In Situ Small Angle X-ray Scattering Studies on the Effects of Reactive Solvents and Gases on Coal Structure

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Chemistry[1] and X-ray Science[2] Divisions

CRL Energy[3], Lower Hutt, New Zealand

Storch Award Symposium

Atlanta ACS Meeting

March 28, 2006

Argonne National Laboratory is managed by
The University of Chicago for the U.S. Department of Energy

Congratulations Colin

Fuel Chemistry 1984

Congratulations Colin

Congratulations Colin

Fifth China — Japan Symposium on Coal and C1 Chemistry
Huangshan China 1996

Congratulations Colin

GORDON RESEARCH CONFERENCES
HYDROCARBON RESOURCES
John Shinn, Chair
January 17-22, 1999

CO_2 and Coal Issues

- It is known that CO_2 dissolves in coal
- Coal swells in CO_2
- Pore structure of coals is variable (molecular to visible holes) and rank dependent – need to be able to access broad range of pore sizes (Angstroms -> microns)

Romanov, Vyacheslav N.; Goodman, Angela L.; Larsen, John W.. Errors in CO2 Adsorption Measurements Caused by Coal Swelling. Energy & Fuels (2006), 20(1), 415-416.

Goodman, A. L.; Favors, R. N.; Hill, M. M.; Larsen, John W.. Structure Changes in Pittsburgh No. 8 Coal Caused by Sorption of CO2 Gas. Energy & Fuels (2005), 19(4), 1759-1760.

Larsen, John W.. The effects of dissolved CO2 on coal structure and properties. International Journal of Coal Geology (2004), 57(1), 63-70.

Purpose and Approach

- To develop a method for predicting CO_2 storage capacity in coal seams
- To link the method with existing techniques for predicting CO_2 storage capacity

- By the use of small angle X-ray scattering (SAXS) – which allows for direct observation of changes in coal structure as CO_2 is injected under pressure

Small Angle X-ray Scattering Analysis of Coal Structure

- SAXS provides pore size, size distribution, shape and surface morphology over broad length scales.
- SAXS is an in situ technique and can work with a variety of high pressure cells.
- SAXS has been used to follow changes in coal structure in gasification and solvent swelling.

Calo, J. M.; Hall, P. J.; Houtmann, S.; Winans, R. E.; Seifert, S. In situ determination of porosity during gasification via SAXS /TGA. Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2001), 46(2), 528-529.

The Scale of Things -- Nanometers and More

Office of Basic Energy Sciences
Office of Science, U.S.DOE
Version 03-05-02

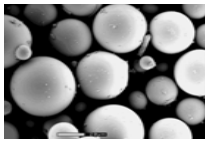
Things Natural

Dust mite

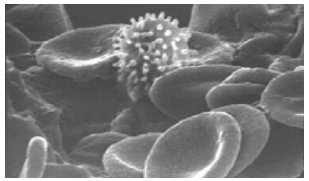
200 μm

Ant
~ 5 mm

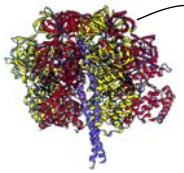
Human hair
~ 10-50 μm wide



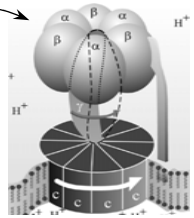
Fly ash
~ 10-20 μm



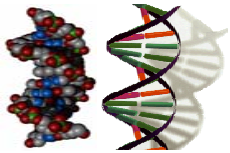
Red blood cells with white cell
~ 2-5 μm



