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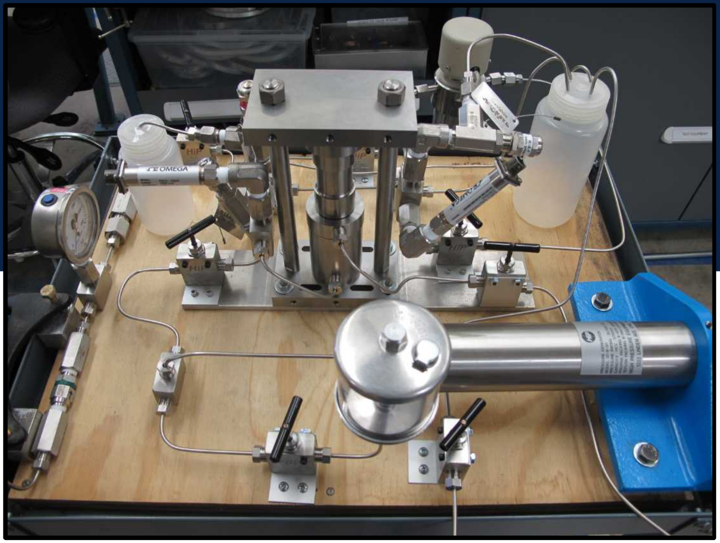

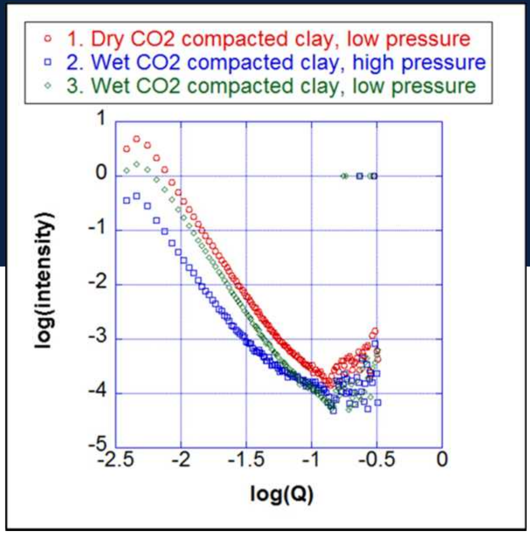

Oedometric Small-Angle Neutron Scattering:

In Situ Observation of Strain in Clay-Rich Samples Under Non-Hydrostatic Stress

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ACS National Meeting, August 20, 2016

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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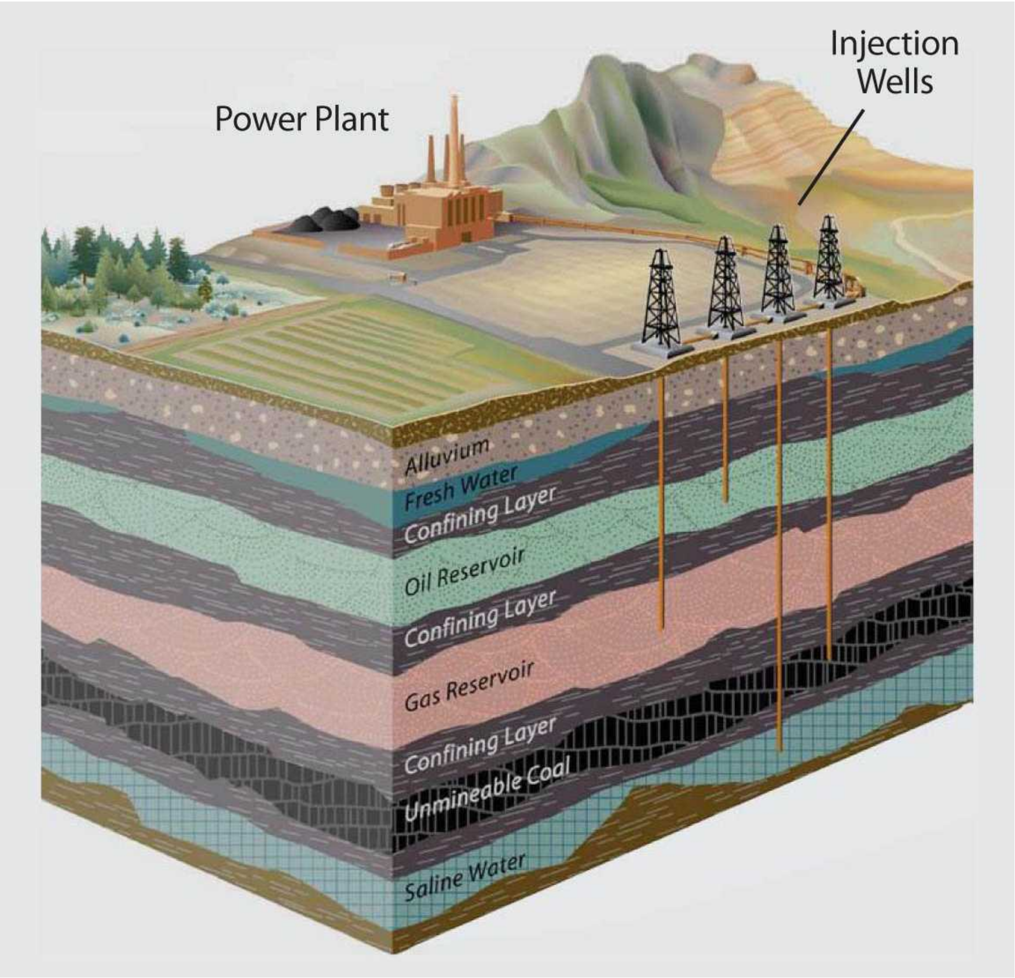
Motivation 1 – Geologic CO_2 Storage



Will initially dry CO_2 dehydrate caprock and exacerbate leakage pathways?

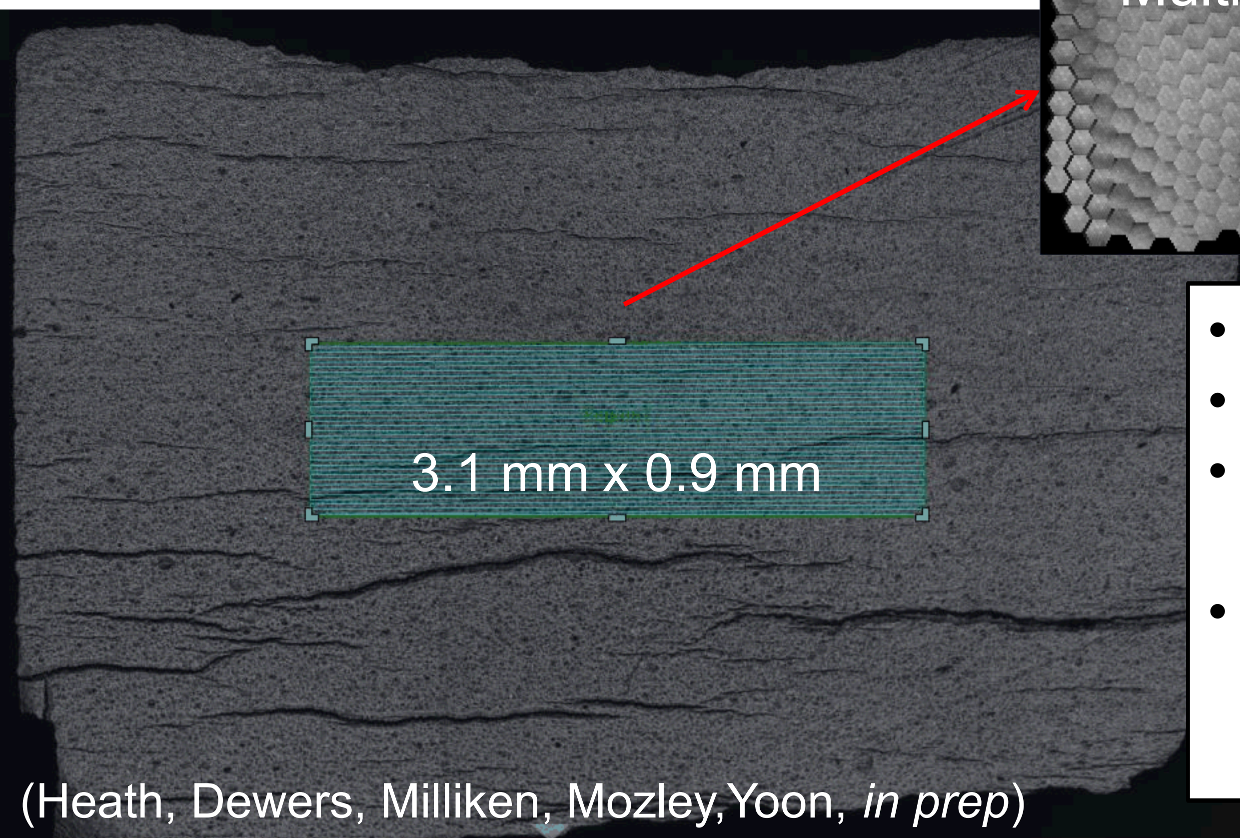
Recent studies investigate intercalation of CO_2 and H_2O in clay and shrink-swell behavior under hydrostatic stress (e.g., Loring et al., 2014)

