Imperial College London

ShaleXEnvironment Dissemination Event

TAMUQ – 18th March 2018

High-pressure gas sorption studies on shales

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Gas adsorption in shale

Of practical relevance, but quantification is still a challenge

- **Most of the porosity in shale is located in pores < 50 nm**
  - What is the accessible pore space? How does it influence fluid behaviour?
  - Gas adsorption contributes to Gas-In-Place (GIP); gas production is limited by the ability to desorb gas from the tight matrix

- **Measurement of HP adsorption isotherms is a technical challenge**
  - Inter-laboratory comparisons are difficult (lack of standards) [*e.g., Lancaster 1993 … Gasparik 2014*]
  - Interactions with shale constituents (e.g., clays and OM) are complex [*e.g., Barrer 1954 … Loring 2012; Busch 2014*]
  - Fluid densification and/or depletion? [*e.g., Rother 2012; Schaef 2014; Jeon 2014*]

Gas adsorption in shale and Gas-In-Place

Material balance analysis with sorption effects

$$GIP = free\ gas + adsorbed\ gas$$

$$= \rho\left[Ah\phi - V^{\mathrm{a}}\right] + n^{\mathrm{a}} = \rho Ah\phi + n^{\mathrm{ex}}$$

Excess sorption

$$n^{\mathrm{ex}} = m^{\mathrm{a}} - \rho V^{\mathrm{a}}$$

fluid density (*P,T,z*) $\left[\frac{mass}{L^3}\right]$

available pore space $[L^3]$

adsorbed volume $[L^3]$

amount adsorbed $[mass]$

- Understand the pore space
- Understand excess adsorption

Pini R 2014 *Energy Procedia* **63**: 5556-61

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Gas adsorption in shale

Of practical relevance, but quantification is still a challenge

- Most of the porosity in shale is located in pores < 50 nm
  - What is the accessible pore space? How does it influence fluid behaviour?
  - Characterization of microporous solids relies on the adsorption *and* transport of confined fluids

- **Measurement of HP adsorption isotherms is a technical challenge**
  - Inter-laboratory comparisons are difficult (lack of standards) [*e.g., Lancaster 1993 … Gasparik 2014*]
  - Interactions with shale constituents (e.g., clays and OM) are complex [*e.g., Barrer 1954 … Loring 2012; Busch 2014*]
  - Fluid densification and/or depletion? [*e.g., Rother 2012; Schaef 2014; Jeon 2014*]

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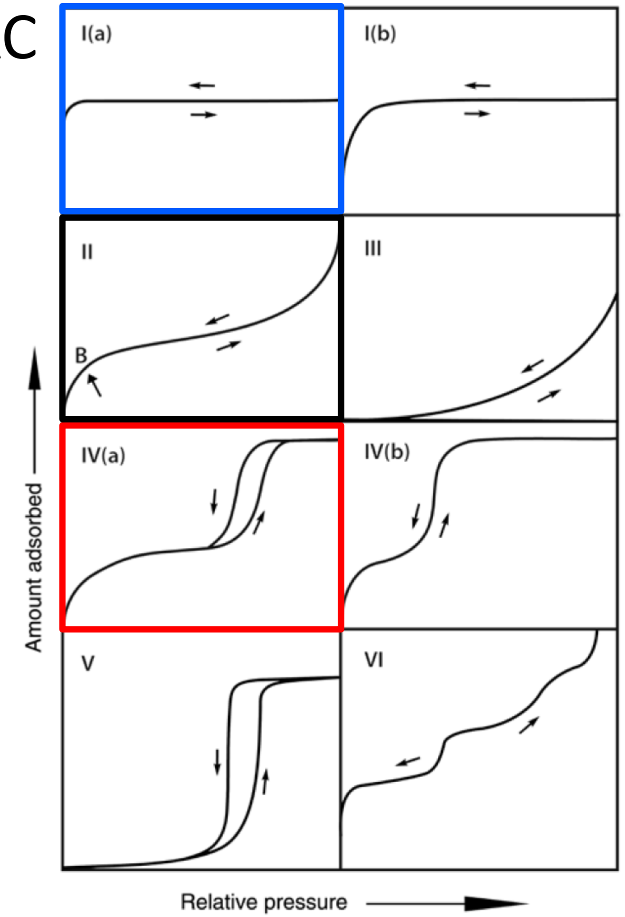
Adsorption 101: Sub- vs. super-critical adsorption

Absolute: m^{a}

IUPAC



Sing K. S. W. et al. **1985** *Pure Appl. Chem.* 57

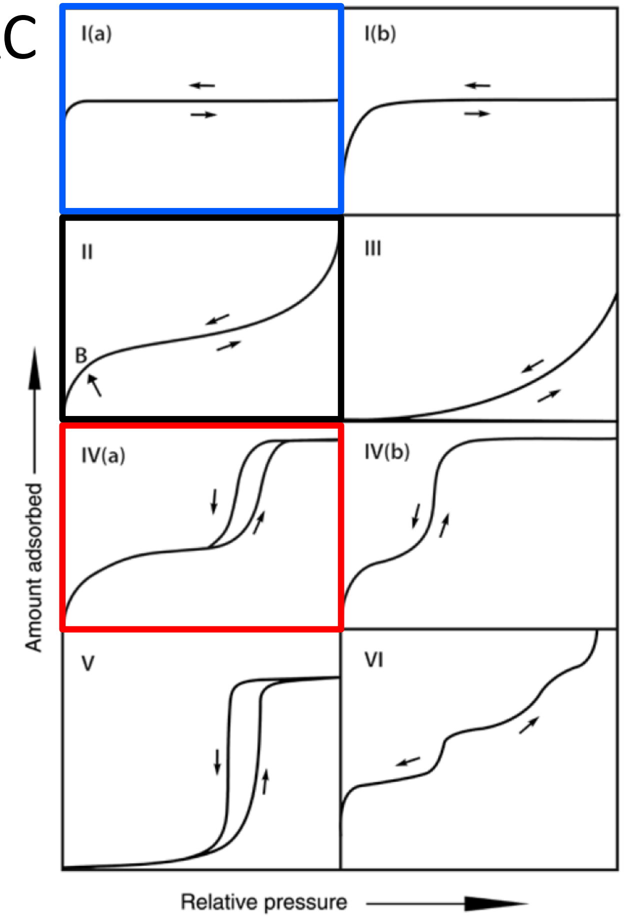
Thommes M. et al. **2015** *Pure Appl. Chem.* 87:1051-69

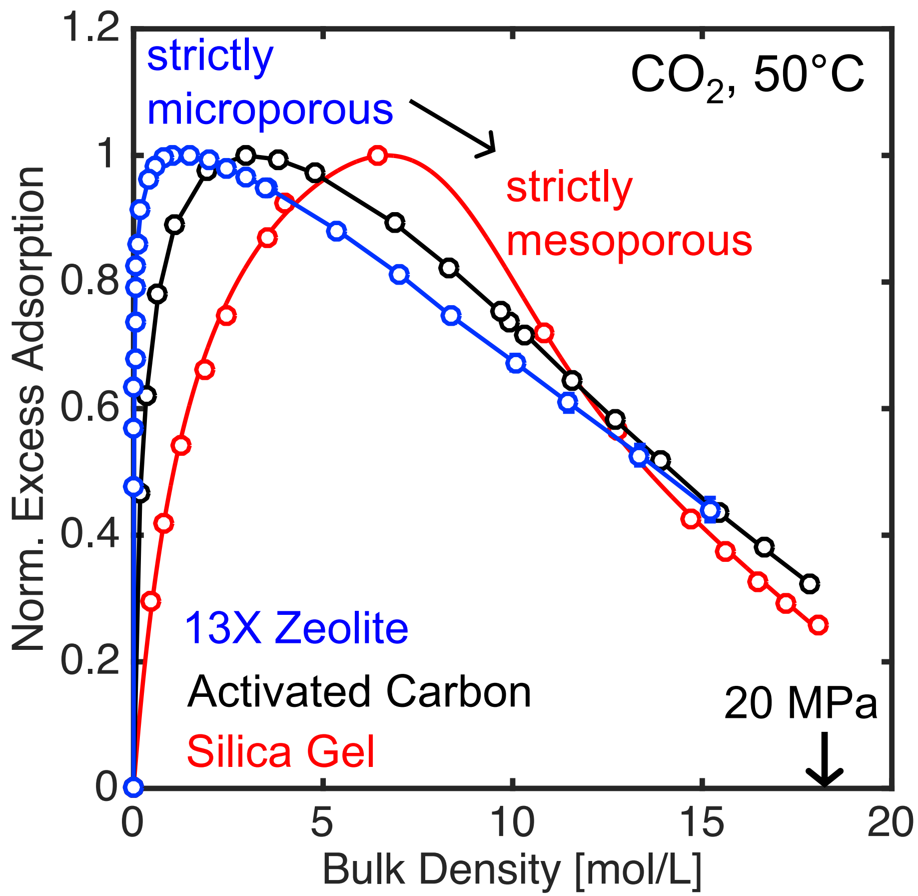
Adsorption 101: Sub- vs. super-critical adsorption

Absolute: m^{a}

Surface excess: $m^{\mathrm{ex}} = m^{\mathrm{a}} - \rho V^{\mathrm{a}}$

IUPAC





Sing K. S. W. et al. **1985** *Pure Appl. Chem.* 57
Thommes M. et al. **2015** *Pure Appl. Chem.* 87:1051-69

