Direct Observation of CO_2 Sorption on Argonne Premium Coal Samples

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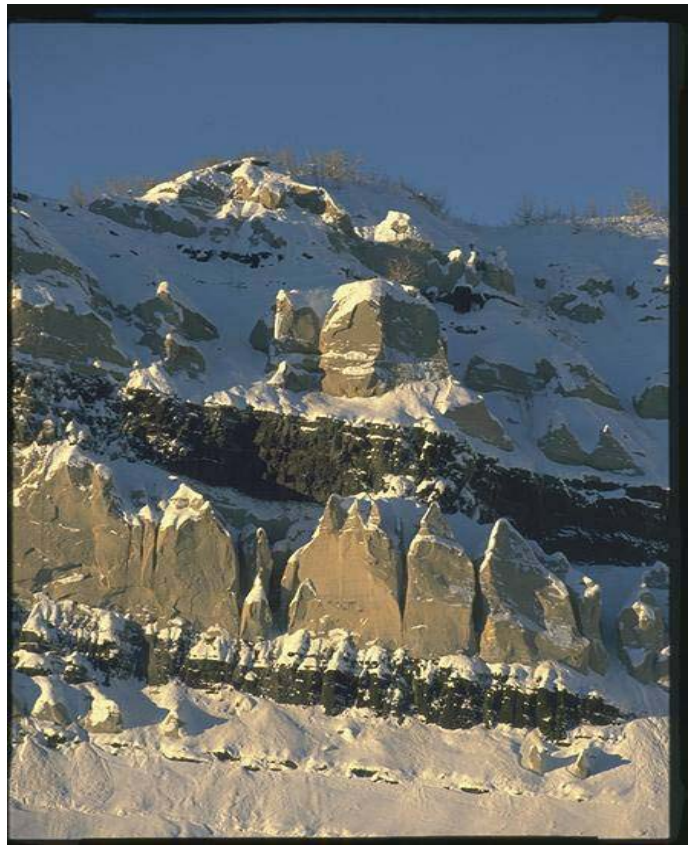
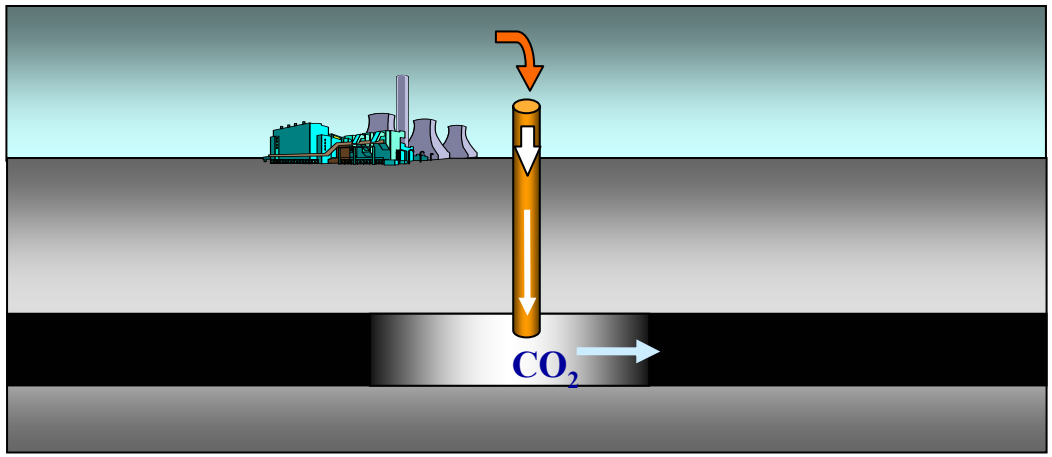


Third Annual Conference on Carbon Capture and Sequestration

Alexandria, Virginia

May 3-6, 2004

CO_2 sequestration in coal seams



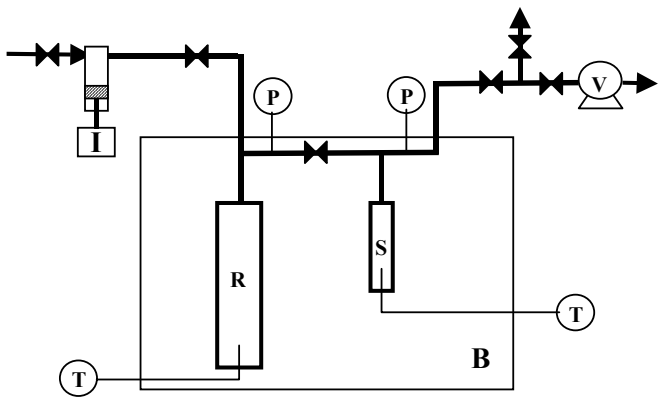
- understanding the mechanism by which CO_2 is stored in coal
- determining the CO_2-coal adsorption isotherm quantitatively

What is the nature of the CO_2–coal interaction?