~10 nm diameter

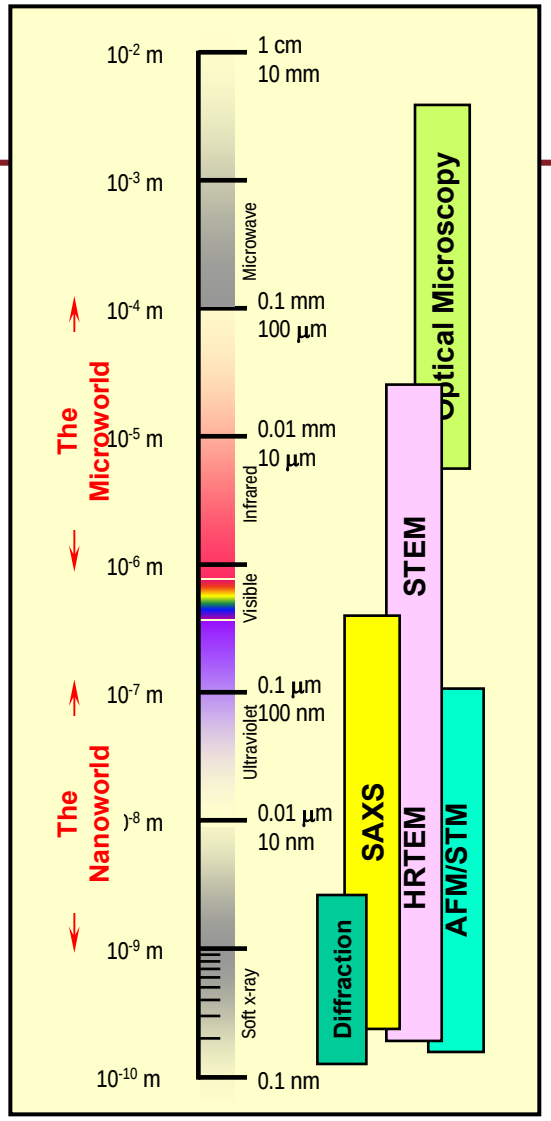


ATP synthase

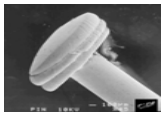


DNA
~2-1/2 nm diameter

Atoms of silicon
spacing ~tenths of nm

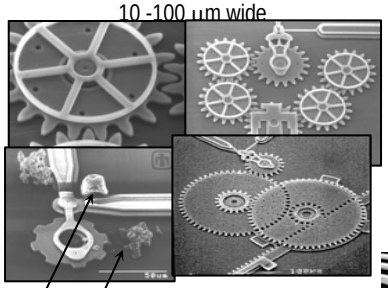


Things Manmade

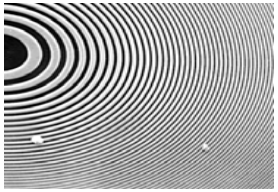


Head of a pin
1-2 mm

MicroElectroMechanical devices
10 -100 μm wide

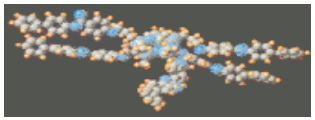


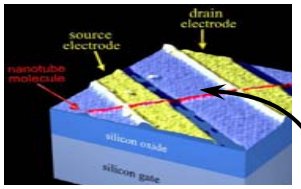
Pollen grain
Red blood cells



Zone plate x-ray "lens"
Outermost ring spacing
~35 nm

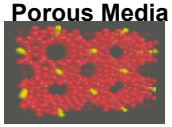
Polymer

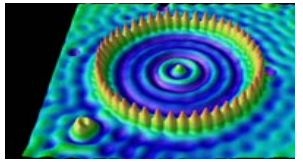




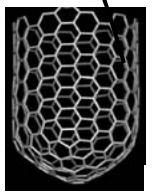
Nanotube transistor

Porous Media



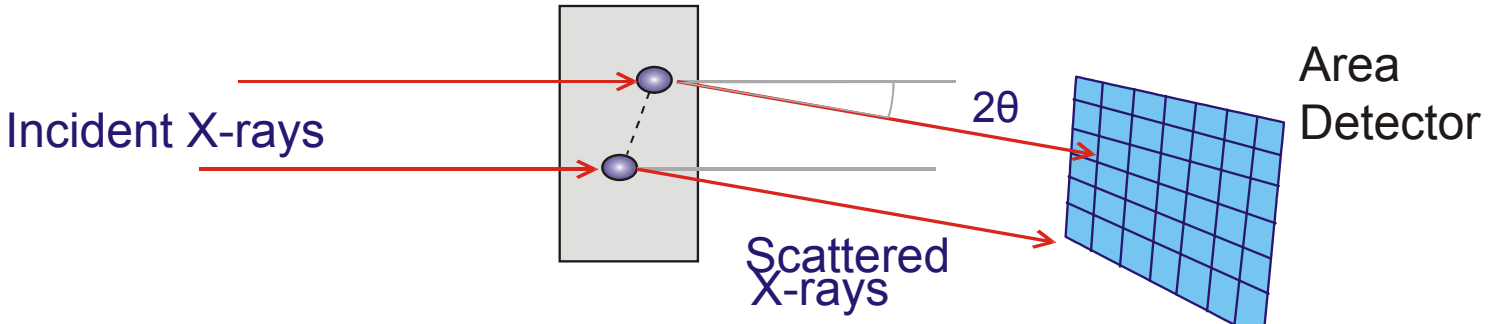


Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral diameter 14 nm

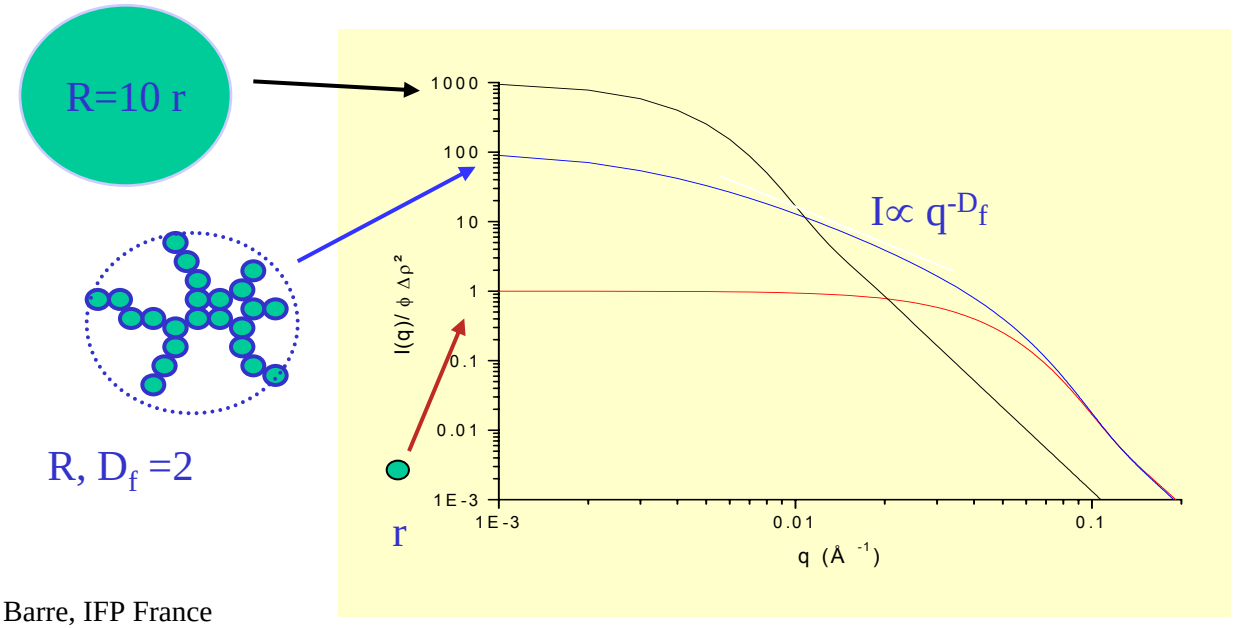


Carbon nanotube
~2 nm diameter

What does small angle scattering measure ?



Scattering Vector: **Q =(4π/λ)sinθ**

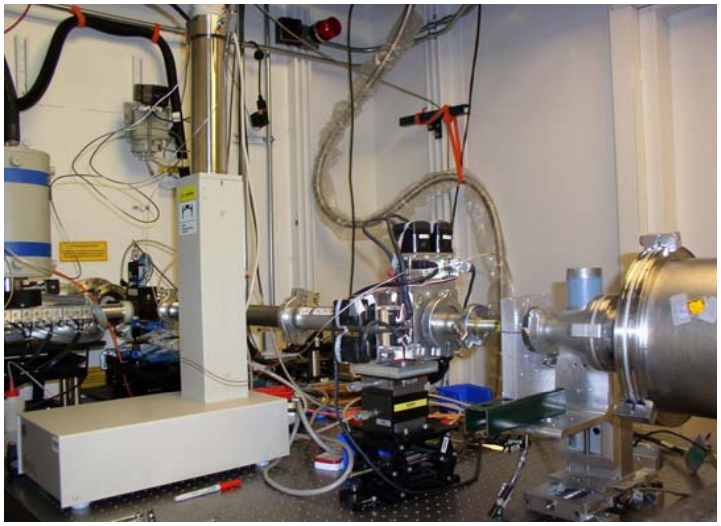


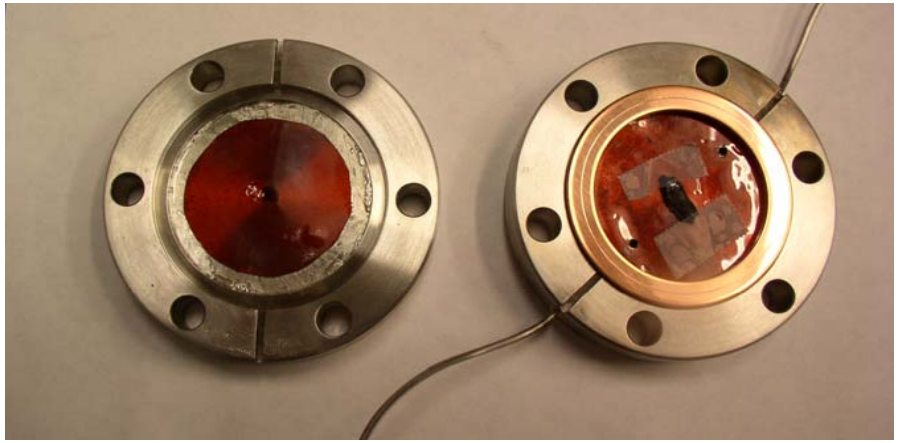
L. Barre, IFP France

Preliminary Experiments Carried Out under the Auspices of the US/NZ Bilateral Partnership for Climate Change Research