Pini R et al. **2006** *Adsorption* 12:393-403;
Pini R et. al **2008** *Adsorption* 14:133-41;
Pini R **2014** *Micropor Mesopor Mat* 187:40-52

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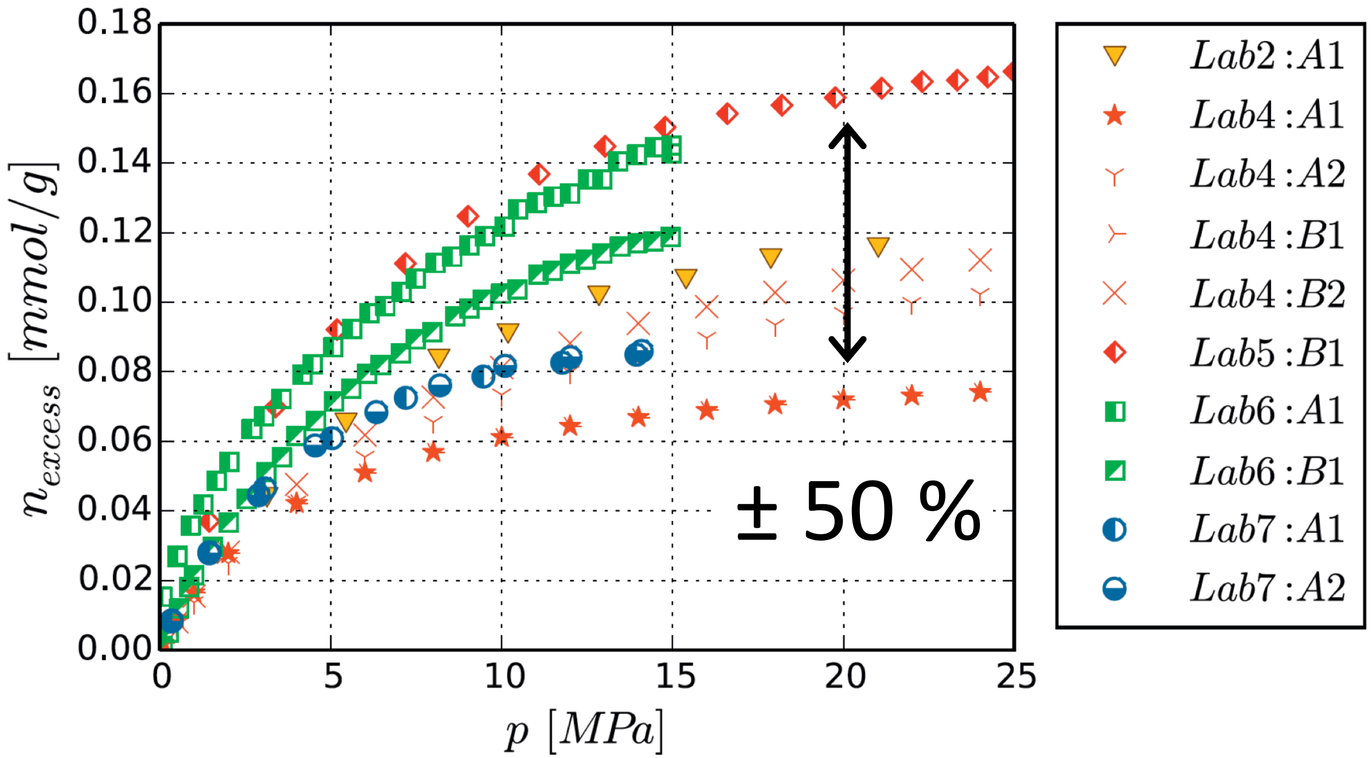
Supercritical gas adsorption: a technical challenge

Lack of reproducibility particularly evident on natural materials

Supercritical CH_4 adsorption on dry Posidonia shale



M. Gasparik et al. **2014** *Int J Coal Geology* 132, 131–146

Supercritical gas adsorption: a technical challenge

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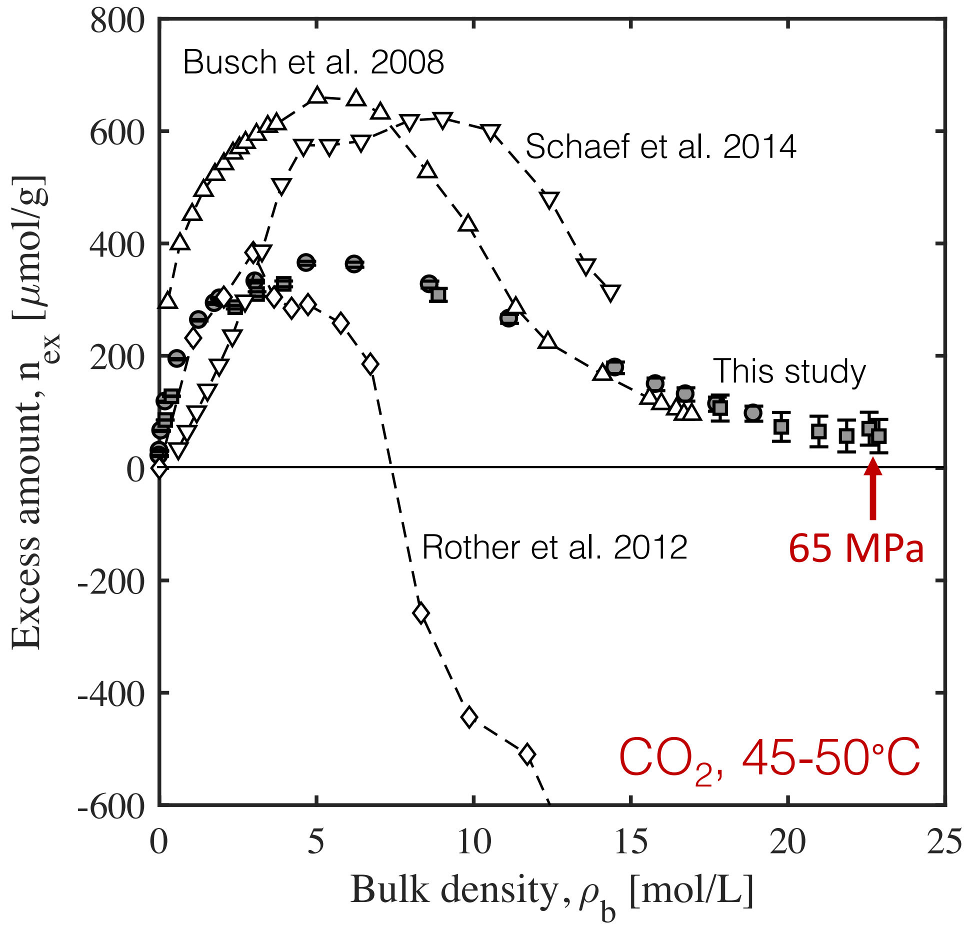


Supercritical CO_2 adsorption on dry Na-Montmorillonite

Schaef et al. **2014** *Energy Procedia,* 63, 7844-7851
Rother et al. **2013**, *Environ Sci Technol*, 47, 205-11
Busch et al. **2008** *Int J Greenhous Gas Control*, 2, 297-308

Measuring supercritical gas adsorption

Gravimetric method – Rubotherm Magnetic Suspension balance

Pressure:

vacuum – 35 MPa

Temperature:

0 – 400°C

Gases:

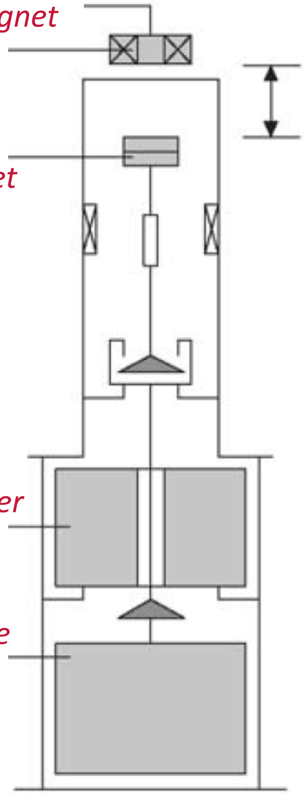
He, CO_2, HCs, N_2,…

Sample:

< 15 g (± 50 μg)

Measuring the adsorption of a dense gas

Operating equations



Apparent weight:

$$M_1(\rho,T) = \underbrace{m^{s} + m^{met}}_{M_1^0 \text{ weight under vacuum}} + m^{a} - \overbrace{\rho_m (V^{met} + V^{s} + V^{a})}^{\text{buoyancy}}$$

Excess adsorbed mass:

$$\begin{aligned} m^{ex} &= m^{a} - \rho_m V^{a} \\ &= M_1(\rho,T) - M_1^0 + \rho_m V^0 \end{aligned}$$

Buoyant solid volume (Helium):

$$V^0 = V^{met} + V^{s}$$

⟶ main source of error [1]

⟶ protocol includes several (repeated) pressure points

[1] Pini R **2014** *Micropor Mesopor Mat* 187:40-52

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Experimental approach

A combination of engineered and natural microporous solids

Bowland Shale (UK)

- Quartz + Carbonate + Clay + OM
- Complex pore structure
- Moderate porosity
- Microporosity (1-200 nm) (>10%)
- Microfracture porosity (< 5-8 %)

