Assessing ultramicropores of shales by CO_2 adsorption at 273K
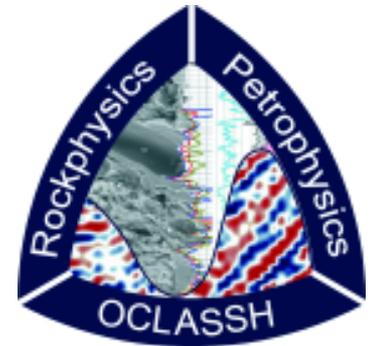
Nerine Joewondo & Manika Prasad

Colorado School of Mines
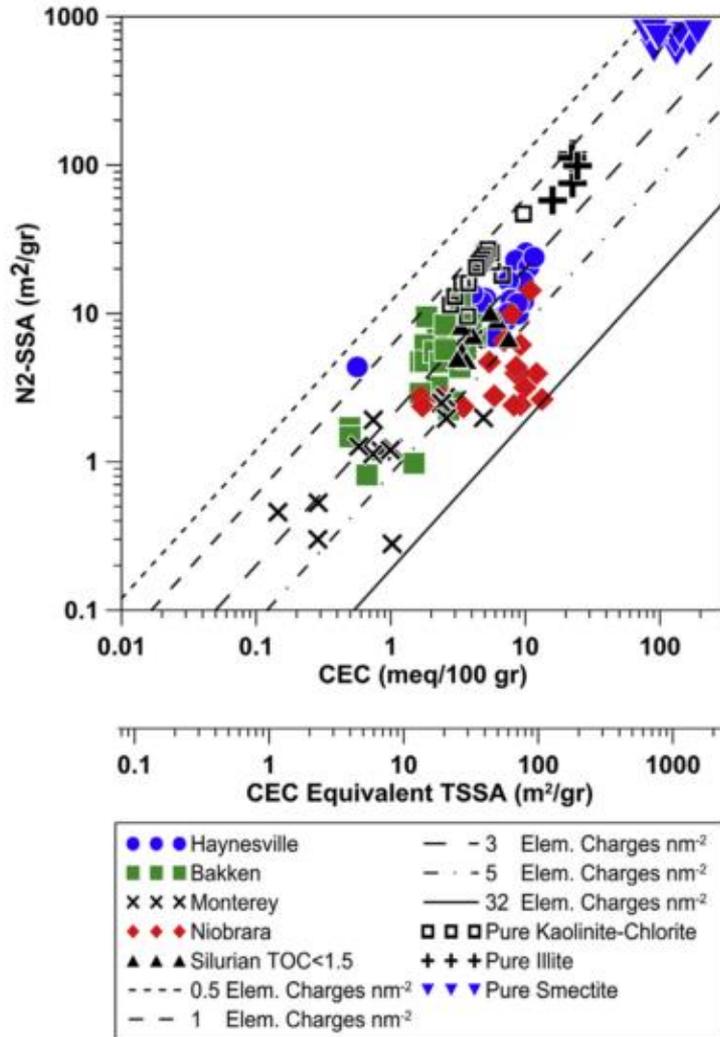
Motivation

- Storage mechanisms in unconventionals
  - Adsorption can account for 80% of estimated GIP in shales (Ambrose et al. 2012)
  - Observed storage capacity in standard clays in reservoir condition increases with BET specific surface area (SSA) (Busch et al. 2008)

Motivation

- Seismic & electrical properties are affected by fluid saturation
  - Shales have large surface area
  - Increased rock – fluid interactions

- Problems: (Saidian et al. 2016)
  - CEC sensitive to clay content & type
  - **N2 – SSA is not as sensitive**

Objectives

- Perform CO_2 adsorption at 273 K to characterize nanopores of shales
  - Study ultramicropores of shales (0.2 -1.4 nm)
  - Compare or compliment N_2 at 77 K results (.7 nm - 50nm)
  - Kinetic diameter of CO_2 is smaller than N_2