- **Non-specific surface and pore filling?**
  - Adsorbed on the coal surface and absorbed within the coal organic matrix
- **Specific interaction between CO_2 and coal functional groups?**
  - carboxyl ($-CO_2H$, $-CO_2R$, $-CO_2Ar$) and / or carbonyl (>C=O) functional groups?
  - hydroxyl (R-OH, ArOH) groups?

  - Nishino "Adsorption of water vapor and carbon dioxide at carboxylic functional groups on the surface of coal" *Fuel* **2001** *80*, 757-764.
  - Adsorption NOT related to hydroxyl groups
  - Found a GOOD correlation between CO_2 adsorption and carboxyl group content for a set of 20 coals.

Calculating the CO_2-coal adsorption isotherm using manometric methods



- R: reference chamber, S: sample chamber, P: pressure transducer, I: syringe pump, V: vacuum pump, T: thermocouples, B: constant temperature bath

$$\Delta n^{ex} = \left(\frac{1}{RT_{iso}m_c}\right) * \left(V_R\left(\frac{P_{ri}}{Z_{ri}} - \frac{P_{rf}}{Z_{rf}}\right) - V_V\left(\frac{P_{sf}}{Z_{sf}} - \frac{P_{si}}{Z_{si}}\right)\right)$$

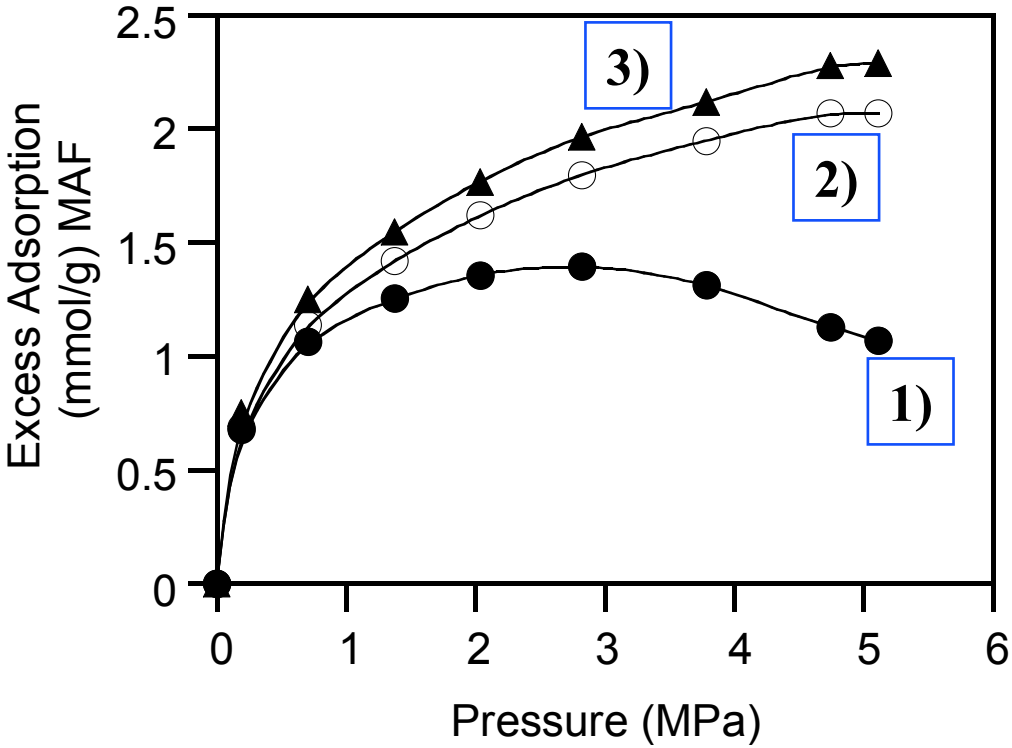
Compressibility Factor

$$n^{ex} = \Delta n_1^{ex} + \Delta n_2^{ex} + \Delta n_3^{ex} + \ldots + \Delta n_i^{ex}$$

$$n^{abs} = \frac{n^{ex}}{\left[1 - \left(\rho_g / \rho_a\right)\right]}$$

Adsorbed Layer Density

Compressibility Factor (Z)