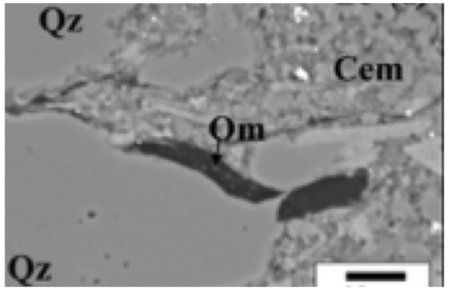
Mesoporous carbons

- Commercially available
- Regular pore structure (10 nm)
- Large porosity

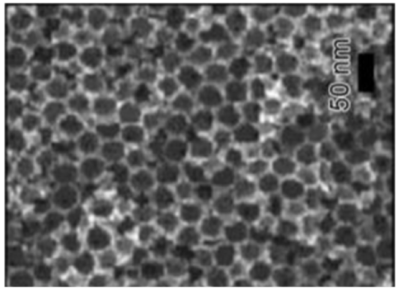
Source clays

- Source clay mineral (Swy-2)
- Hydrous layer silicates (2:1)
- Micro- *and* meso-pores (< 50nm)
- Large porosity

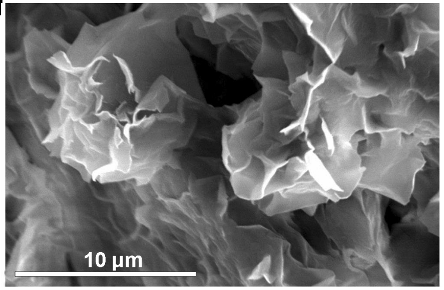
[1]



[2]



[3]



Images reproduced from:

[1] Fauchille A. L. et al. **2017** *Marine and Petroleum Geology*, 86, 1374-1390
[2] Liang C. et al. **2008** *Angew. Chem. Int. Ed.*, 47, 3696 – 717
[3] 'Images of Clay Archive' of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society

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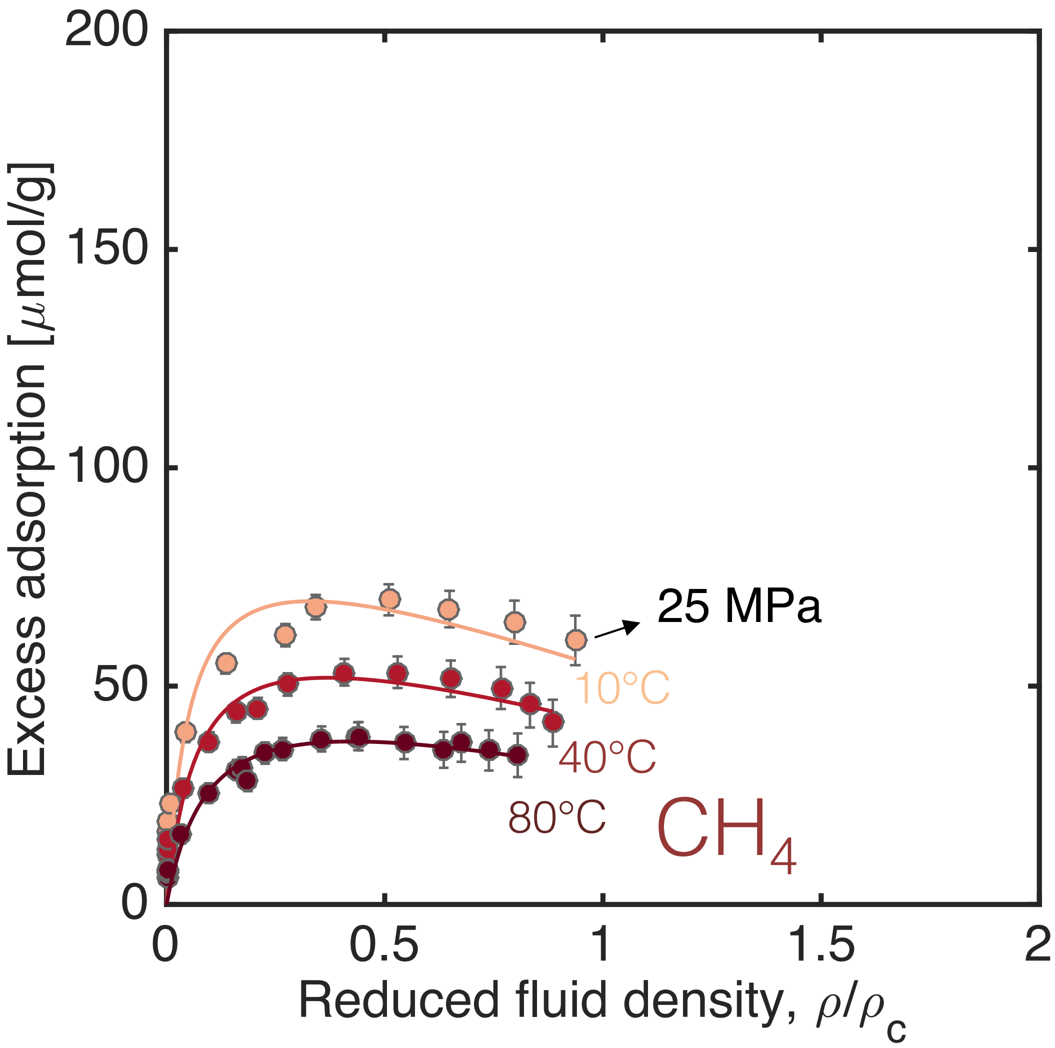
CO_2 and CH_4 adsorption on Bowland Shale (UK)

- Experimental conditions:

  vac. – 25 MPa, 10 – 80°C



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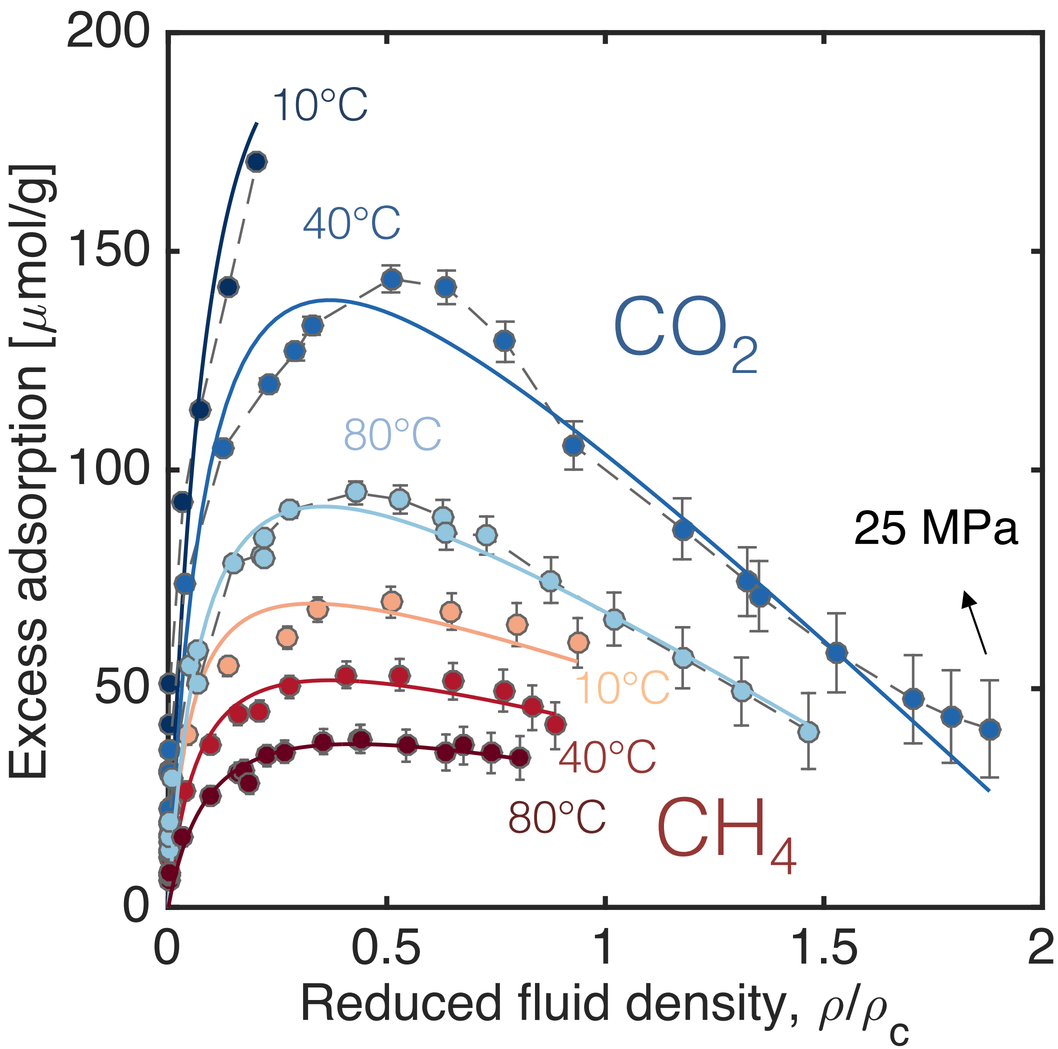

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CO_2 and CH_4 adsorption on Bowland Shale (UK)

- Experimental conditions:

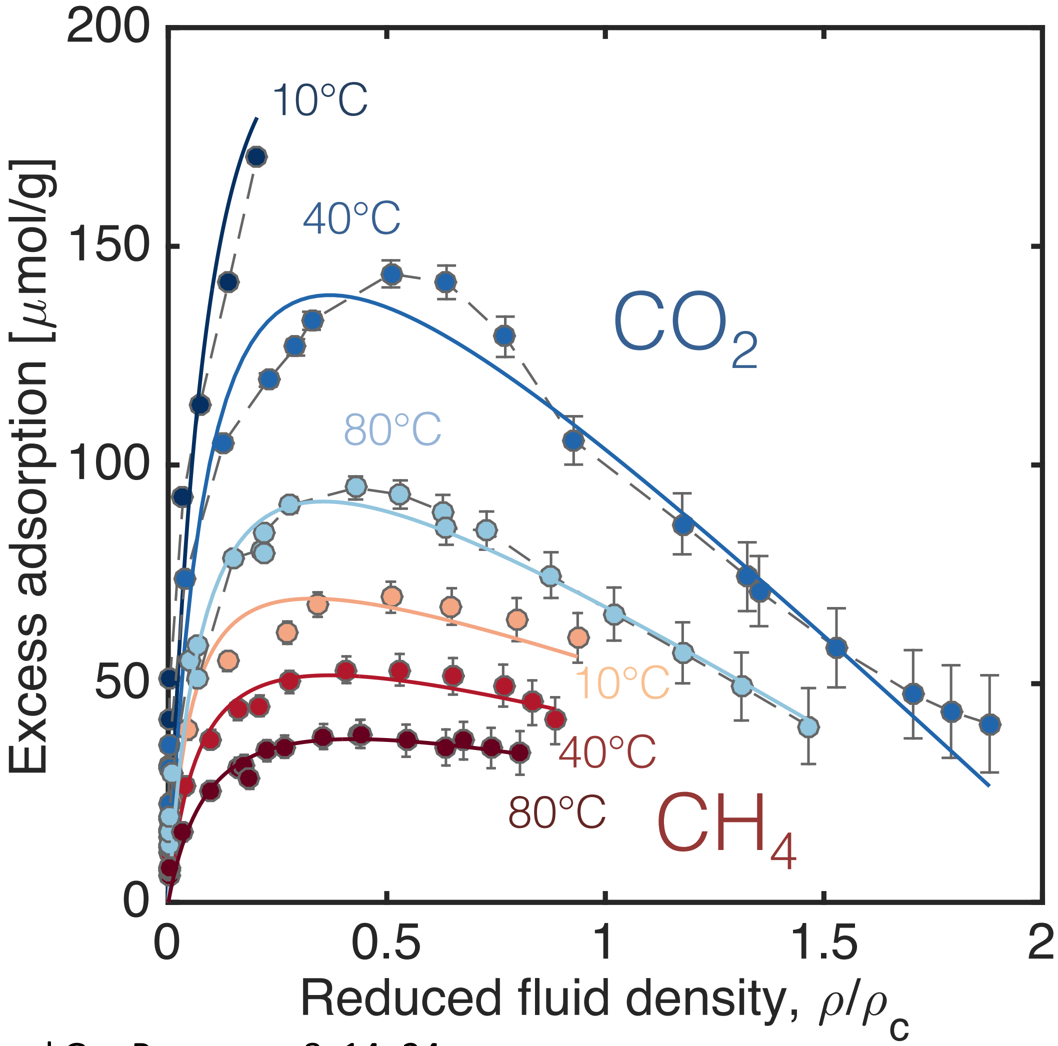
vac. – 25 MPa, 10 – 80°C

- Adsorption Capacity:

m^3_{STP} / t	CO_2	CH_4
Bowland	3 – 5	1.5 – 2
Eagle Ford	~ 9***	~ 4*
Barnett**	~ 5	~ 2

- Selectivity:

$$H_{CO_2}/H_{CH_4} \approx 5-8$$



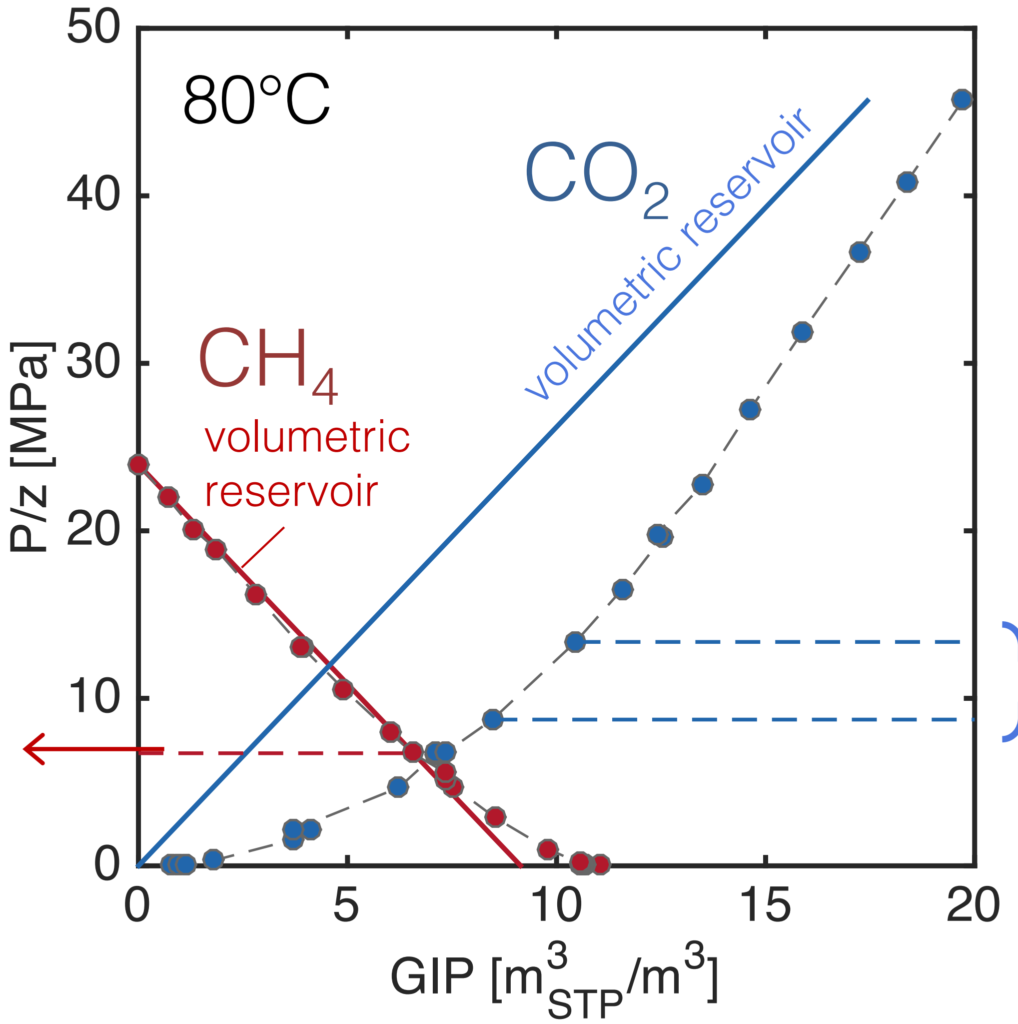
*Jang et al. **2016** *Energy Sources*,38(16), 2336-2342
** Heller and Zoback **2014** Journal of Unconventional Oil and Gas Resources 8, 14–24
***Carey JW, Pini R et al. **2017** *Caprock Integrity in Geological storage – AGU Monograph.*

CO_2 and CH_4 adsorption on Bowland Shale (UK)

Potential for *enhanced* gas recovery?