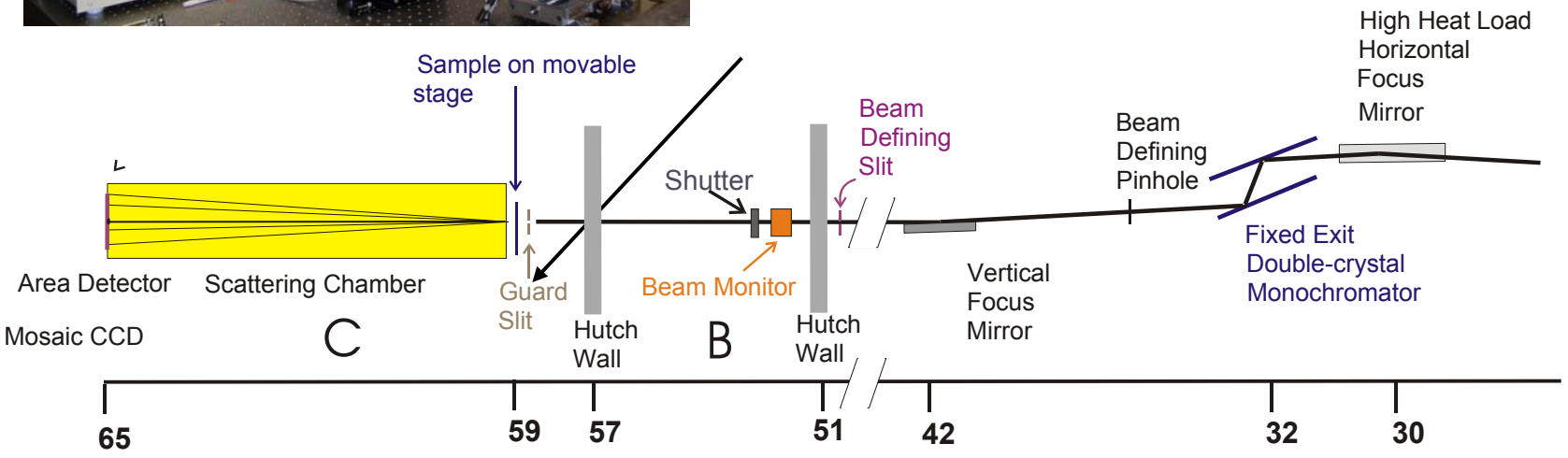
- CO_2 uptake of a suite of four NZ coals and three APCS coals were observed for the first time by in situ SAXS over the lower end of pore size range.
  - Ohai Subbituminous
  - Maramarua Subbituminous
  - Hawkdun Lignite
  - Mataura Lignite
  - Illinois No. 6
  - Pittsburgh No. 8
  - Upper Freeport
- Reproducible data were obtained.

