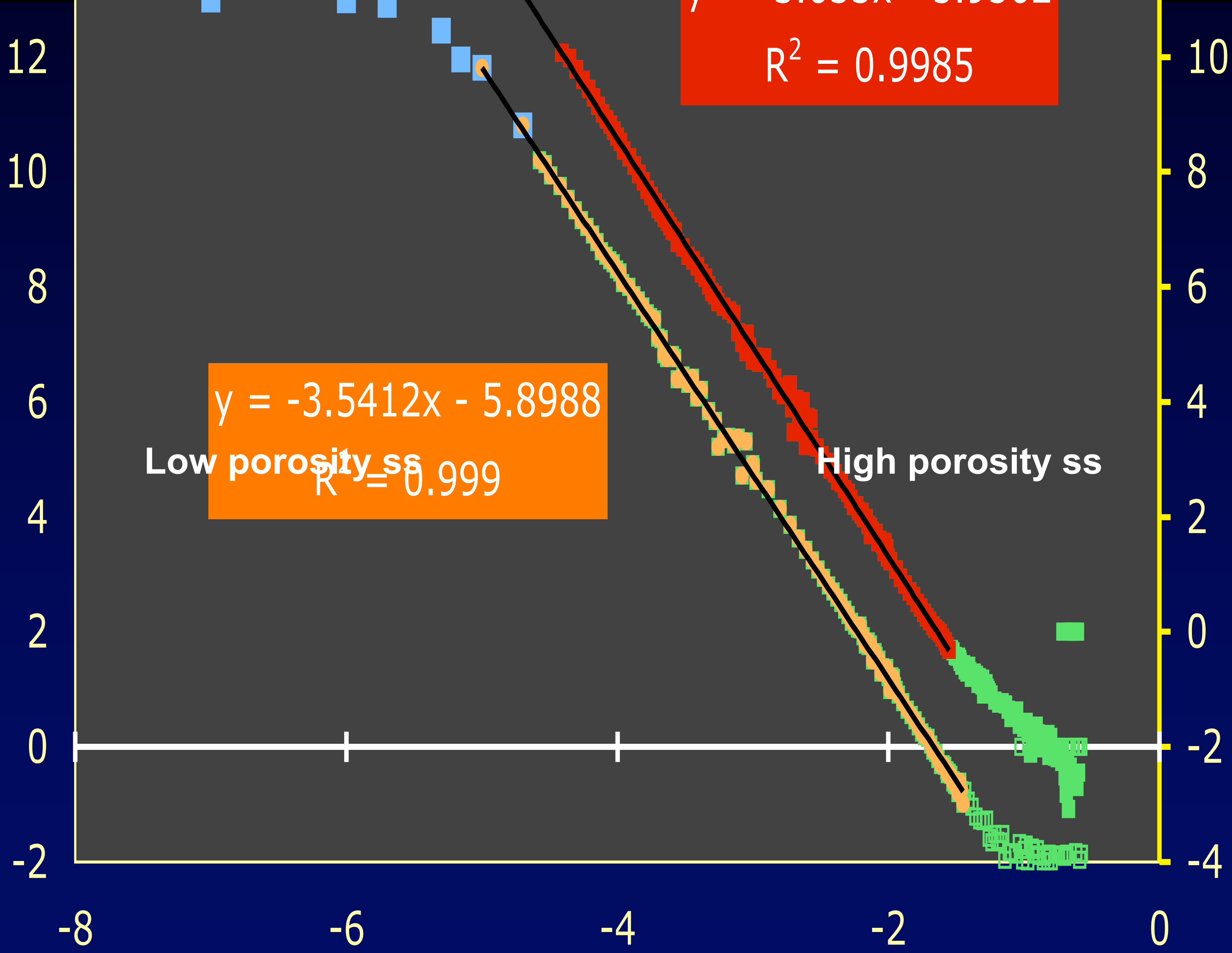
Images can also be used for multifractal analysis

