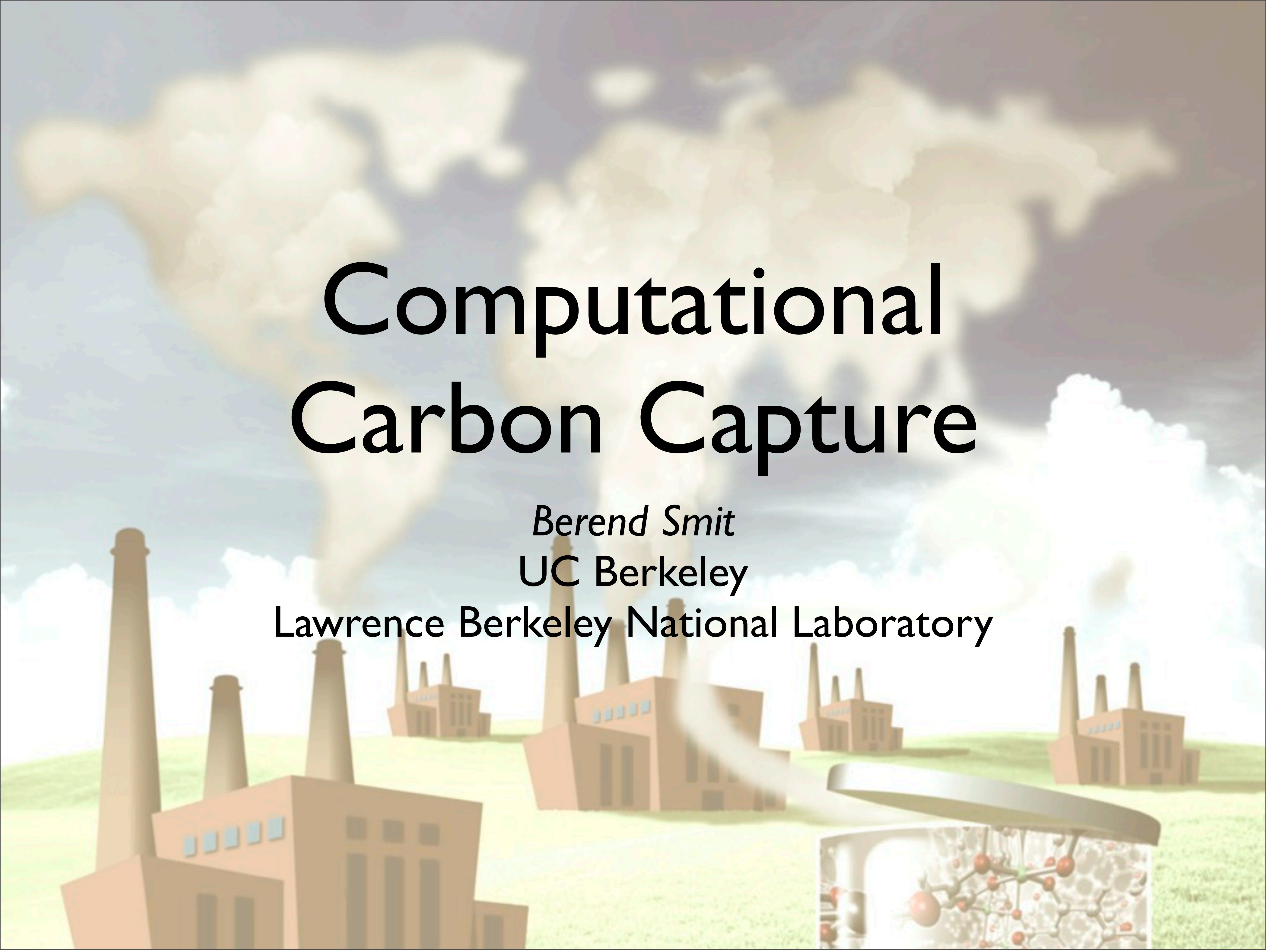
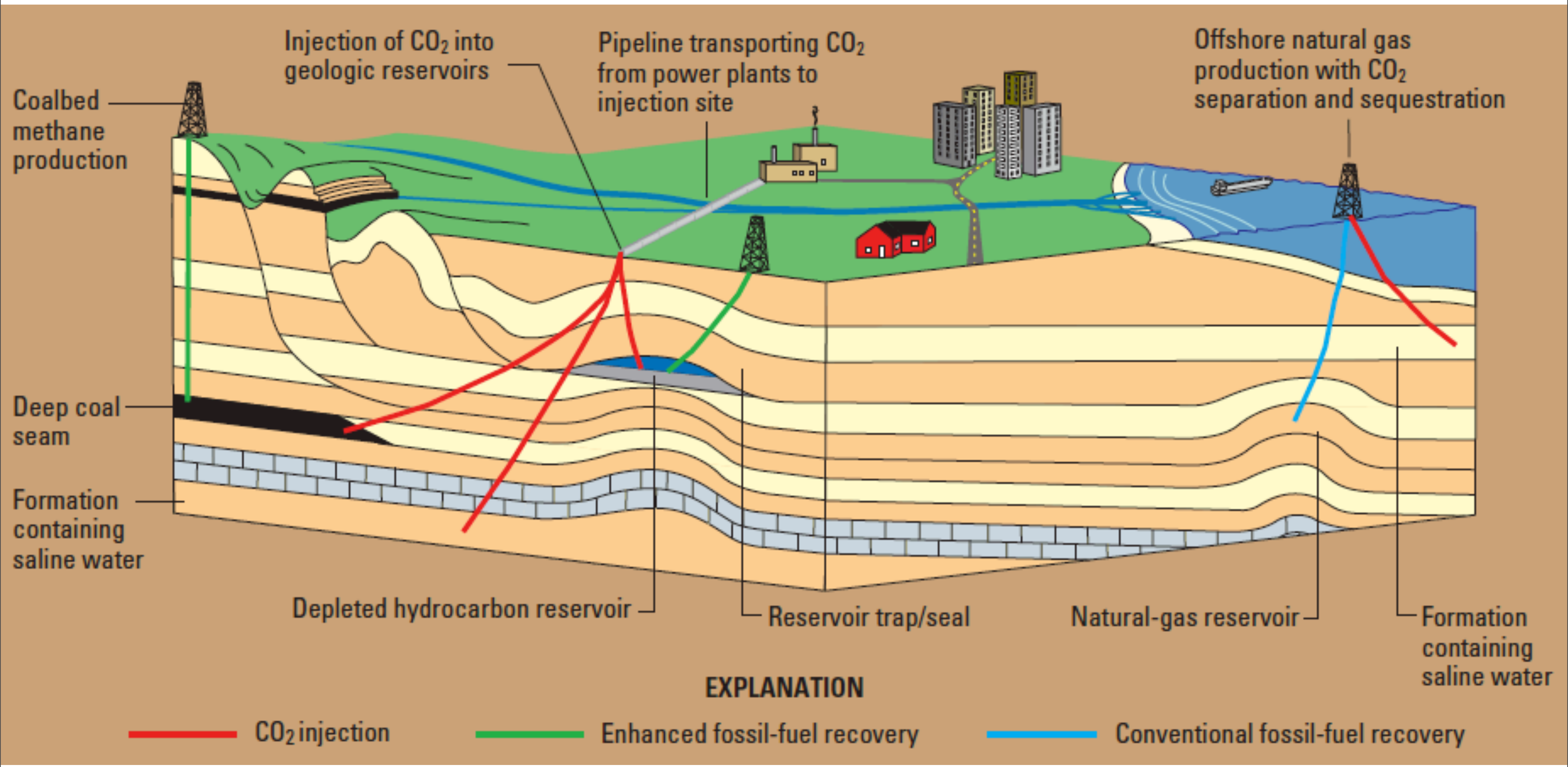