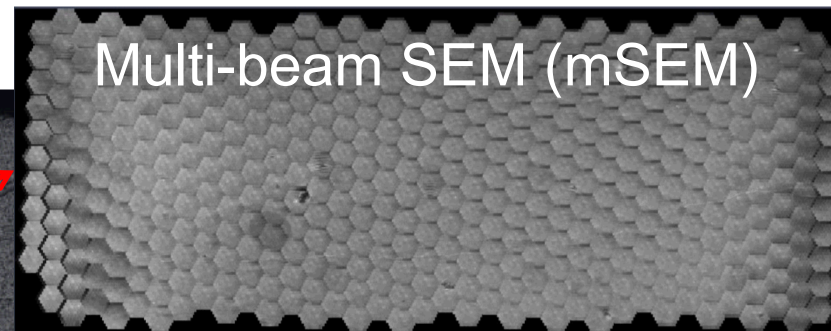
How does lithostatic stress affect shrink-swell of clay?

Motivation 2 – Shale Pores

Characterization of multiscale porosity alone is difficult. Including coupled processes is even harder…

Example of large-area porosity characterization for context





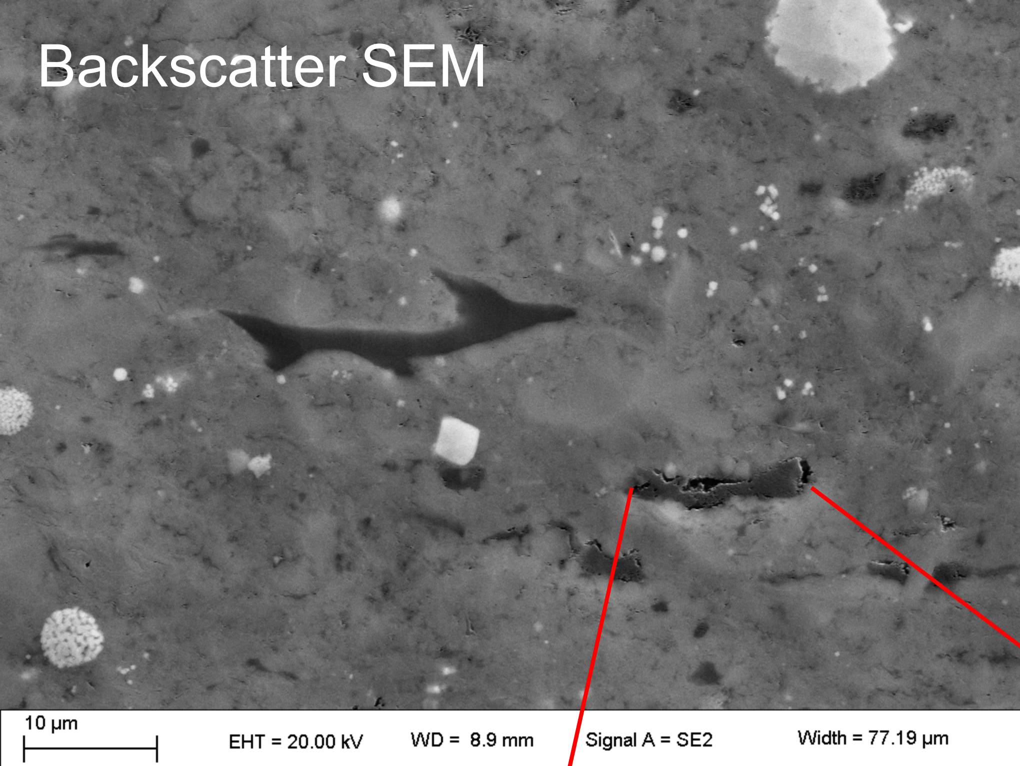
- ~ 3 x 1 mm area
- 4 nm resolution, 3 keV
- Data collection time: ~16 min.
- 26,657 images
  - Single image: 12.5 x 10.9 µm

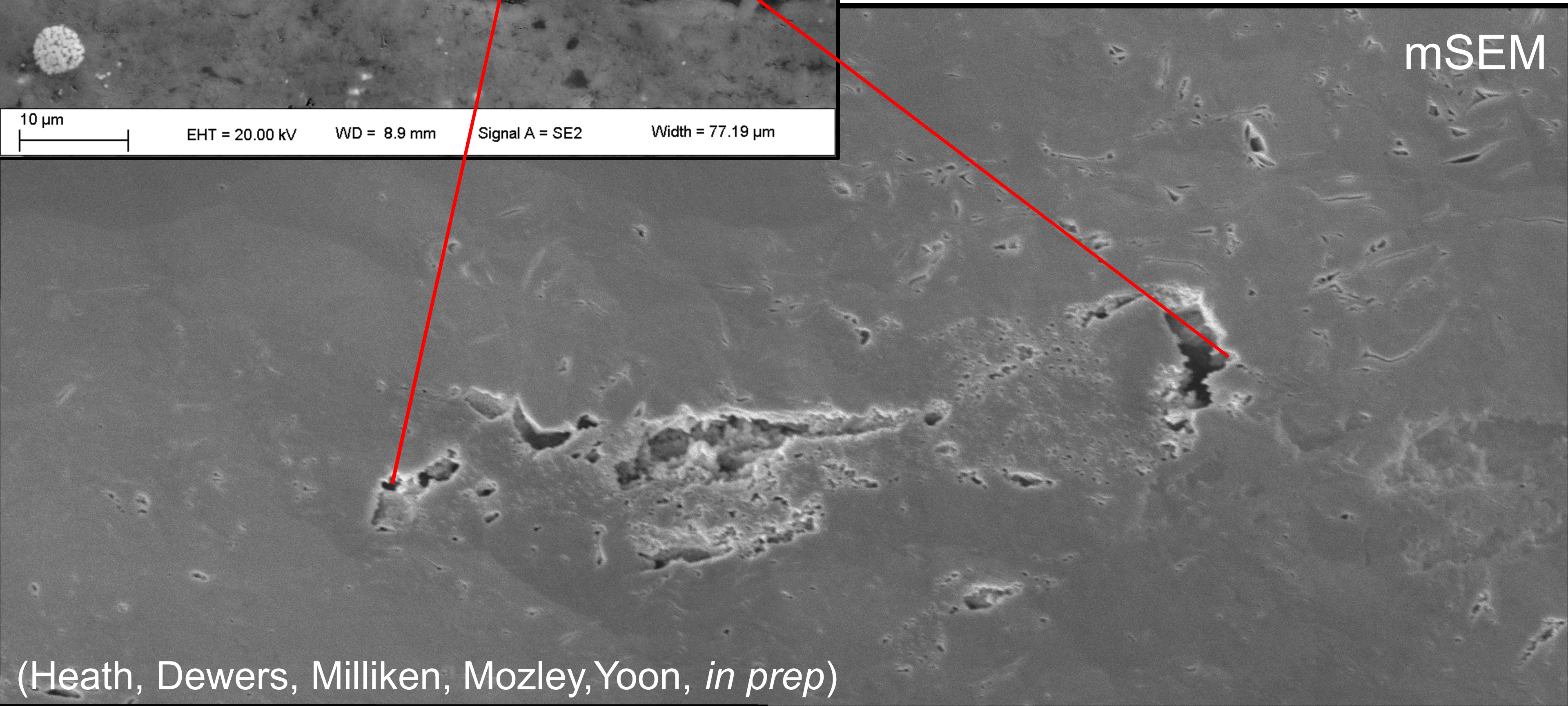
(Heath, Dewers, Milliken, Mozley,Yoon, *in prep*)