Pore Features in Sandstone

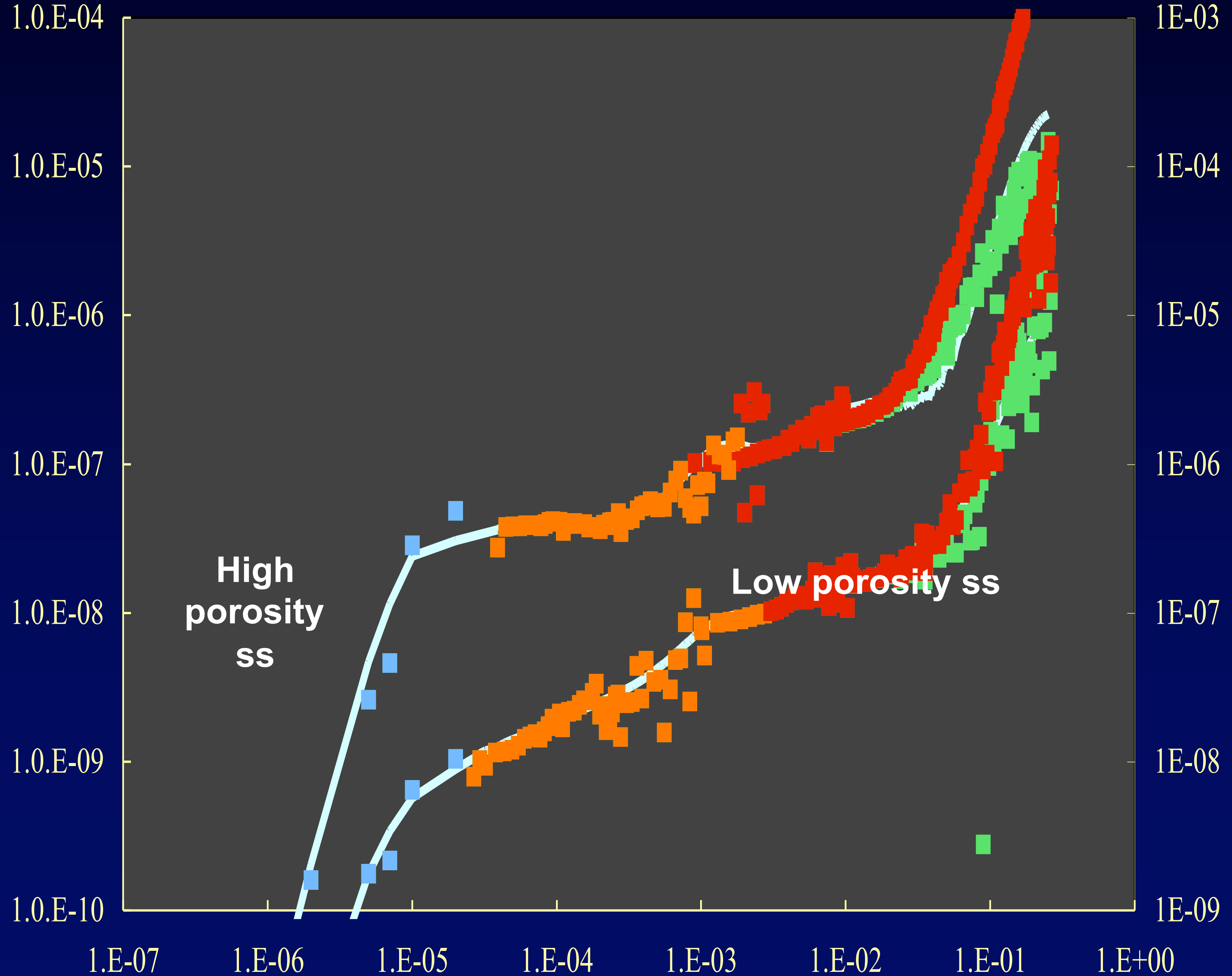


Imaging Reservoir Rock



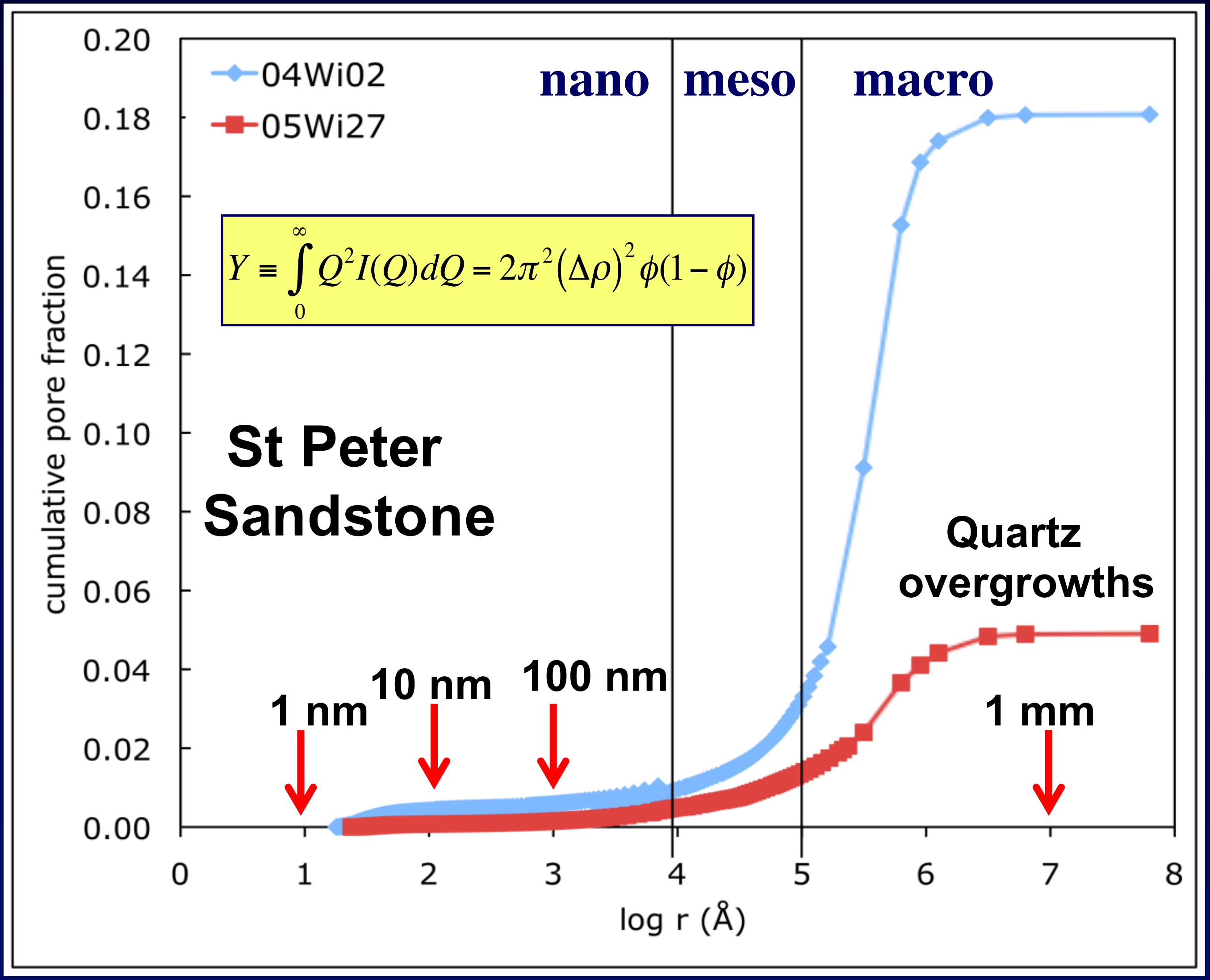


R2 = 0.9985
y = -3.5412x - 5.8988
R2 = 0.999
Low porosity ss
High porosity ss
12
10
8
6
4
2
0
-2
-8
-6
-4
-2
0
10
8
6
4
2
0
-2
-4



1.0.E-04
1.0.E-05
1.0.E-06
1.0.E-07
1.0.E-08