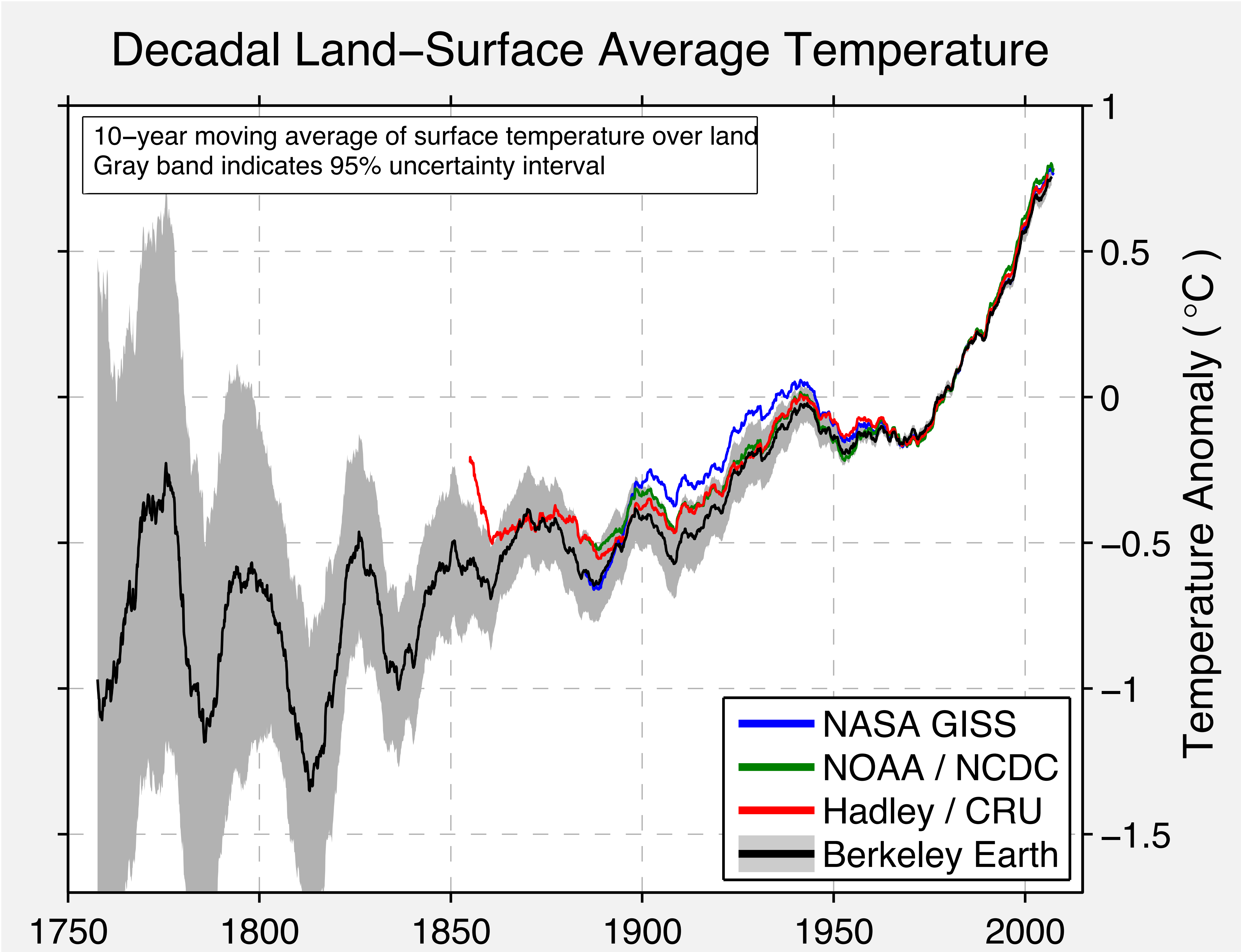


