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In situ studies of coal pressurized with CO_2 by small angle X-ray scattering

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ACERC Conference 2010
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New Zealand Foundation for Research, Science and Technology
and New Zealand Industry Consortium
US/NZ Bilateral Partnership for Climate Change Research

PROGRAMS

- **In situ studies of nano catalysis – XSD, CSE, CNM**
- **CO_2 uptake in coals – XSD, CRL, Brown**
- **Characterization of oil shales – XSD, U. Utah, Chevron, BYU**
- **Catalytic combustion – XSD, U. Utah, Penn State, Cal Tech…**

APPROACHES

- **Global information – SAXS, PDF, SANS, XAFS, NMR**
- **Molecular Specific information – high resolution mass spectrometr**
  GCMS of extracts

Tony Clemens CRL New Zealand 1951 - 2010

Direct Observation of CO_2 Injection into Coal using Small Angle X-Ray Scattering (SAXS)

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2009 Pittsburgh Coal Conference

CRL Energy Ltd

Purpose and Approach

- Understand the mechanisms of CO_2 uptake in coals
- 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

CO_2 and Coal Issues

- It is thought 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)

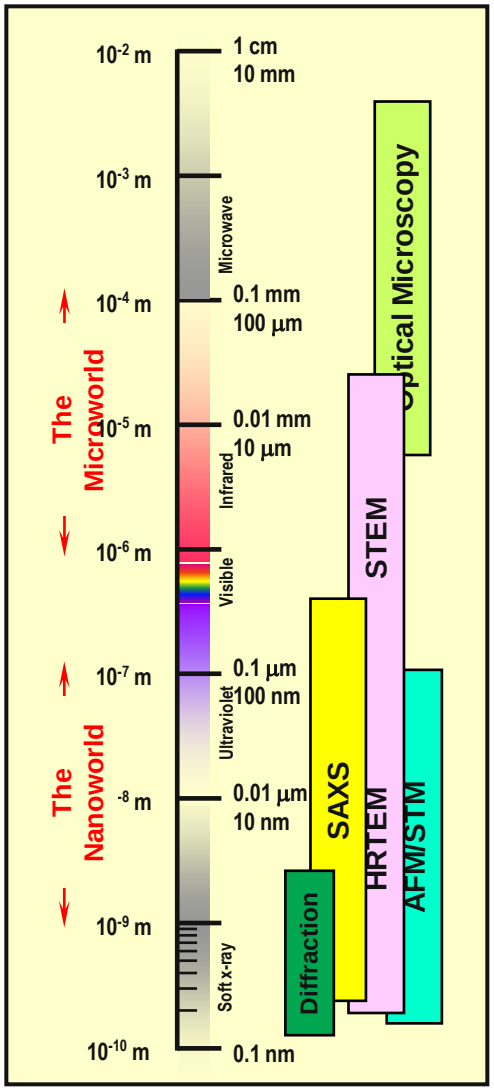
Romanov, Vyacheslav N.; Goodman, Angela L.; Larsen, John W.. Errors in CO2 Adsorption Measurements Caused by Coal Swelling. Energy & Fuels (2006), 20(1), 415-416.

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.

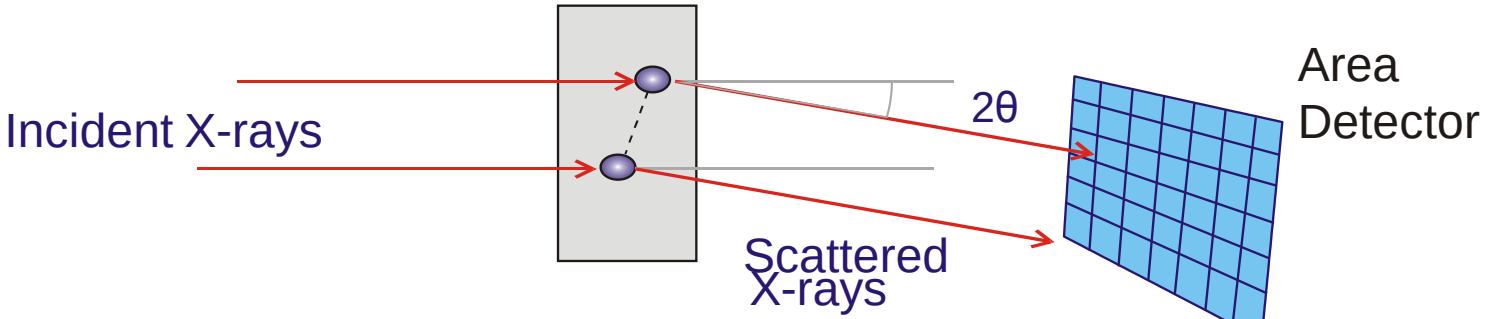
Small Angle X-ray Scattering Analysis of Coal Structure

- 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.

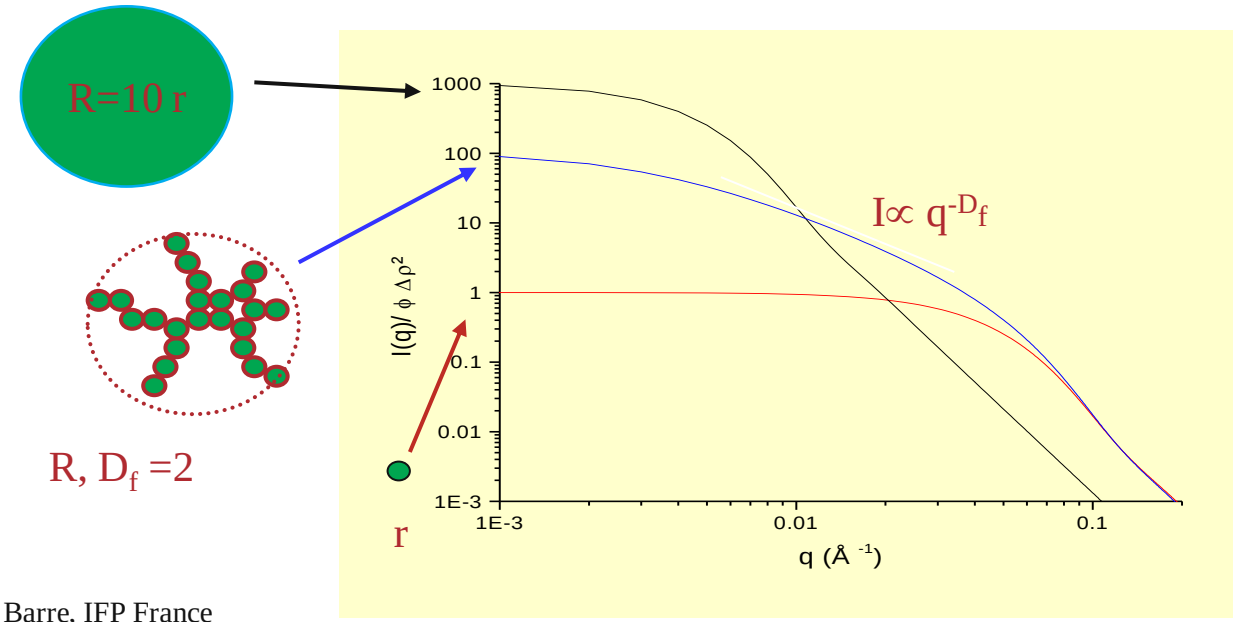


Calo, J. M.; Hall, P. J.; Houtmann, S.; Lozano-Castello, D.; Winans, R. E.; Seifert, S. "Real time" determination of porosity development in carbons: A combined SAXS/TGA approach. Studies in Surface Science and Catalysis (2002), 144(Characterization of Porous Solids VI), 59-66.

What does small angle scattering measure ?

