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4th Biennial CO_2 for EOR as CCUS Conference 2019

Uptake capacity and pore accessibility of illite-smectite source clay minerals for supercritical CO_2 and CH_4

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Introduction

Adsorption at elevated pressure (often supercritical)

Sequestration
&
Enhanced recovery

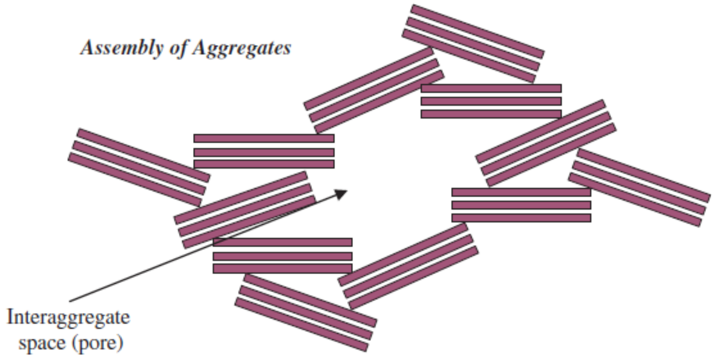
- Shales
- Coal
- Clay minerals

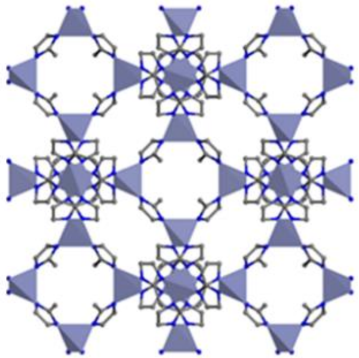
Broad porosity
Low surface area

Capture
&
Separation

- Zeolites
- MOFs

Mostly microporous
High surface area
(> 1,000 m^2/g)





[1] F. Bergaya, B.K.G. Theng, and G. Lagaly. *Handbook of Clay Science* Elsevier 2006
[2] D. Fairen-Jimenez *et al. J. Am. Chem. Soc.* 133 (2011) 8900-8902

Introduction: adsorption

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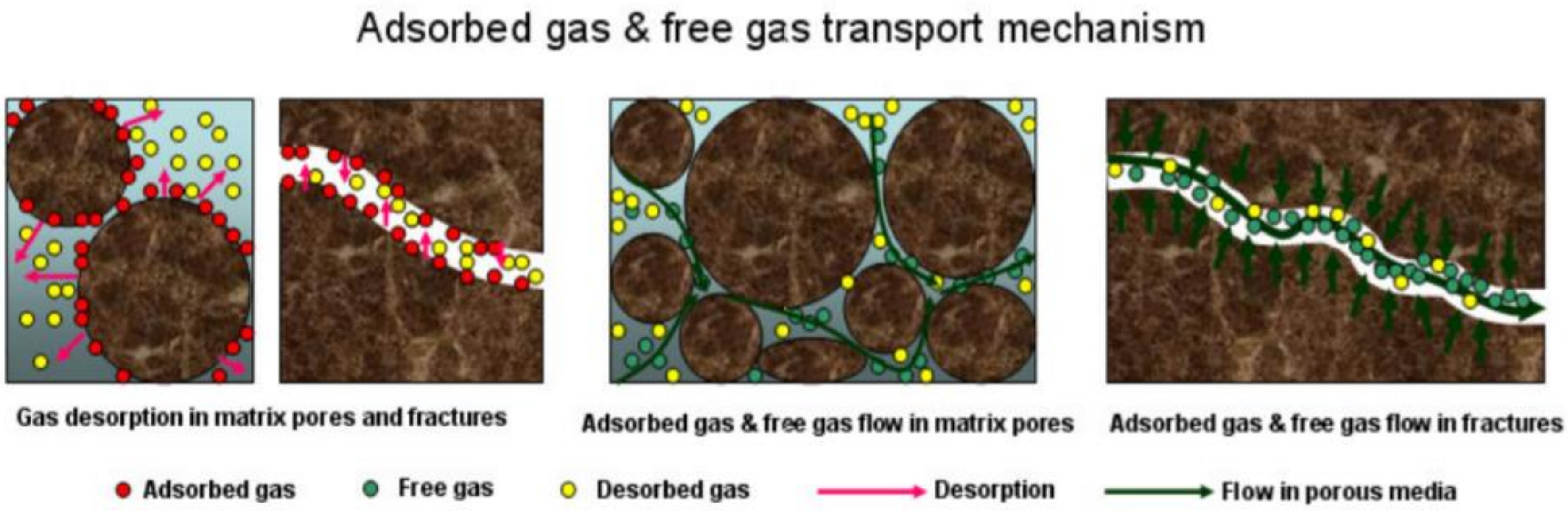
Adsorption in carbon sequestration



[7]

- Liquid-like dense phase on surface leading to increased gas storage capacity[1,2]
- Enhanced sealing efficiency[3]
- 20 - 85% of total gas-in-place (GIP)[4-6]

[1] A. Busch et al. *Geomech. Geophysics Geo-energy Geo-resources* 2 (2016) 111-130
[2] J. Wan et al. *PNAS* 115 (2018) 873-878
[3] J. Wollenweber et al. *IJGGC* 4 (2010) 231-241
[4] X. Lu and F. Li *Fuel* 74 (1995) 599-603
[5] J. Curtis *AAPG Bulletin* 86 (2002) 1921-1938
[6] S. Montgomery et al. *AAPG Bulletin* 89 (2005) 155-175
[7] B. Song et al. SPE 140555 (2011)

Introduction: clay minerals

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Dominant presence in underground formations

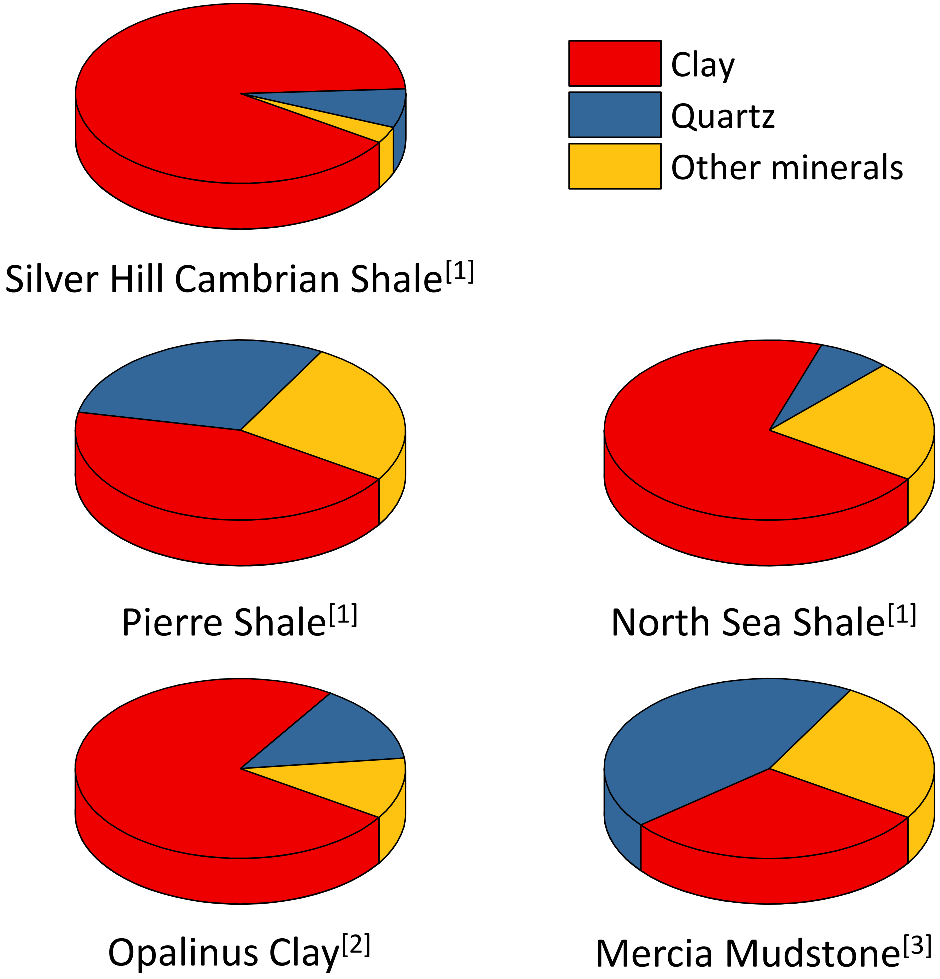
Clay minerals are present in geological formations in large fractions