TR/ASAXS Instrument on the APS BESSRC ID-12-B&C Undulator Beamline



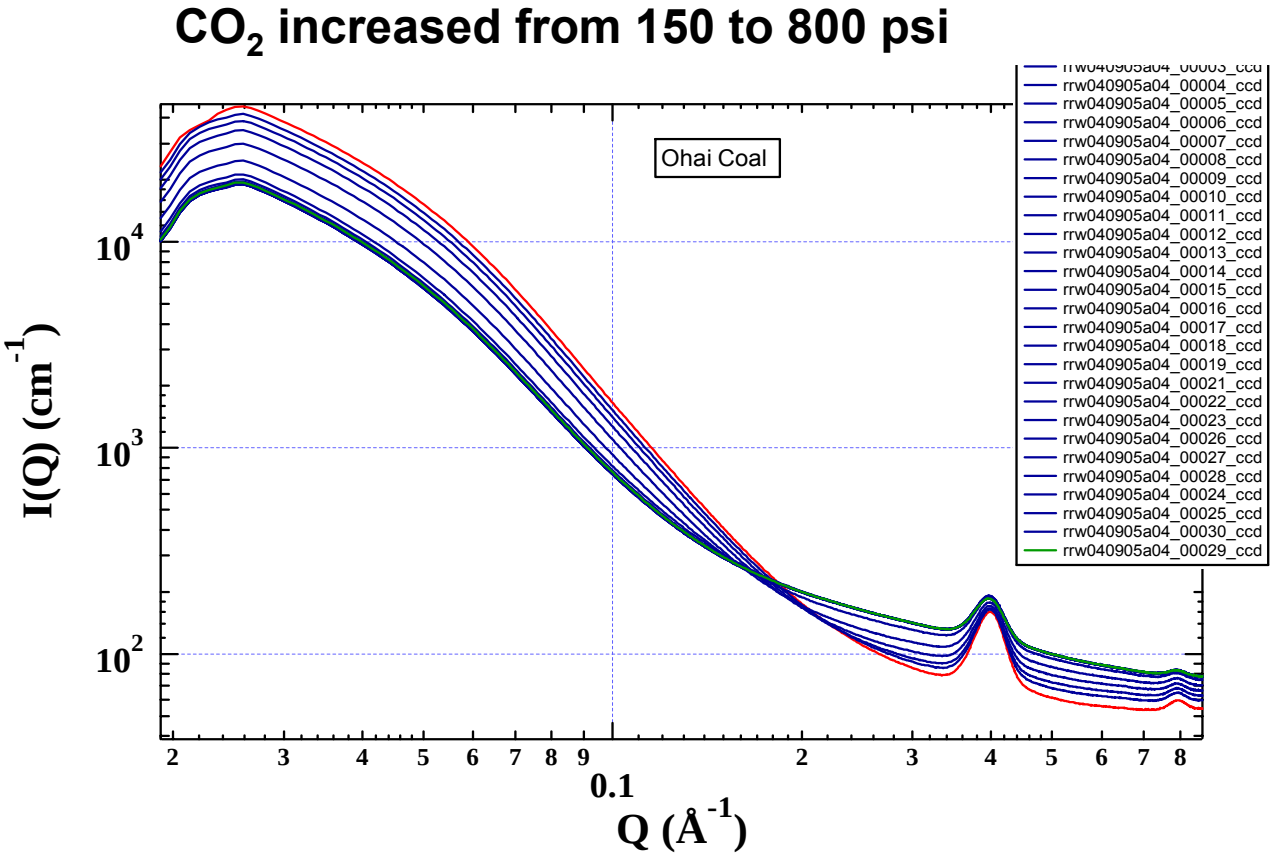


CO2 increased from 150 to 800 psi

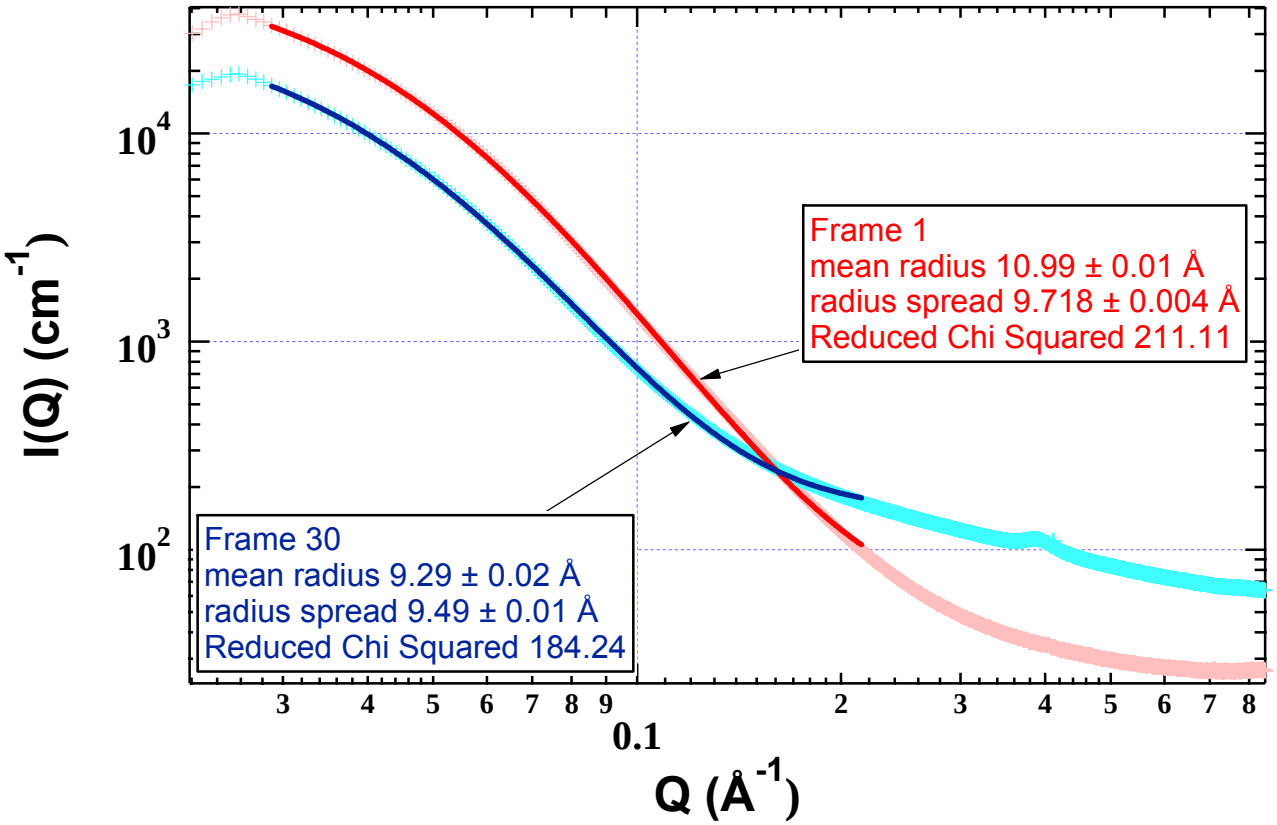


Distance from source in meters

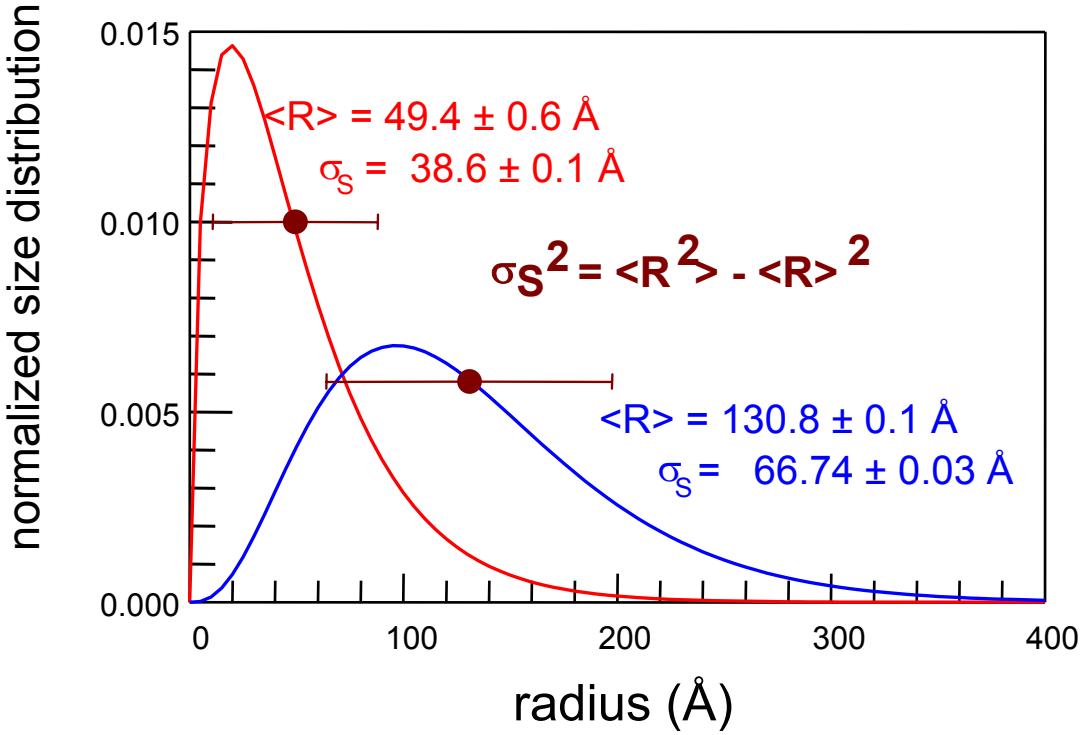
Ohai Subbituminous Coal



Ohai Coal