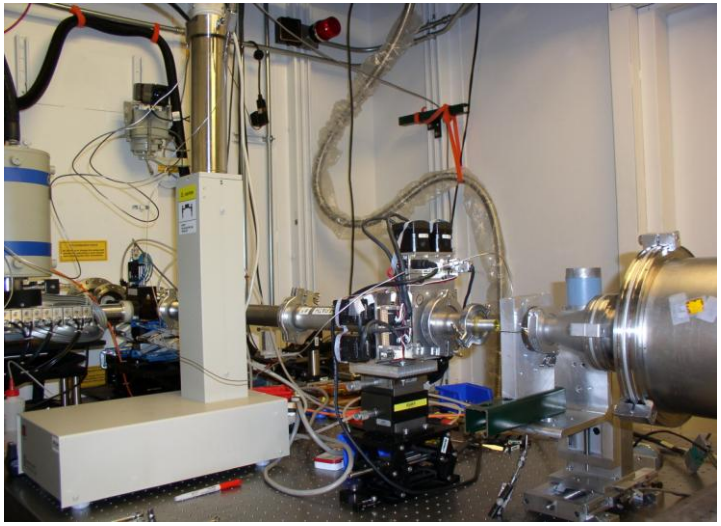


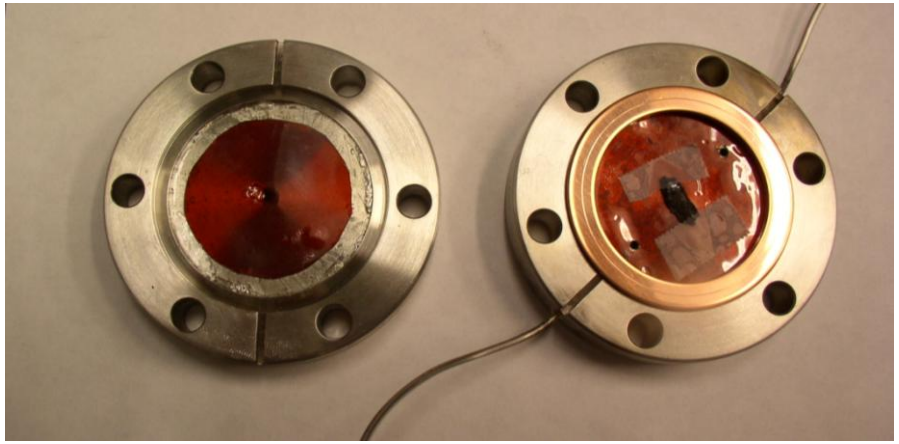
Scattering Vector: **Q =(4π/λ)sinθ**



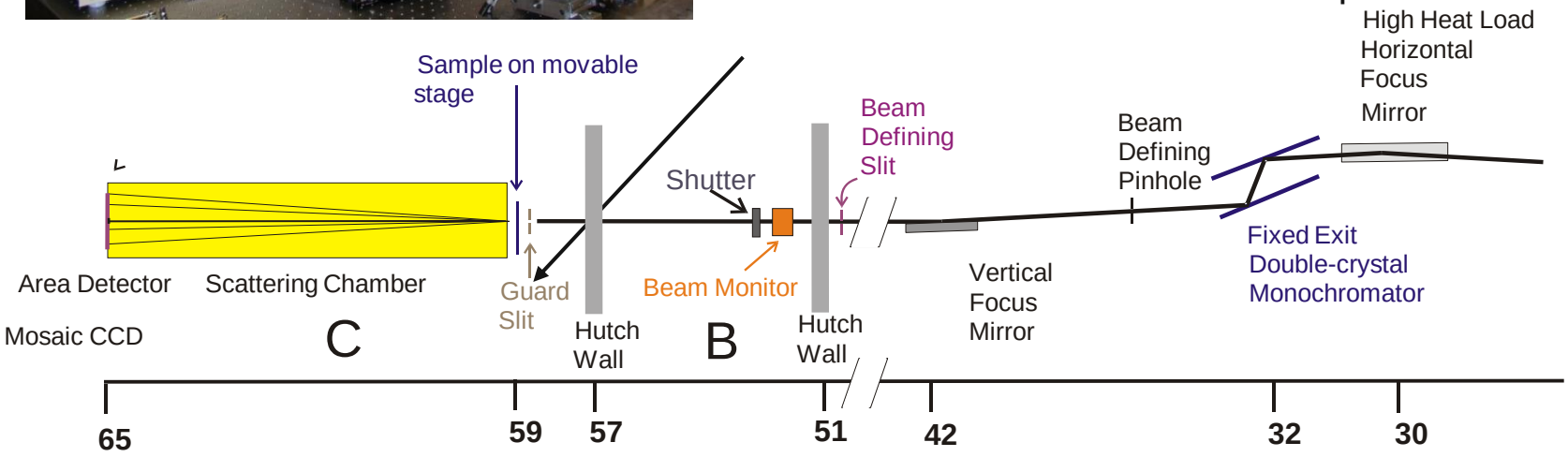
L. Barre, IFP France

SAXS Instruments at 12-ID APS





CO2 increased from 150 to 800 psi



Distance from source in meters

Analysis of the Argonne Premium Coals

www.anl.gov/PCS/

Coal Seam	Rank	No	%C	O/1000C	N/1000C	S/1000C
Beulah-Zap	Lignite	8	74.1	210	14	3.6
Wyodak-Anderson	Subbituminous	2	76.0	180	13	2.3
Illinois No. 6	hvC Bituminous	3	80.7	130	15	11.5
Blind Canyon	hv Bituminous	6	81.3	110	17	1.7
Pittsburgh No. 8	hvA Bituminous	4	85.0	80	17	4.0
Lewiston-stockton	hvA Bituminous	7	85.5	90	16	3.0
Upper Freeport	mv Bituminous	1	88.1	70	15	3.2
Pocahontas	lv Bituminous	5	91.8	20	13	2.1

>35,000 Samples shipped world wide

Coal Properties

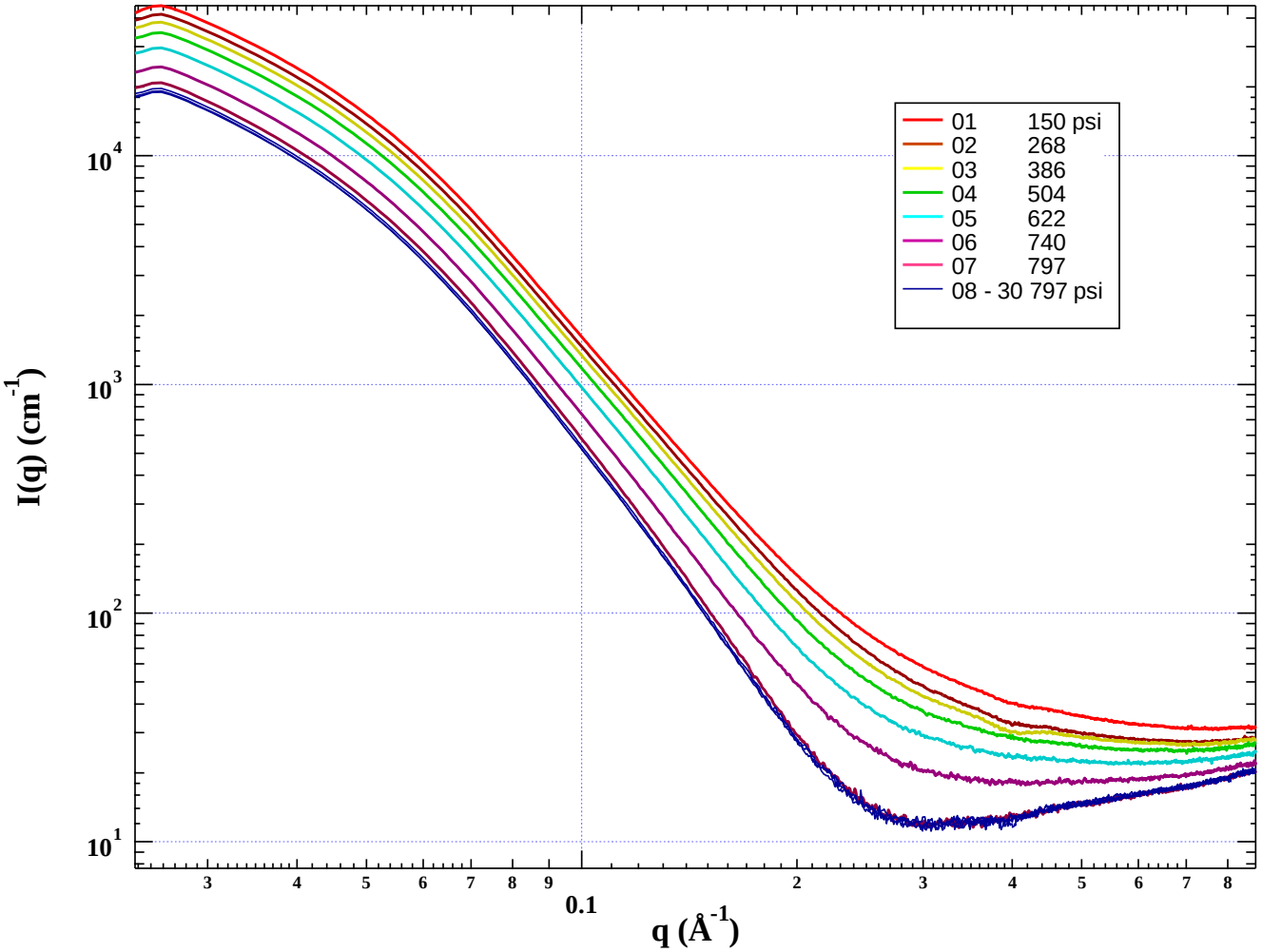
Coal	Rank	%C (daf)	%H (daf)	%N (daf)	%S (daf)	%O (daf)	% ash	%H_2O	CO_2 (m^3/t)	f_a
Mataura	Lignite	68.8	5.01	0.73	0.89	24.6	7.23	42.6	<1(<2)	0.62
Hawkdun	Lignite	69.2	5.16	0.64	0.62	24.4	4.71	40.5	12 (18)	0.53
Maramarua	Subbituminous	75.0	5.23	1.26	0.17	18.4	4.10	26.9	14 (18)	0.65
Ohai	Subbituminous	75.3	4.36	1.31	0.42	18.6	4.16	23.1	21 (27)	0.70
Illinois 6	hvC bituminous	77.7	5.00	1.12	2.38	13.5	15.5	7.97	20	0.72
Pittsburgh 8	hvA bituminous	83.2	5.32	1.64	0.89	8.83	9.25	1.65	21	0.75
Upper Freeport	mv Bituminous	85.5	4.70	1.55	0.74	7.51	13.8	1.13	21	0.81

CO_2 - records data obtained by CO_2 absorbance measurements at 3 MPa (5 MPa) for the New Zealand coals [6] and at 3 MPa for the Argonne coals [7,8.]