Shale Pores

mSEM: 2D imaging; pores visible but organics not-so-much; difficult sample prep.; static sample

Helpful but not enough for in situ coupled processes





(Heath, Dewers, Milliken, Mozley,Yoon, *in prep*)

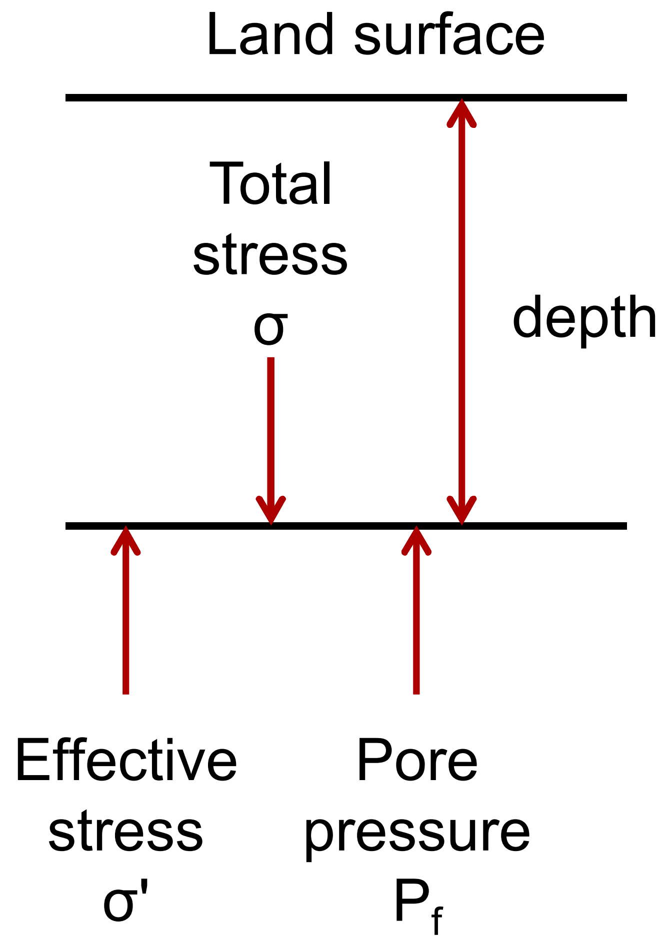
Oedometric SANS

Key advances:

- Data collection over 1 to 1000 nm (or to 10s of microns if used with USANS)
- Accommodates pore fluids at high pressure and temperature
- Non-hydrostatic stress state applied to sample

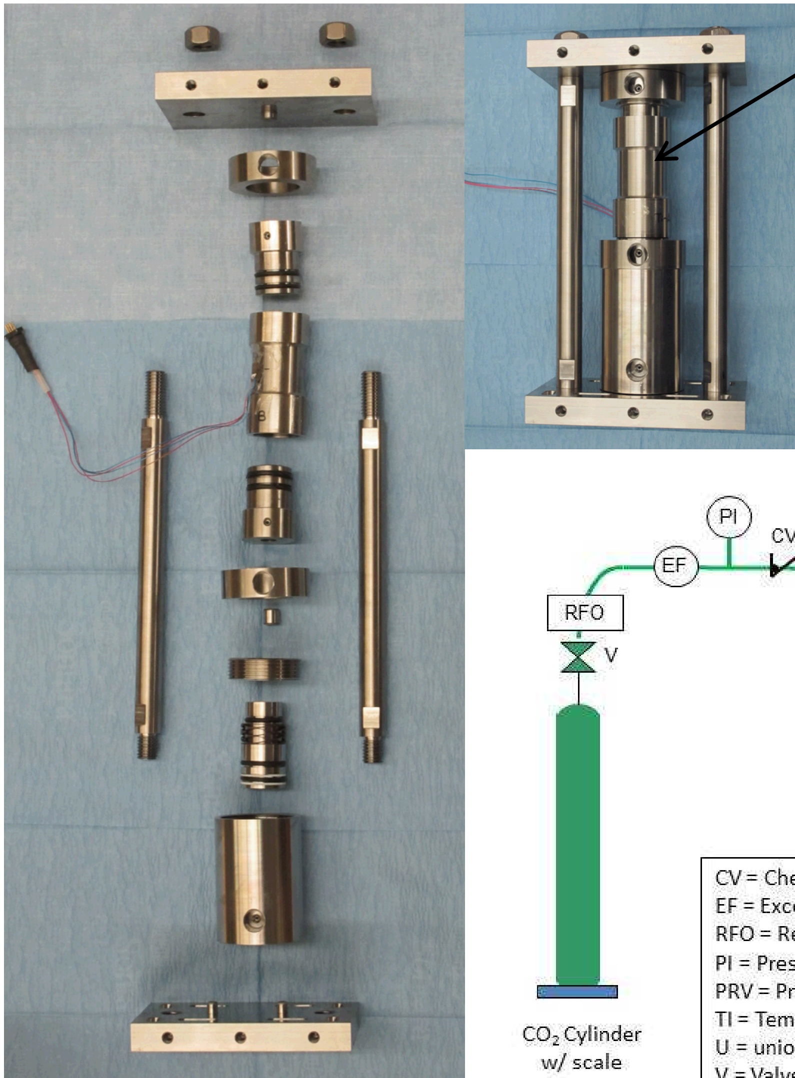
Difficulties and opportunities:

- We are developing oedometer v4.0…
- Sample preparation for *in situ* fluids, pressure, and temperature at beam facilities (LANSCE; NIST with USANS); thin sample
- Data interpretation – you don't "see" pores