- ~30 wt% of sedimentary rocks
- Found in shales and oil sands up to 90 wt%
- Determines physical characteristics

This study:

Smectite I-S mixed Illite

[1] Kuila and Prasad. *Geophysical Prospecting* 61 (2013) 341-362
[2] Busch *et al*. *Geological Society London* 454 (2017)
[3] Armitage *et al*. *J. Geological Society* 170 (2013) 119-132



Introduction: clay minerals

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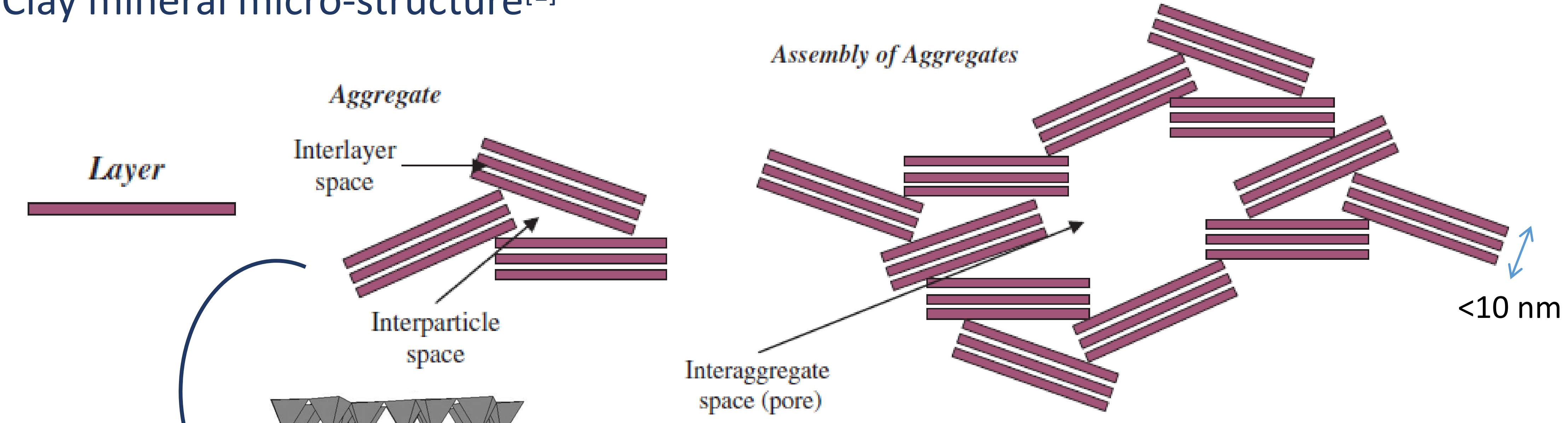
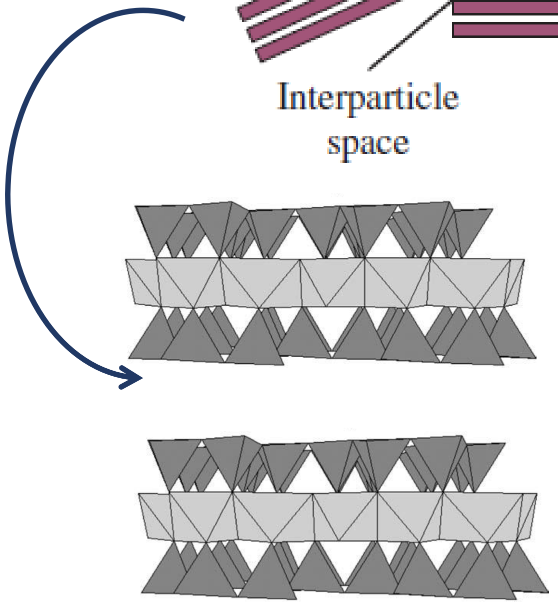
Clay mineral micro-structure[1]





- Mesopores (>2 nm, <50 nm) from inter-particle/aggregate spaces
- Small micropores (< 2nm) from interlayer spaces
- Interlayer *internal* surface area (700 – 1000 m^2/g)[2] compared to external surface area (~30 m^2/g)[3]

[1] F. Bergaya, B.K.G. Theng, and G. Lagaly. *Handbook of Clay Science* Elsevier 2006
[2] C. Tournassat *et al*. *Natural and Engineered Clay Barriers* Elsevier 2015
[3] R. Mooney *et al*. *J. Am. Chem. Soc*. 74 (1952) 1367–1371

Research objectives

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- Textural characterization of clay minerals via adsorption
- Supercritical single-component adsorption of CO_2 and CH_4 on clay minerals
- CO_2 and CH_4 inside clay nanopores under subsurface conditions
- High-pressure adsorption of CO_2 and CH_4 mixtures

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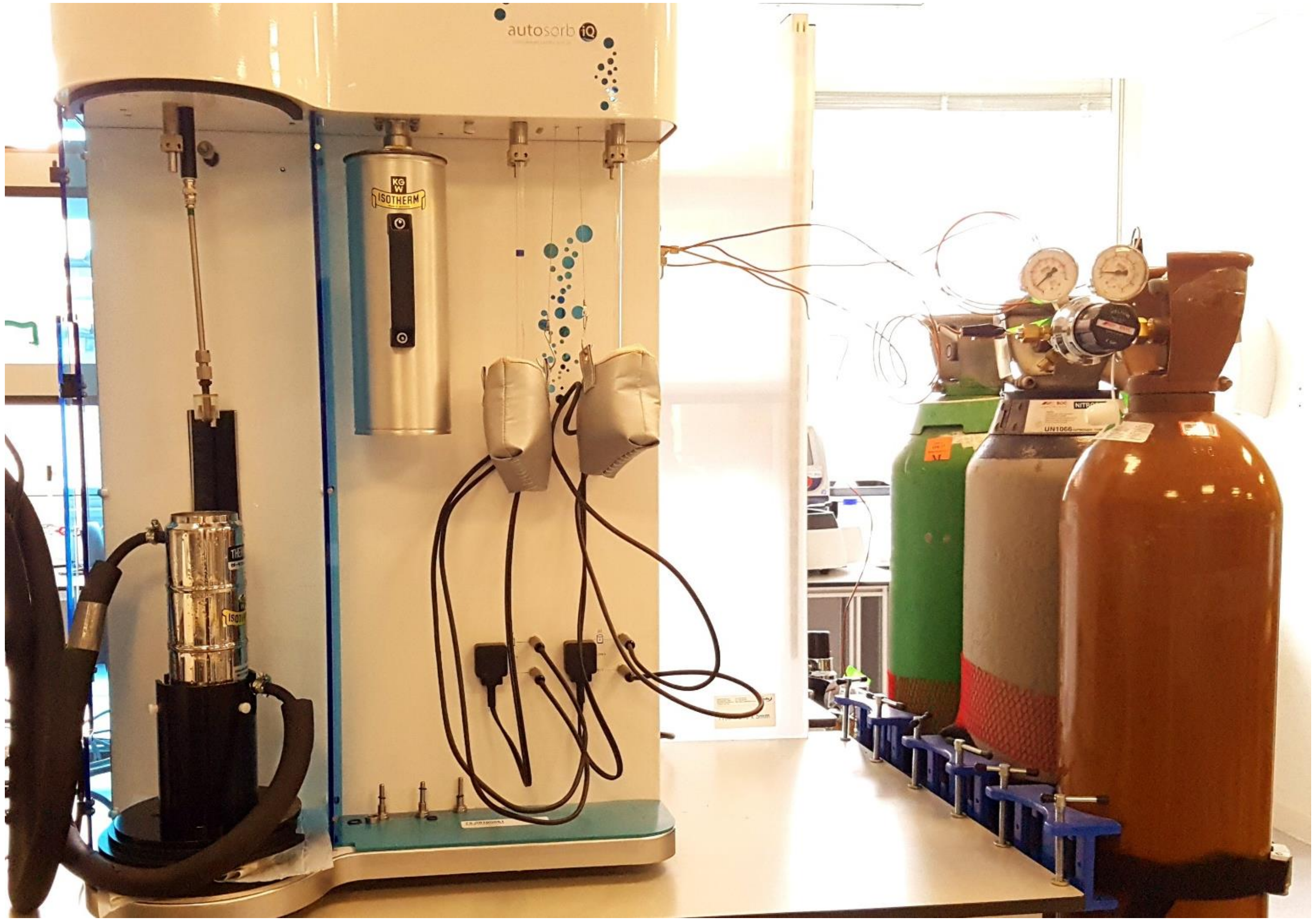
Experimental methodology