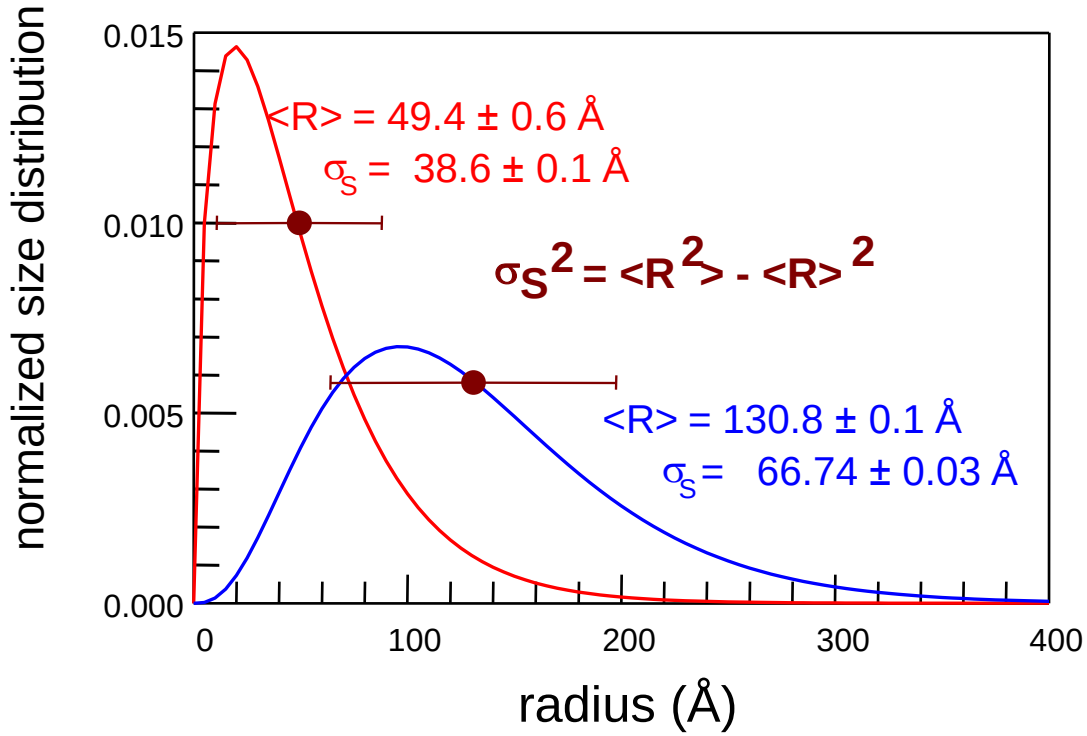
F_a - refers to the degree of aromaticity of the coal by ^{13}C solid NMR [9,10]

Ohai Subbituminous Coal

CO_2 increased from 150 to 800 psi, CO_2 blank subtracted

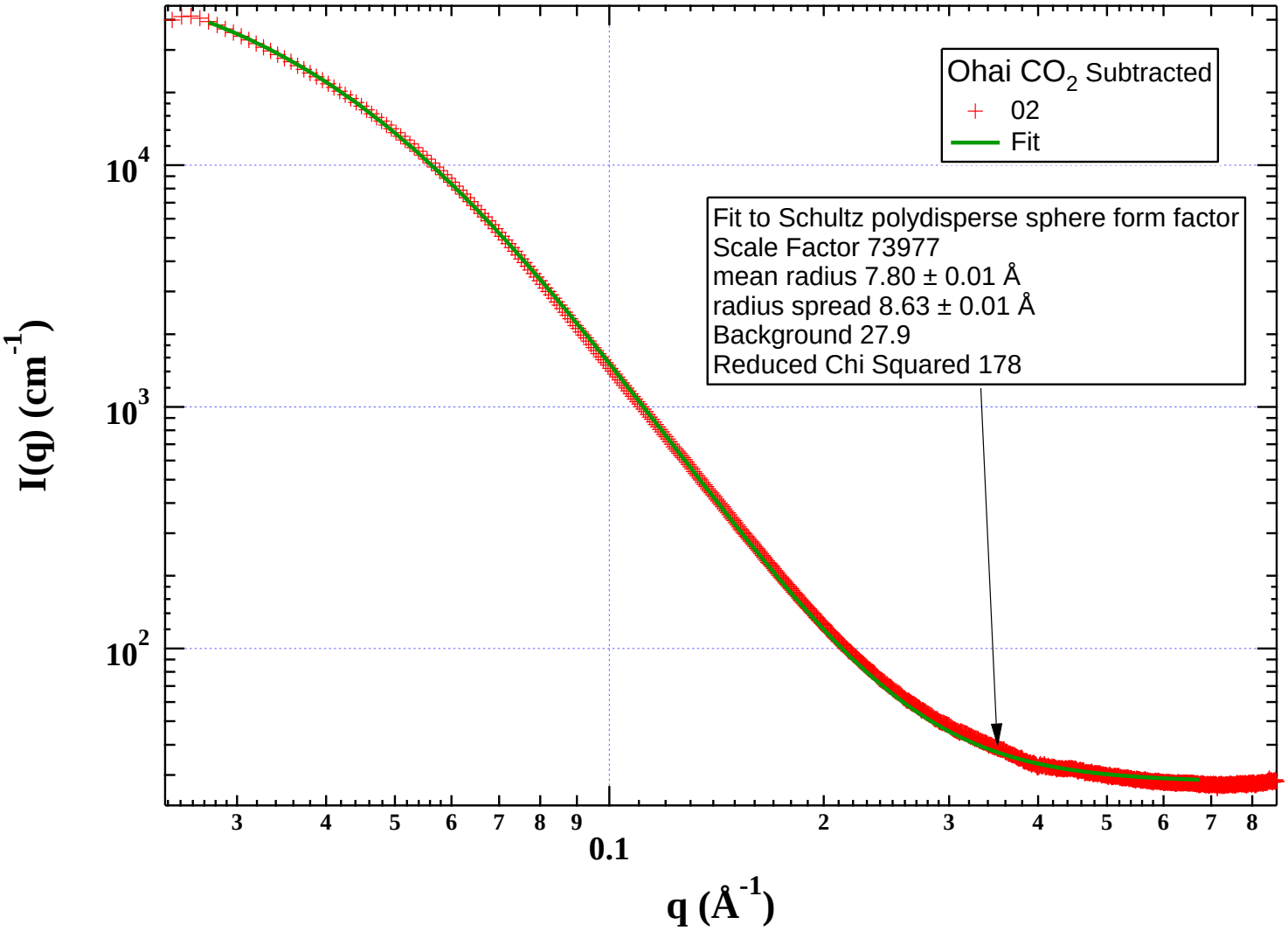


Schulz Distribution: Analysis of Polydispersed SAXS Data

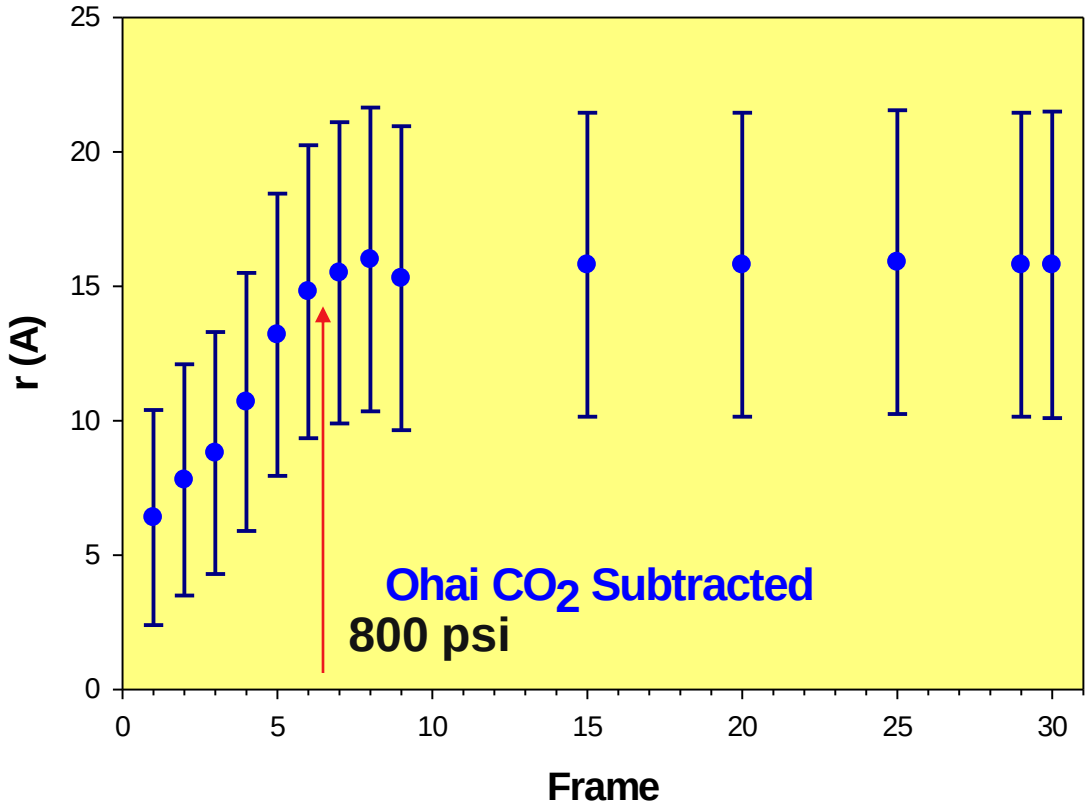


Polydispersity analysis of scattering data from self-assembled systems
Eric Y. Sheu, *Phys. Rev. A* **45** , 2428-2438 (1992)