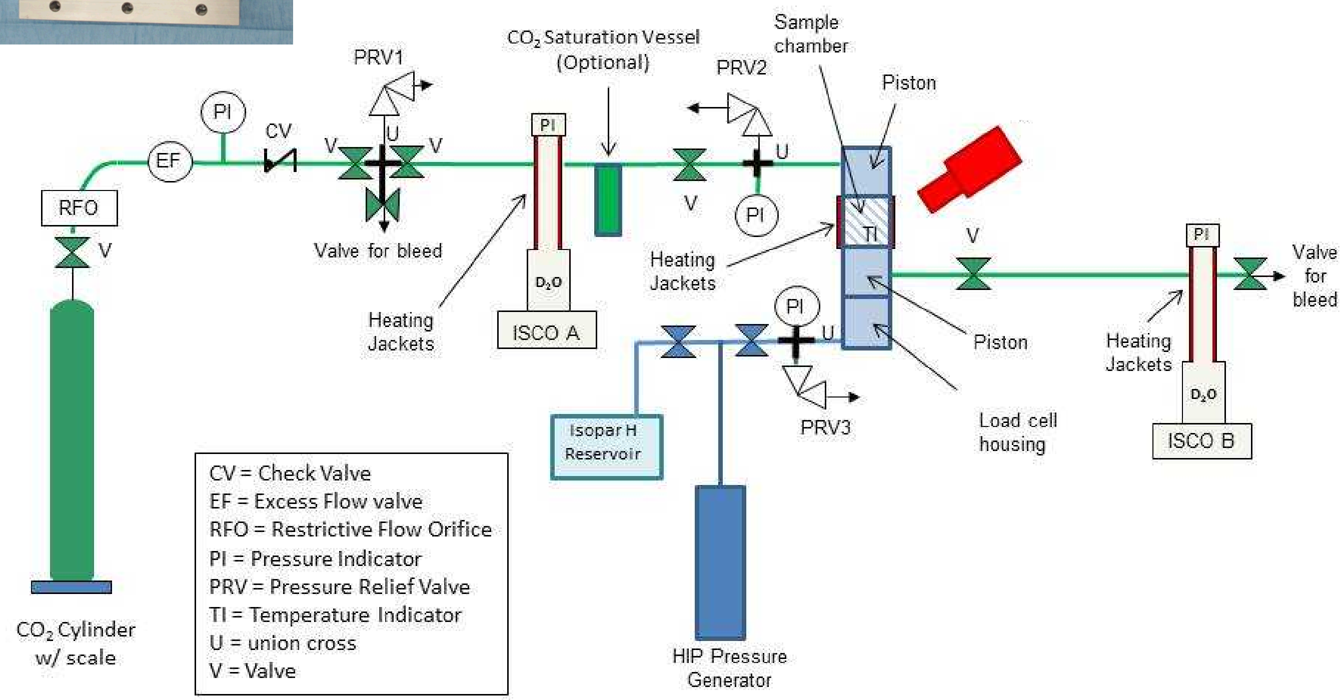


Oedometer v1.0

SWy-2

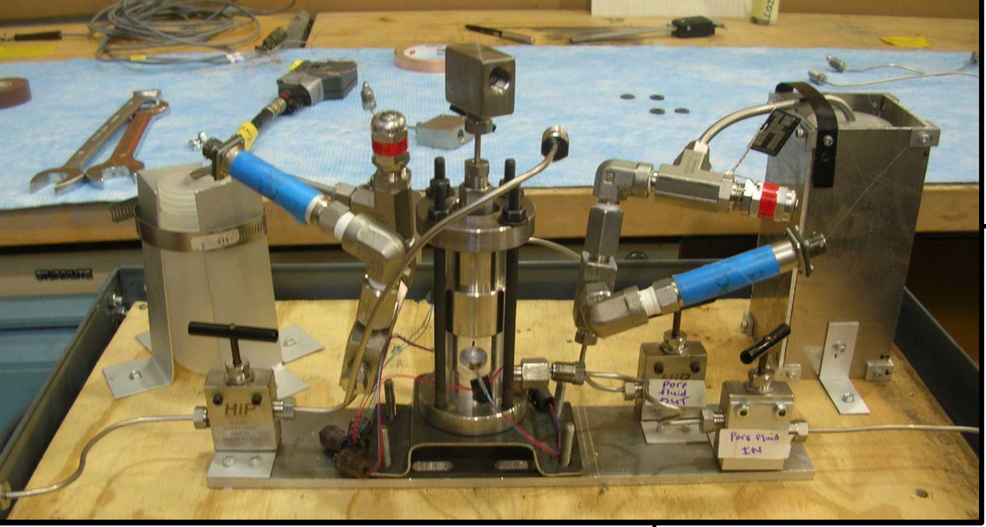


- MAWP: 27.6 Mpa
- Made of Ti
- Designed for geomechanics
- Drawback: 1-inch sample chamber
- Multiple scattering



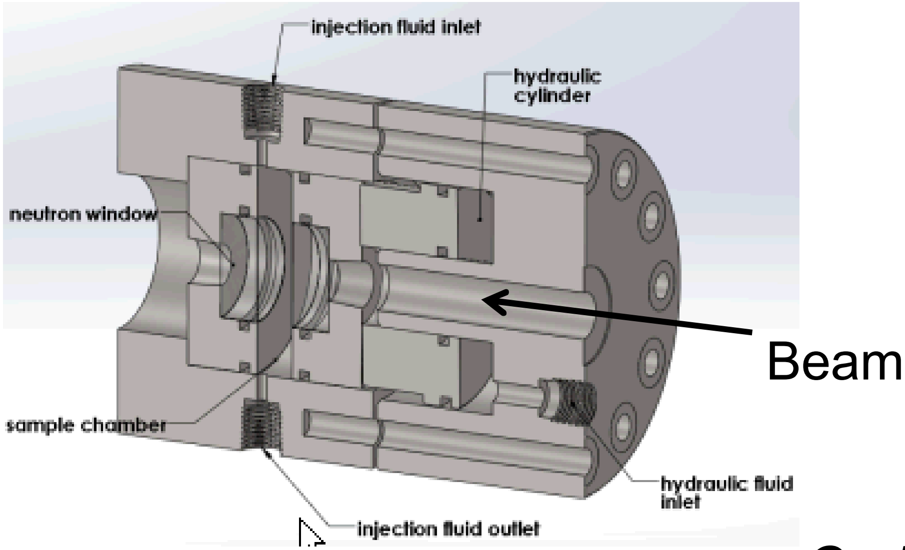
High Pressure Piping System

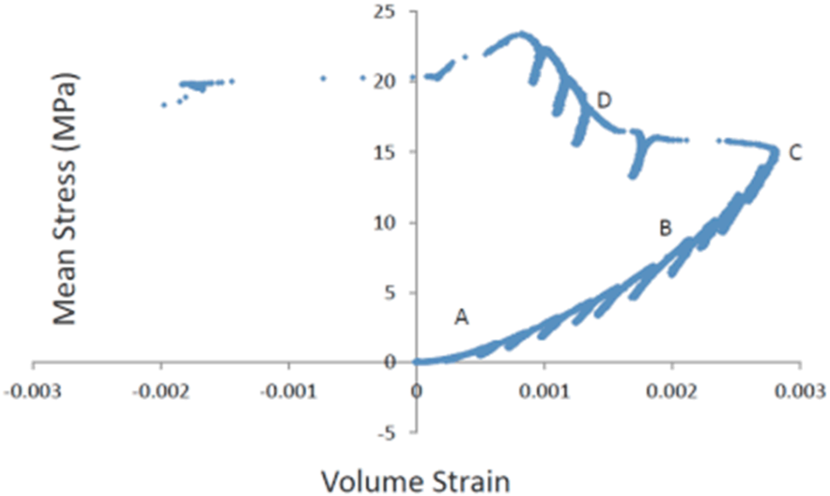
Oedometer v2.0



- MAWP: 6.89 MPa
- Al window; steel
- Designed for SANS neutron optics
- Drawback: “penny-shaped” crack in metal…

Oedometer v3.0





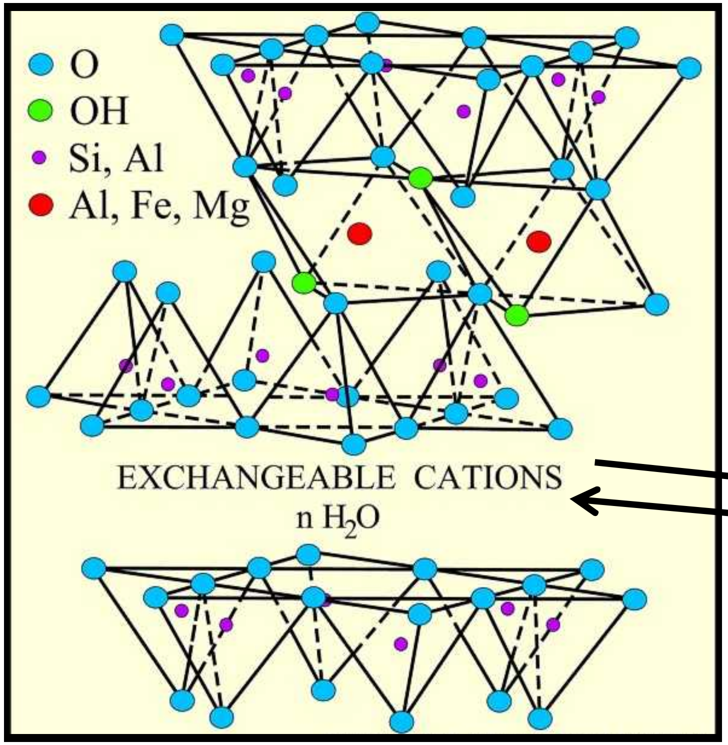
A - Elastic Regime
B - Initiation of yielding
C - Near dilational "turn-around"
D - Approaching sample failure

Oedometric-SANS performed on Mancos Shale

- New oedeometer design with sapphire windows acting as pistons for uniaxial loading
- MAWP: 60 MPa axial and pore pressure
- Stress parallel to beam
- Used successfully on SANS and USANS instruments (at NIST)
- Fluid injection for contrast measurements

Example from Oedometer v2.0

What is the change in <u>pore structure</u> of montmorillonite (SWy-2) as a function of non-hydrostatic stress conditions and dissolved water in CO_2?