Clay mineral porosity characterization

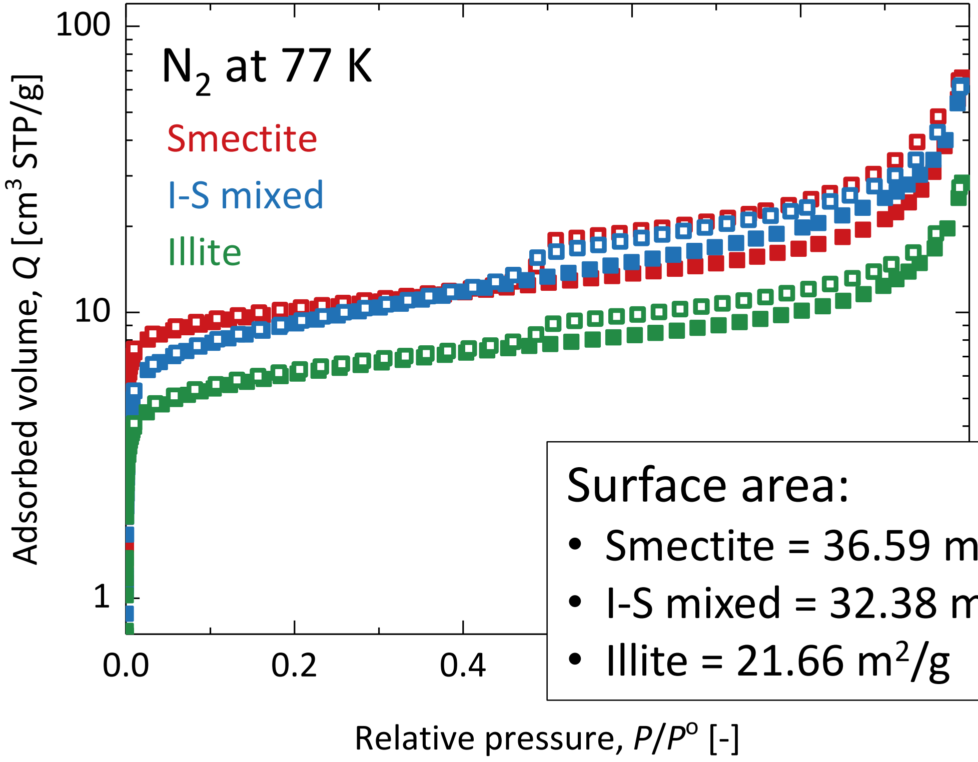


- Quantachrome Autosorb iQ
- CryoSync and cooling bath
- Using N_2 (77 K), Ar (87 K), and CO_2 (273 K) for micro- and mesopores analysis
- Recommended by the IUPAC report[1]

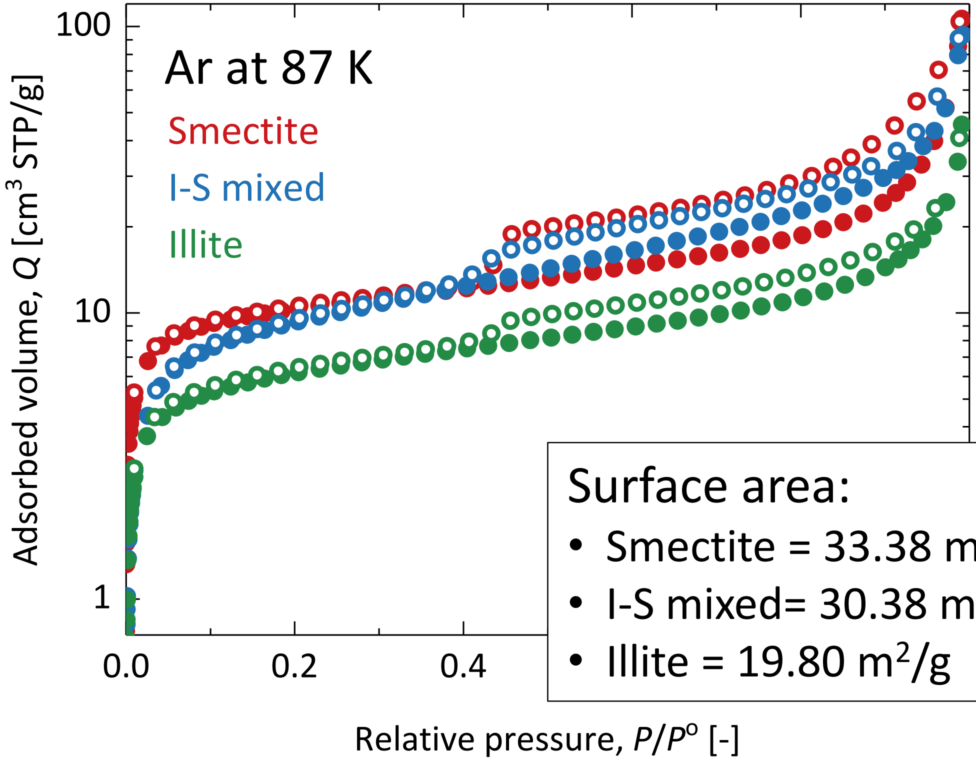
[1] M. Thommes *et al*. *Pure and Applied Chemistry* 87 (2015) 1051-1069

Clay nanopores characterization

N_2 (at 77 K) and Ar (at 87 K) sorption isotherms



Surface area:
- Smectite = 36.59 m^2/g
- I-S mixed = 32.38 m^2/g
- Illite = 21.66 m^2/g



Surface area:
- Smectite = 33.38 m^2/g
- I-S mixed= 30.38 m^2/g
- Illite = 19.80 m^2/g

Low-pressure (< 1 bar) adsorption characterization shows

- Total pore volume (≤ 0.110 cm^3/g): smectite> I-S mixed > illite
- Clay minerals are dominated by mesoporosity (≈ 50 - 60 %)
- Contain microporosity (≈ 10 %): smectite > illite > I-S mixed

Clay nanopores characterization

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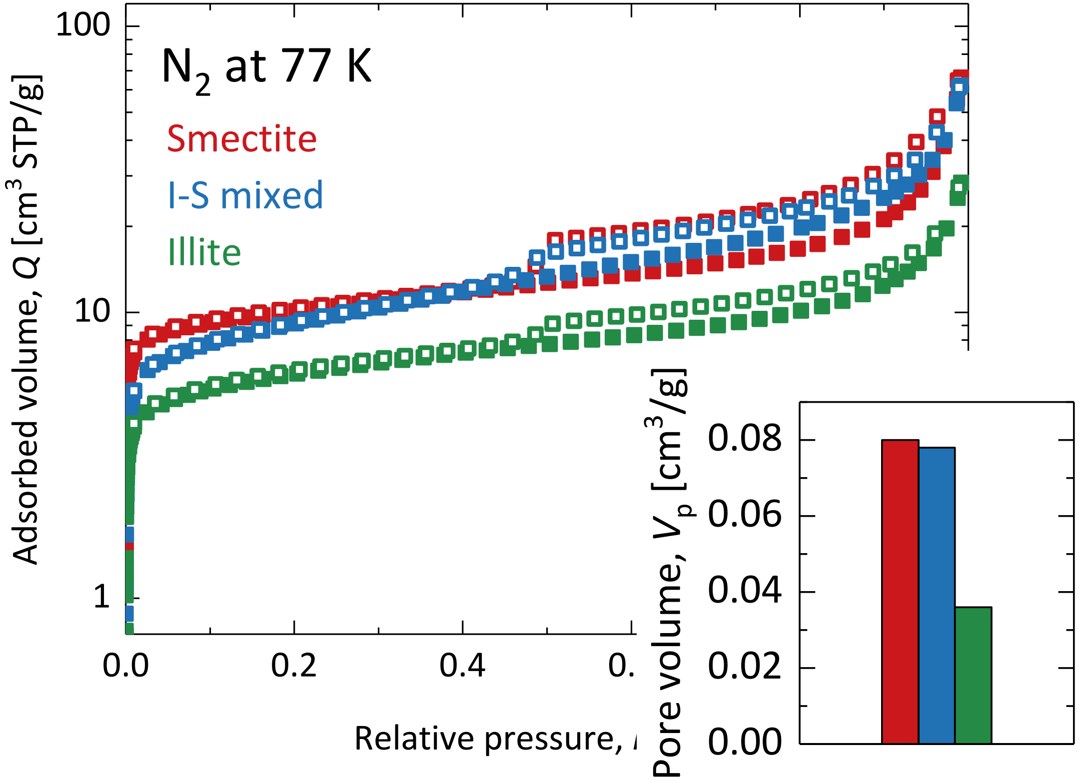