Ohai Coal - Schulz Polydispersed Spheres



Ohai Coal - Schulz Polydispersed Spheres



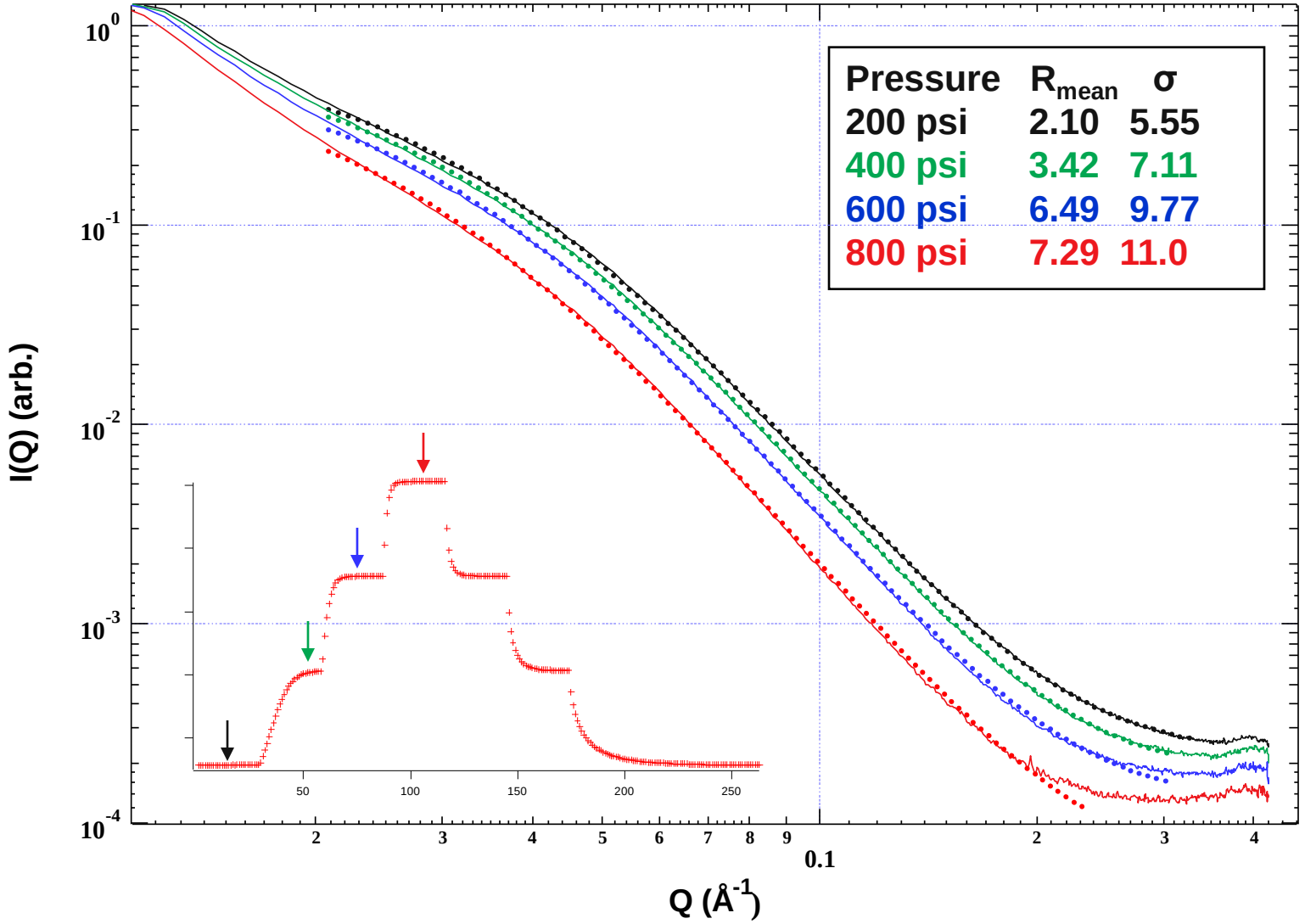
Individual New Zealand Coal Summaries

Coal	CO_2 adsorbed (m^3/t, 50 atm)	SAXS Results
Ohai (subbit)	27	Overall porosity decrease Small Pore increase in size
Maramarua (subbit)	18	Some pore decrease
Hawkdun (lignite)	17	Slight large pore collapse
Mataura (lignite)	Very low	No large pore change

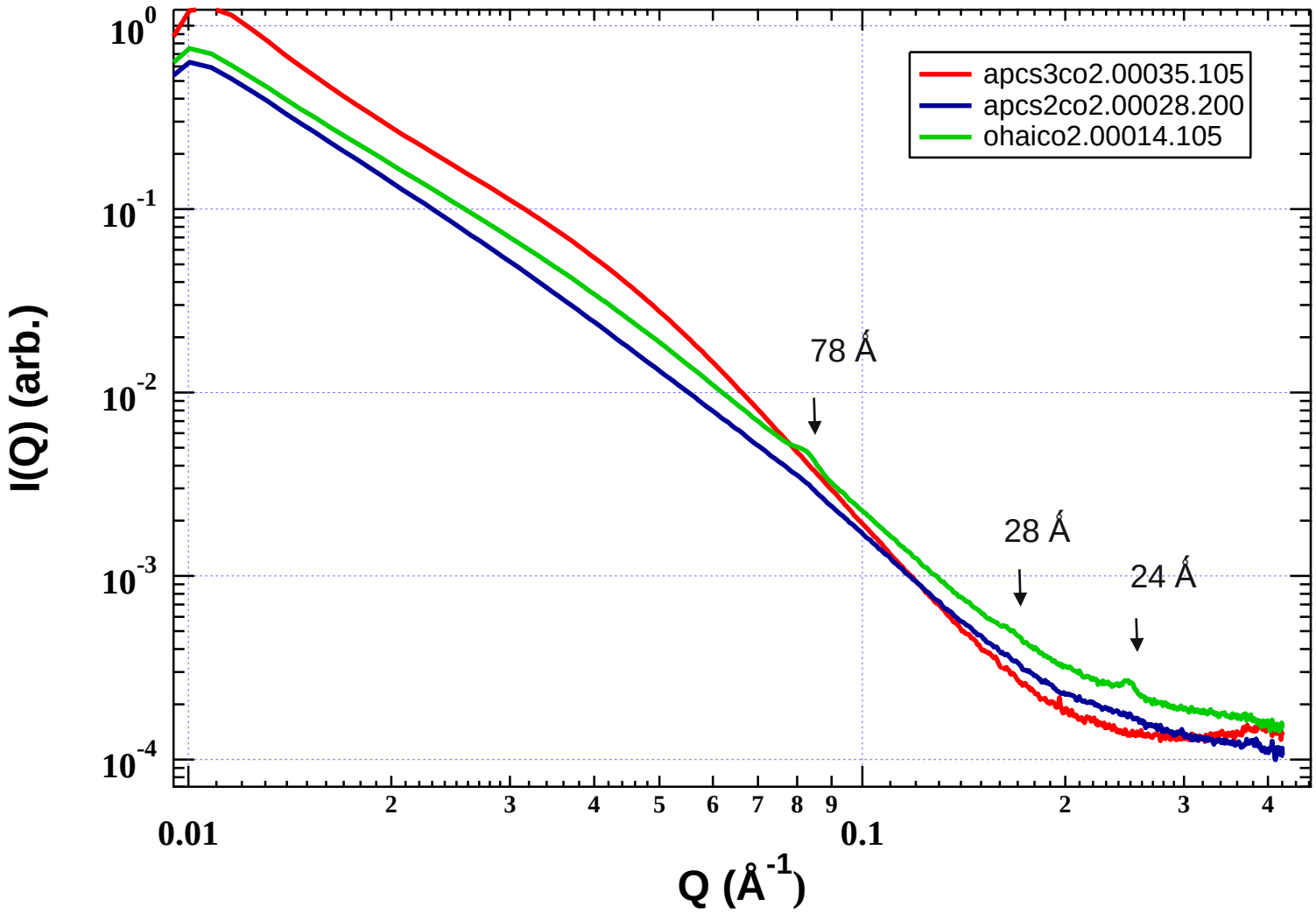
*CO_2 Absorbed – CRL Energy Report 04-11043