Gas recovery

Production of adsorbed gas kicks in



Gas storage

Gas sorption most effective

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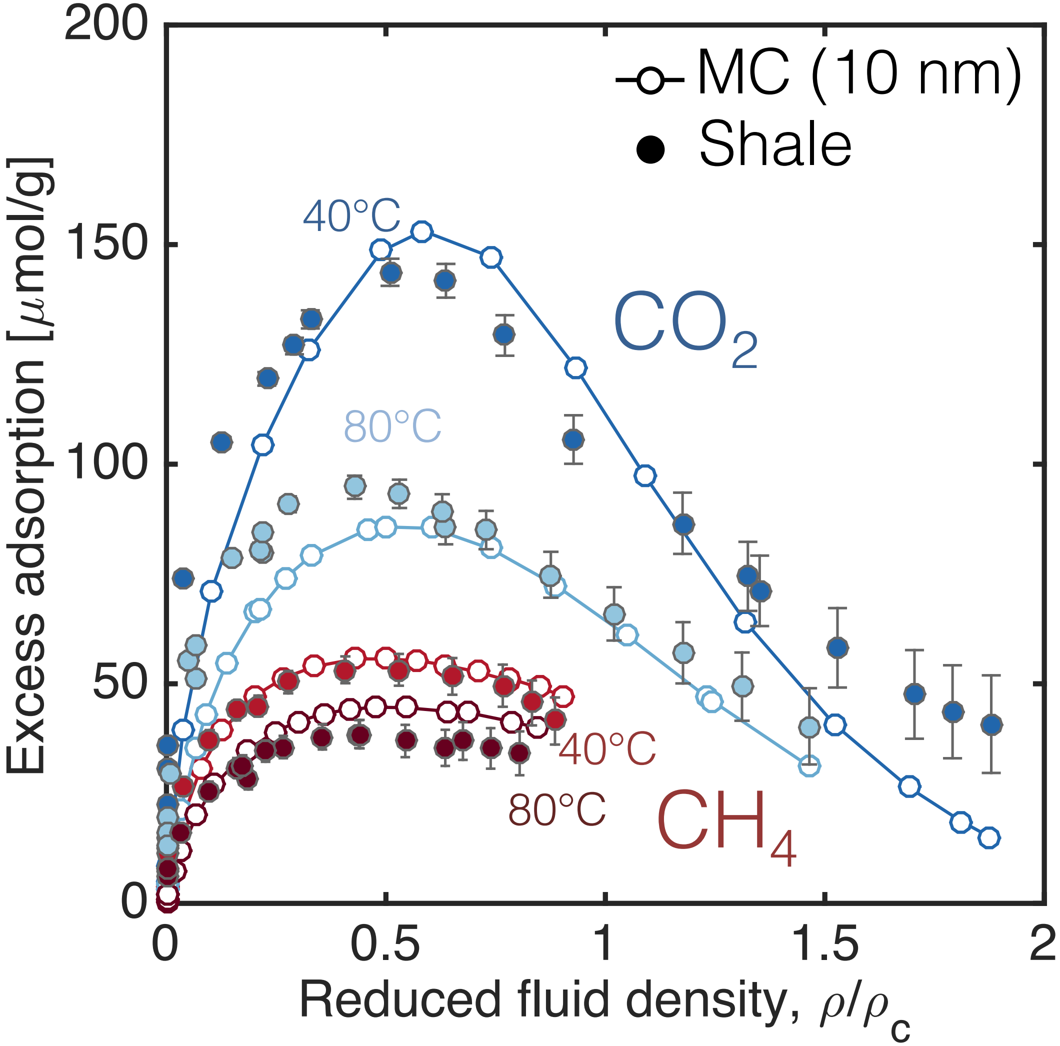
Scaling of shale data: the role of organics

- Independent measurements on mesoporous carbon
- Scaling factor (5%) ≈ shale sample TOC (6%wt.[1])
- Observations
  - Pronounced features of mesoporosity



[1] Fauchille A. L. et al. **2017** *Marine and Petroleum Geology*, 86, 1374-1390

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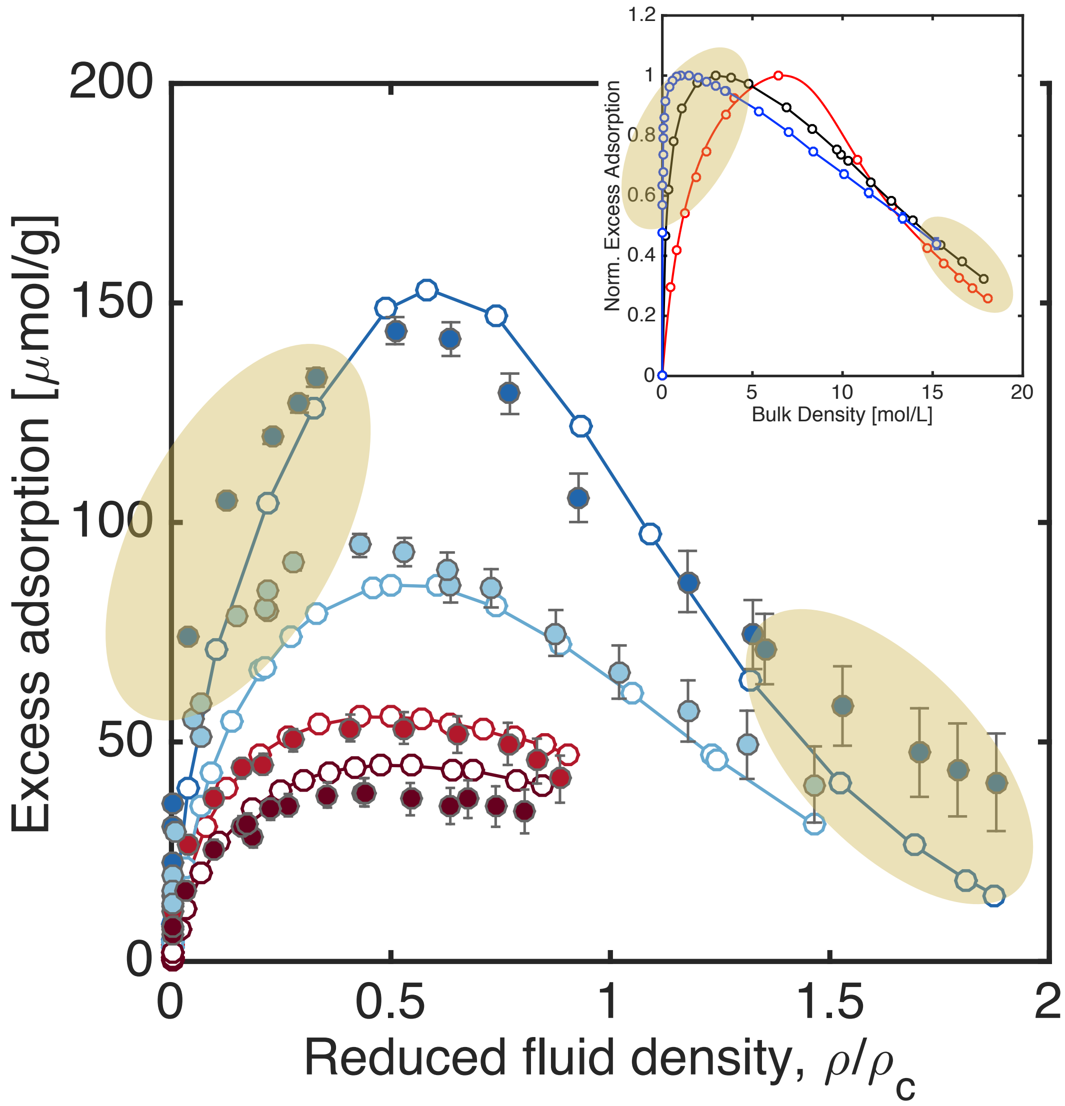
Scaling of shale data: the role of organics

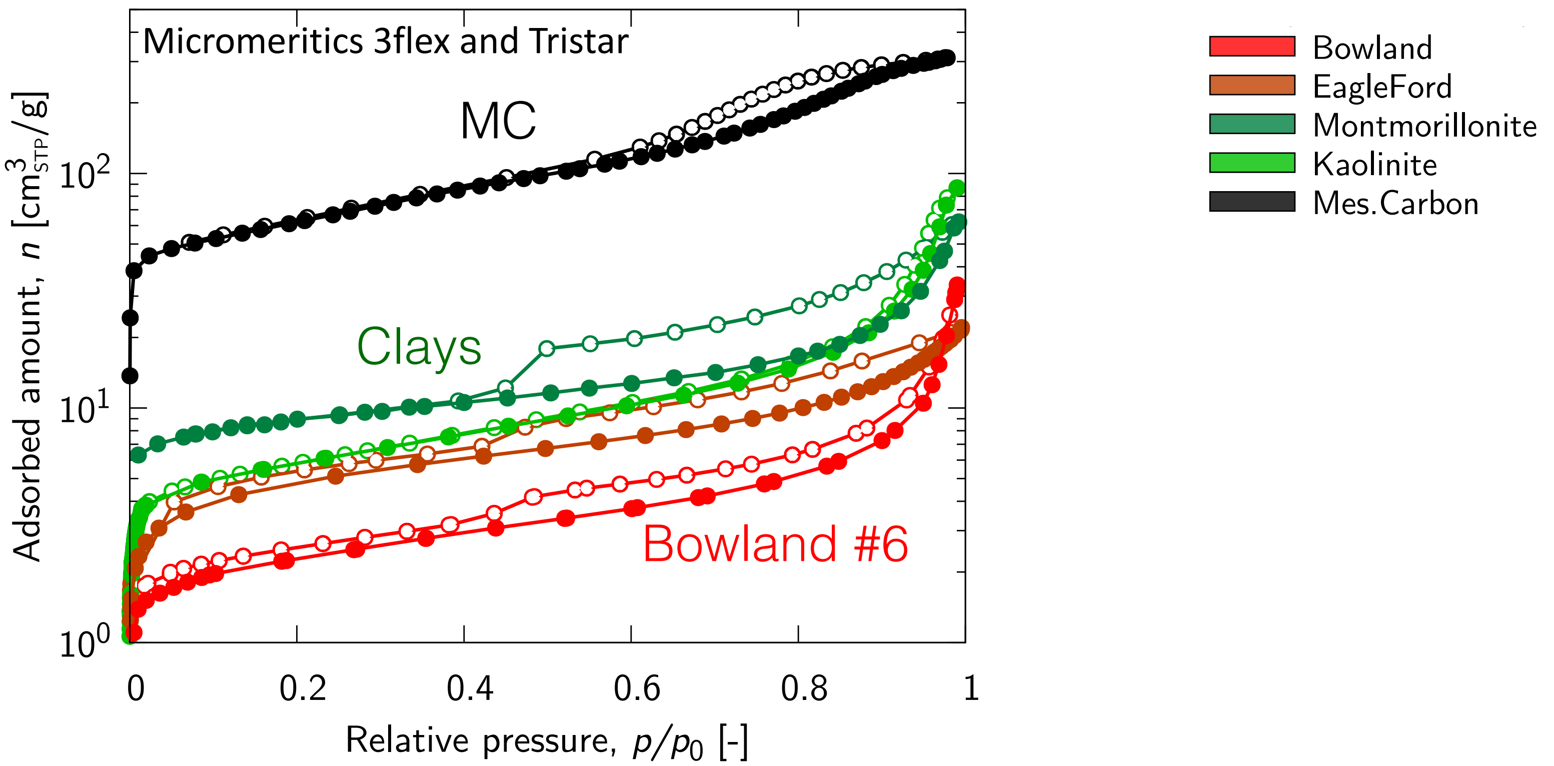
- Independent measurements on mesoporous carbon
- Scaling factor (5%) ≈ shale sample TOC (6%wt.[1])
- Observations
  - Pronounced features of mesoporosity
  - Some indications of microporosity
  - MC analogue for TOC (?)