Adsorption mechanism
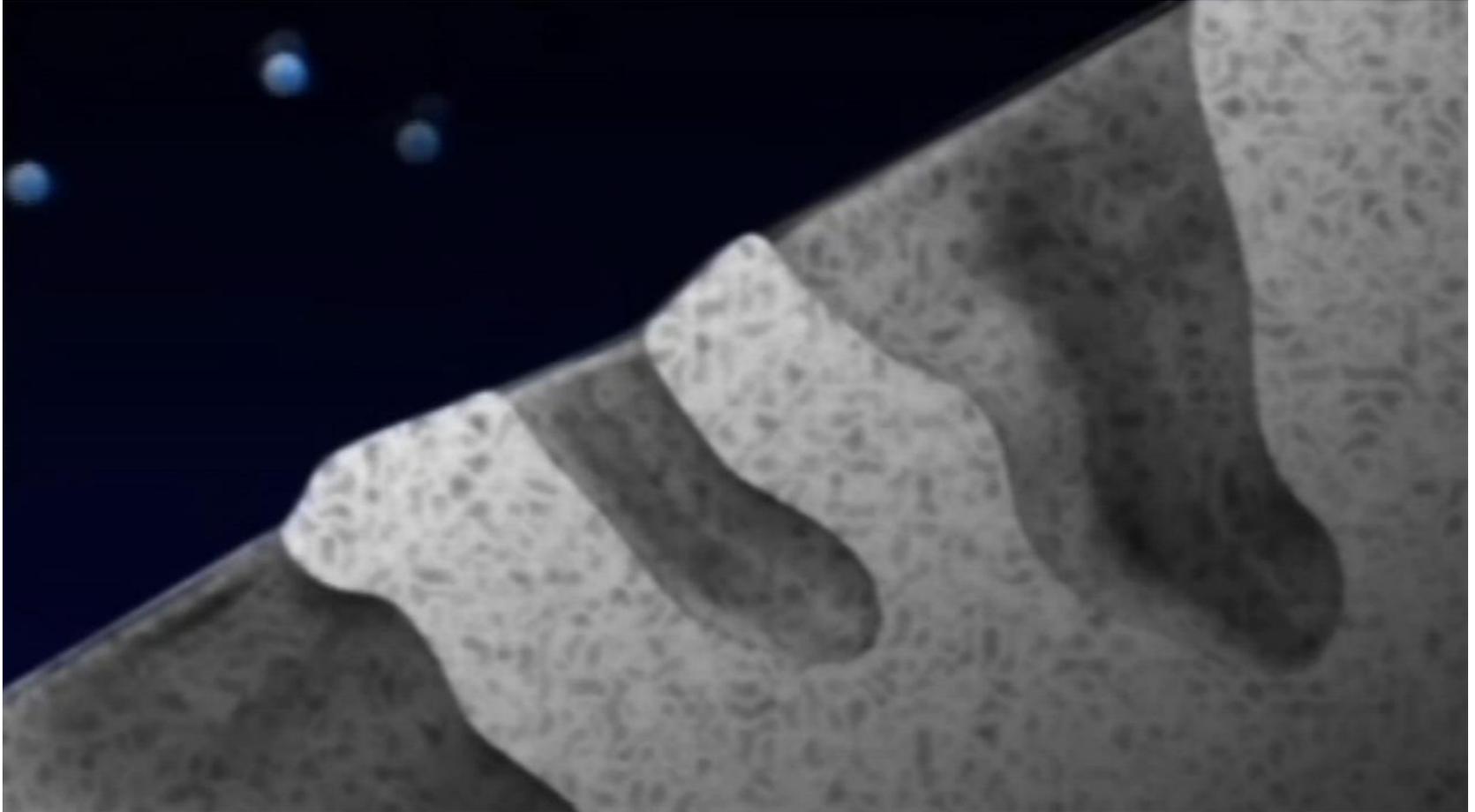
Video modified from Quantachrome

IUPAC Definitions

- ## Ultramicropores
  - Pore diameter ≤ 1 nm

- ## Micropores
  - Pore diameter ≤ 2 nm

- ## Mesopores
  - Pore diameter 2-50 nm

- ## Macropores
  - Pore diameter ≥ 50 nm

  * IUPAC (Thommes et al. 2014)

TEM resolution :0.2 nm
(Curtis, 1989)

CO_2 : < 1.4 nm
IUPAC (Thommes et al. 2014)

SEM resolution : 2 nm
(Shao et al. 2017)

N_2 range : 0.7 – 50 nm
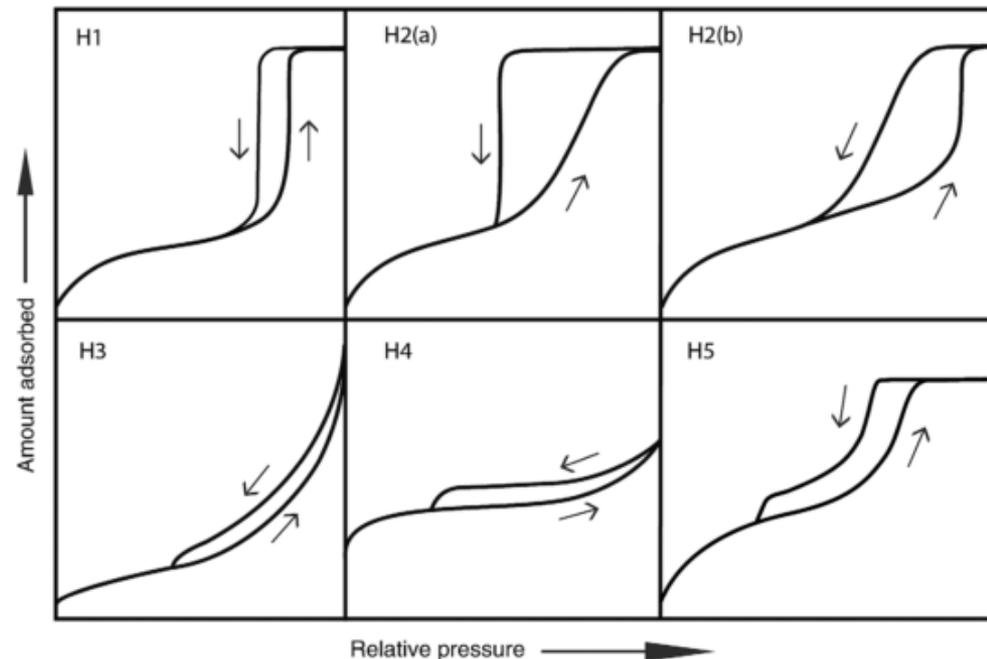IUPAC (Thommes et al. 2014)