Illinois No. 6 Bituminous Coal – APCS 3

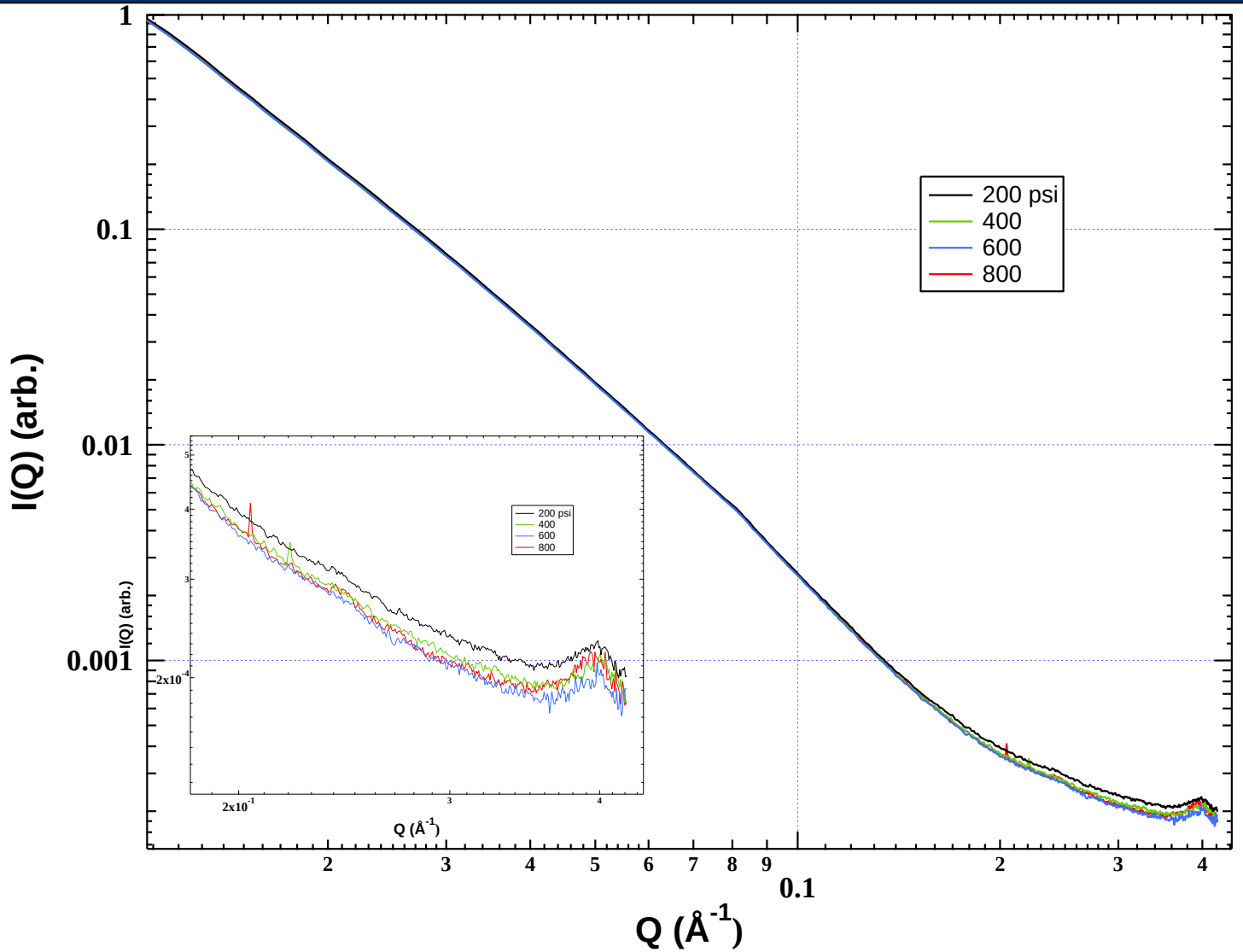
Fit to Schultz polydisperse sphere form factor