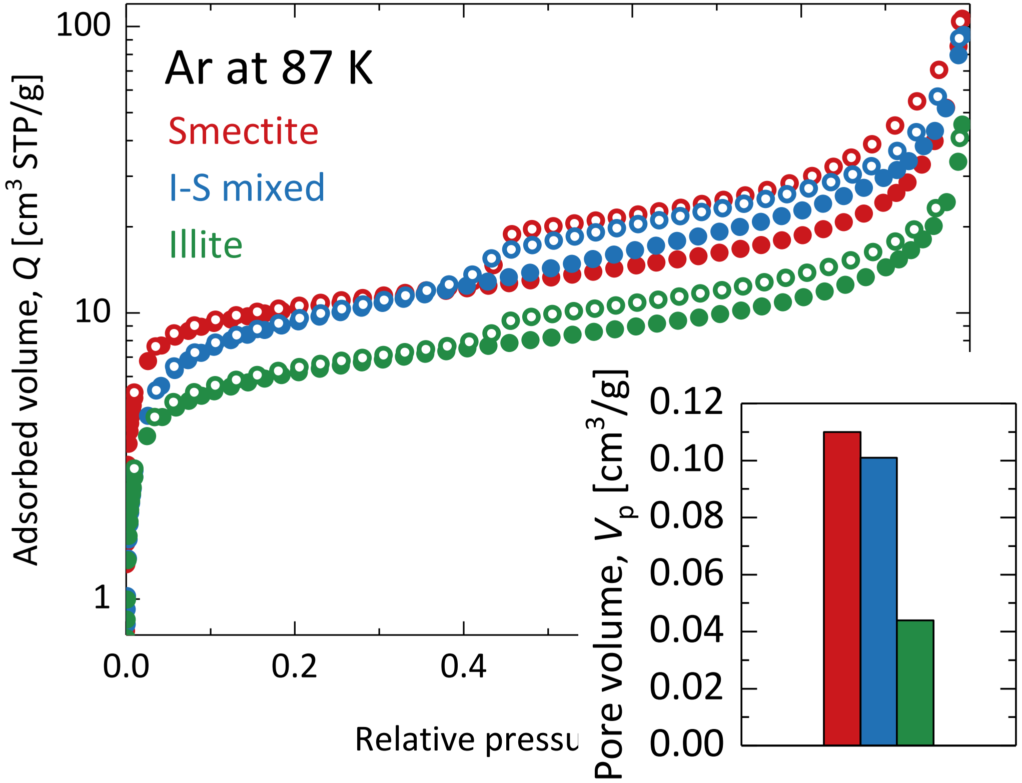

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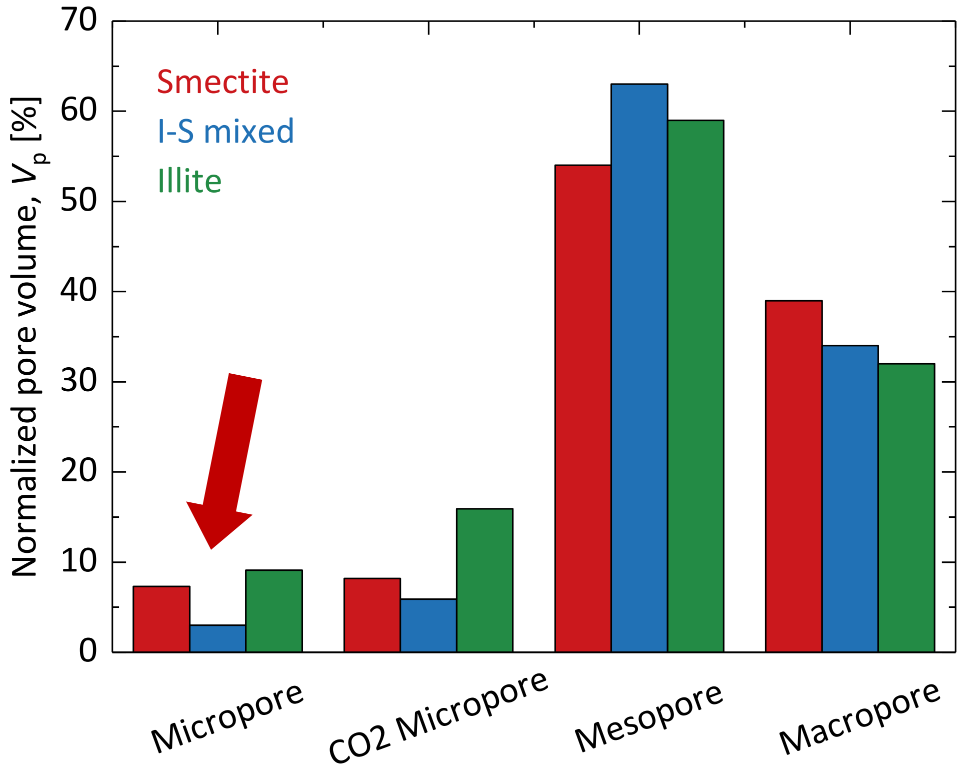