1.0.E-09
1.0.E-10
1E-03
1E-04
1E-05
1E-06
1E-07
1E-08
1E-09
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
High porosity ss
Low porosity ss

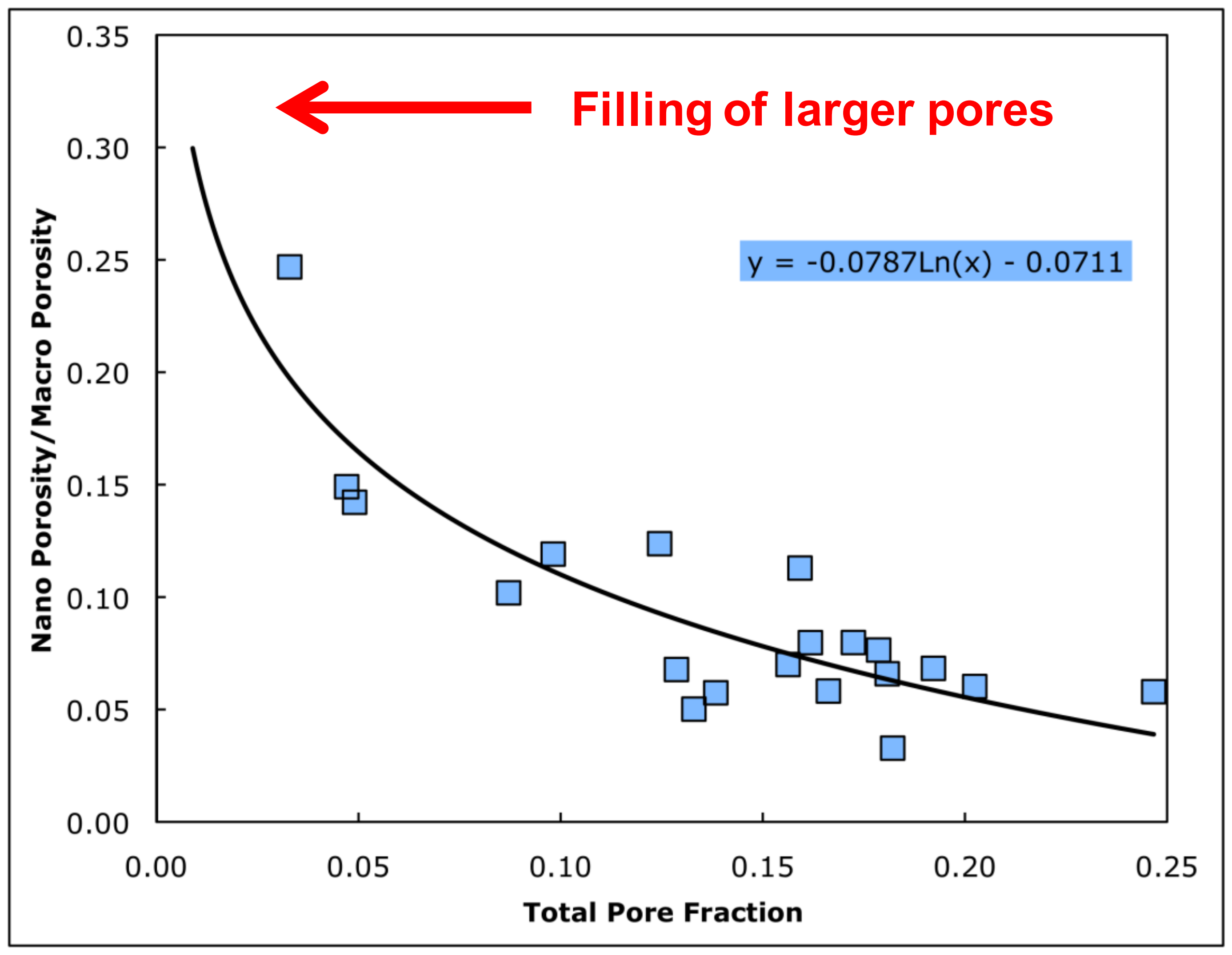
Cumulative Porosity



Reduced porosity at all scales

Anovitz L.M., Cole D.R., et al, *Geochim. Cosmochim. Acta*, (2013; 2015)