[1] Fauchille A. L. et al. **2017** *Marine and Petroleum Geology*, 86, 1374-1390

Pore space characterisation of shale

Low-pressure (< 1 bar) N_2 adsorption isotherms at 77K



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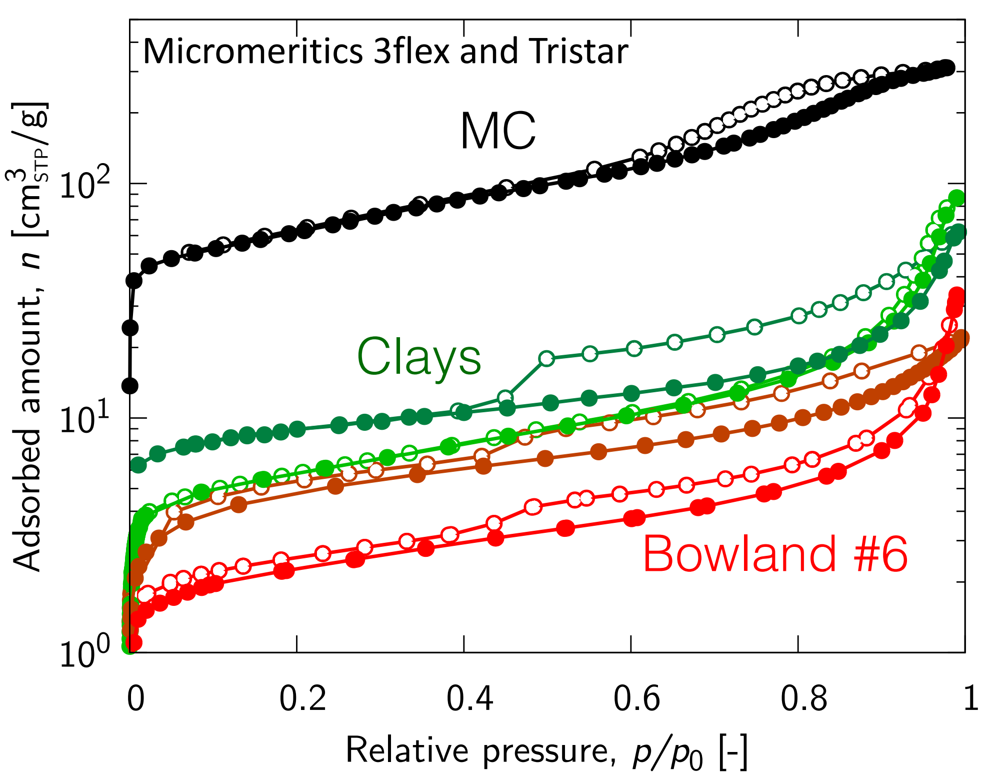
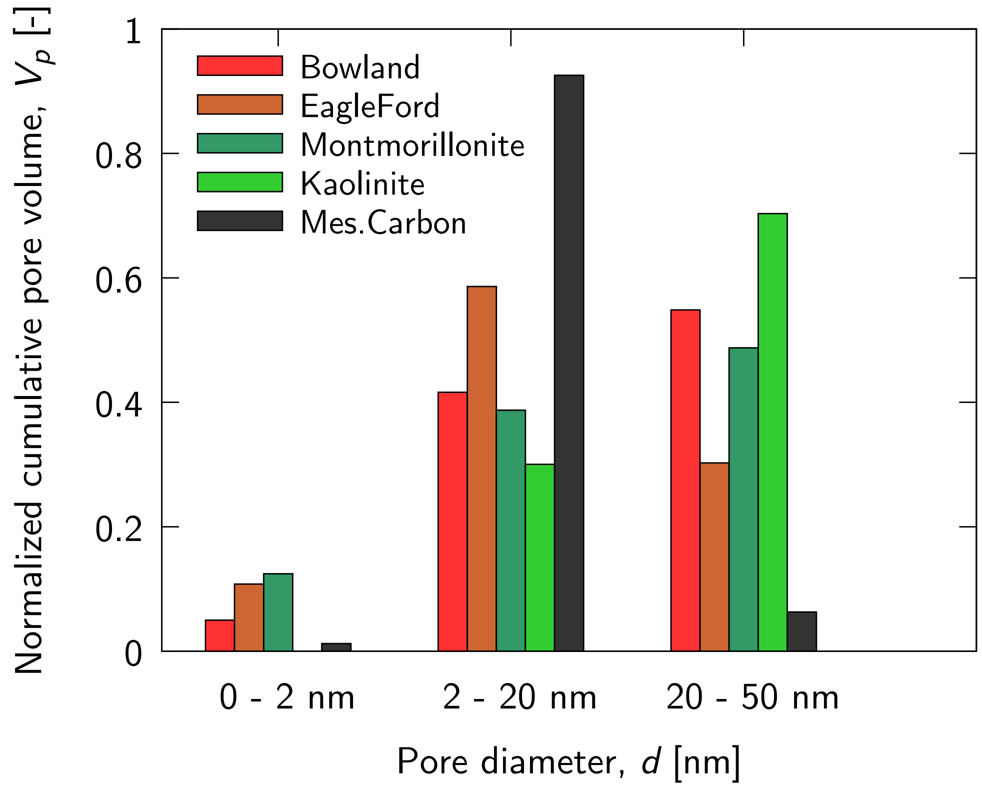