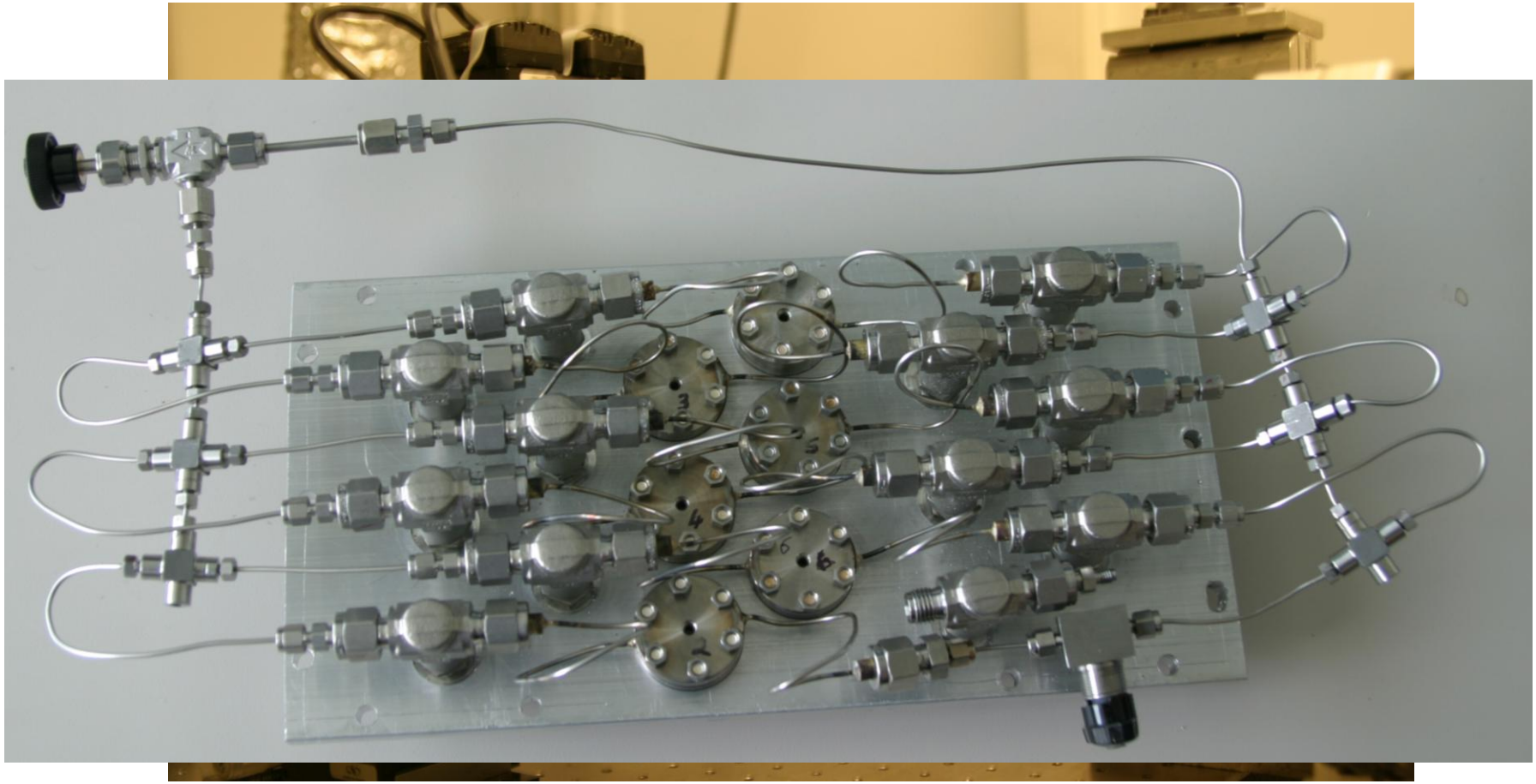
Comparison of Three Coals at 800 psi



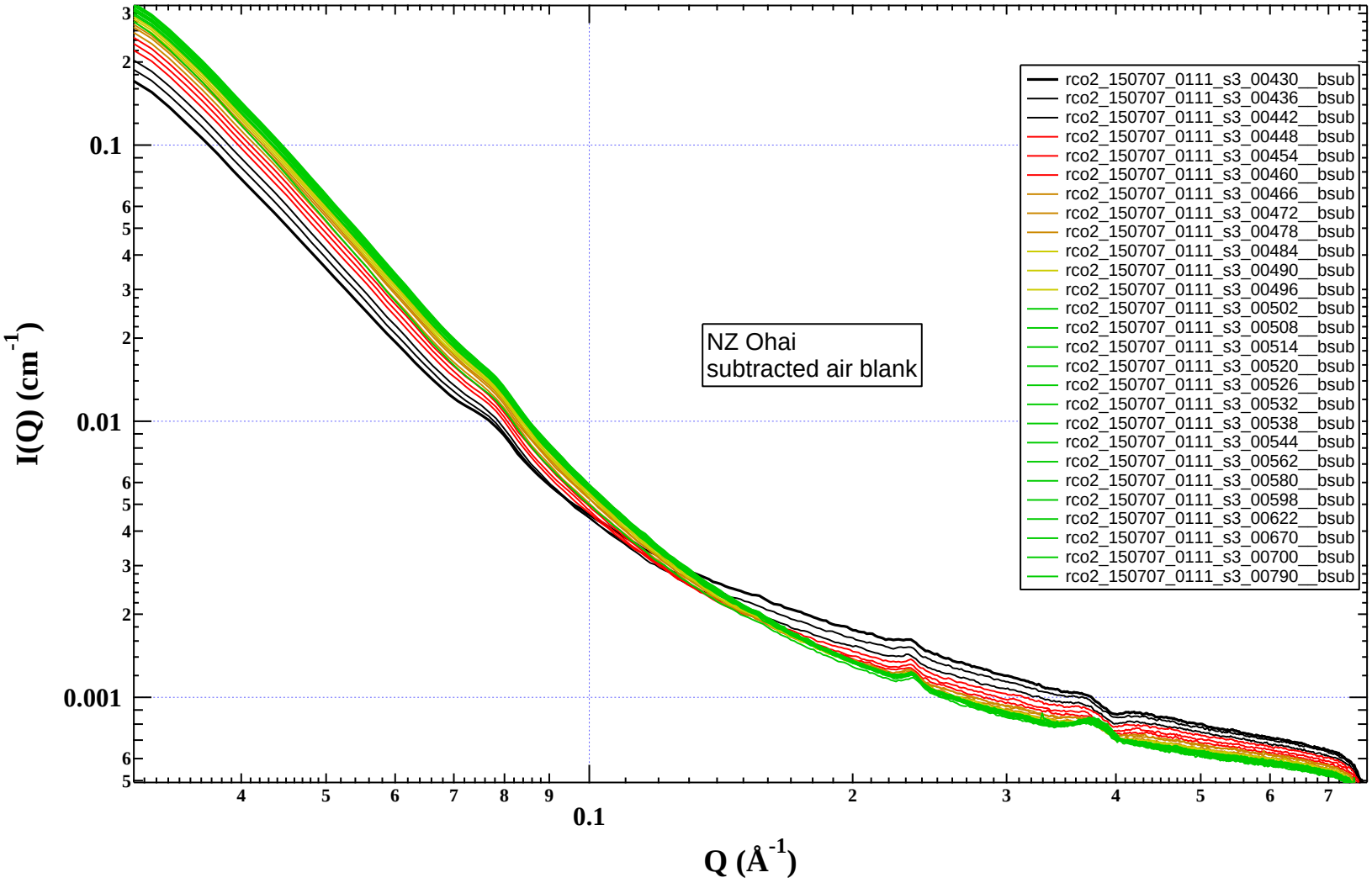
WyoDak (APCS 2) with Argon



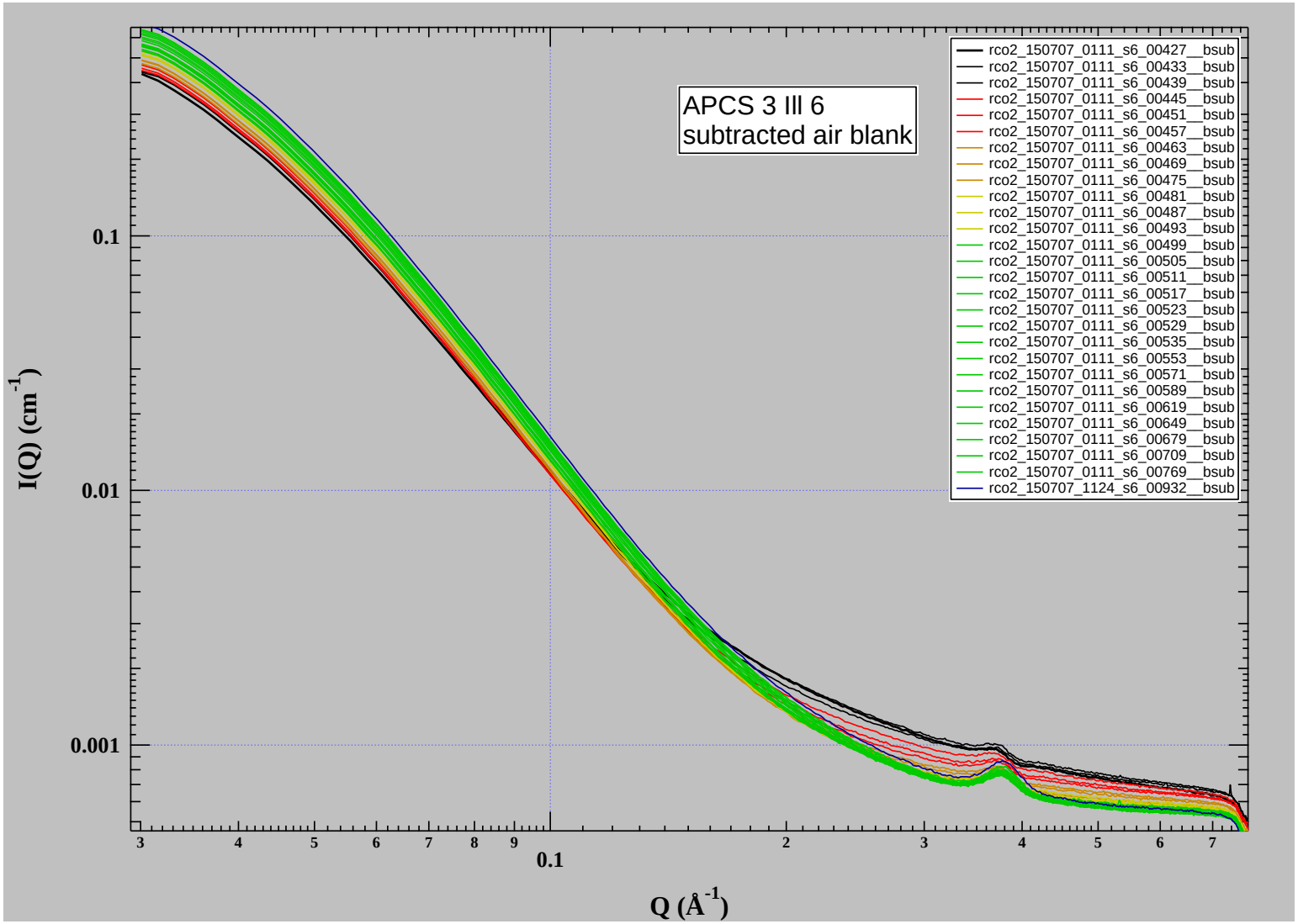
SAXS Instruments at 12-ID APS



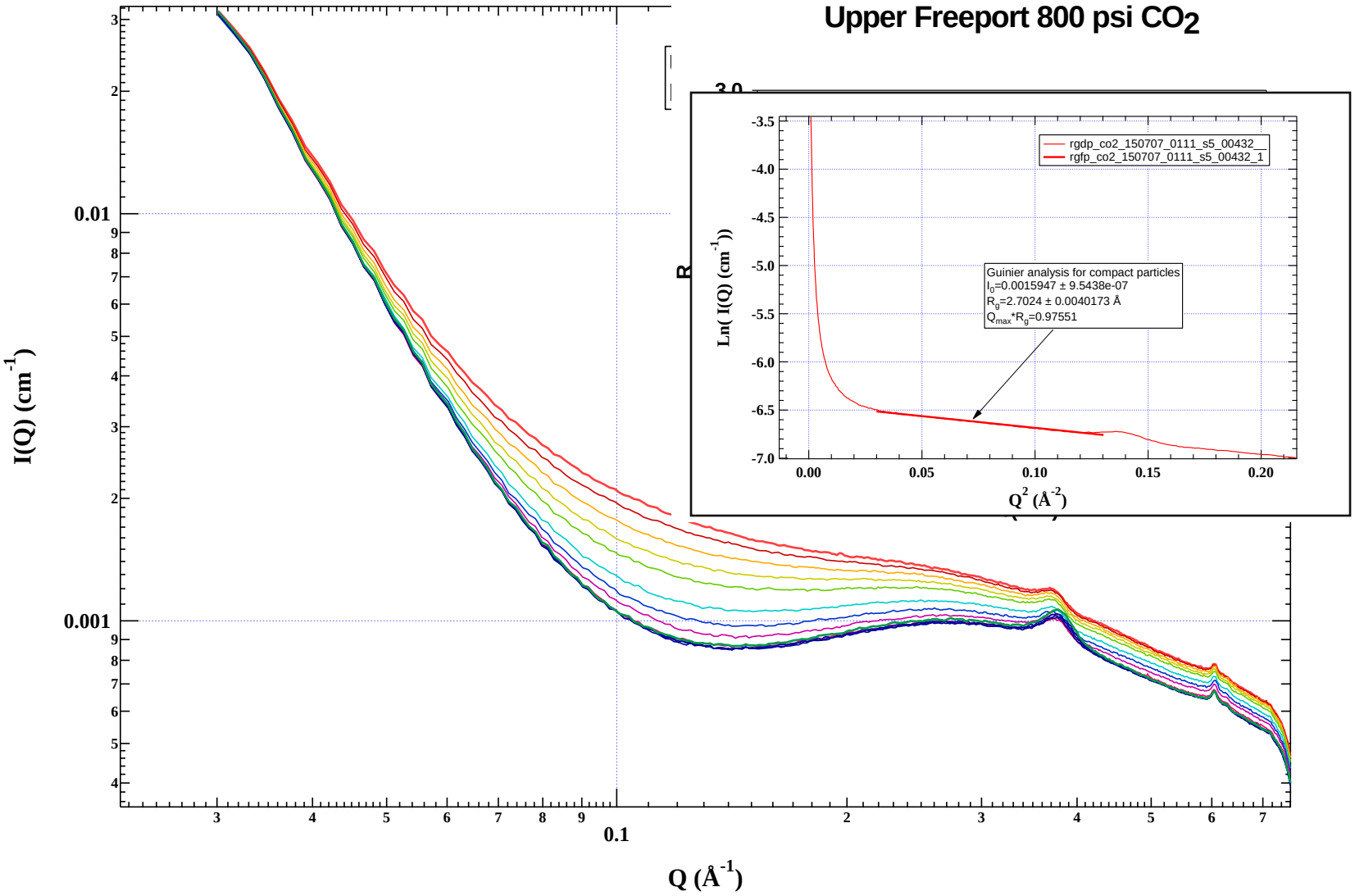
New Zealand Ohai Subituminous Coals – 800 psi