Approach:

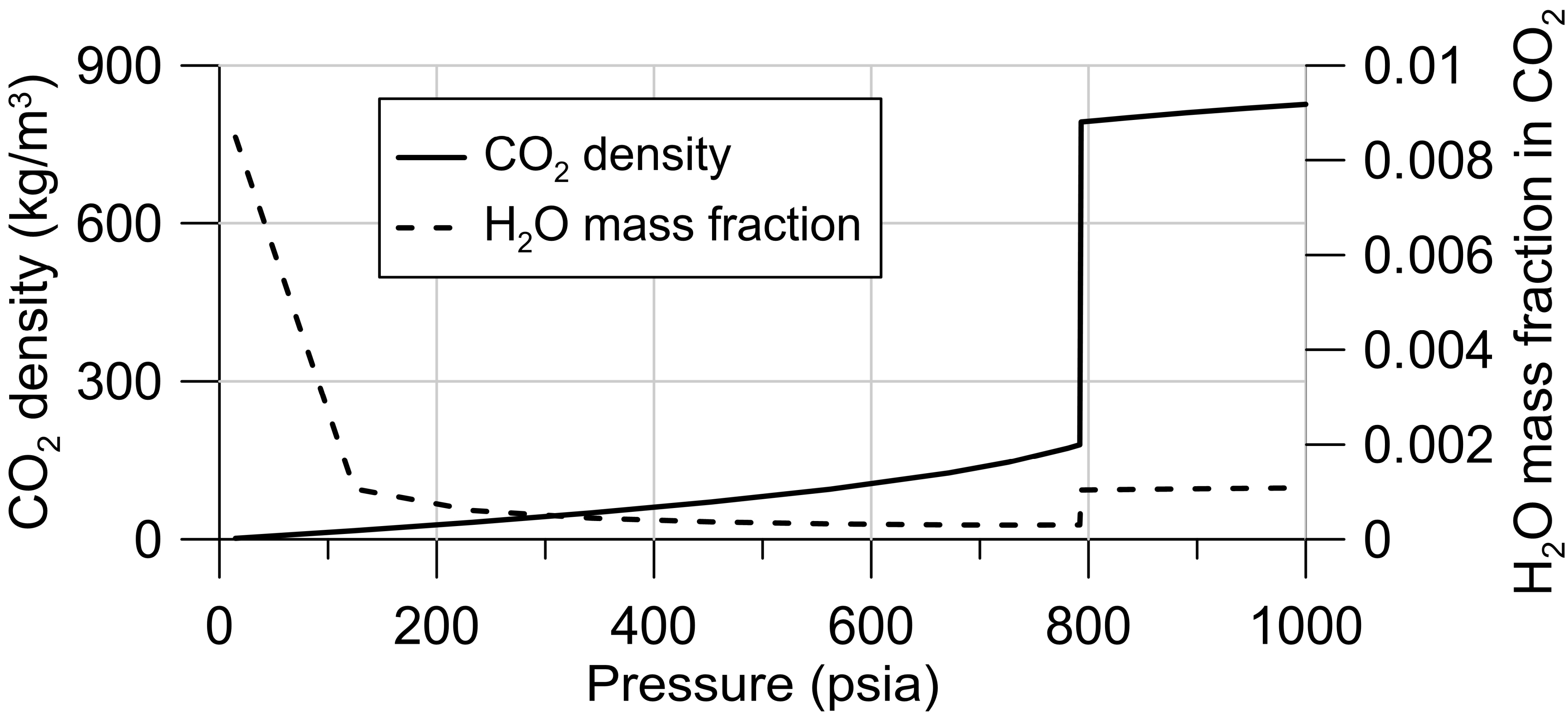
- Measure compaction or swelling with oedometer, coupled to SANS
- Take the same clay sample through a stress path with different pore fluids (dry and wet CO_2) and measure pore structure with SANS

H_2O?

CO_2?