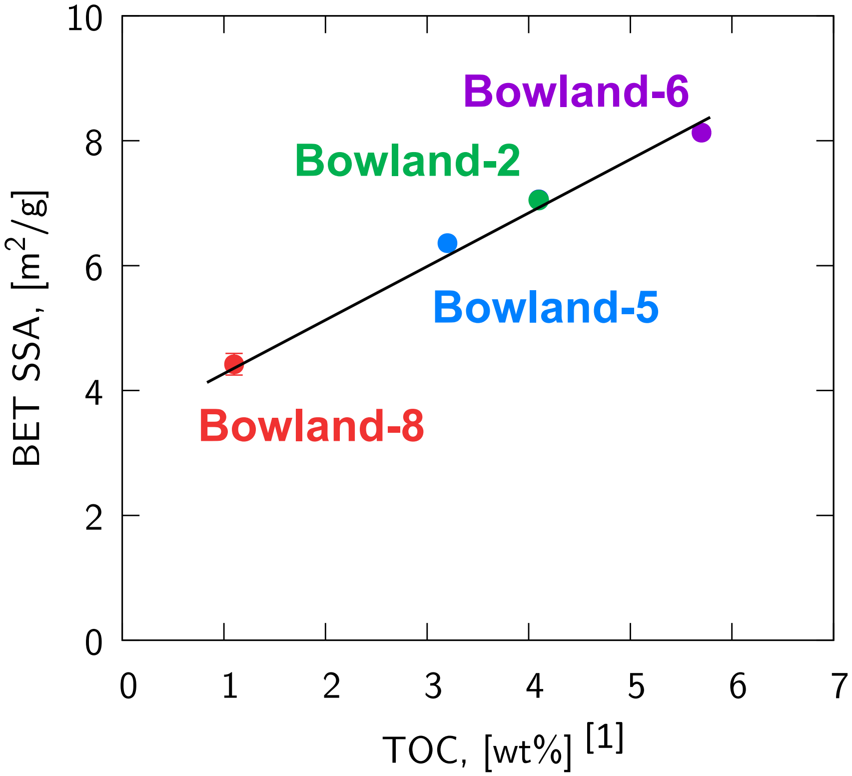


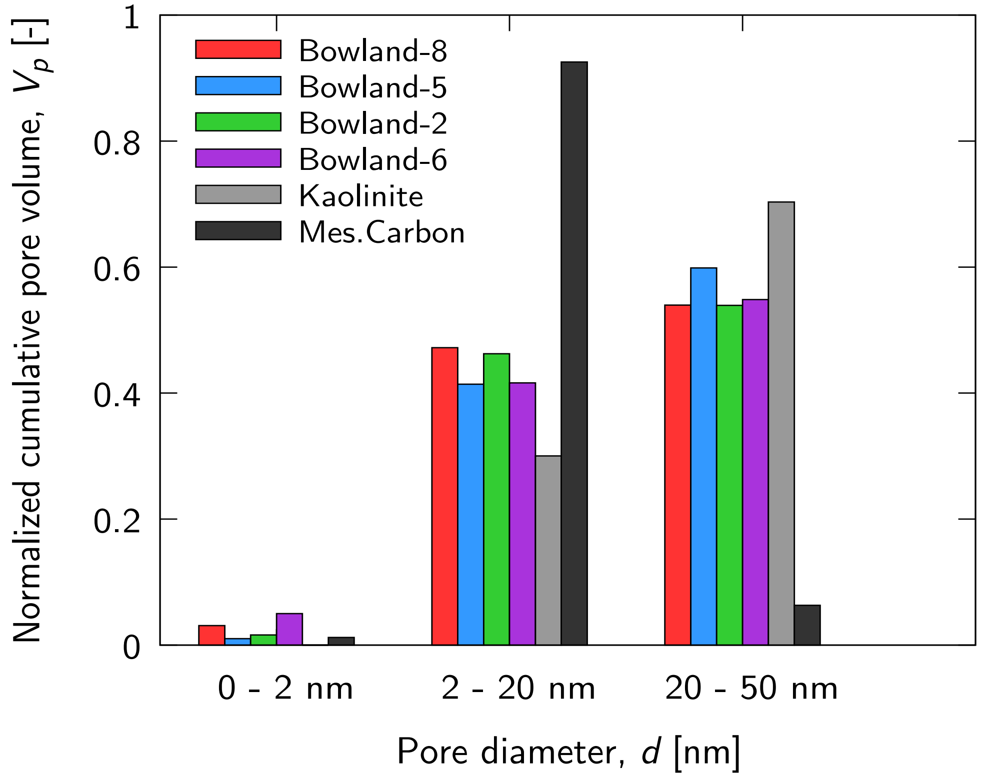
- Mesopores occupy majority of pore space in shale (> 80%)
- Shale does contain microporosity (5 – 10%)
- Clays contribute to microporosity (Bowland ~ 7%wt.[1])

[1] Fauchille A. L. et al. **2017** *Marine and Petroleum Geology*, 86, 1374-1390

Pore space characterization: Bowland shale

Low-pressure (< 1 bar) N_2 adsorption isotherms at 77K





- Mesopores occupy majority of pore space in shale (> 80%)
- Shale does contain microporosity (5 – 10%)
- Bowland case study: apparent correlation between SSA_{N2} and TOC

[1] Fauchille A. L. et al. **2017** *Marine and Petroleum Geology*, 86, 1374-1390

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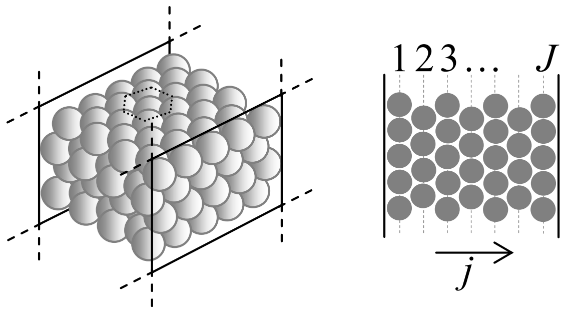
Modelling of gas adsorption in shale

How can we account for the complexity of shale's pore space?

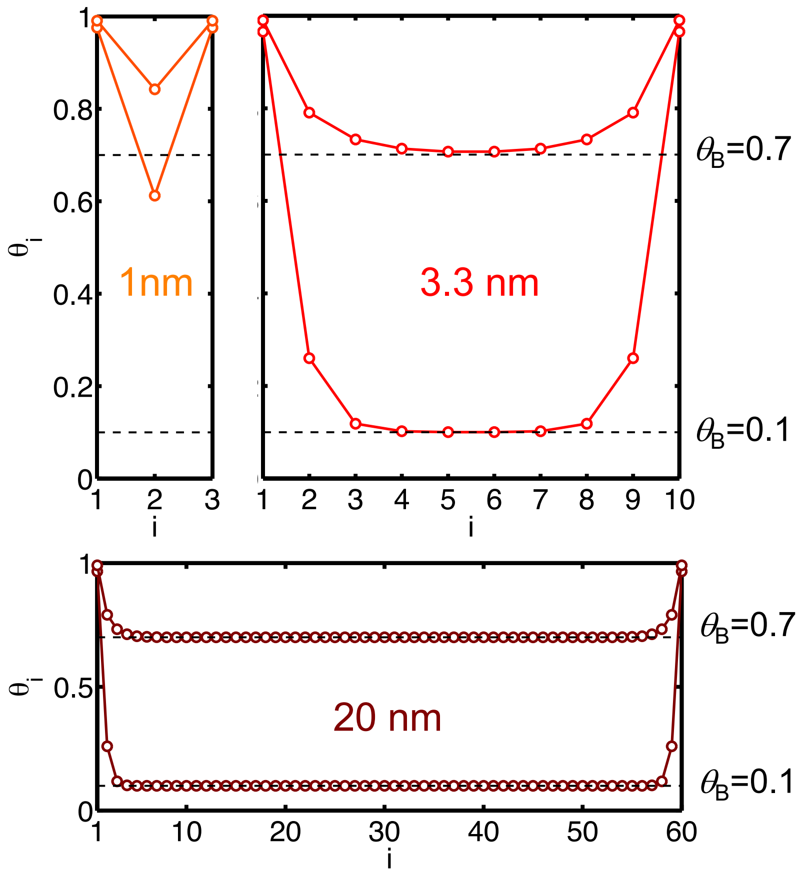
- Lattice DFT model[1]:
  - Discretization of the pore space



  - Slit pores, hexagonal lattice
  - Nearest-neighbors interactions
  - Successfully applied to both engineered materials [2] and rocks [3-5]

Density profiles in the pores

CO_2, T = 45°C

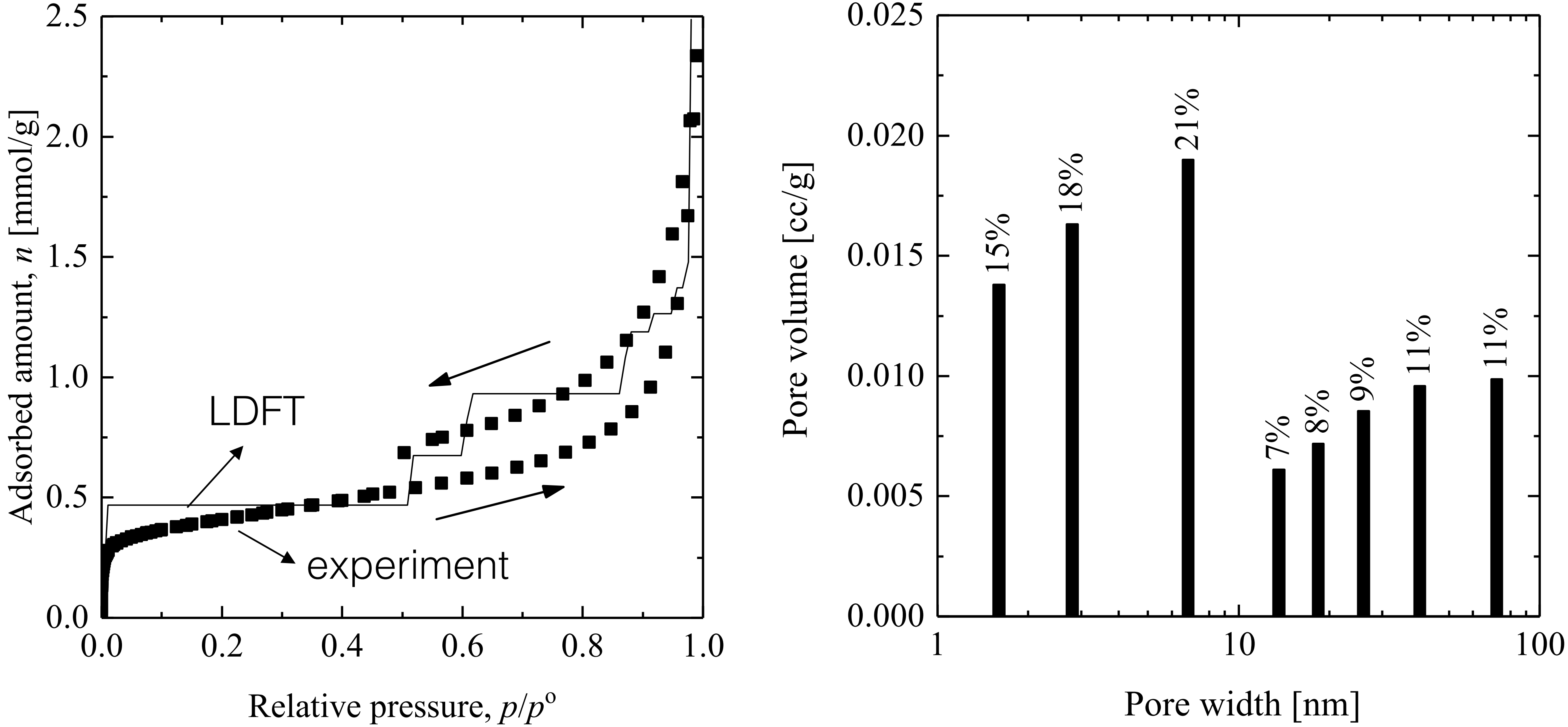


[1] Aranovich and Donohue *J Colloid Interface Sci* **1998**, 200: 273-90
[2] Hocker et al, *Langmuir* **2003,** 19: 1254-67
[3] Ottiger et al. *Langmuir* **2010**, 24: 9531-40
[4] Pini et al. *Adsorption* **2010**, 16: 37-46
[5] Qajar et al. *Fuel* **2016**, 163: 205-13

Application example: source clay (SWy-2)