Schulz Polydispersed Spheres

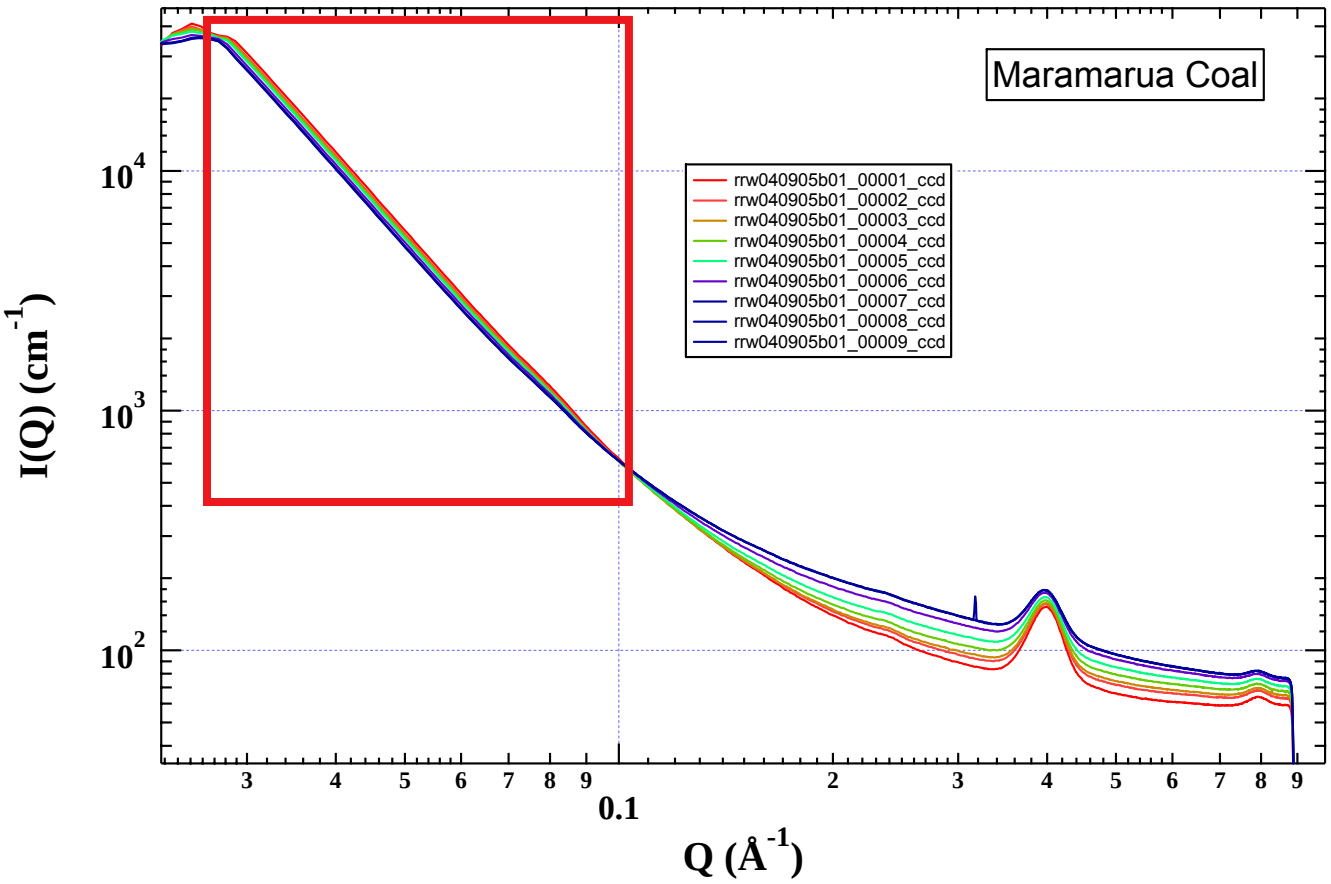


Schulz Distribution: Analysis of Polydispersed SAXS Data

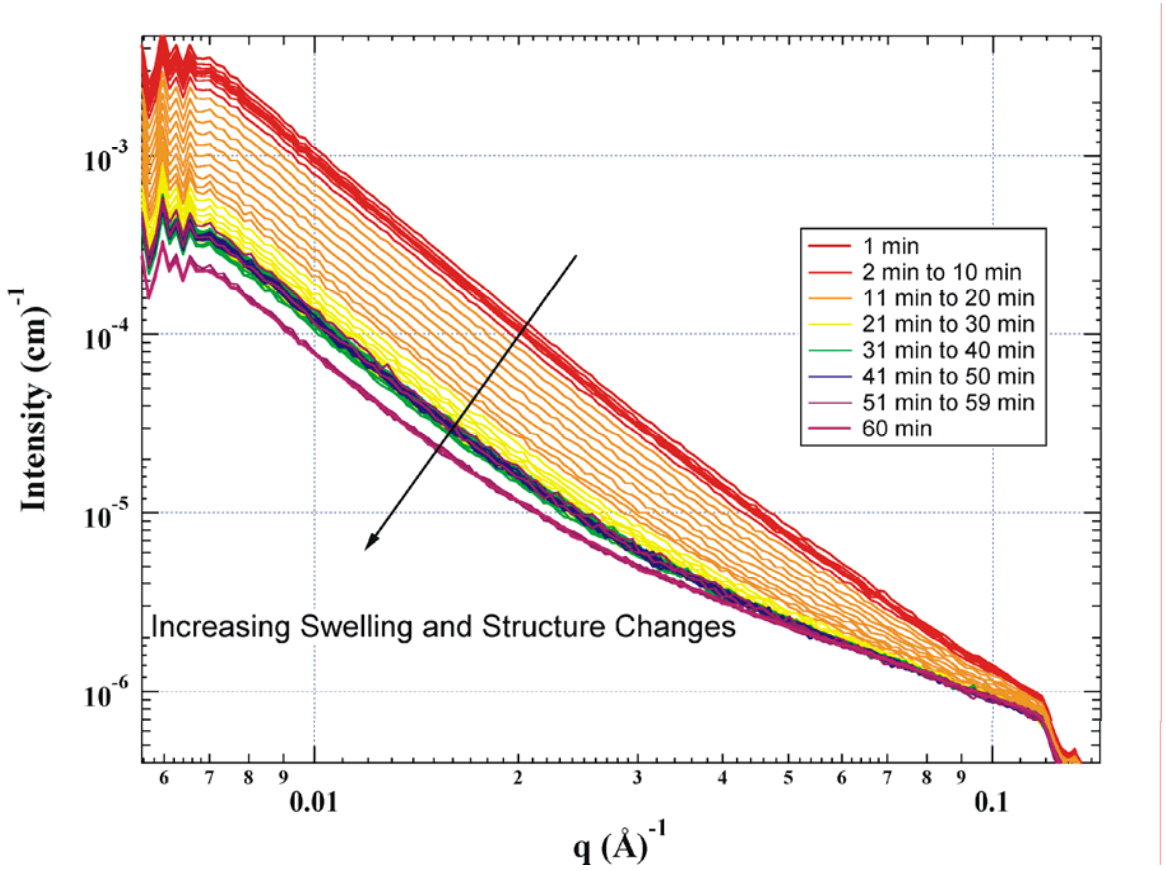


Polydispersity analysis of scattering data from self-assembled systems
Eric Y. Sheu, *Phys. Rev. A* **45** , 2428-2438 (1992)