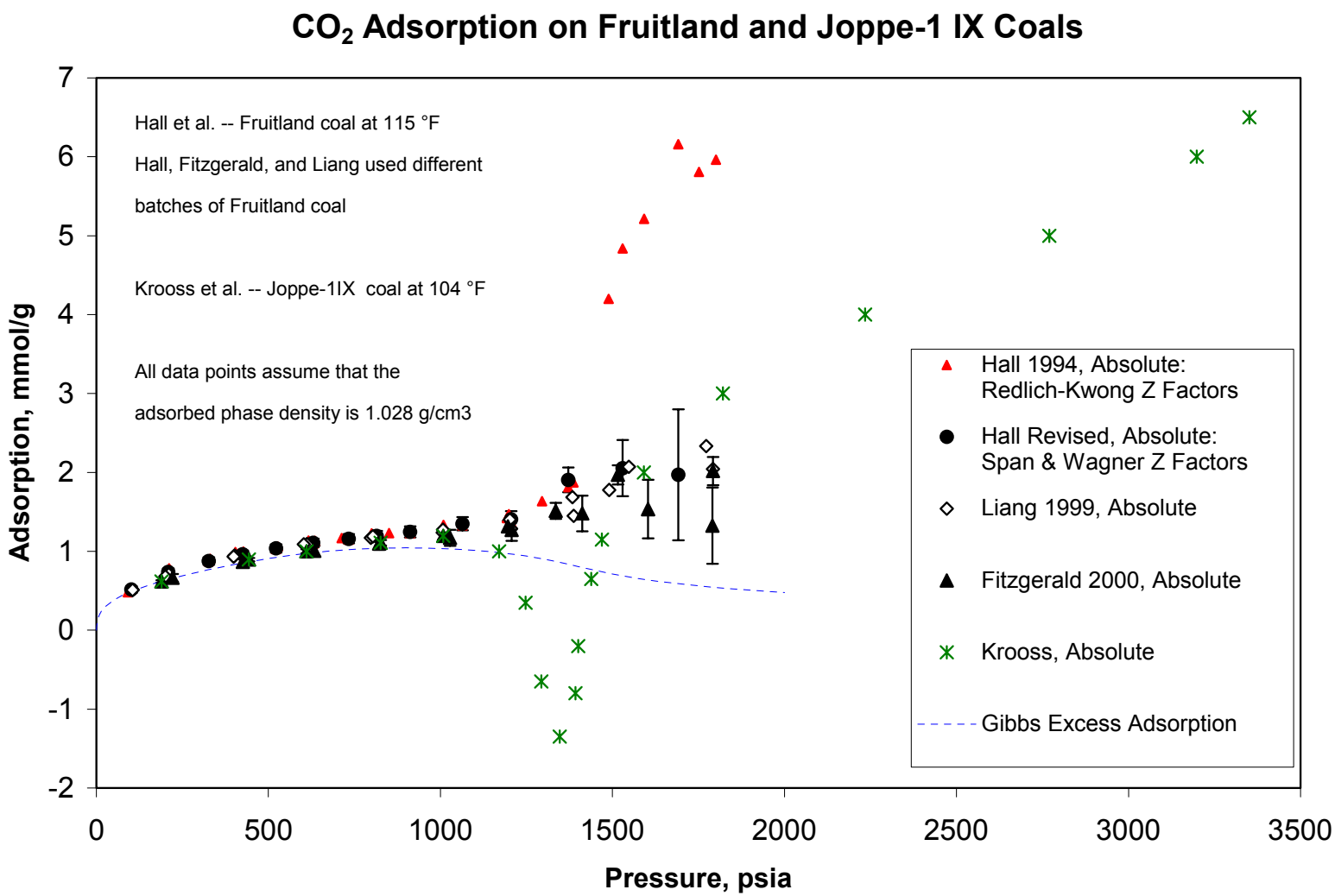
- 1) Z = 1 (ideal gas law)
- 2) Z value from Air Liquid Gas Encyclopedia, 1976
- 3) R. Span, W. Wagner, *J. Phys. Chem. Ref. Data* **25**, 6, **1996**