Sub- and super-critical data in a unique, consistent framework

N_2 adsorption at 77K ⟷ **Pore size distribution**



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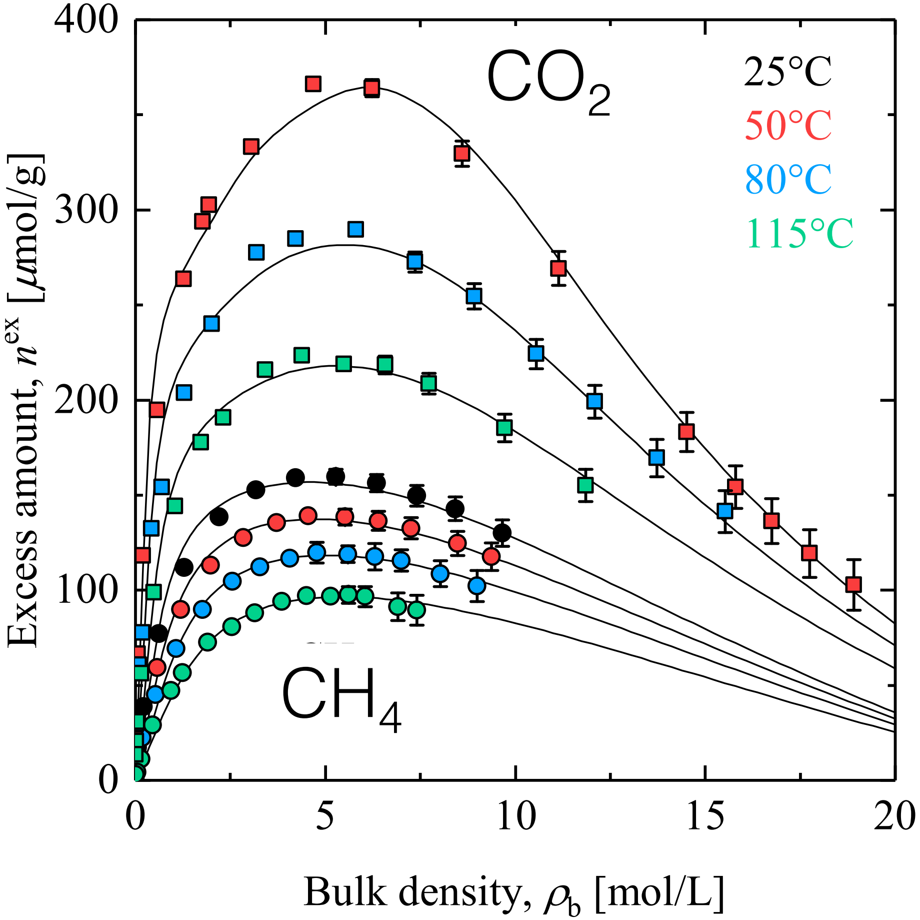
Application example: source clay (SWy-2)

Sub- and super-critical data in a unique, consistent framework

Supercritical adsorption



Identification of relevant pore-classes from N_2 physisorption ✓

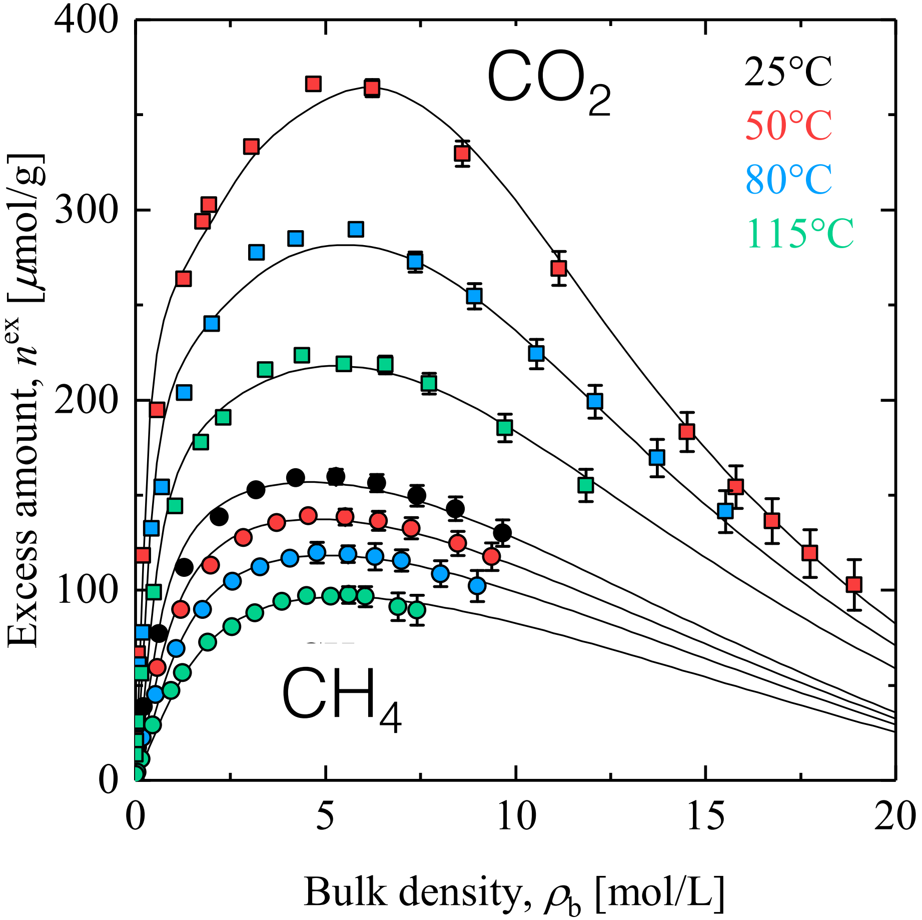
Calibrated model applied to match supercritical isotherms

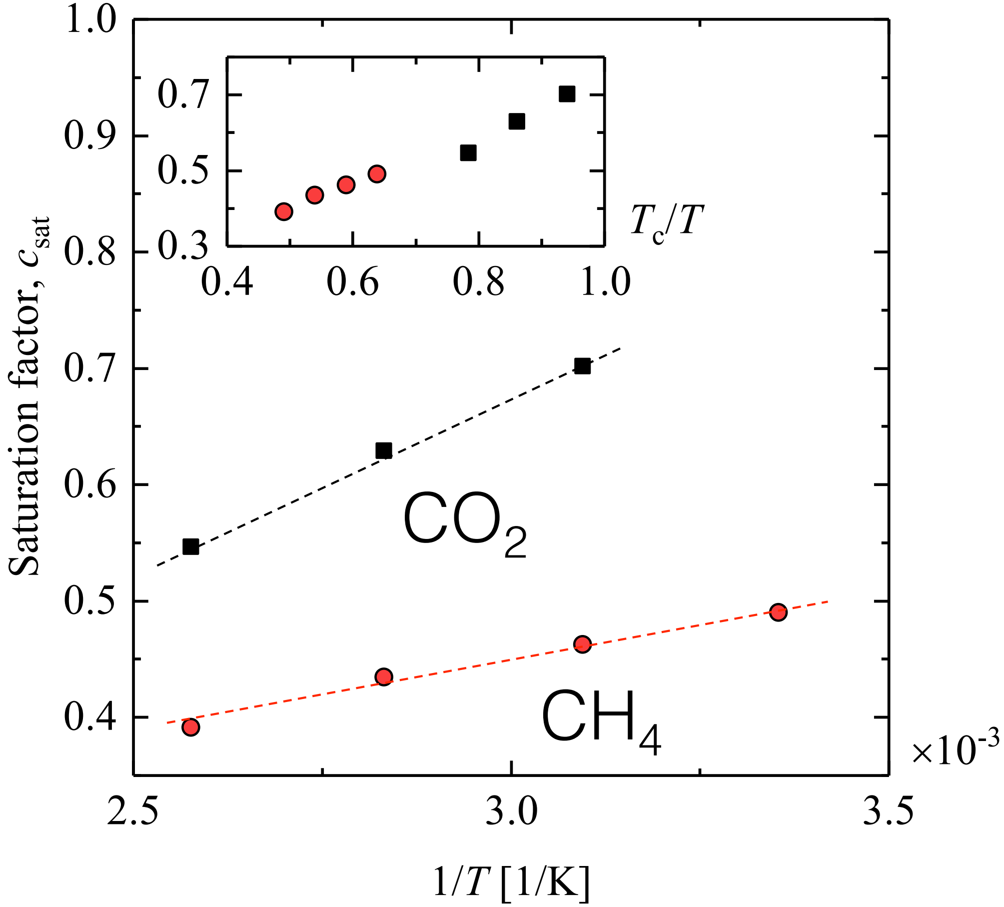
Solid-fluid interaction used as a fitting parameter (fluid-dependent)

Application example: source clay (SWy-2)

Sub- and super-critical data in a unique, consistent framework

Supercritical adsorption → **Filling capacity**





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Concluding remarks

- Understanding the shale's pore space requires understanding gas adsorption (and vice versa)
- Shale and clay-rich systems retains characteristics of a mesoporous material
- The presence of microporosity is confirmed from both sub- and supercritical adsorption studies
- Mesoporous carbon as analogue of OM?
- Significant adsorption selectivity of CO_2 vs. CH_4
- The complexity of the pore space requires rigorous modeling approaches that incorporate PSD and chemical heterogeneity

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  Prof. Martin Trusler, Imperial College London

  Prof. Alberto Striolo, University College London

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  QATAR SCIENCE & TECHNOLOGY PARK
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