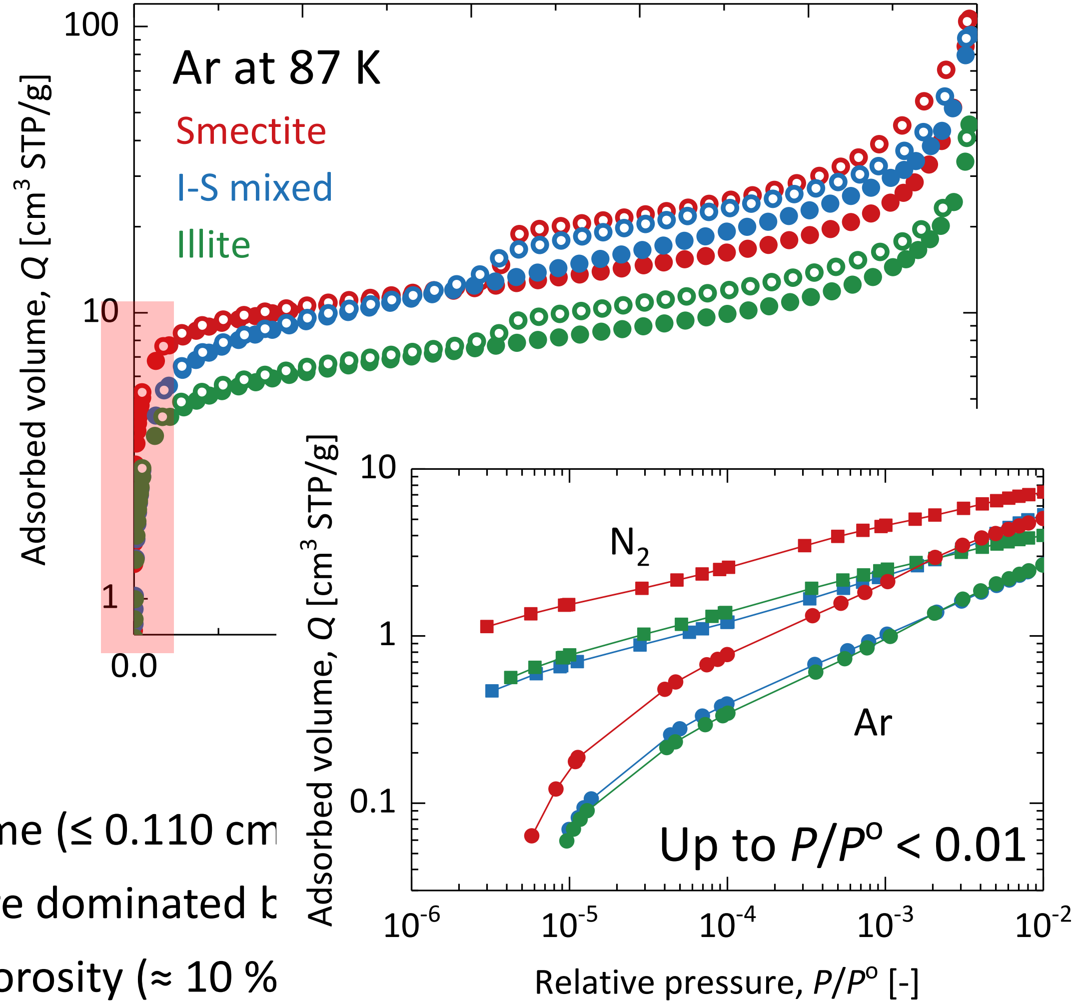

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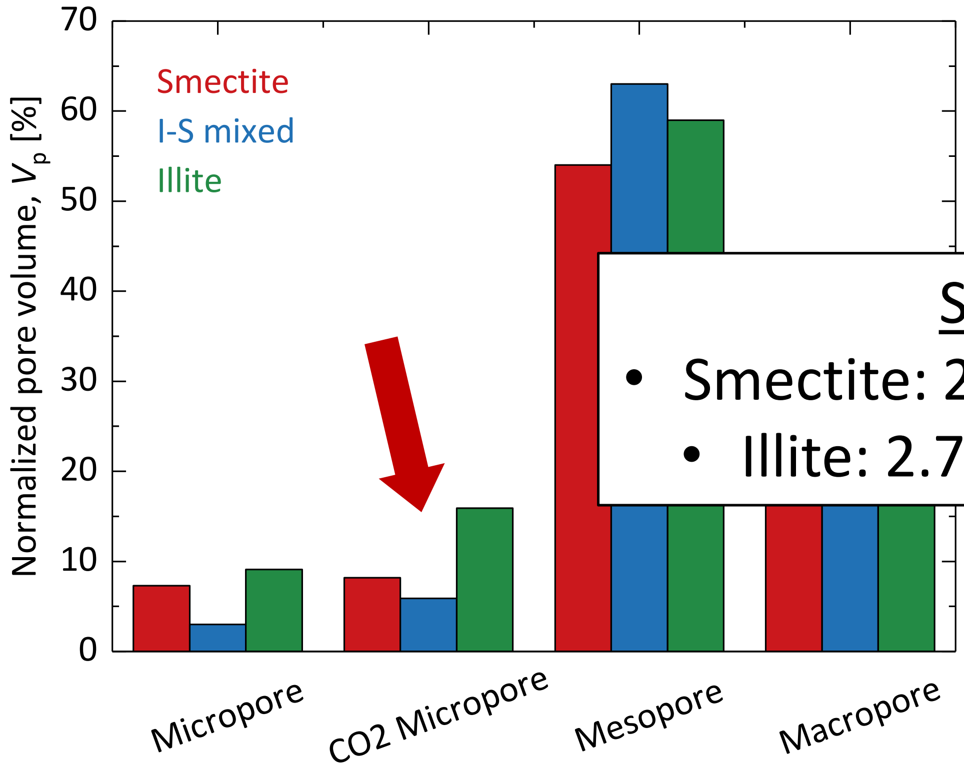
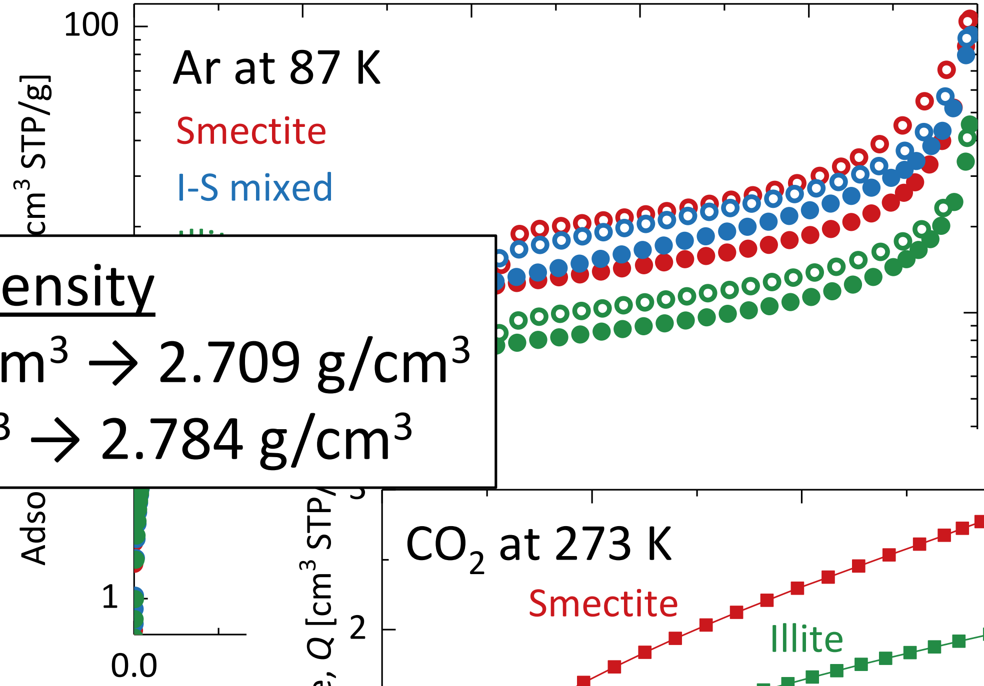
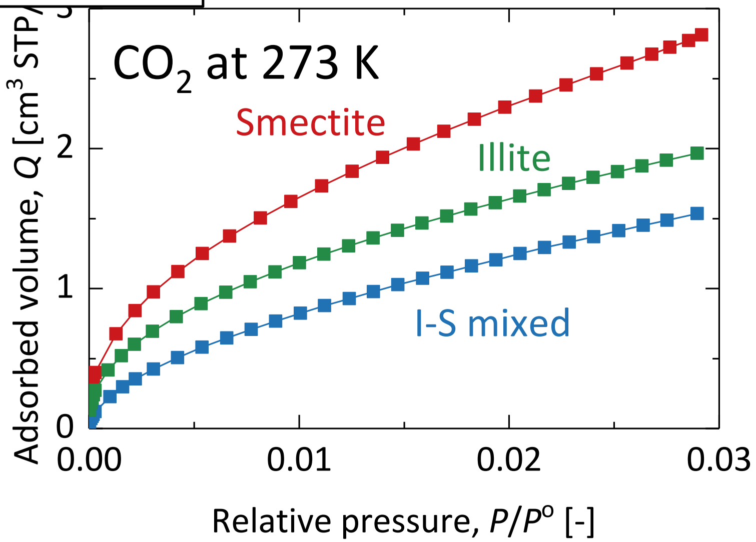