Maramarua Subbitumious Coal

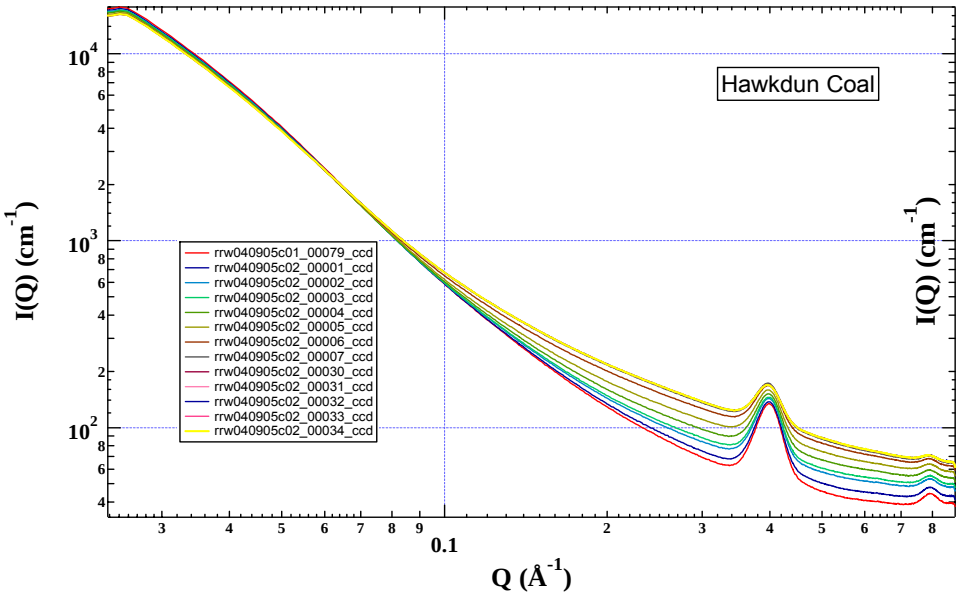


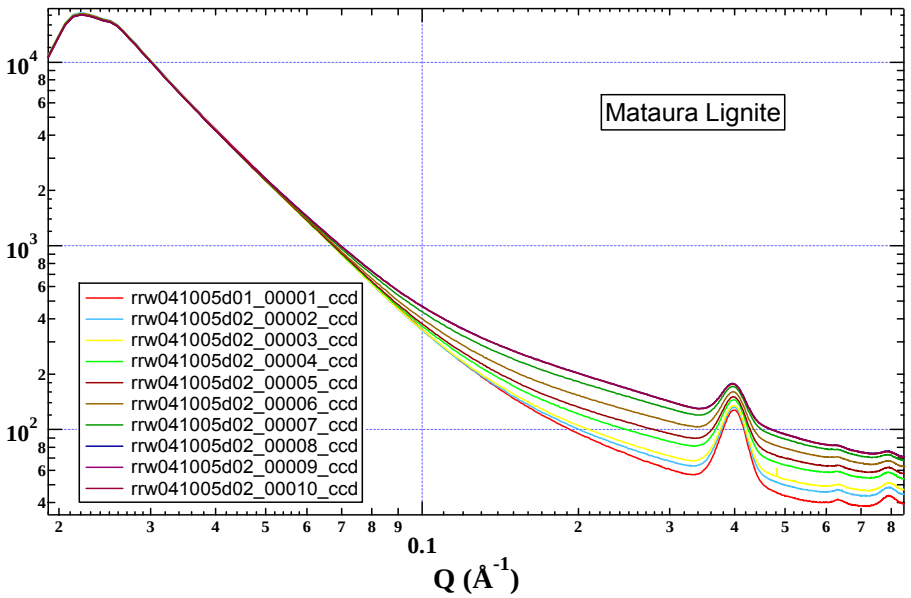
Pyridine Swelling of a Subbituminous Coal (APCS 2)

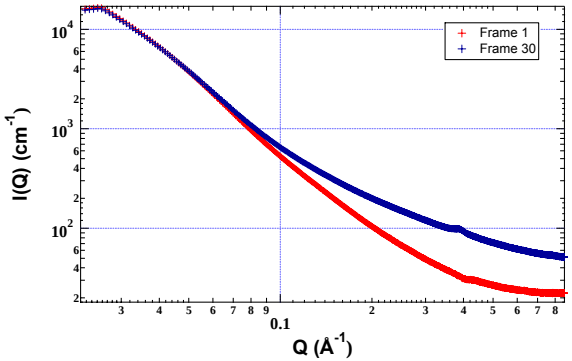


Cylindrical Pores are formed after swelling

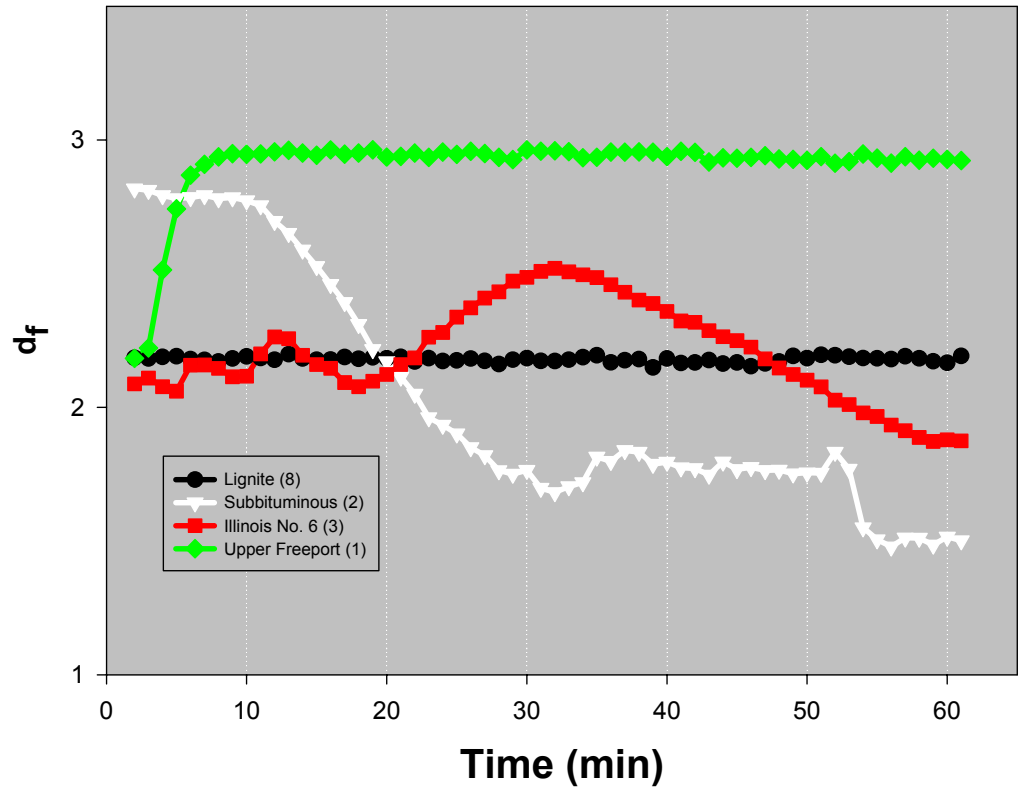
Comparison of the NZ Lignites







Power law slopes (fractal dimensions) for coal swelling in pyridine at low Q, as a function of solvent contact time.