Initially dry supercritical CO_2 in pores

CO_2 density and H_2O solubility



Timeline of oedometer stress path

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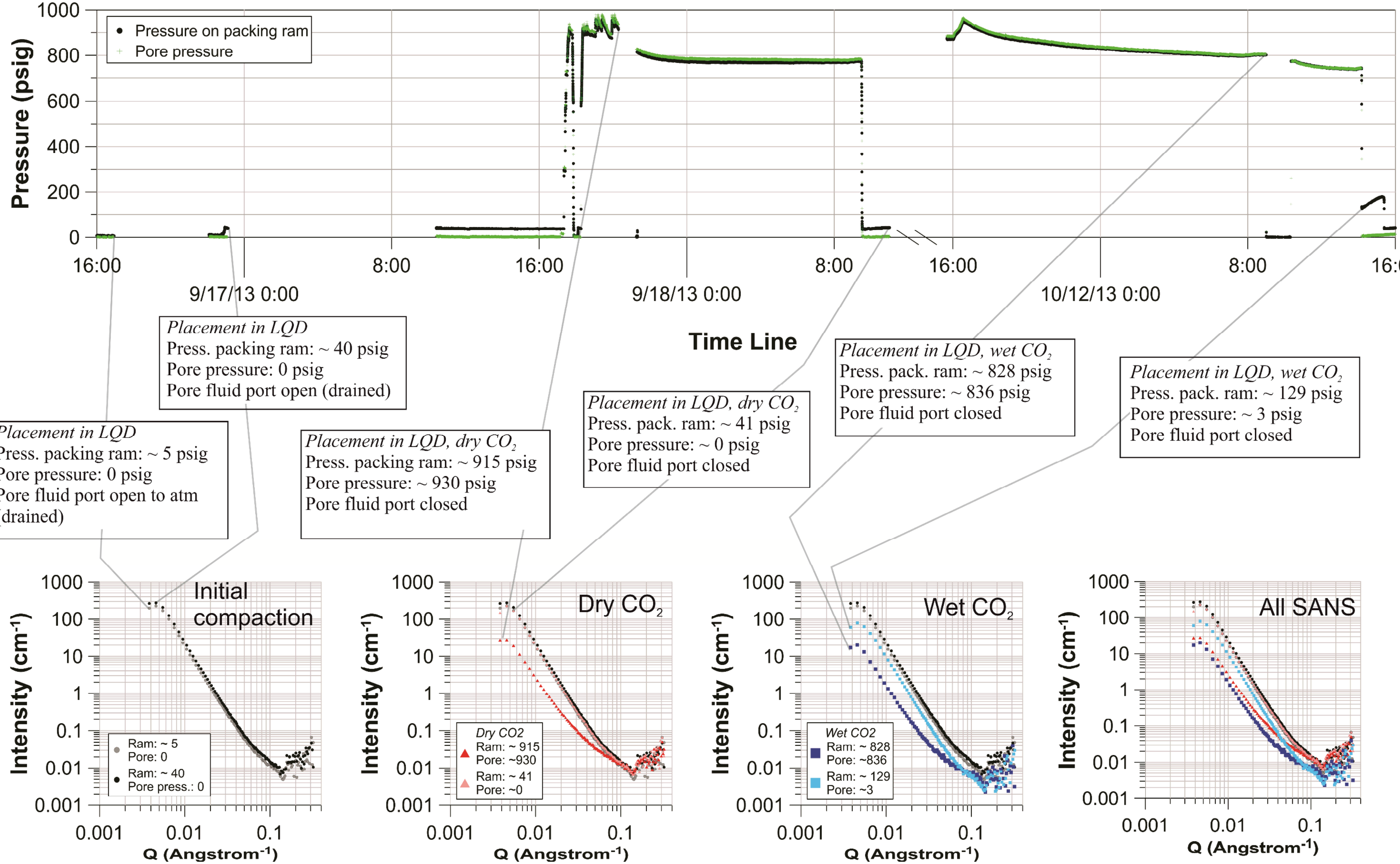
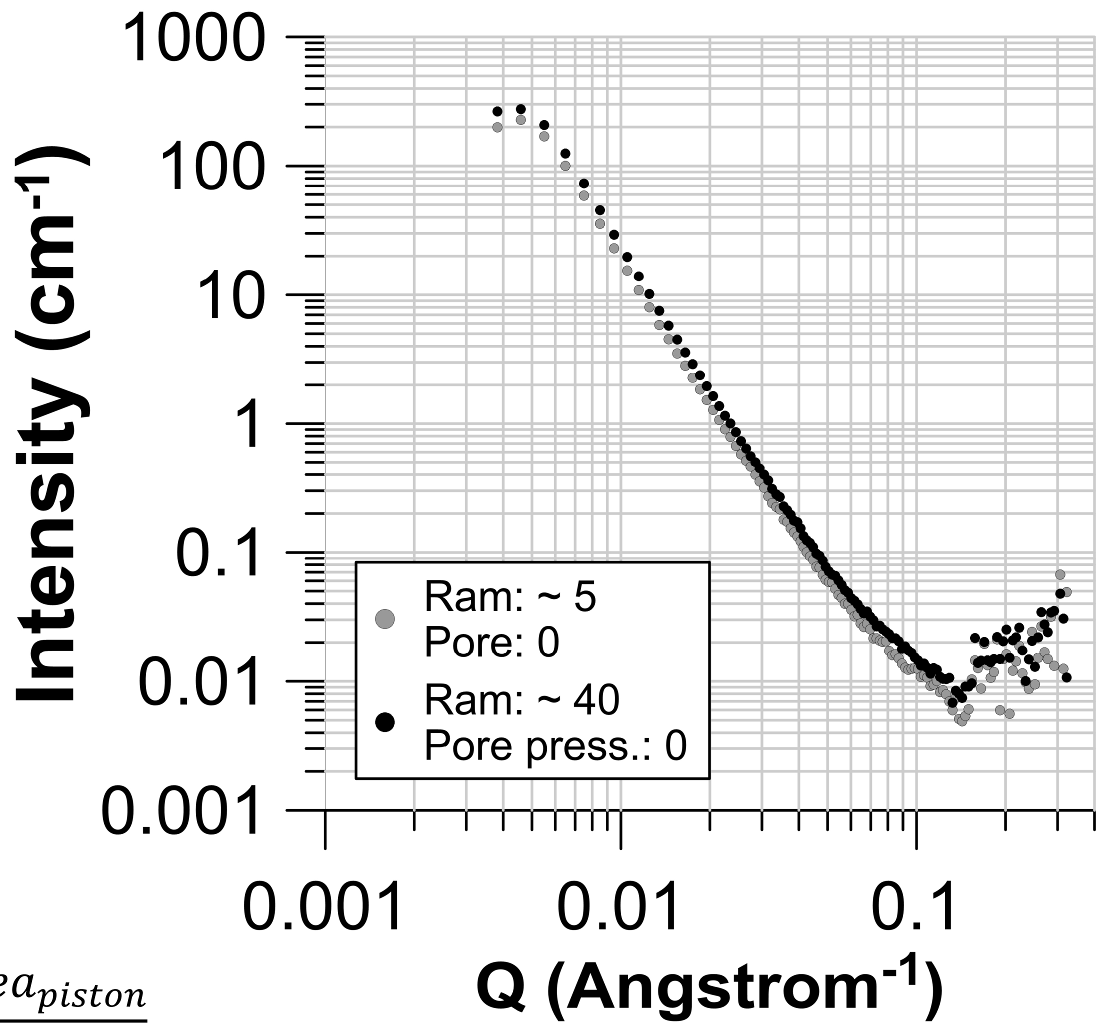
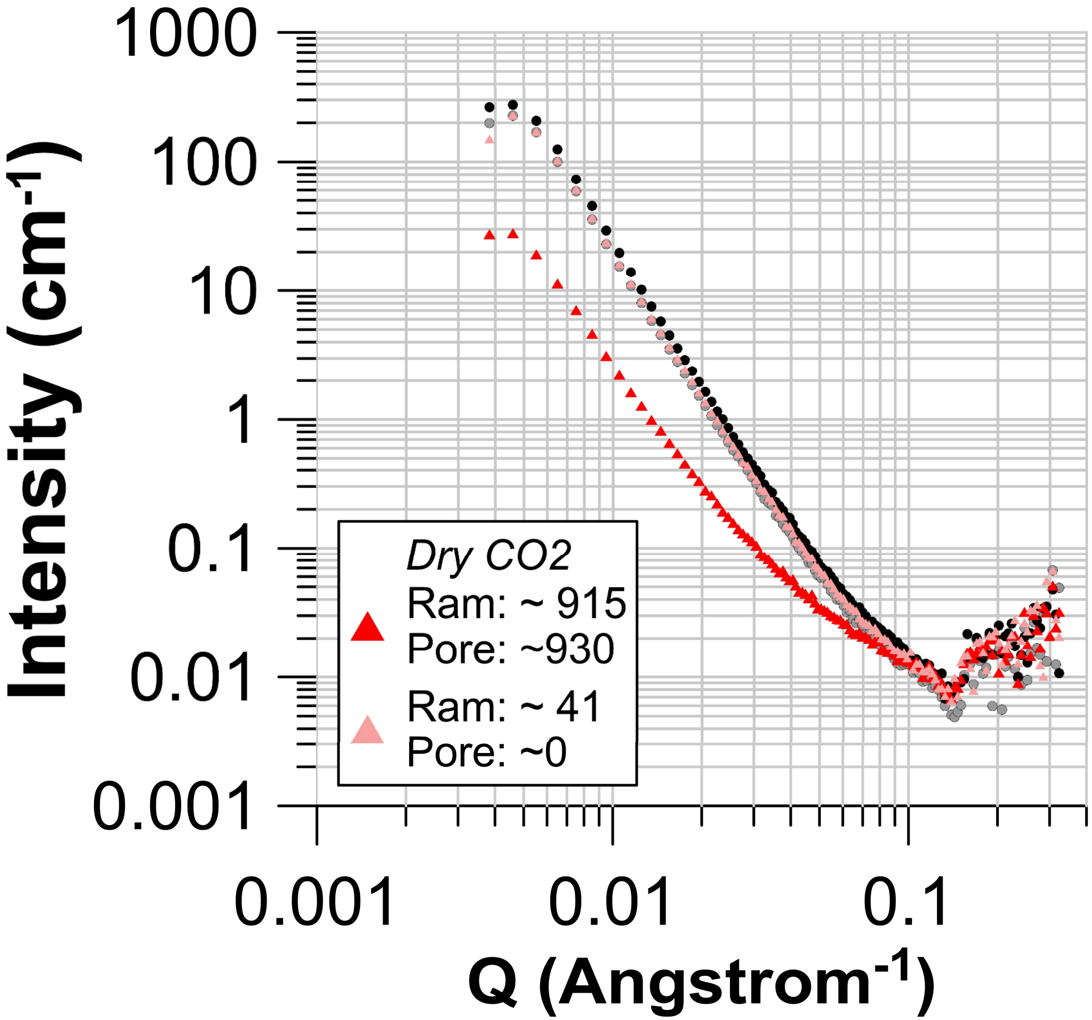
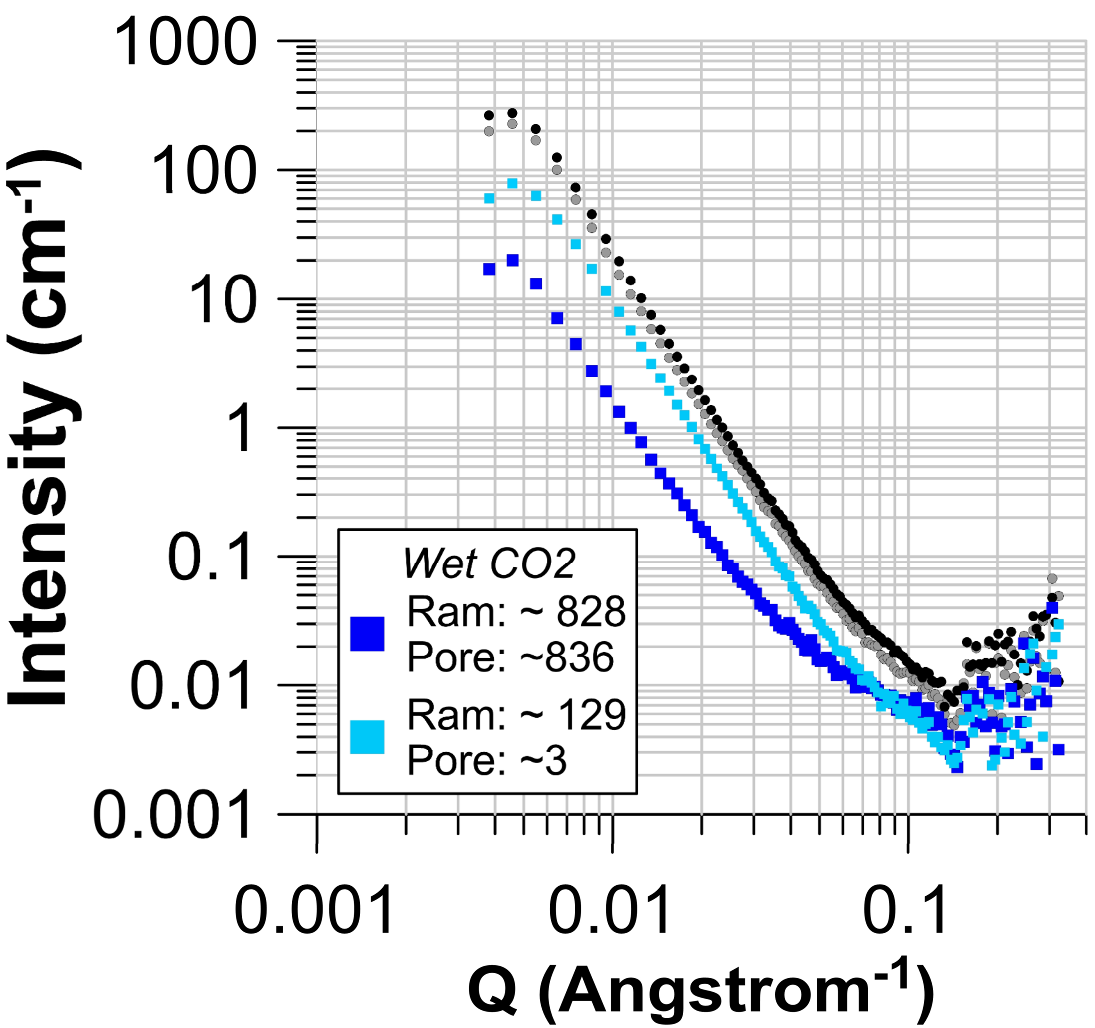