Adsorbed Layer Density

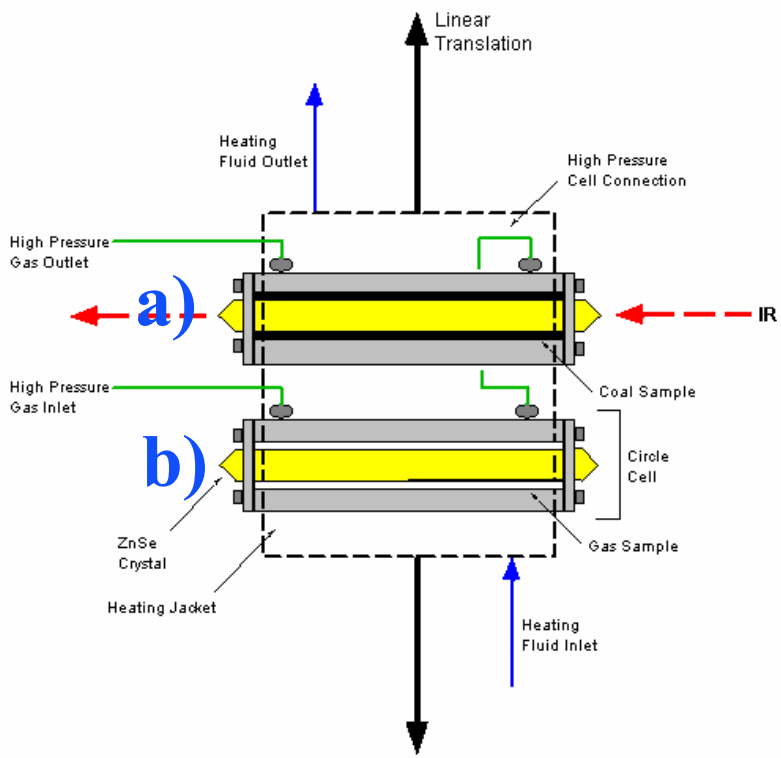
method	Adsorbed layer density (g/cm^3)
VDW	1.03
Solid density estimate	1.18
ONO-Kondo Model	0.996
ZGR EOS	0.982

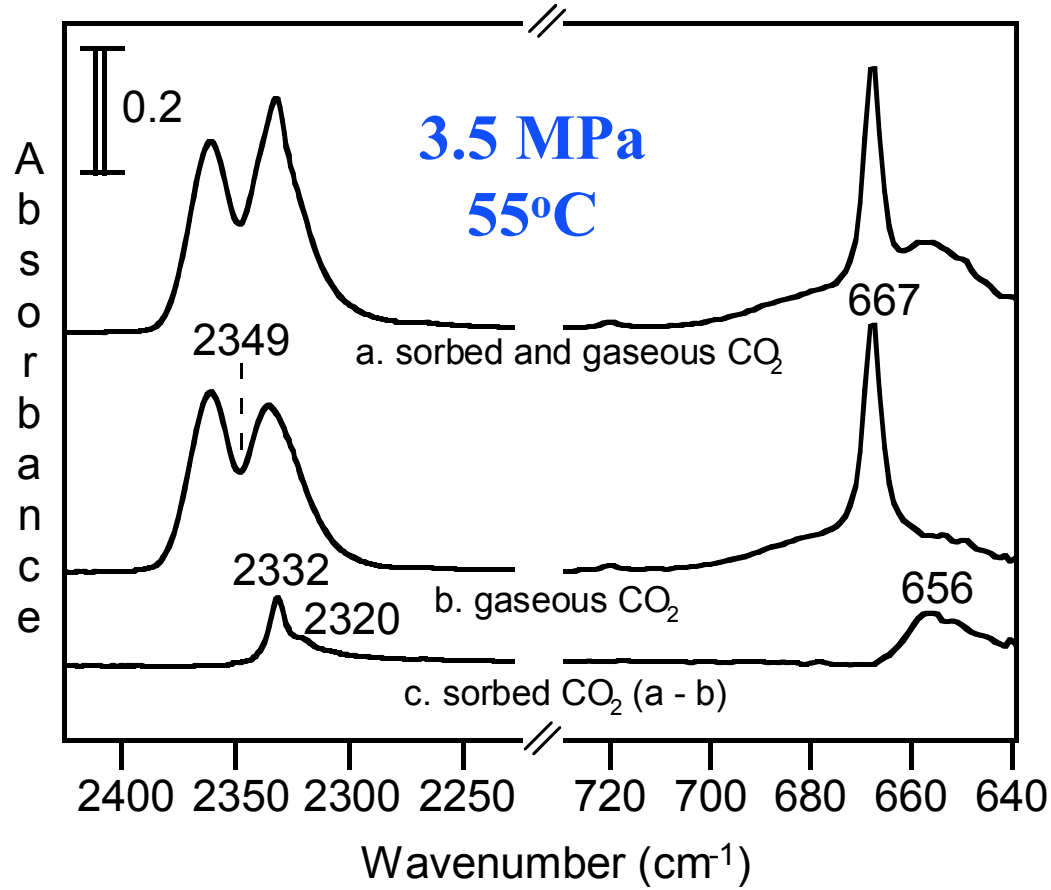
Sudibndriyo et al, *Langmuir* **2003**, *19*, 5323-5331