NMR : > 2nm
(Klobes & Meyer 2014)

MICP: > 3 nm (400 MPa)
(Rouquerol et al. 2014)

Adsorption mechanism

Adsorbed amount at **constant temperature** and **volume** is a function of

Pressure, pore structures (geometry, size) & materials (composition, gas used)


(IUPAC 2015)

Inversion methods

- **Macro**scopic thermodynamics based method
  - **BJH**, t-plot, BET
  - Most widely used

- **Micro**scopic thermodynamics/ statistical mechanics based methods
  - Most recent development due to advances in computational methods
  - **DFT**, molecular simulation
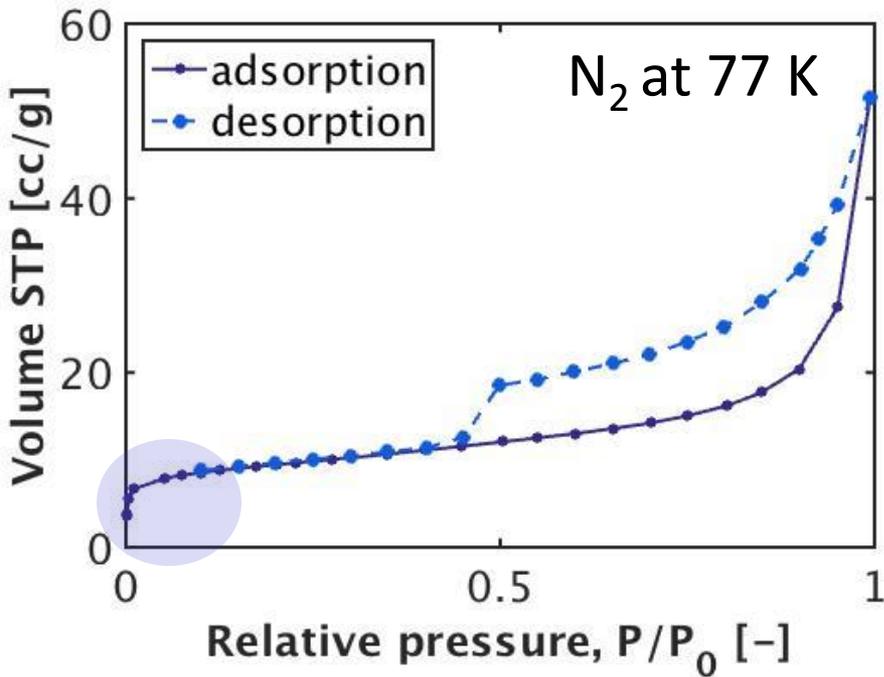 - recommended for nano-scale phenomena