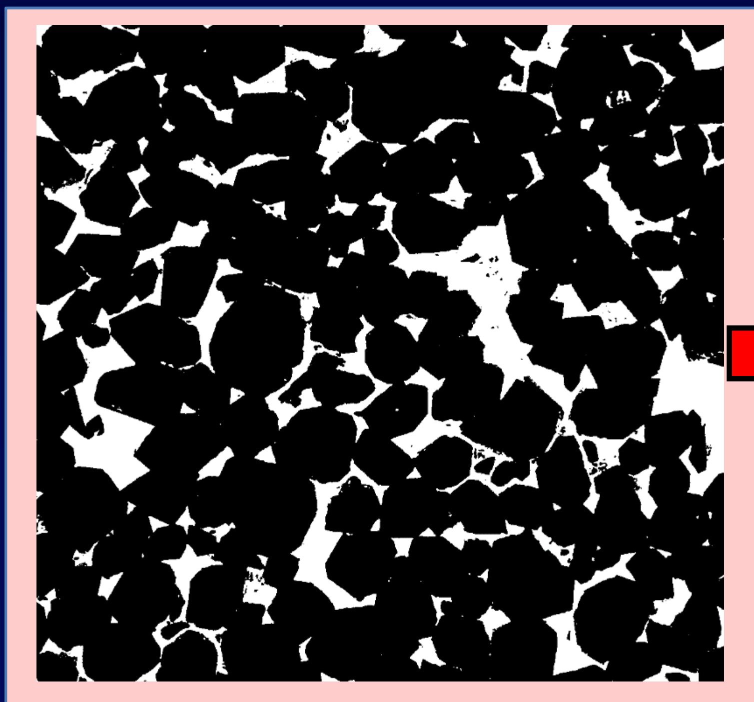
Nano/Macro Porosity as f(Total Porosity)



- Most change in total porosity is at macro scales

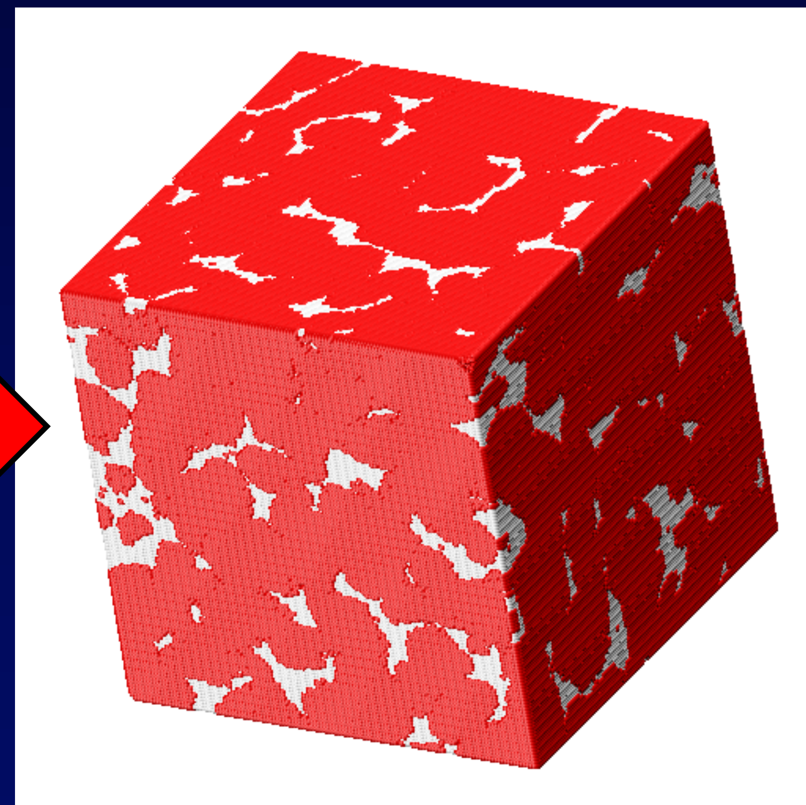
Multi-Point Geostatistics (MPS)

St. Peter sandstone, porosity ~20%
Backscattered electron (BSE) image[1]
coupled with U(SANS)



2mm x 2mm

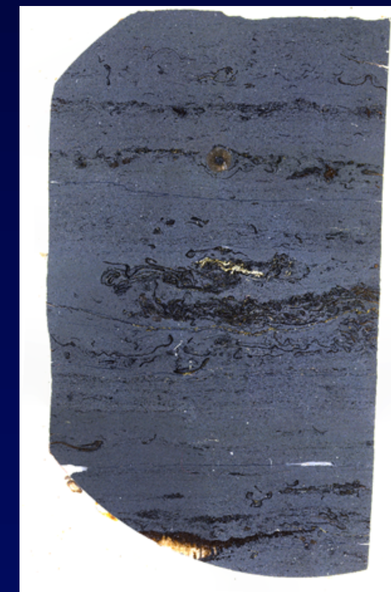
Reconstruction using MPS[2]
porosity ~17%