CO_2 adsorption on coal at high pressures



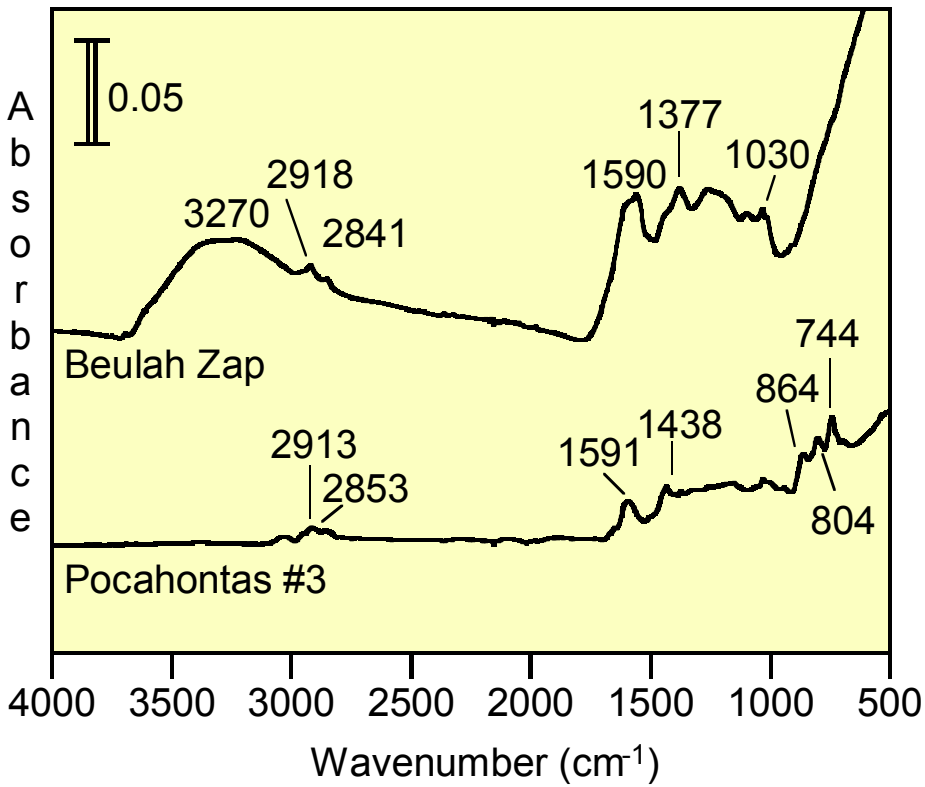
The ATR-FTIR experiment



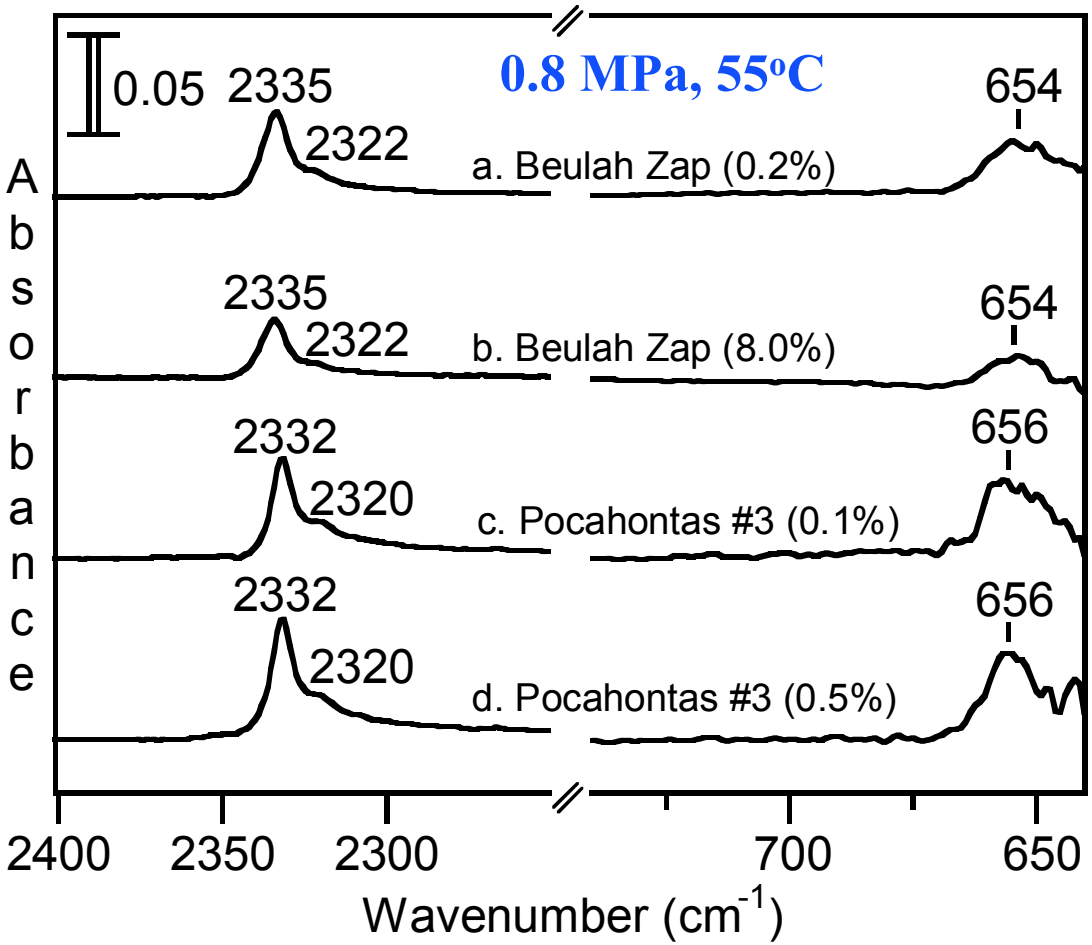


Argonne premium coals

- Pocahontas #3 (low volatile bituminous) and Beulah Zap (lignite).
- coals are well-characterized, providing the research community with a large database of physical and chemical properties of coal
- samples were supplied as powders (-100 mesh).
- Prepared in an inert environment



Spectral data indicate that there is no specific CO_2 – carbonyl nor CO_2 – carboxyl interactions.



Polymers Containing Carbonyl and Carboxyl Functional Groups:

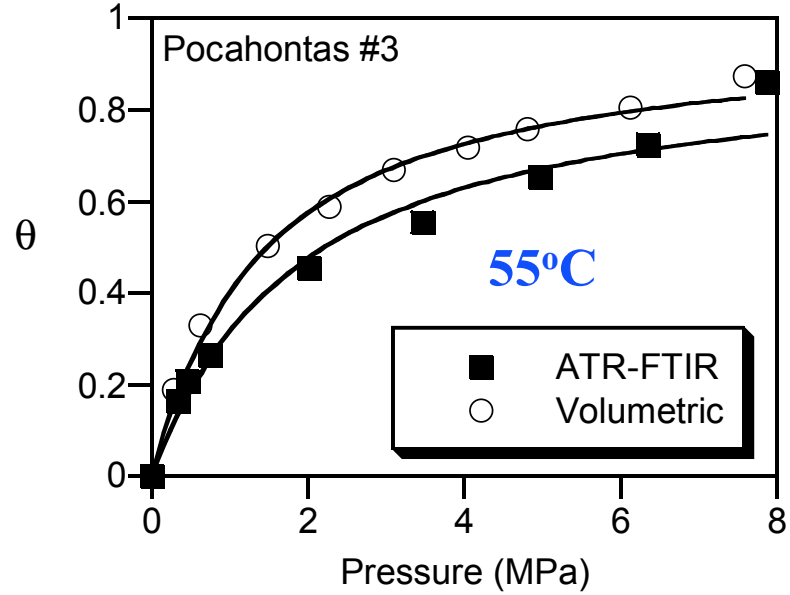
2338.0 - 2339.5 cm $^{-1}$

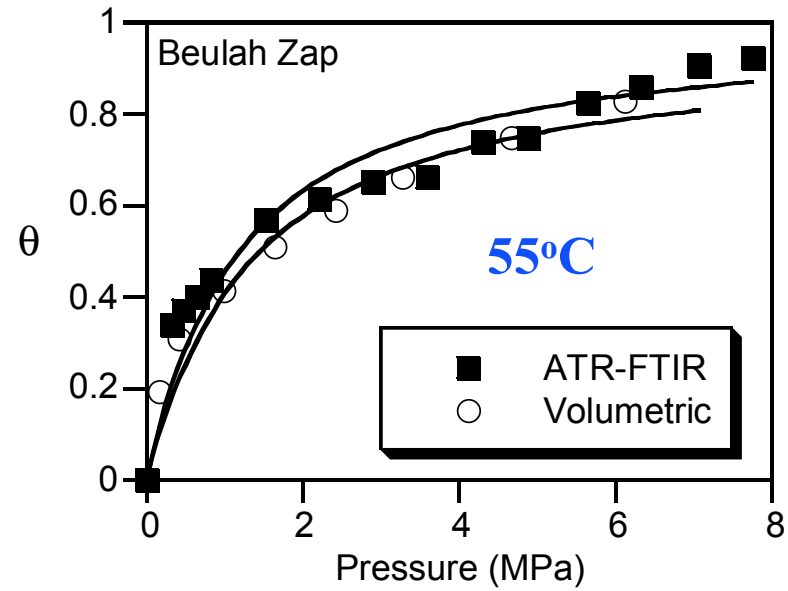
Polymers That Don't Contain Carbonyl and Carboxyl Functional Groups :

2334.5 - 2335.5 cm $^{-1}$

Kazarian et al. "Specific Intermolecular Interaction of Carbon Dioxide with Polymers" *J. Am. Chem. Soc.* **1996,** *118,* 1729-1736.

Comparing ATR-FTIR and manometric techniques for CO_2 adsorption on Argonne coals





For the manometric method:

1. Z values calculated from Span and Wagner EOS

2. Adsorbed layer density = 1.03 g/cm^3

Energy of Adsorption

- **Langmuir Equation**

$$\theta = \frac{bP}{1 + bP} \qquad b = b_o e^{Q/RT} \qquad b_o = \frac{N\sigma\tau_o}{(2\pi MRT)^{1/2}}$$

Technique	Coal	% Moisture	Q (kJ/mol)	b (1/Mpa)
ATR-FTIR	Beulah Zap	8.0[a]	19.9	0.711
ATR-FTIR	Beulah Zap	0.2[b]	20.5	0.878
Manometric	Beulah Zap	4.0[c]	20.2	0.787
ATR-FTIR	Pocahontas #3	0.5[a]	20.0	0.706
ATR-FTIR	Pocahontas #3	0.1[b]	18.8	0.471
Manometric	Pocahontas #3	0.5[c]	19.9	0.708

Conclusions

- **one type of sorption site for CO_2**
- **physical sorption process (18.8-20.5 kJ/mol)**
- **the nature of the CO_2 – Coal interaction:**
  - no specific interactions with coal functional groups.
- **Isotherm shape was generated by ATR-FITR**
  - No assumption for the compressibility factor or adsorbed layer density