Skeletal density

- Smectite: 2.798 g/cm^3 → 2.709 g/cm^3
  - Illite: 2.780 g/cm^3 → 2.784 g/cm^3



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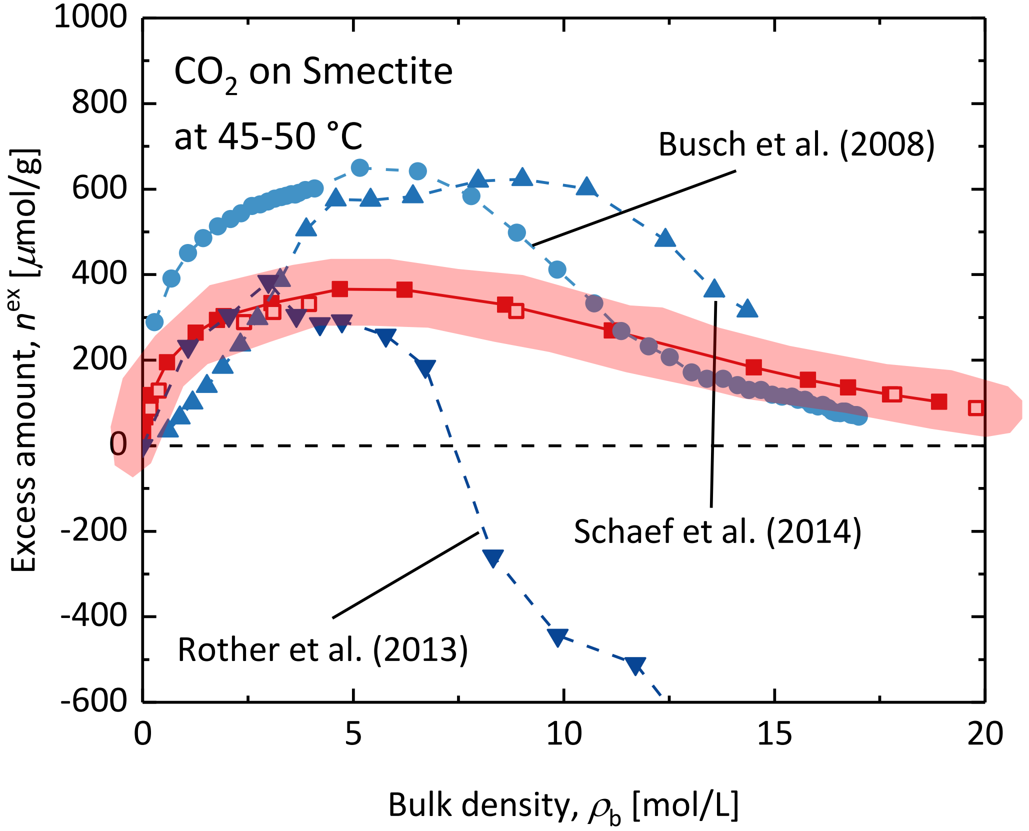
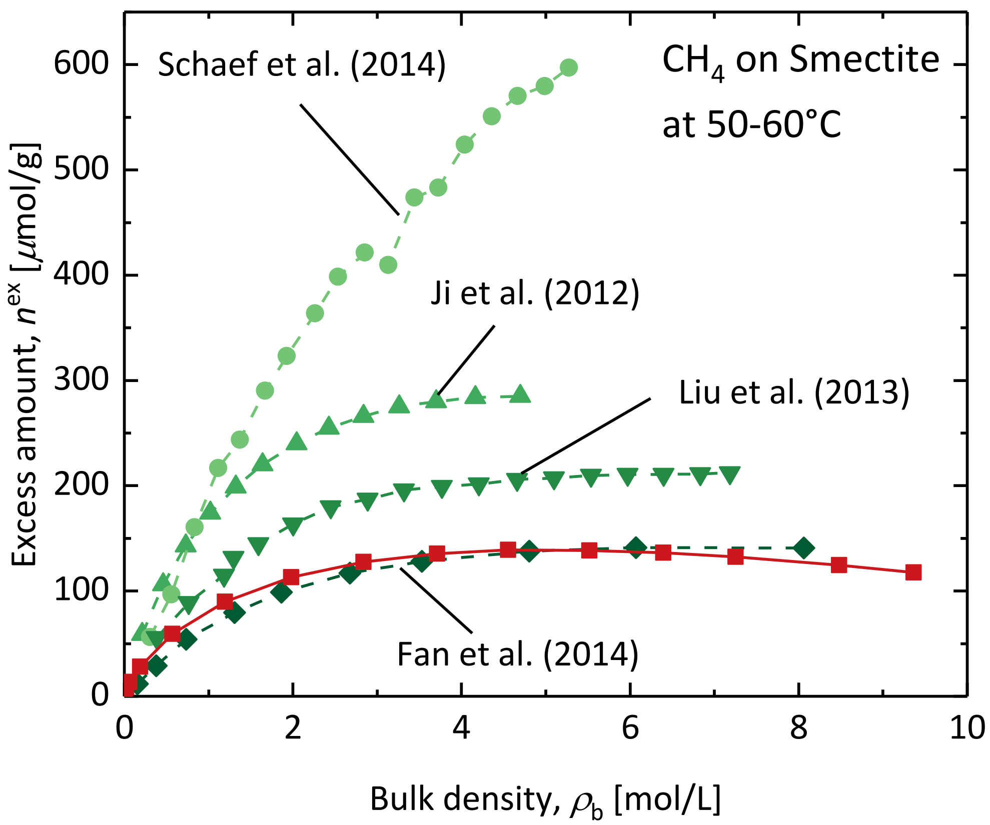
Sorption isotherms on clay minerals

Adsorption isotherms on clays at elevated pressures: literature data





[1] A. Busch *et al. Int. J. Greenh. Gas Con.* 2 (2008) 297-308
[2] H. Schaef *et al. Energy Procedia* 63 (2014) 7844-7851
[3] G. Rother *et al. Environ. Sci. Technol.* 47 (2013) 205-211
[4] L. Ji *et al. Appl. Geochem.* 27 (2012) 2533-2545
[5] D. Liu *et al. Appl. Clay Sci.* 85 (2013) 25-30
[6] E. Fan *et al. Energy Explor. Exploit.* 32 (2014) 927-942

Experimental methodology

High pressure sorption measurement apparatus

- Rubotherm MSB (Bochum, Germany)
- From vacuum to 350 bar
- Up to 150°C
- *in situ* measurement of excess adsorption and fluid bulk density

CO_2 and CH_4 sorption on illite-smectite clay minerals

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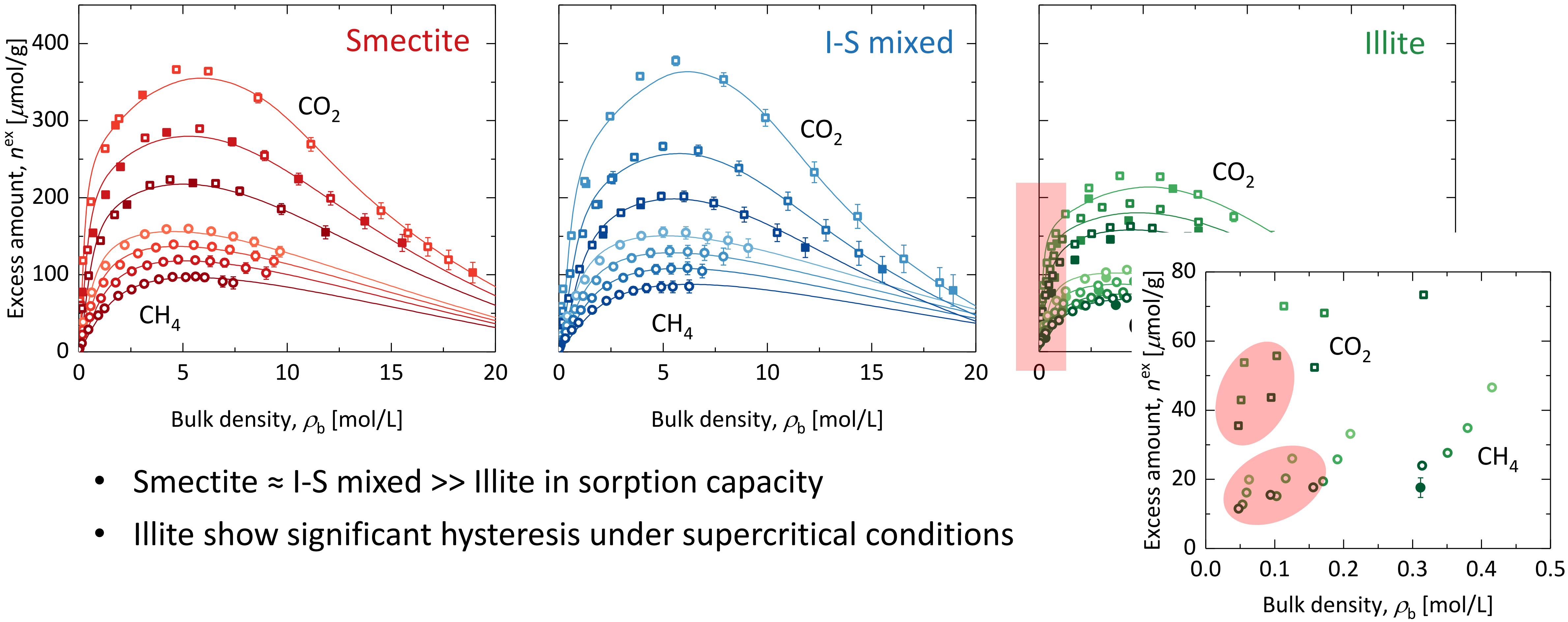
High pressure supercritical sorption isotherms



- Smectite ≈ I-S mixed >> Illite in sorption capacity
- Illite show significant hysteresis under supercritical conditions