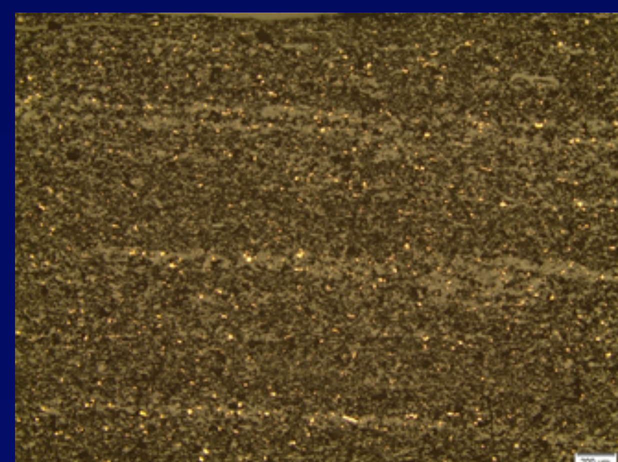


1mm x 1mm x 1mm

1) Anovitz L.M., Cole D.R., et al, *Geochim. Cosmochim. Acta*, (2013)
2) Mariethoz G., Kelly B.F.J, *Water Resour. Res*. **47**, W07527 (2011)

Pore Features in Shale





The Mildner Legacy in Earth Sciences

On the analysis of small-angle scattering with elliptical azimuthal symmetry

Peter L. Hall and D. F. R. Mildner
Research Reactor Facility, University of Missouri, Columbia, Missouri 65211

J. Appl. Phys. **54**, 427-428 (1983)

Pore size distribution of shaly rock by small angle neutron scattering

P. L. Hall[a] and D. F. R. Mildner
Research Reactor Facility, University of Missouri, Columbia, Missouri 65211
R. L. Borst
Phillips Petroleum Company, Research and Development, Bartlesville, Oklahoma 74004

Appl. Phys. Lett. **43**, 252-254 (1983)

Small-angle scattering of shaly rocks with fractal pore interfaces

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Phillips Petroleum Company, Research and Development, Bartlesville, Oklahoma 74004

Appl. Phys. Lett. **48**, 1314-1316 (1986)

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 91, NO. B2, PAGES 2183–2192, FEBRUARY 10, 1986

Small-Angle Scattering Studies of the Pore Spaces of Shaly Rocks

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J. Phys. D: Appl. Phys. **19** (1986) 1535–1545. Printed in Great Britain

Small-angle scattering from porous solids with fractal geometry

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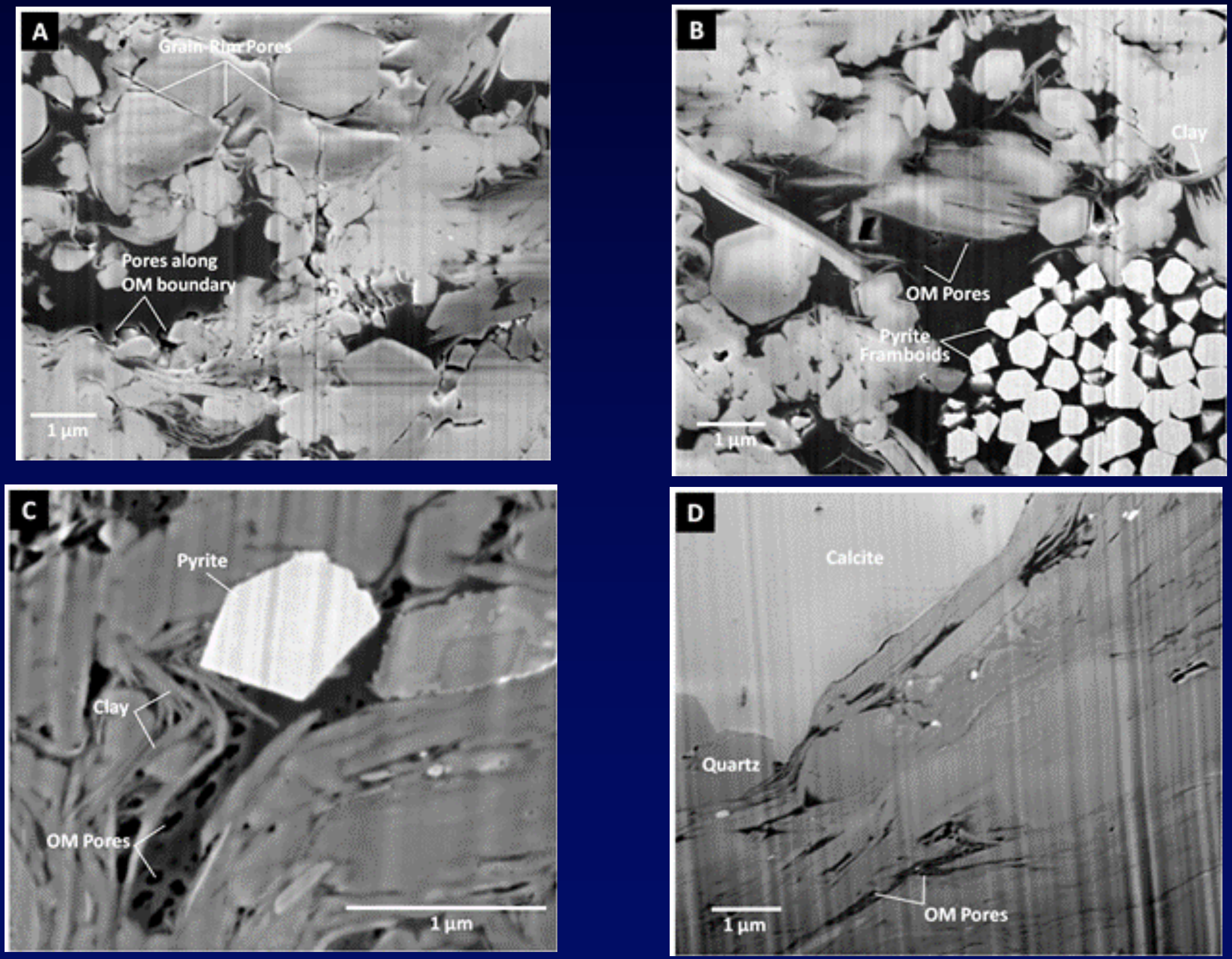
Pore Features in the Marcellus Shale