Materials

- SWy-2* : Na-rich montmorillonite

- ISCz-1* : Illite smectite

- IMt-1* : Illite

- Utica 2.7% TOC, 53.3% clay, Carbonate 12%, QFPP 32%

- Niobrara 3% TOC, 35% clay, Carbonate 32%, QFPP 30%
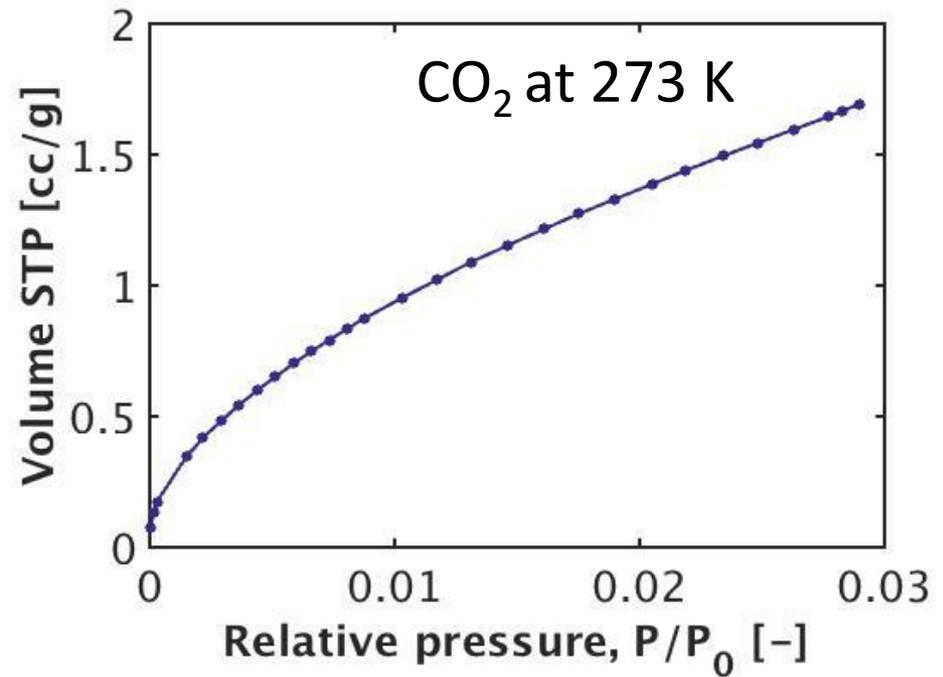
* from The Clay Mineral Society
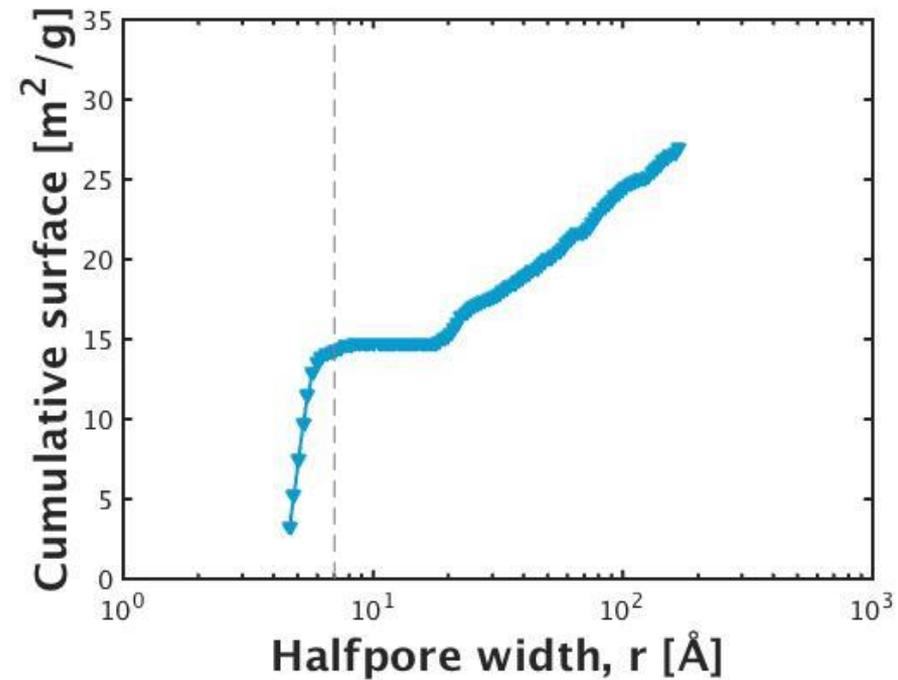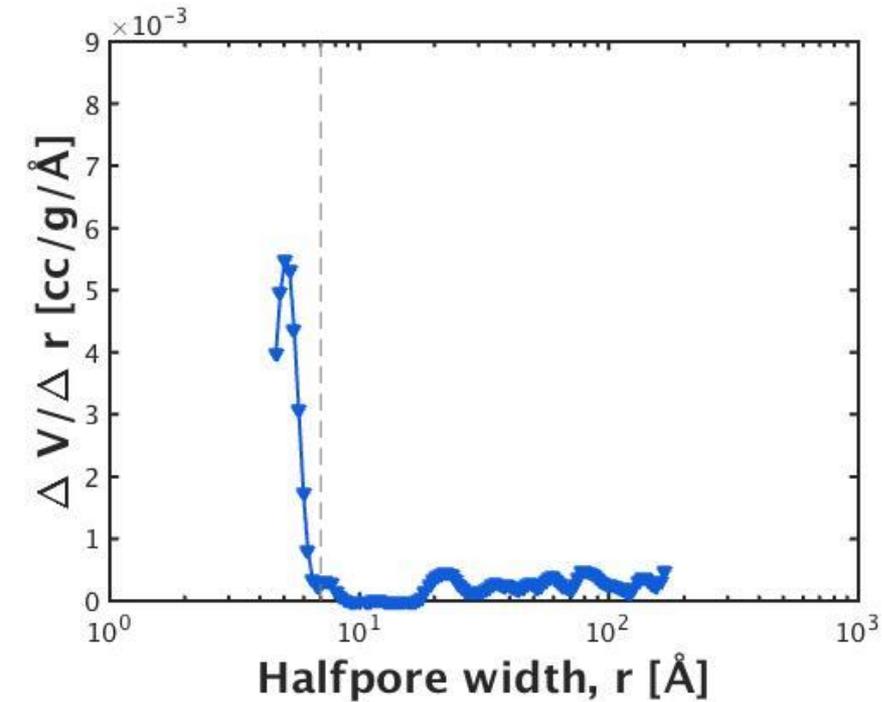
Isotherms of SWy-2