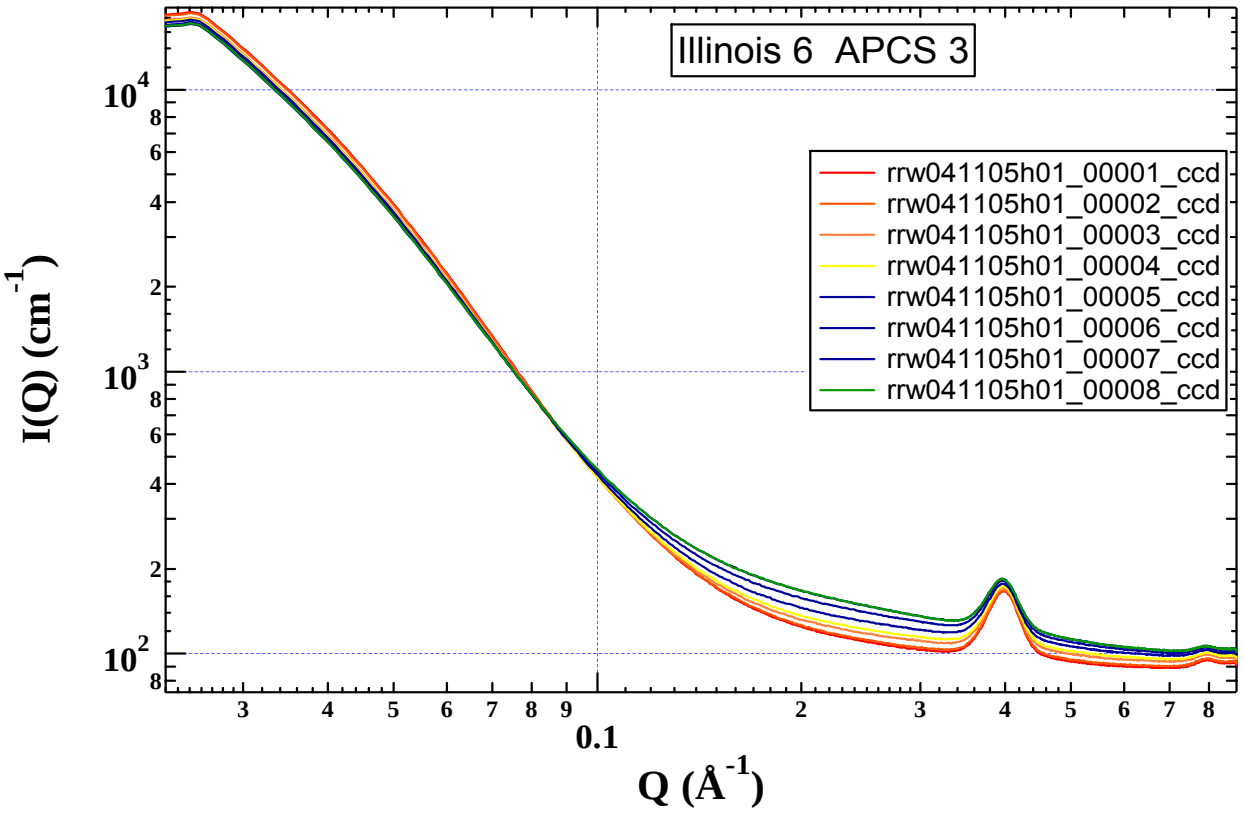


Individual New Zealand Coal Summaries

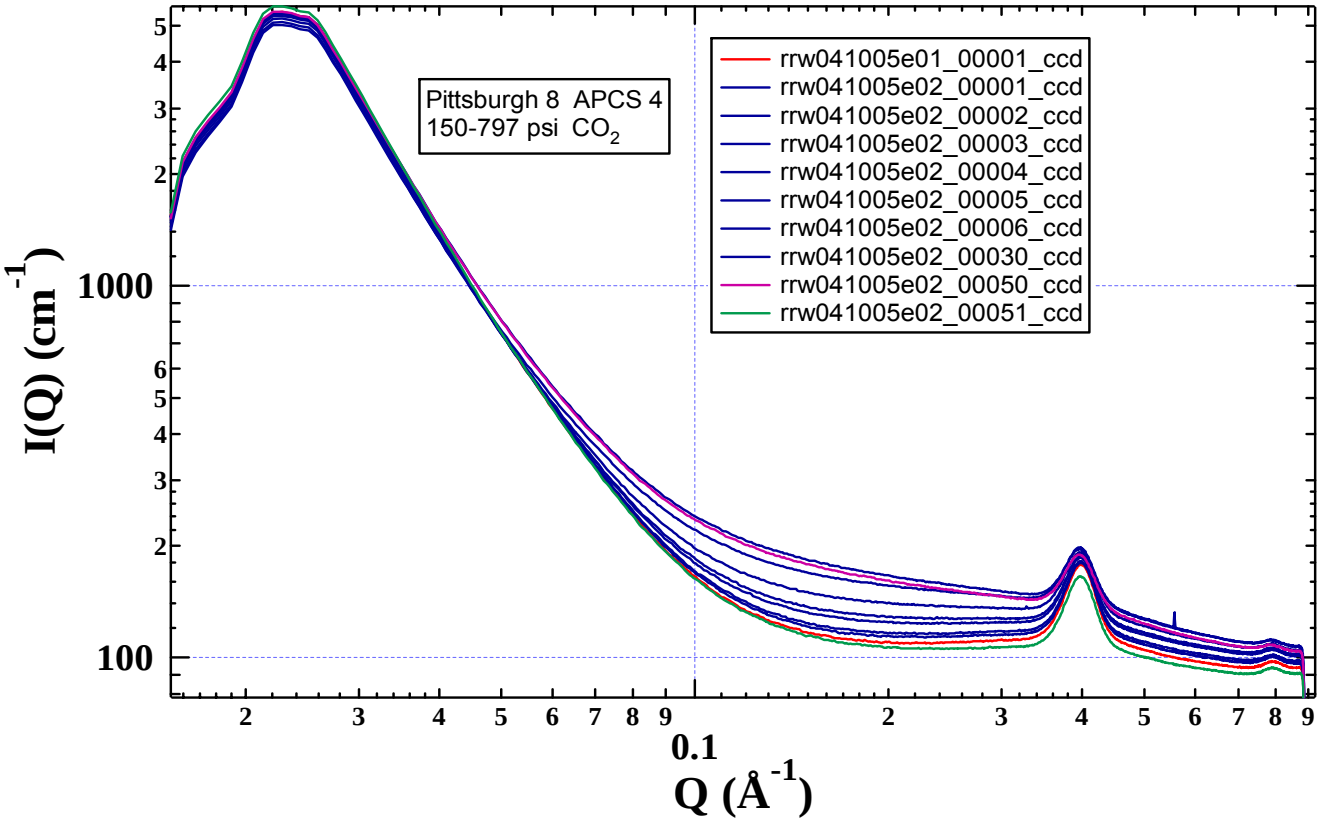
Coal	CO_2 adsorbed (m^3/t, 50 atm)	SAXS Results
Ohai (subbit)	27	Large pore decrease and small pore growth
Maramarua (subbit)	18	Some pore decrease and small pore growth
Hawkdun (lignite)	17	Slight large pore collapse and small pore growth
Mataura (lignite)	Very low	No large pore change and significant increase in small pores