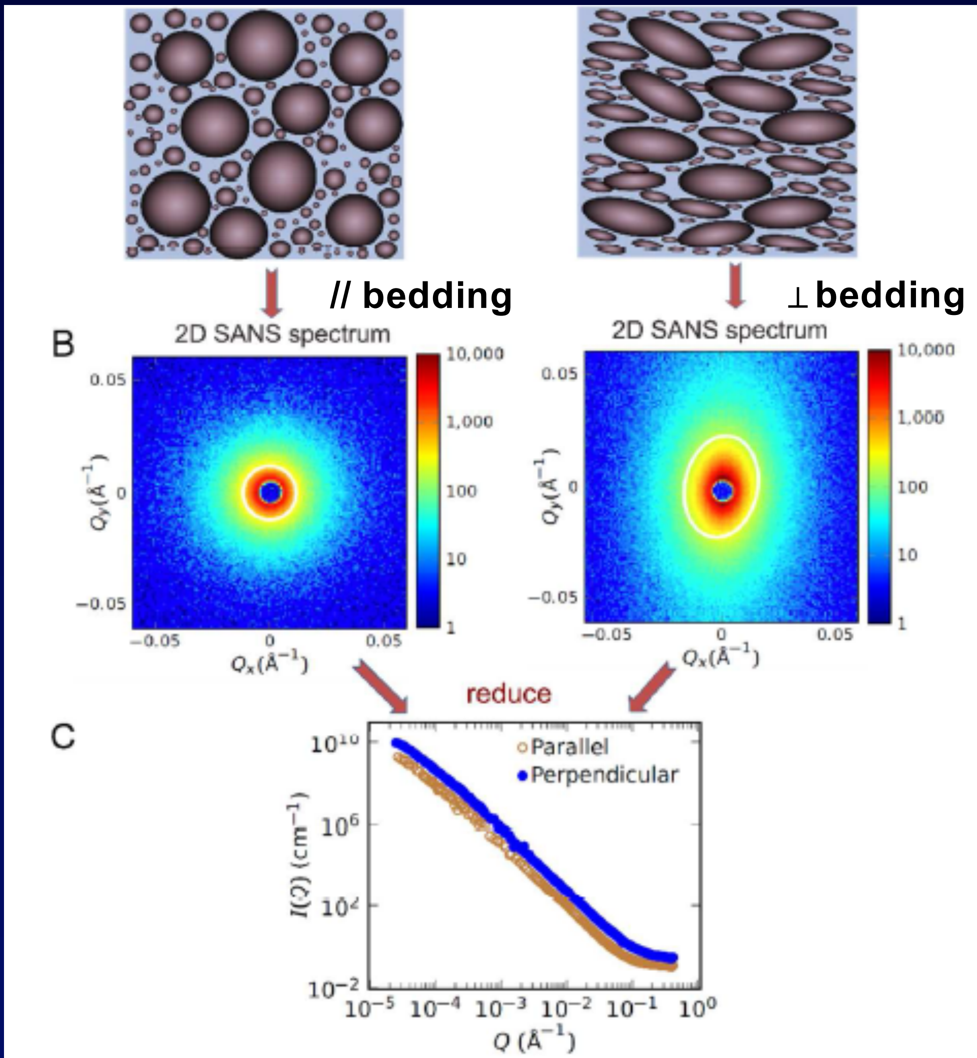


X. Gu et al. (2015) *Energy & Fuels*

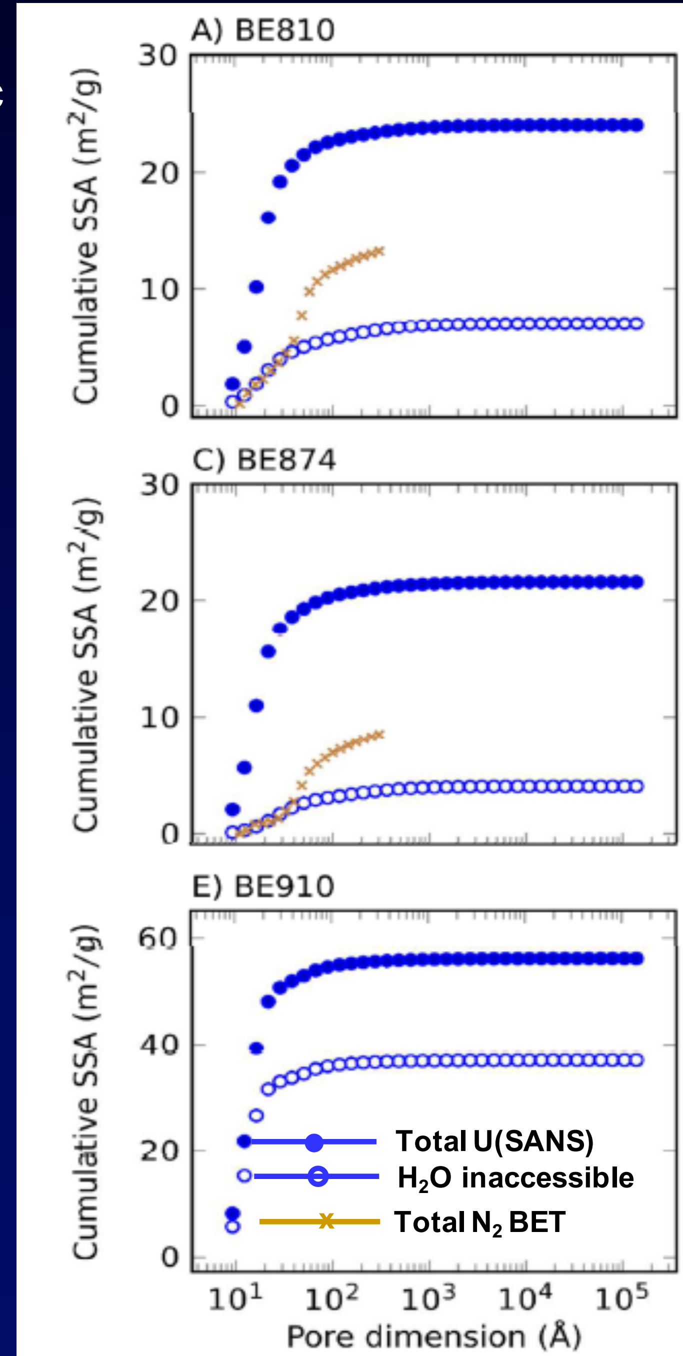
U(SANS) Results

Isotropic

Anisotropic

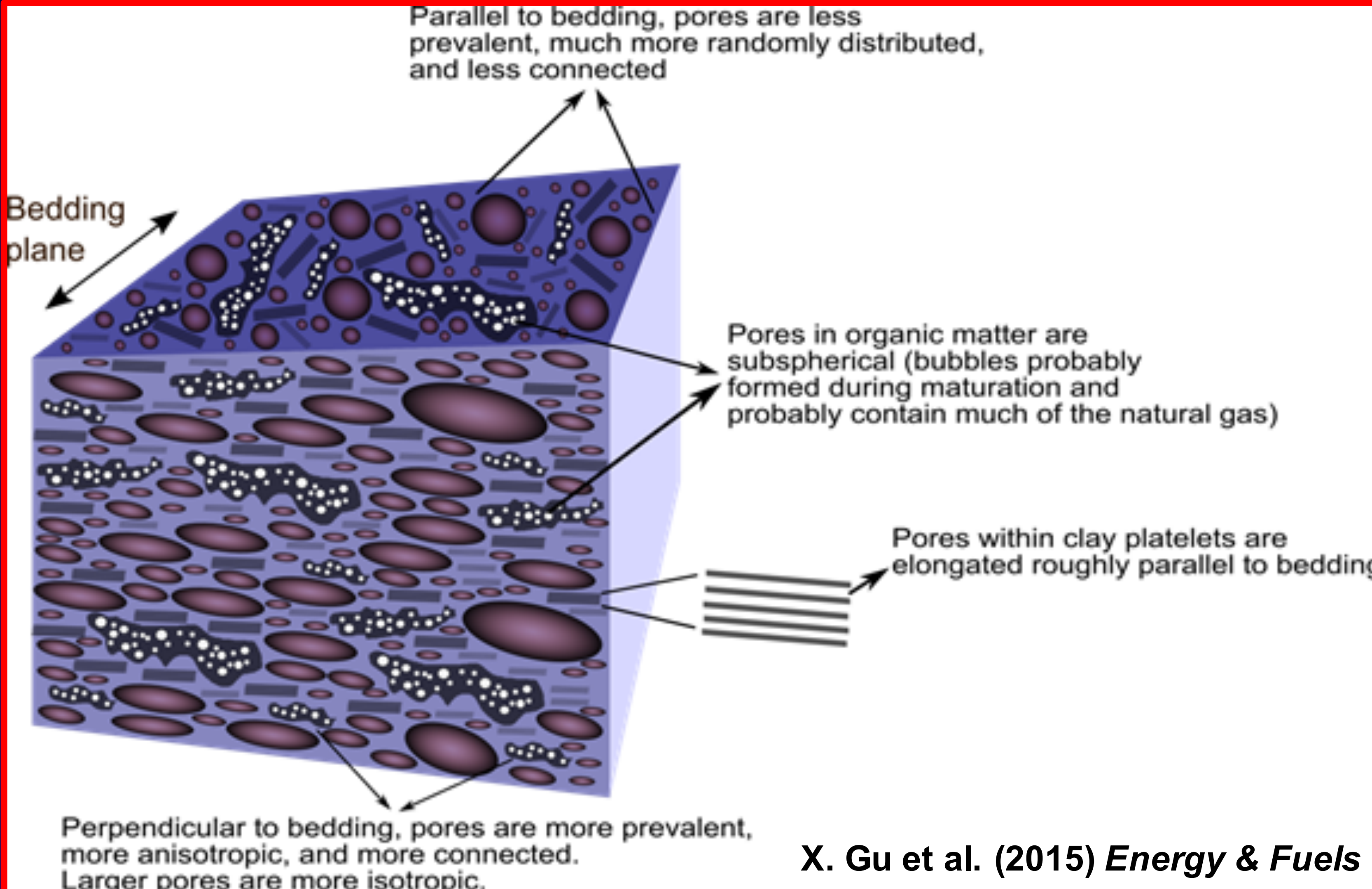


Specific Surface Area



X. Gu et al. (2015) *Energy & Fuels*

Insights from Scattering and Microscopy for the Marcellus



X. Gu et al. (2015) *Energy & Fuels*

The Mildner Legacy

Introduced SANS as a complement to TEM, BET, MICP

Demonstrated shale viewed normal to bedding exhibited anisotropy; isotropic behavior observed parallel to bedding