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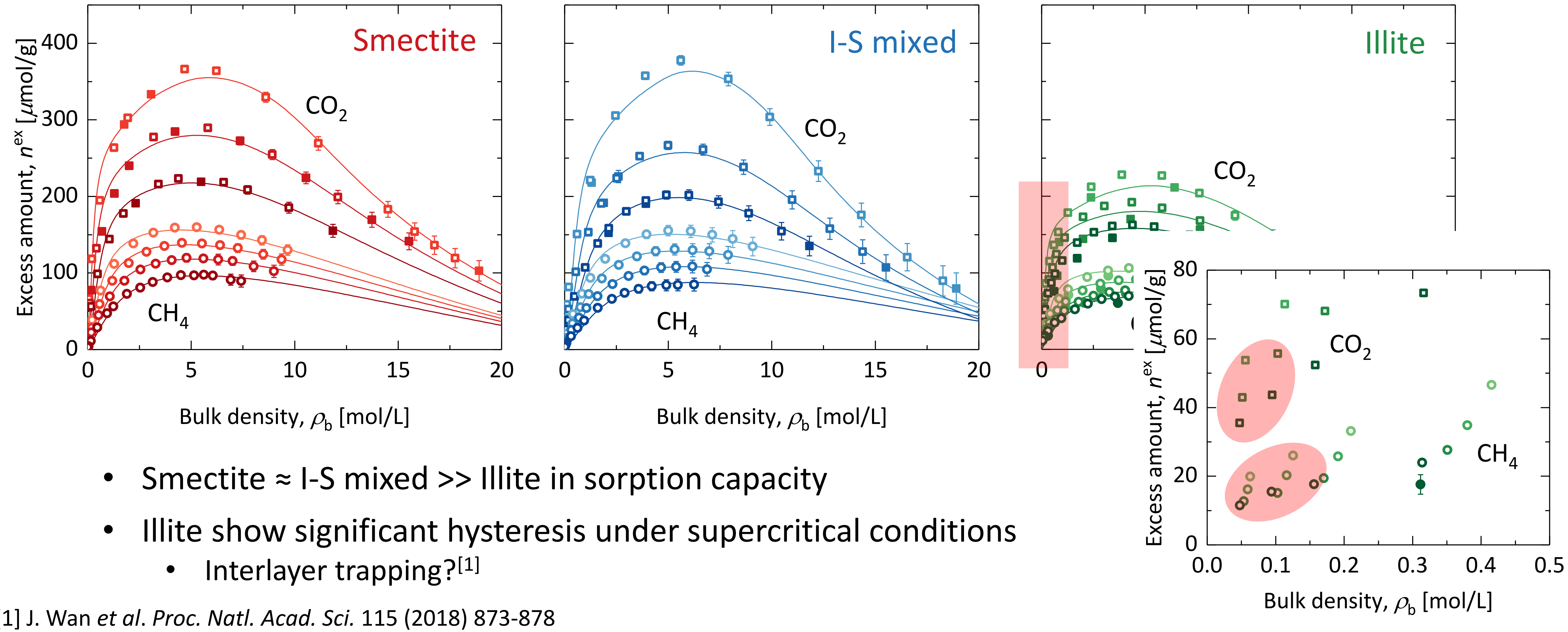
High pressure supercritical sorption isotherms



- Smectite ≈ I-S mixed >> Illite in sorption capacity
- Illite show significant hysteresis under supercritical conditions
  - Interlayer trapping?[1]

[1] J. Wan *et al*. *Proc. Natl. Acad. Sci.* 115 (2018) 873-878

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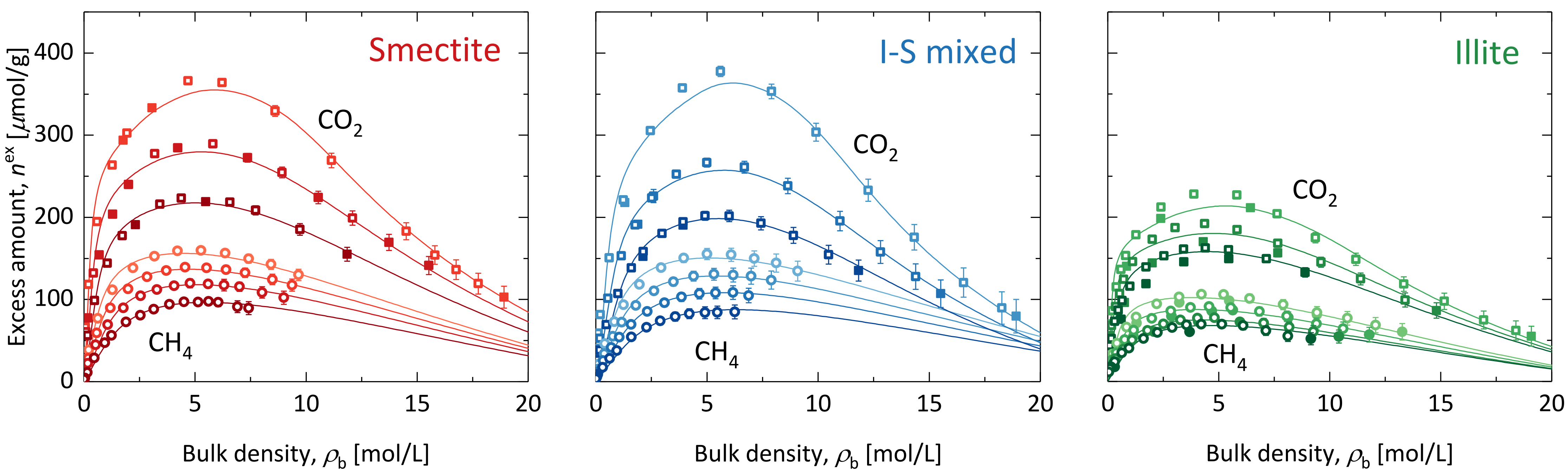
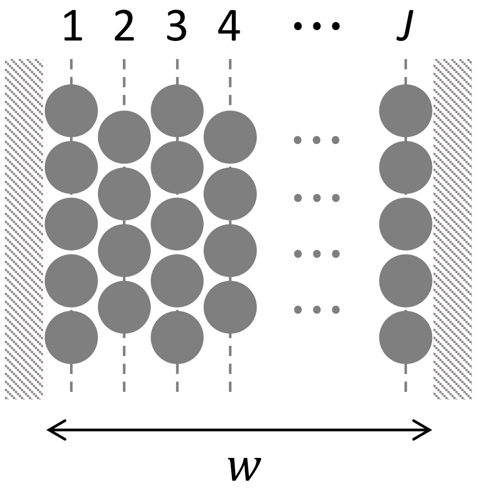


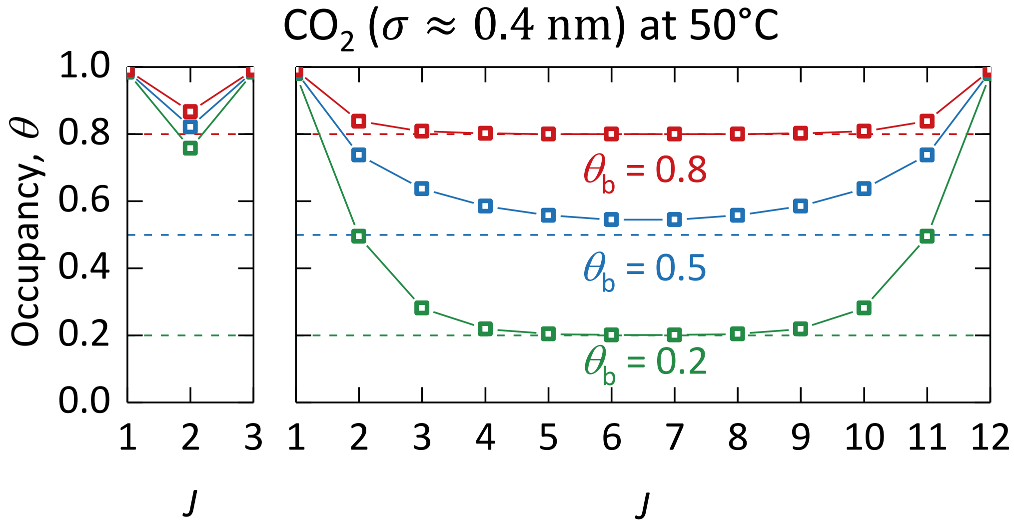
Supercritical adsorption model for slit pores