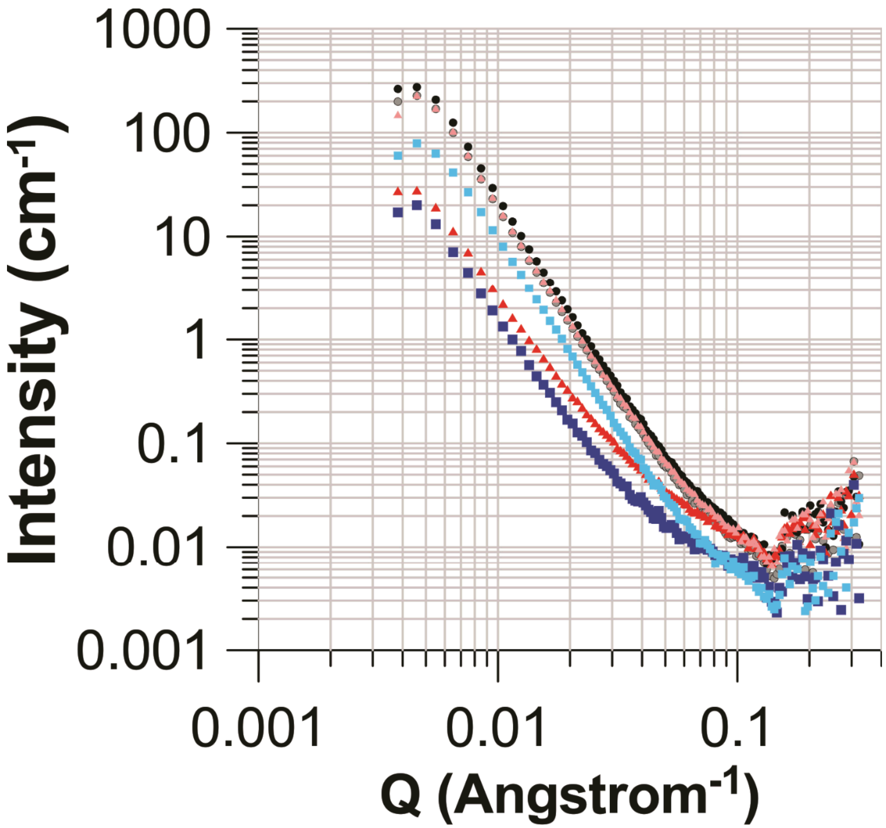


$$Pressure \times \frac{Area_{piston}}{Area_{ram}}$$


1000
100
10
1
0.1
0.01
0.001
Intensity (cm-1)
0.001
0.01
0.1
Q (Angstrom-1)
Dry CO2
Ram: ~ 915
Pore: ~930
Ram: ~ 41
Pore: ~0


Intensity (cm-1)
1000
100
10
1
0.1
0.01
0.001
0.001
0.01
0.1
Q (Angstrom-1)
Wet CO2
Ram: ~ 828
Pore: ~836
Ram: ~ 129
Pore: ~3

Unified and Fractal Fitting



Stage	Avg. pore size (nm)	n	D
1st comp.	37.9	3.64	2.36
2nd comp.	37.5	3.66	2.34
HP, dry CO_2	34.4	2.83	3.17
LP, dry CO_2	37.6	3.60	2.40
HP, wet CO_2	39.5	3.14	2.86
LP, wet CO_2	34.6	3.71	2.29

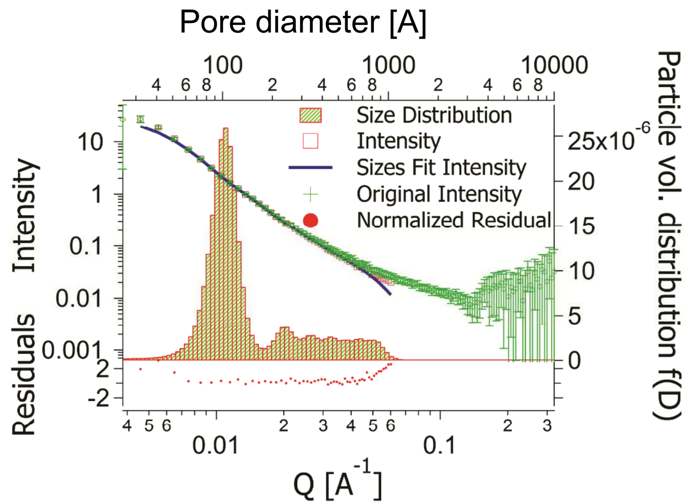
- Increase in fractal dimension under load
- Recoverable changes in fractal dimension relate to elastic compression
- Irreversible changes in D relate to plastic and/or creep strains
- Intercalation not obvious

Power-law relationship:

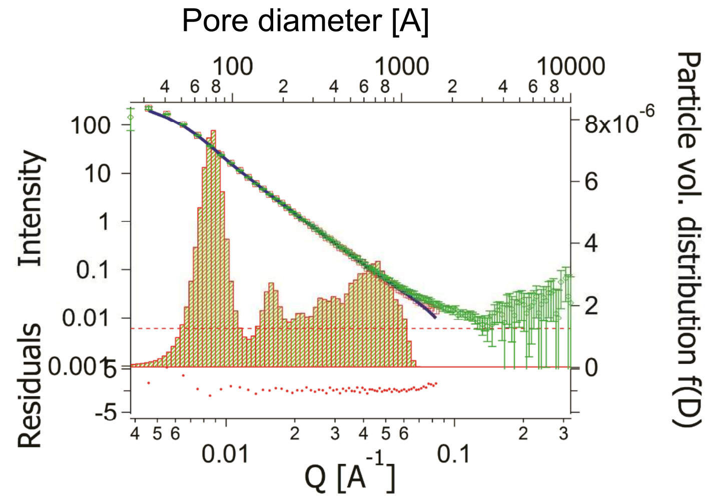
$$I(Q) = \frac{A}{Q^n} + B$$

Fitting used Irena Tool Suite: Ilavsky and Jemian, P.R., 2009

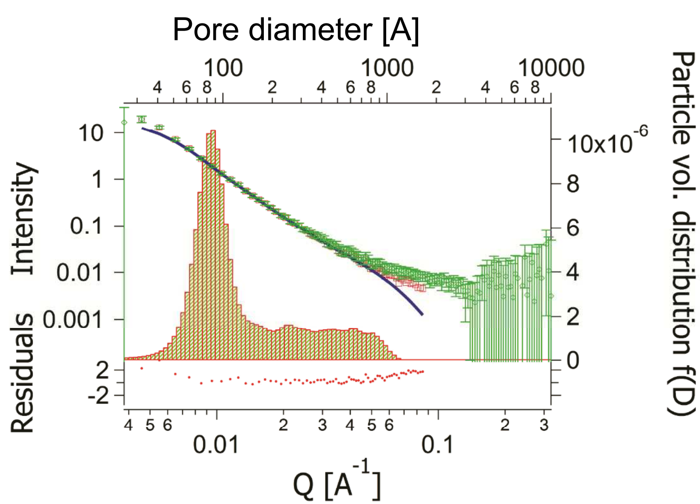
Dry CO_2 at 930 psig



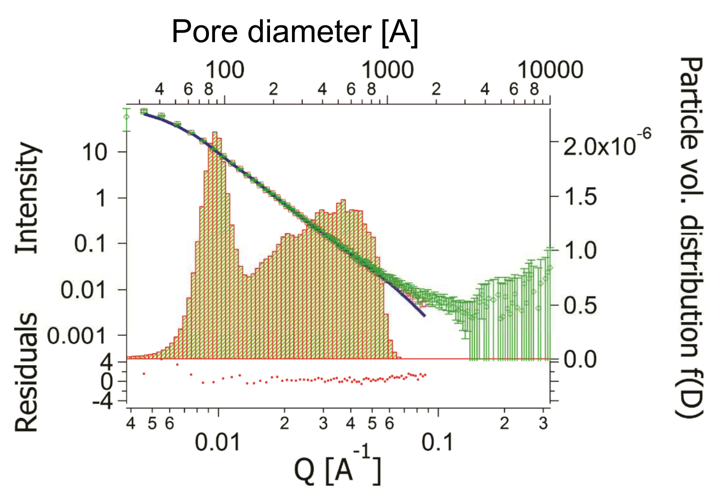
Dry CO_2 at 0 psig



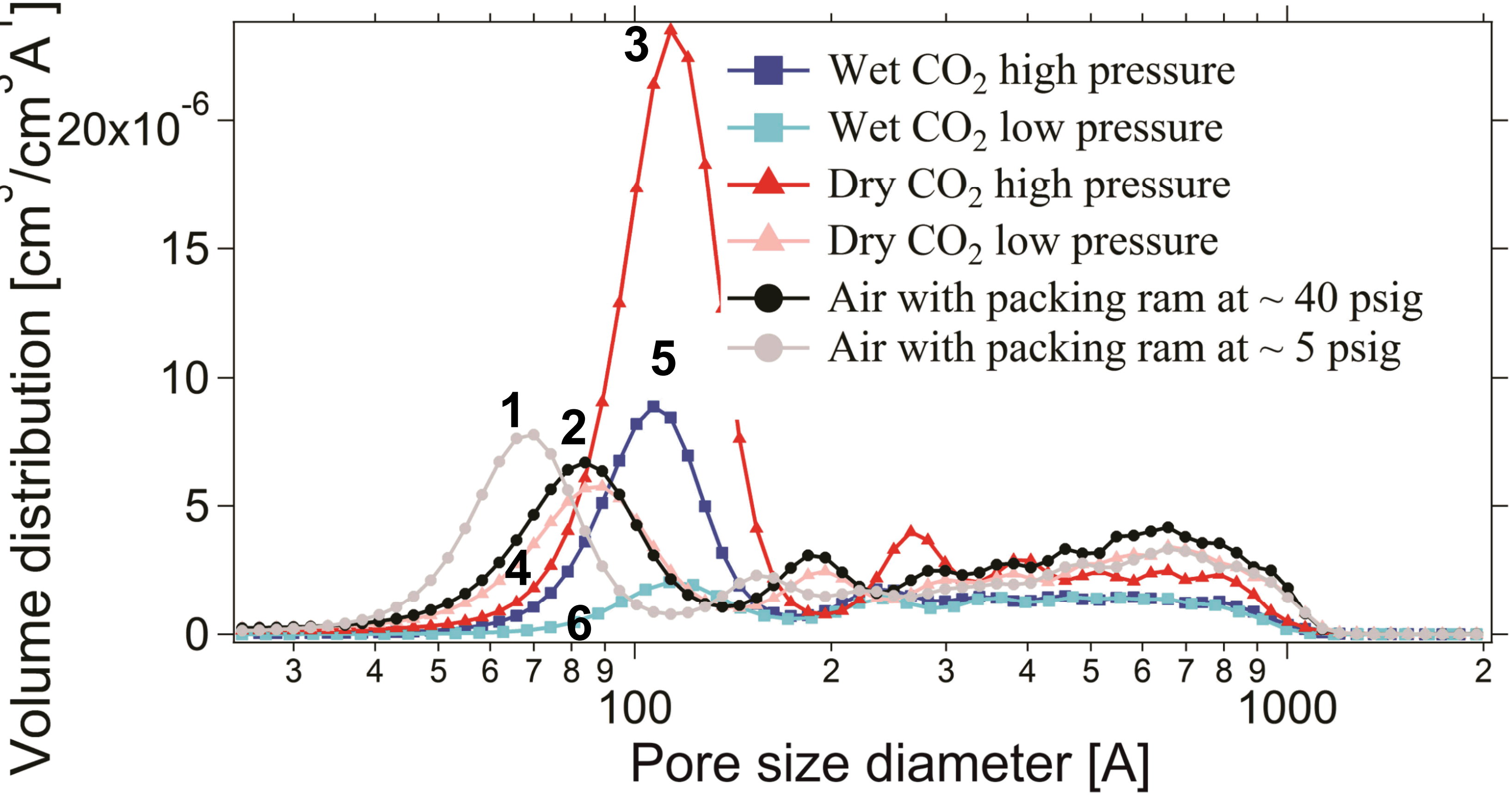
Wet CO_2 at 836 psig



Wet CO_2 after bleed to 129 psig



Pore Size Distributions



- Release of pore pressure for dry CO_2 seems reversible (falls back near initial compaction curve – elastic strain)
- To release to lower pressure of wet CO_2 shows a major change to broader pore sizes (irreversible strain)

PSD obtained with: Irena Tool Suite: Ilavsky and Jemian, P.R., 2009

Acknowledgements

- Many thanks to the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award Number DE-SC0006883 for funding.
- This work has benefited from the use of Low-Q Diffractometer at LANSCE at the Lujan Center at Los Alamos Neutron Science Center, funded by DOE Office of Basic Energy Sciences. Los Alamos National Laboratory is operated by Los Alamos National Security LLC under DOE Contract DE-AC52-06NA25396.
- For contributions to the design of oedometers and pressure systems
  - Steve Bauer, Jiann Su, Greg Flint, SNL
  - Mark Taylor, LANL

Transmission and multiple scattering