Extent of asymmetry due to clay content but not always

Calculated porosity and observed a bimodal distribution

SLD could be exploited to better resolve pore features in organic-rich samples

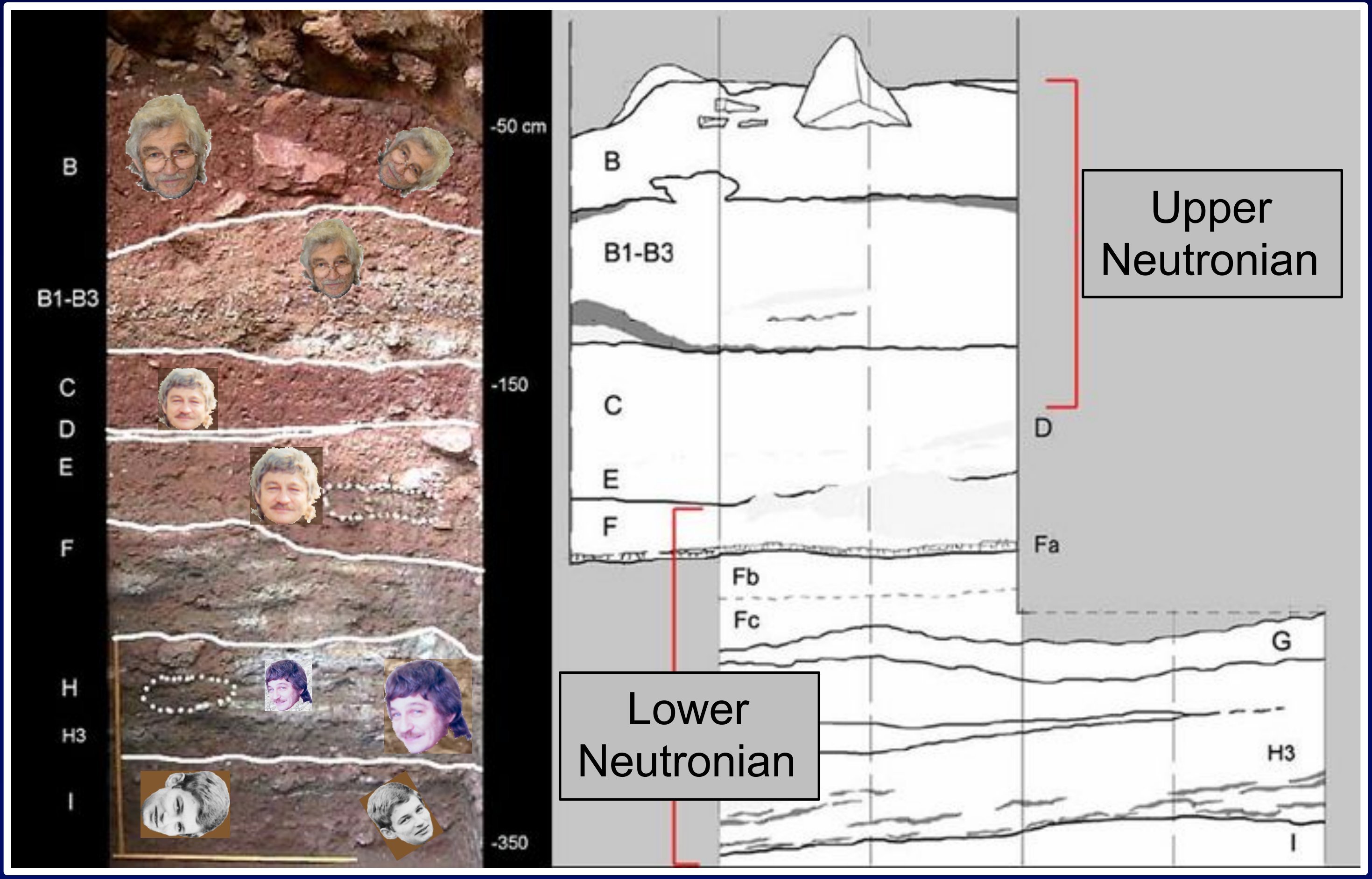
Observed the contribution by incoherent scattering > than predicted by chemistry – microheterogeneity (as well as Bragg peaks in clays)

Identified the value of SANS for delineating fractal behavior of pores

UNIVERSITY OF

OXFORD PALEONTOLOGICAL SOCIETY

"New fossil discovery named after alumnus David F. R. Mildner called *Davidus Mildnerinia.* Remarkably the fossil looks very much like the esteemed Oxford graduate it is named after. The discovery was in "Neutronian" Age rocks"



Ad Hoc Commission on "Neutron Scientists are Important People Too"

A proposal to the U.S. Dept. of Interior to update Mt. Rushmore