Lattice density functional theory (Ono-Kondo)[1]



- Applied to commercial materials[2,3] and natural rocks[4]
- Density profiles from occupancy profiles

Lattice occupancy profiles in slit pores



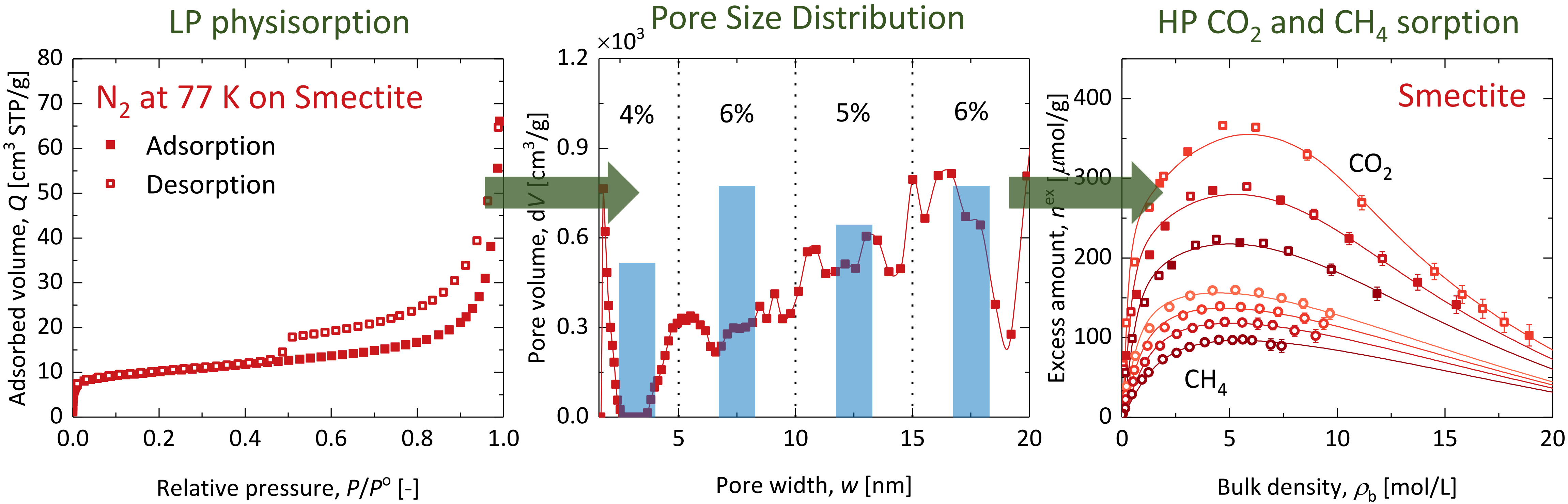
Pore volume PSD → Lattice DFT → HP sorption isotherms

Similar approach with molecular simulations[5-7]

[1] G. Aranovich and M. Donohue. *J. Chem. Phys.* 105 (1996) 7059-63
[2] P. Benard and R. Chahine. *Langmuir* 17 (2001) 1950-1955
[3] T. Hocker *et al*. *Langmuir* 19 (2003) 1254-1267
[4] S. Ottiger *et al*. *Langmuir* 24 (2008) 9531-9540
[5] L. Firlej *et al. J. Chem. Phys. C* 118 (2014) 955-961
[6] Y. Liu and J. Wilcox. *Int. J. Coal Geol.* 104 (2012) 83-95
[7] P. Kowalczyk *et al*. Langmuir 21 (2005) 5639-5646

Framework for supercritical CO_2 and CH_4 sorption

Investigation of supercritical adsorption of CO_2 and CH_4 on smectite[1]



- Quantachrome
- P: vac. to 760 mmHg

- Rubotherm MSB
- P: vac. to 25 MPa
- T: 25 – 115 °C

[1] J. Hwang *et al*. *Micropor. Mesopor. Mat.* 273 (2019) 107-121

CO_2 and CH_4 in clay nanopores

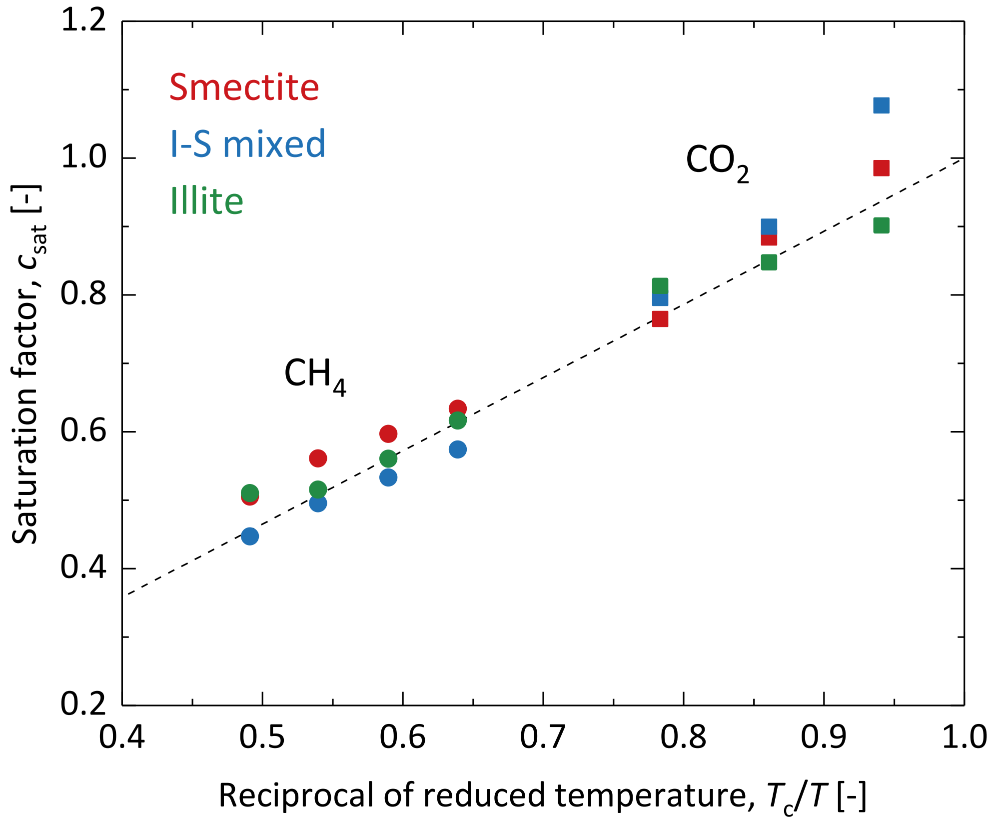
Maximum fluid density = liquid density?

Fluid	ρ_{max} [mol/L]	ρ_{GCMC}[1] [mol/L]	$\rho_{Smectite}$ [mol/L]	$\rho_{I\text{-}S\ mix}$ [mol/L]	ρ_{Illite} [mol/L]
CO_2	25.72	25.53	22.09	20.52	21.35
CH_4	26.45	17.42	15.26	15.26	15.09

Adsorbed phase density estimated from the first two layers at 150 bar and 60 °C

Clay nanopore saturation

- Pore space not completely saturated beyond T_c[2,3]
- Common correlation found for CO_2 and CH_4 for all clays with respect to T_c



[1] H. Zhao *et al*. *Fuel* 224 (2018) 412-423

[2] P. Benard and R. Chahine. *Langmuir* 12 (1997) 808-813

[3] D. Do. *Adsorption Analysis: Equilibria and Kinetics*; Imperial College Press 1998

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Concluding remarks and future work

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- Adsorption and desorption of CO_2 and CH_4 were measured on three illite-smectite clay minerals under subsurface conditions
- Sorption isotherms were described with the LDFT model with porous properties
  - Characterization via low-pressure N_2, Ar, and CO_2 adsorption isotherms
- Temperature dependent pore saturation found by the model
  - Common correlation found for all clays and for both fluids
- Binary mixture adsorption is planned to obtain the experimental evidence of CO_2 to CH_4 selectivity
- J. Hwang and R. Pini. *Environ. Sci. Technol.* 2019. DOI: 10.1021/acs.est.9b03638

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S4CE Science4CleanEnergy