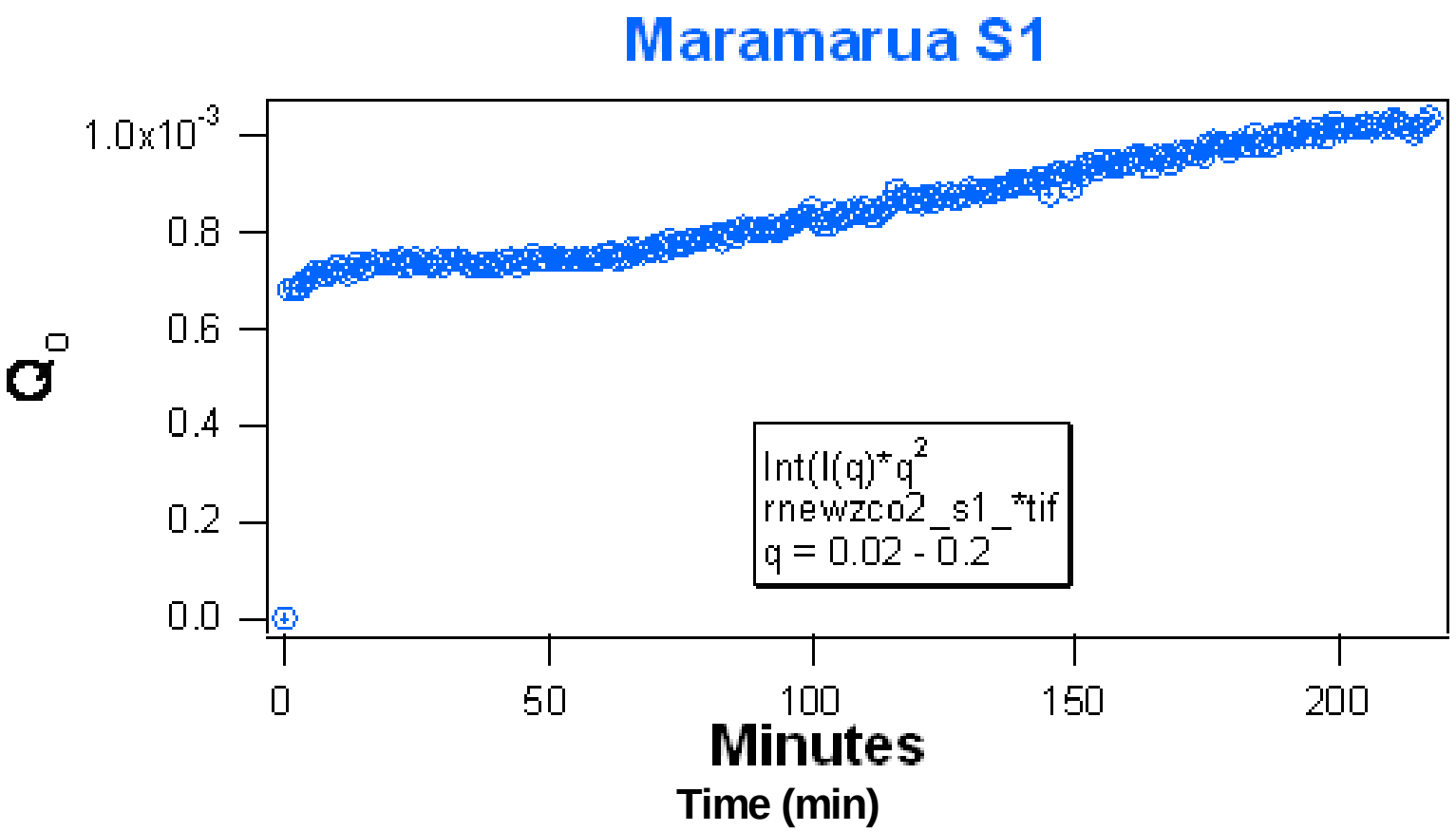
Illinois 6 Coal – 800 psi



Upper Freeport APCS 1 – 800 psi



Invariant Calculated for Coals at 900 psi

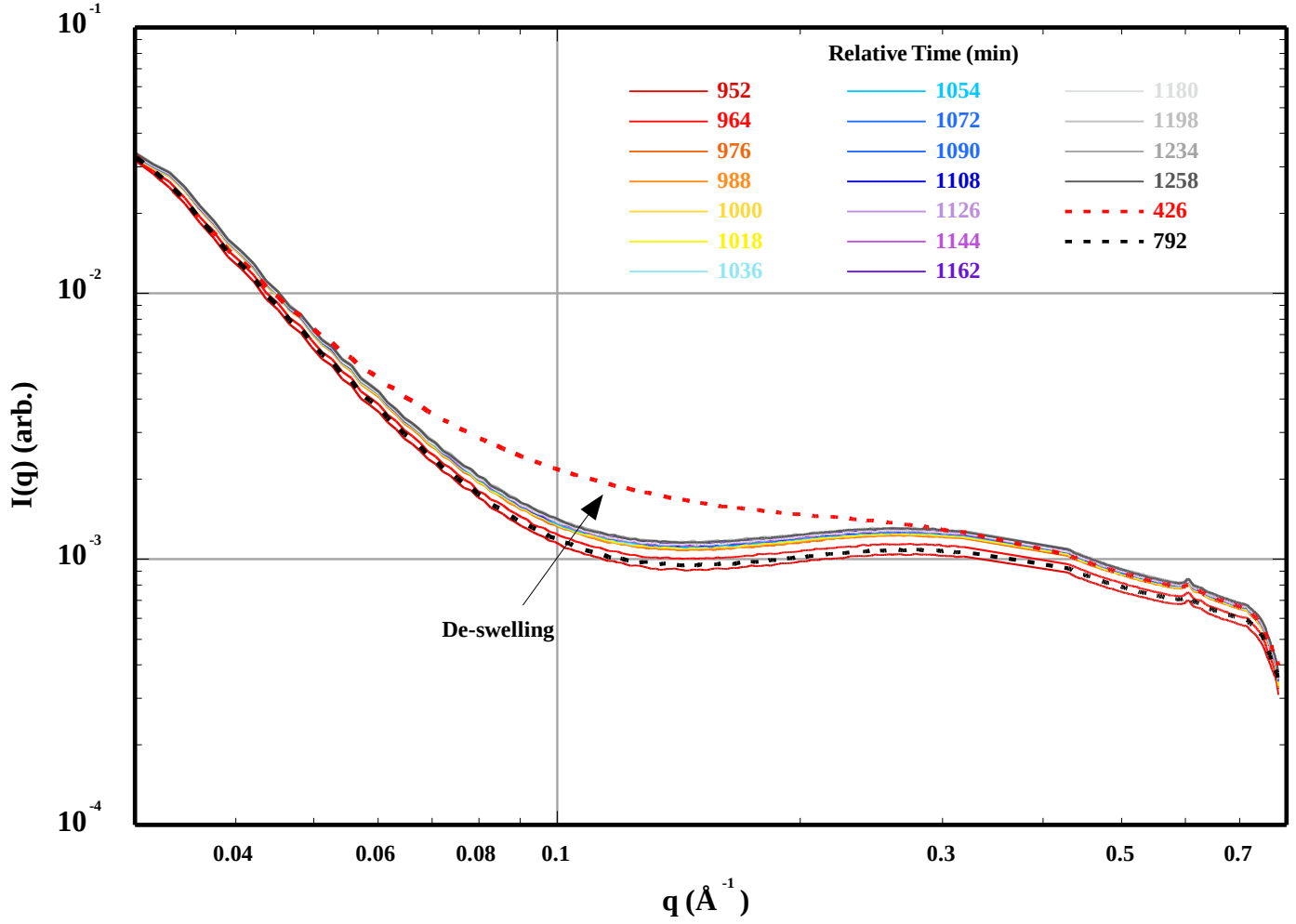


$$Q = \int_0^\infty q^2 dq \cdot I(q)$$

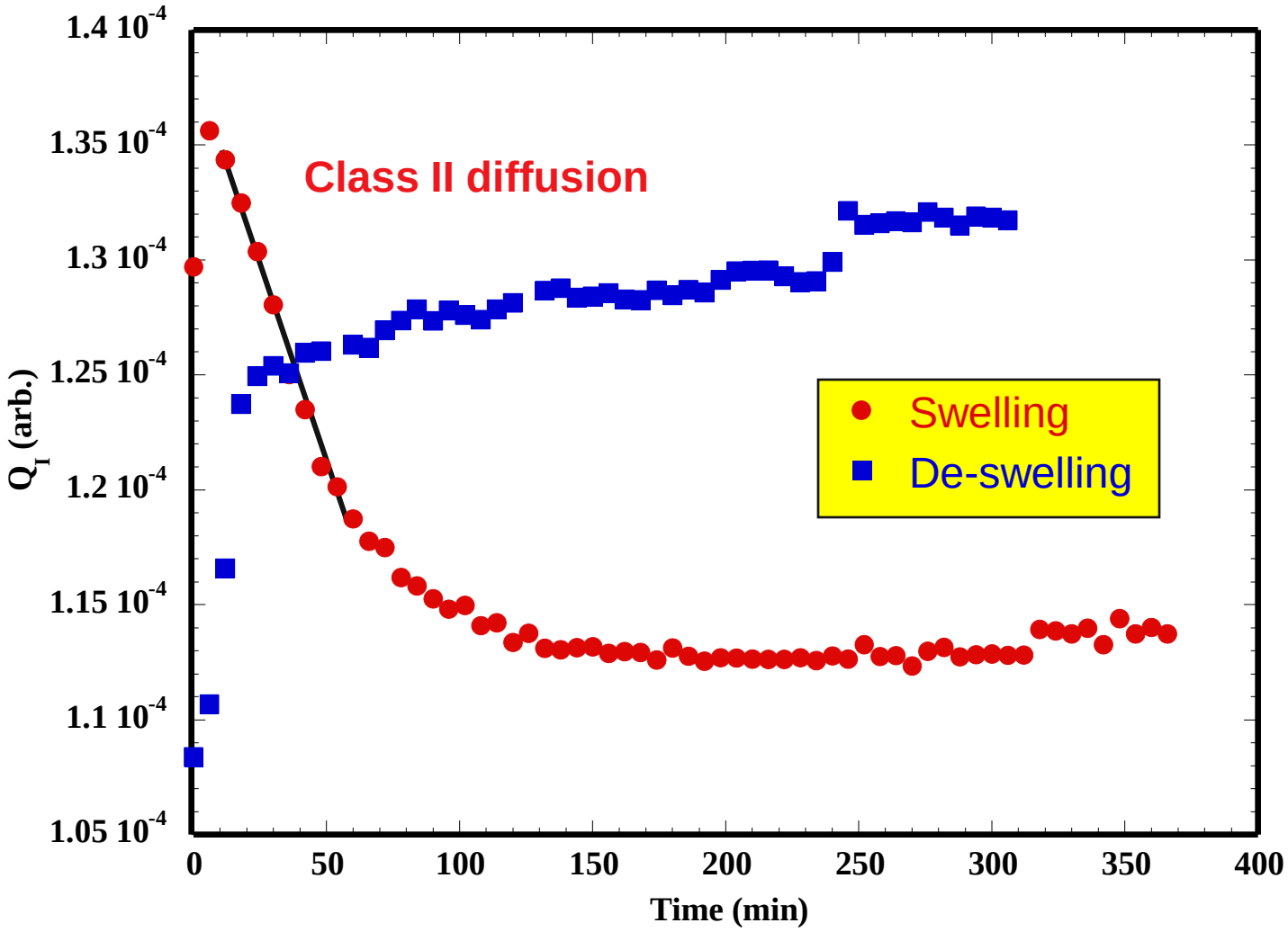
Decrease in the invariant is the result of a decrease in difference in electron density, which occurs as the CO_2 is filling the pores.

Upper Freeport APCS 1 – 800 psi

Scattering intensity of the APCS 1 coal following depressurization of the sample cell to atmospheric pressure air from 800 psig CO2 at ambient temperature.



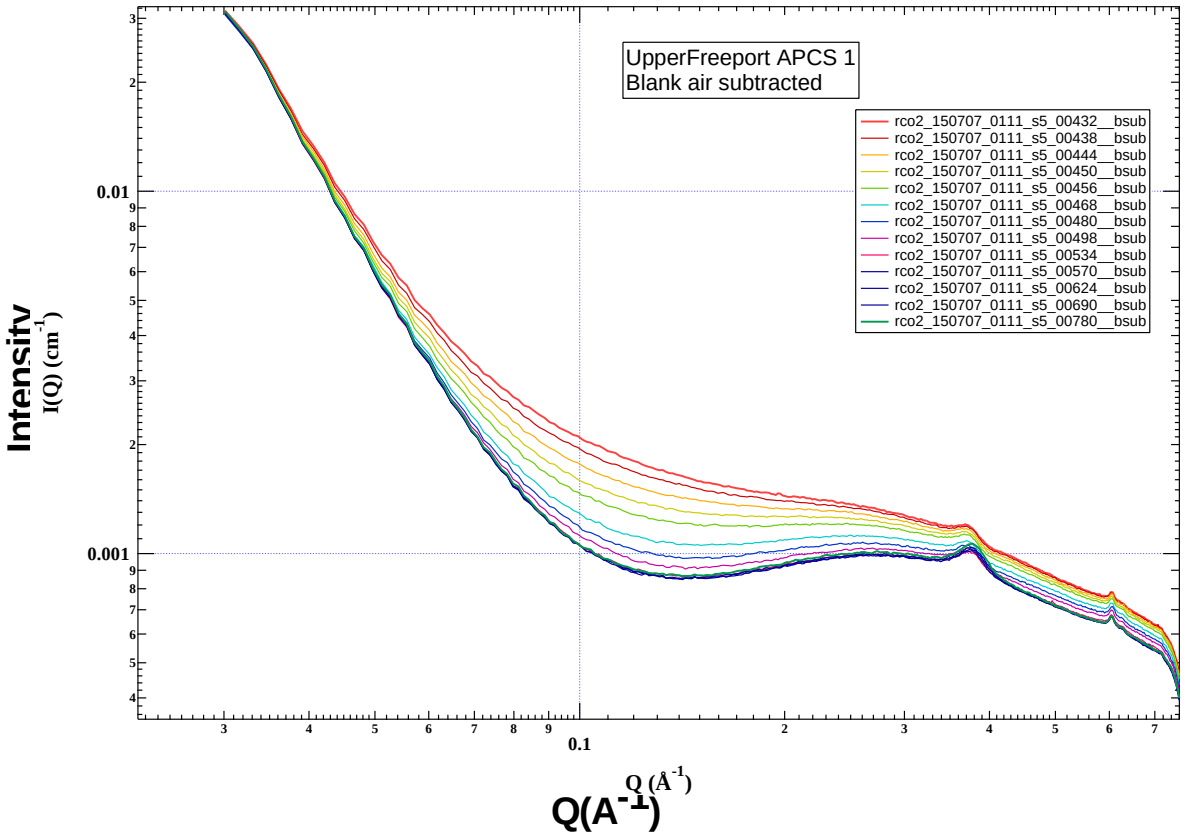
Upper Freeport APCS 1 – 800 psi - Invariant

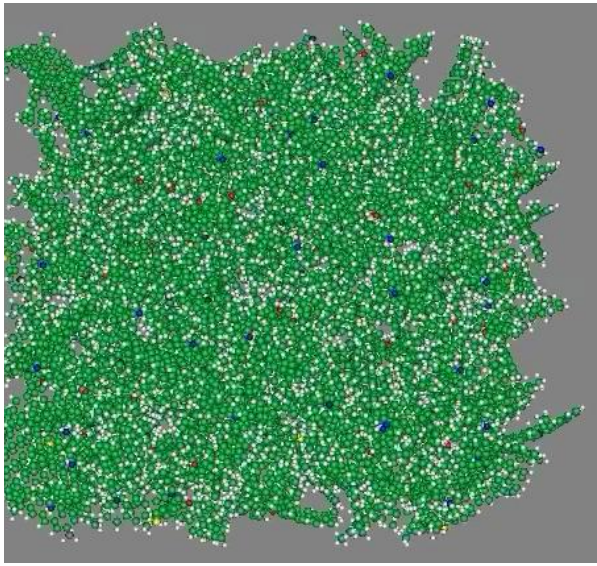


SAXS Calculated from Coal Models

SAXS calculated using CRYSOL

Svergun D.I., Barberato C. & Koch M.H.J. (1995) J. Appl. Cryst., 28, 768-773.





Models from:

Narkiewicz, M. R. and Mathews, J. P. Visualization of carbon dioxide sequestration issues within coal using a molecular representation of Pocahontas No. 3 coal, 12th International Conference on Coal Science and Technology, 2005, October 9-14, Okinawa, Japan, *Energy & Fuels* 2008, *22,* 3104–3111

Conclusions

- In short times of exposure to CO_2 the PDF results suggest that there are no changes in short length scales.
- In higher rank coals observed a slow uptake of CO_2 with a decrease in porosity.
- Model for CO_2 uptake in a high rank coal qualitative agrees with SAXS results
- Rank dependence is again observed in long exposures to CO_2

- The CO_2 uptake process can be interpreted in terms of a simplified two-phase model beginning with shorter term void/pore filling and gas adsorption onto the solid matrix followed by longer term coal swelling

Future

- Expand the coal set and the experimental parameters (pore size range, temperature, pressure and time).
- Look at PDF experiment over longer exposure times.
- Correlate with CO_2 uptake volume measurements obtained by other methods.
- Study the uptake and expulsion of CH_4.
- Use these results in combination with other approaches to predict sequestration behavior of selected coal seams.