Isotherms of SWy-2

N_2 at 77 K

$P_{max} = 1$ atm
$P_0 = 1$ atm

CO_2 at 273 K
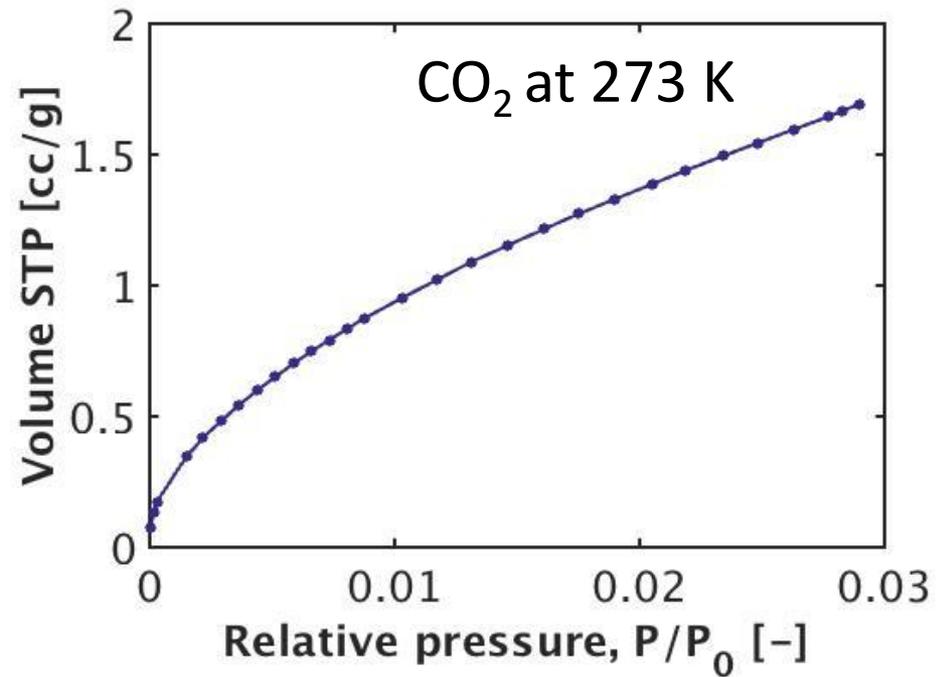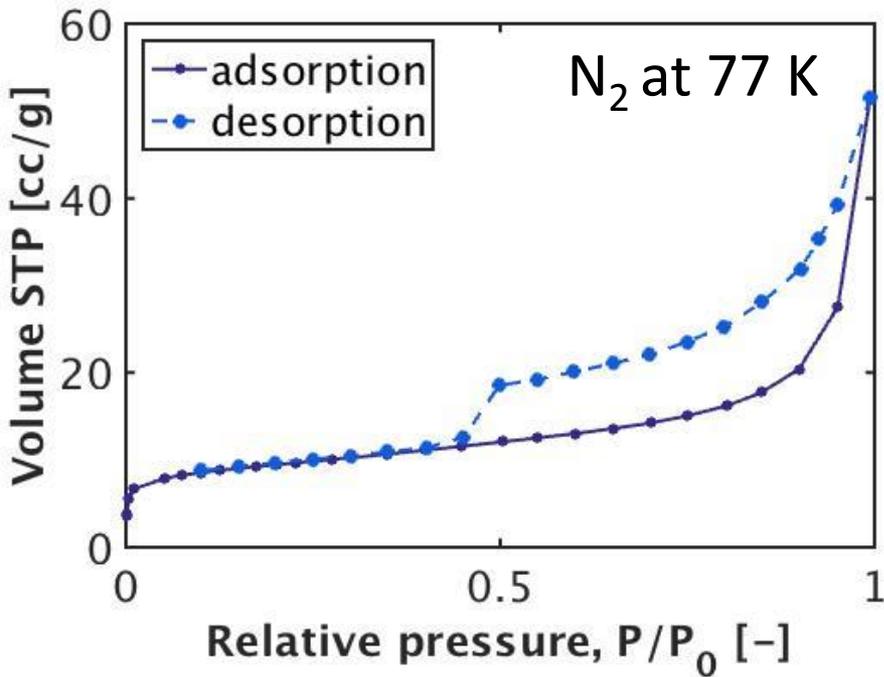
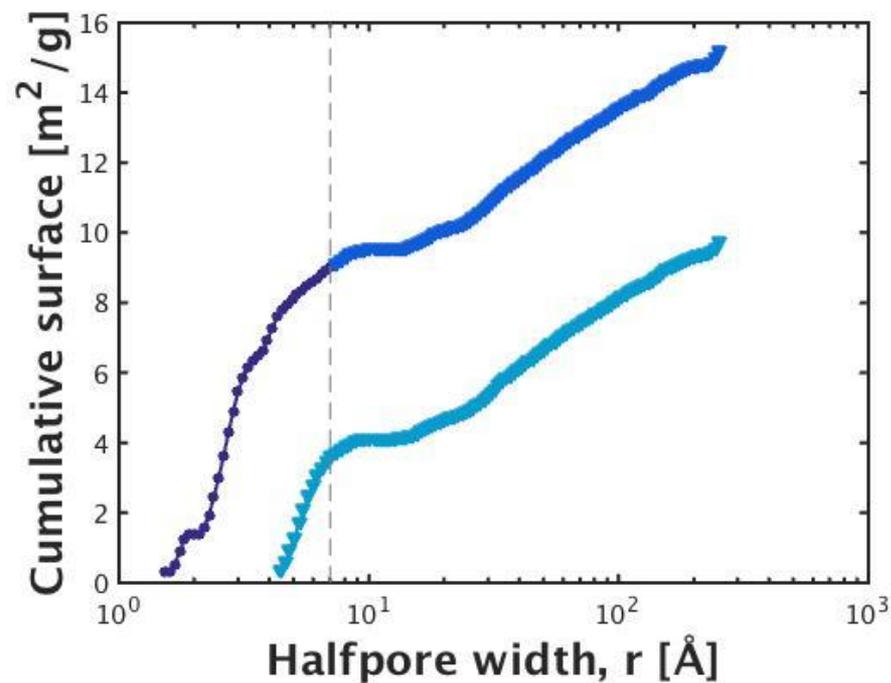$P_{max} = 1$ atm
$P_0 = 2600$ atm