*CO_2 Absorbed – CRL Energy Report 04-11043

Illinois 6 Bituminous Coal APCS 3

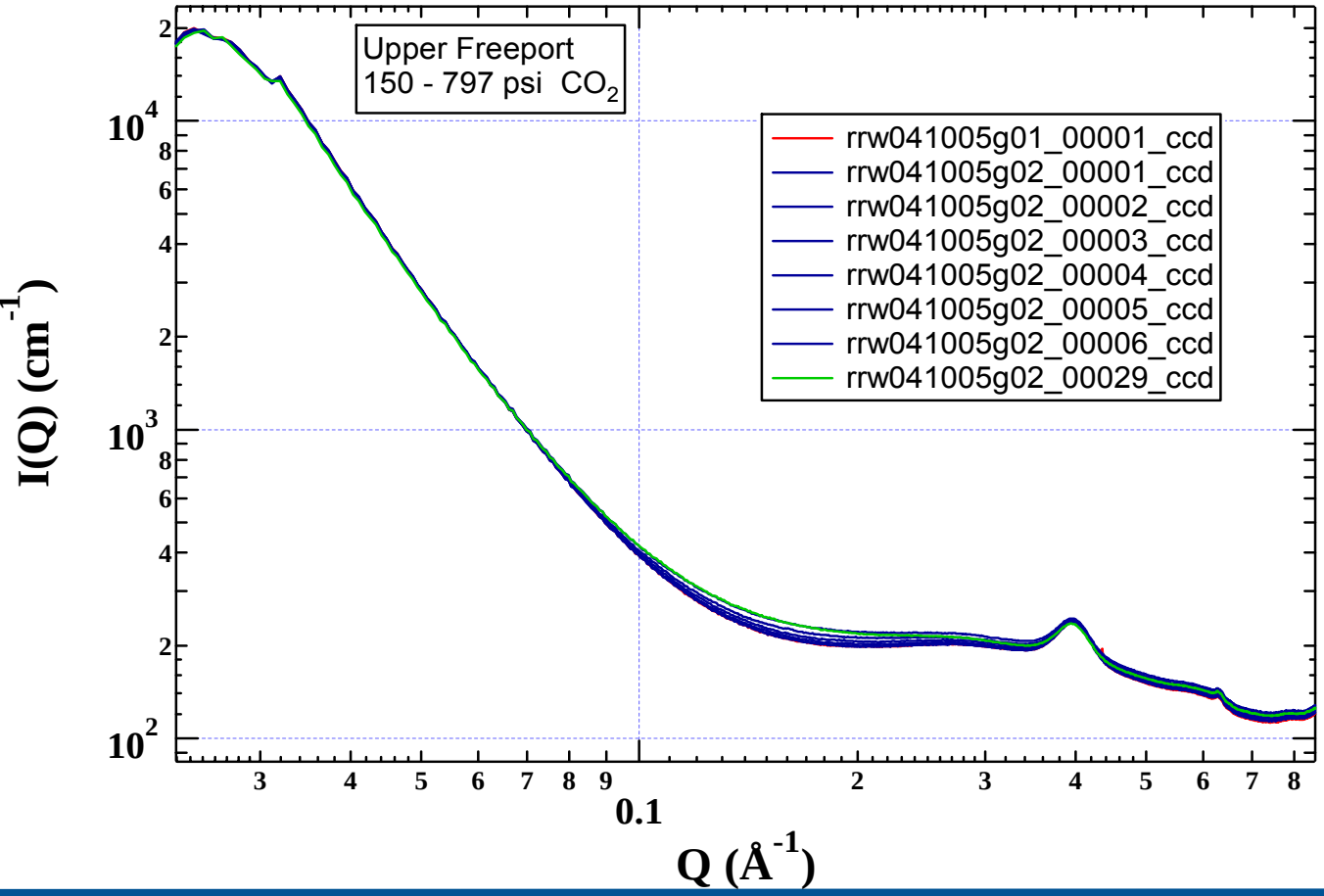


Pittsburgh 8 APCS 4

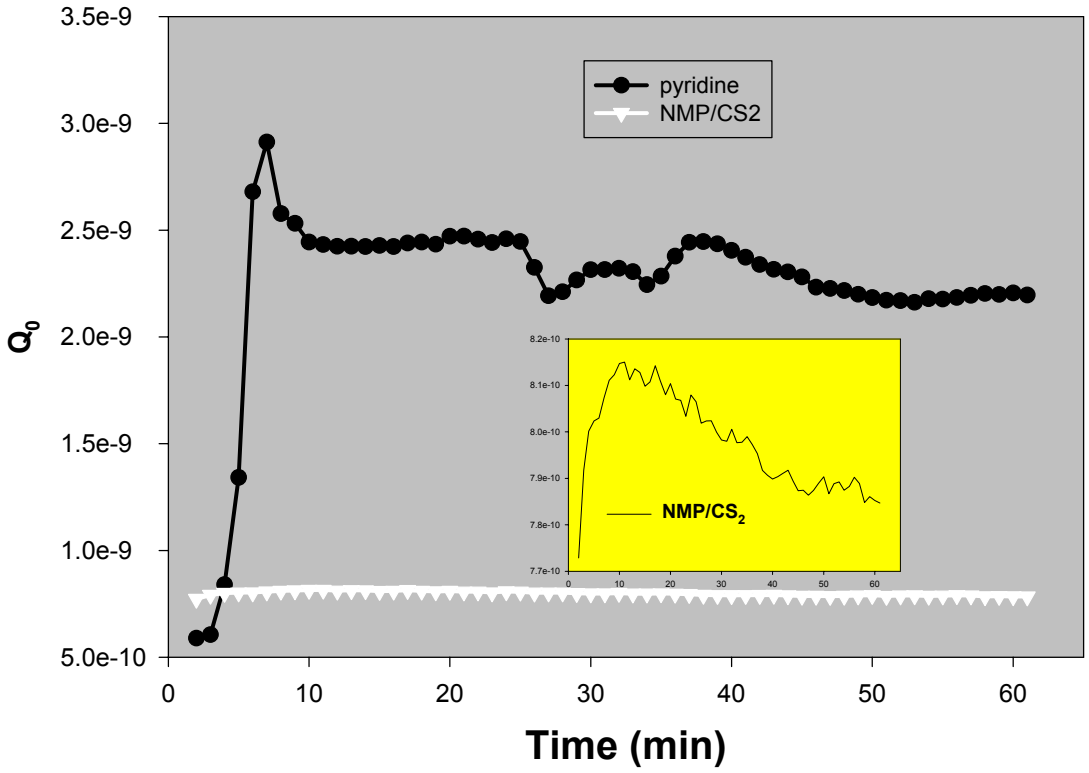


Overall increase in porosity

Upper Freeport mv Bituminous Coal APCS 1



Invariant change with swelling in pyridine and NMP/CS2 for the Upper Freeport coal.



The inset is an exploded view in Q0 for the NMP/CS2 data.

Summary of SAXS Results on Four New Zealand and Three Argonne Premium Coals(APCS)

- With SAXS changes are observed in pore size and distribution with CO_2 uptake at sequestration pressures as it happens.
- There is a significant rank dependence.
- The number of small pores increase in all coals (CO_2 dissolving?).
- In a NZ coal (Ohai) the contribution to large pore scattering is reduced very quickly, possibly due to the filling of larger pores.
- High rank coal Upper Freeport (APCS) shows little change.
- In bituminous coals the effects are reversible.

Future

- Expand the coal set and the experimental parameters (pore size range, temperature, pressure and time).
- Correlate with CO_2 uptake volume measurements obtained by other methods.
- Correlate with in-seam sequestration data if available.
- Use these results in combination with other approaches to predict sequestration behavior of selected coal seams.