PSD of SWy-2 Nitrogen

PSD of SWy-2 N$_2$ CO$_2$
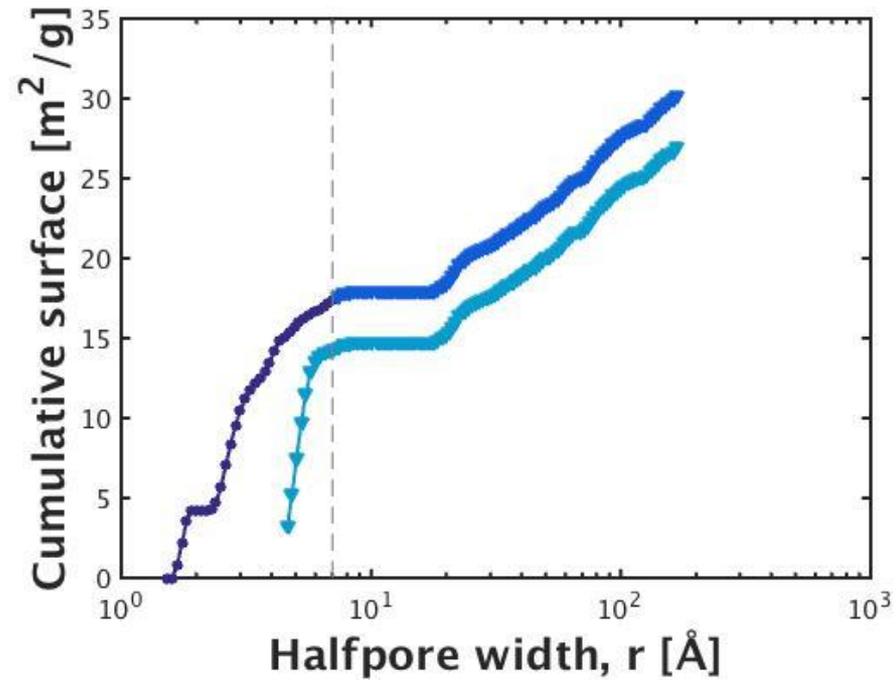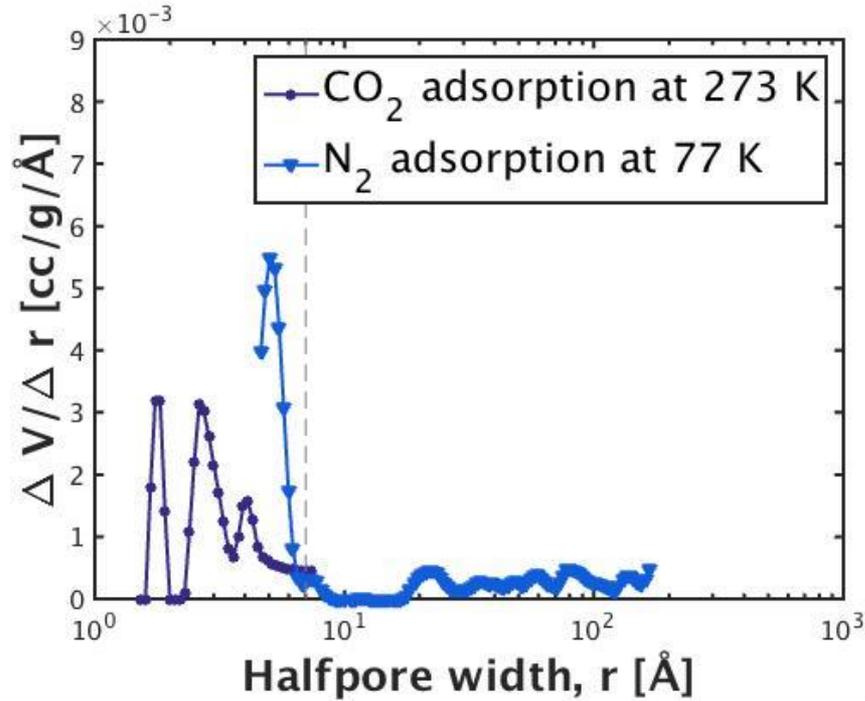
PSD of Niobrara
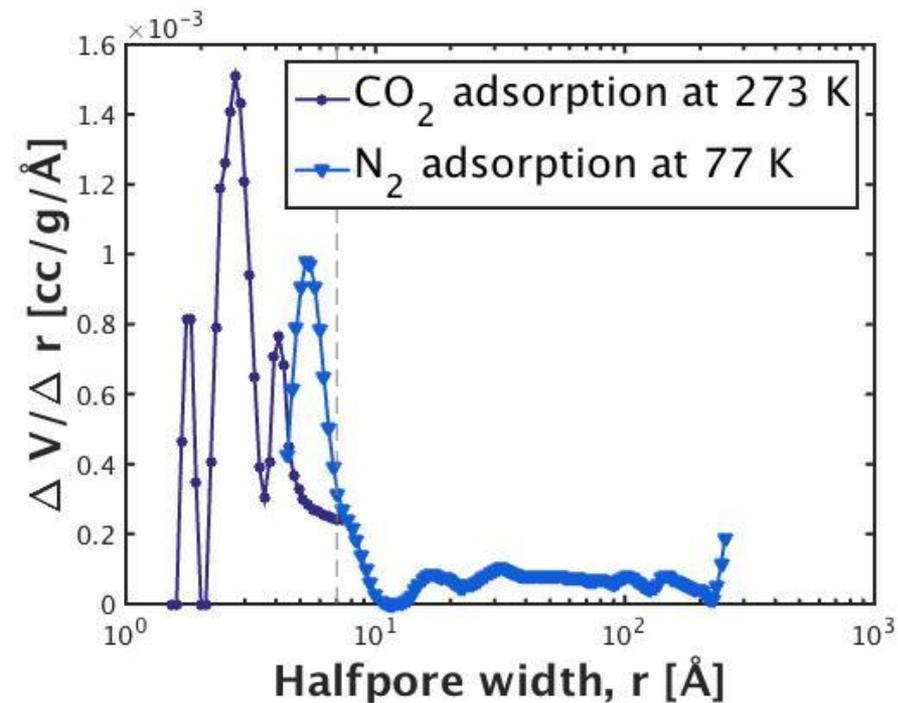
Summary
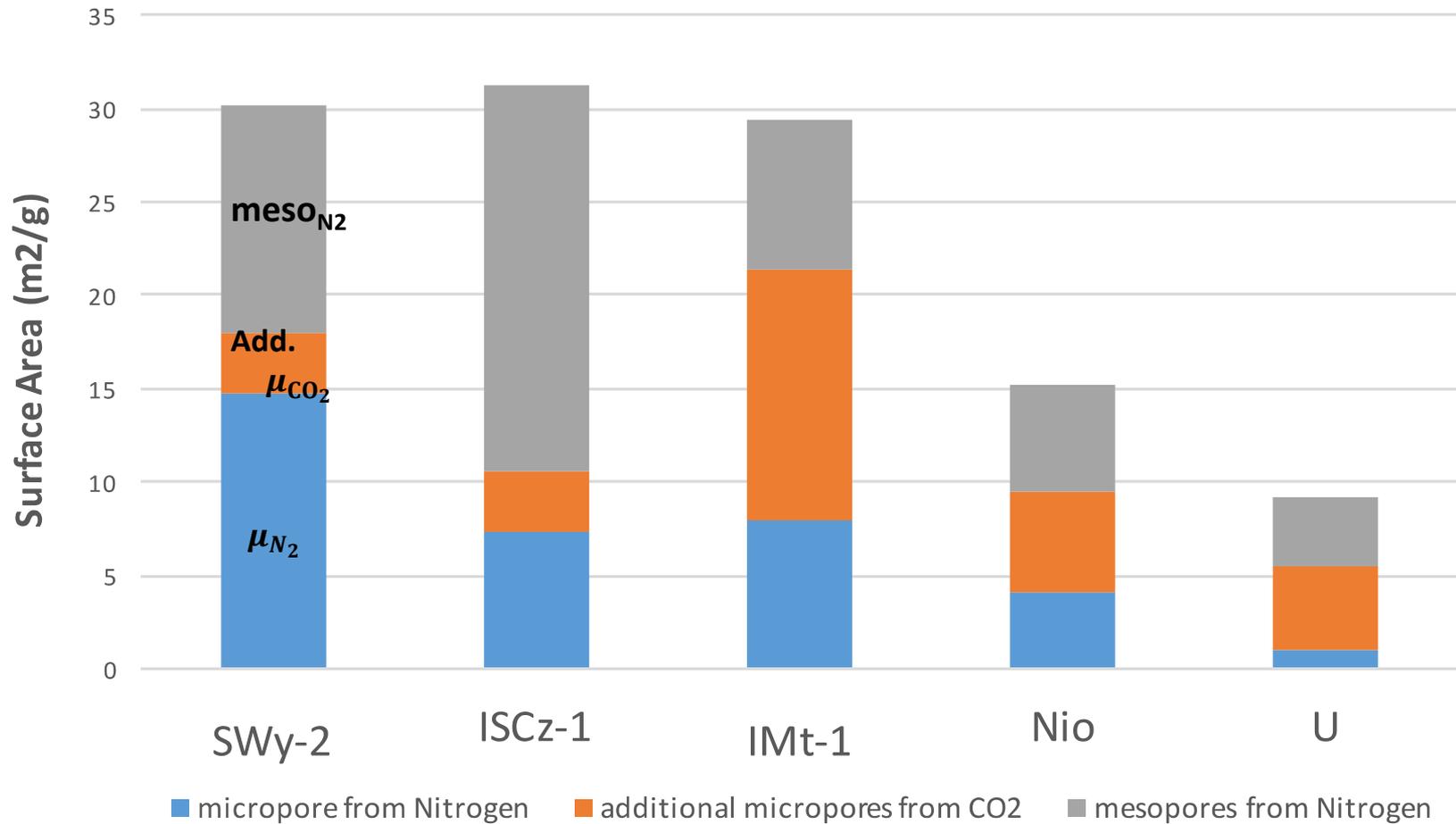
Summary
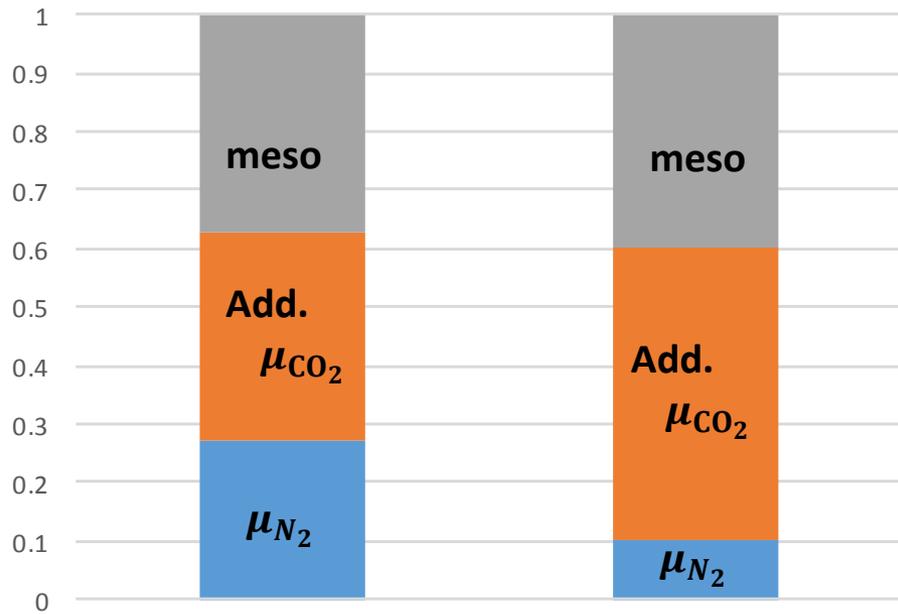
Fraction from total surface area (%)
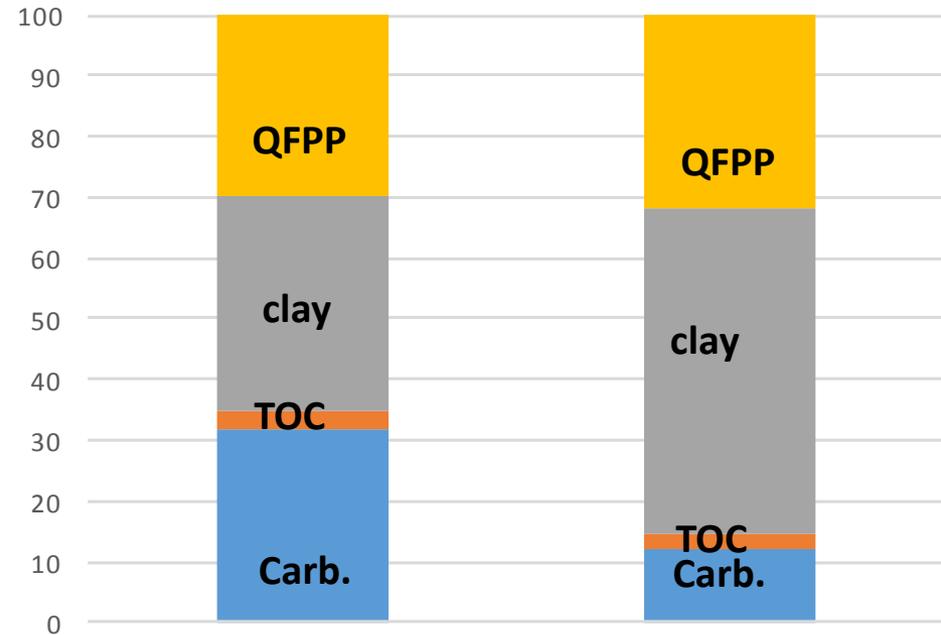
Mineralogy by weight (%)

Learnings

- Would've missed large surface area if one only measure N_2 adsorption

- Mineralogy controls pore size distribution

- Clay types may contribute to different pore size distribution

Future works

- Further investigation of micropore region
  - Low temperature, pressure CO_2 adsorption
    - Samples with varying TOC and clay content
- Mineralogy – PSD relationship
  - Fluid coverage?

Thank you!

Questions?