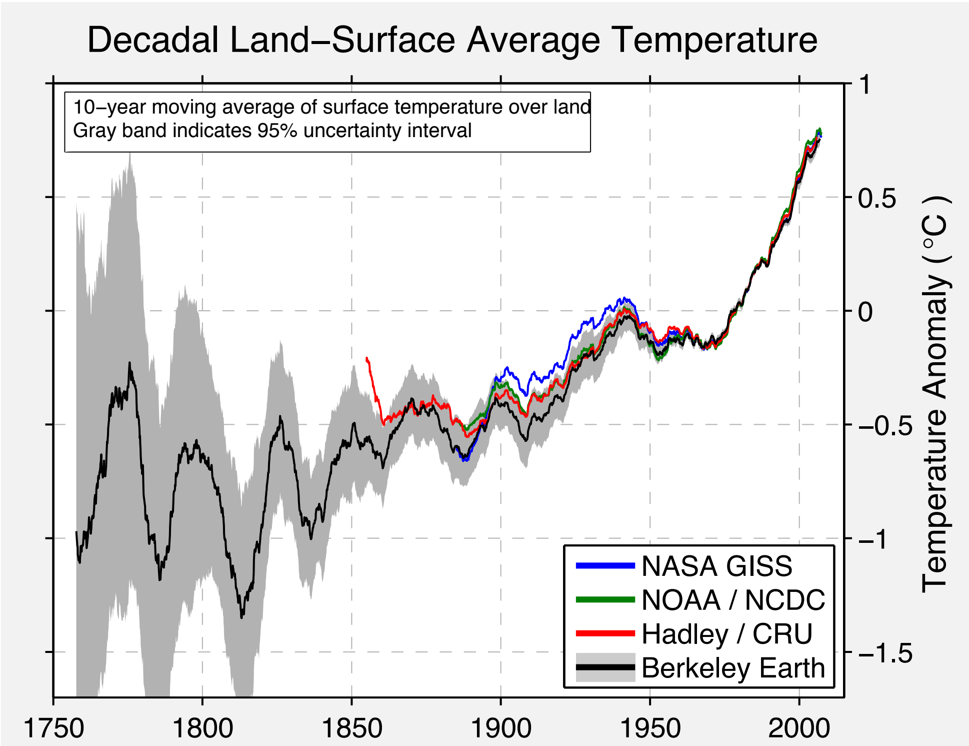
Computational Carbon Capture

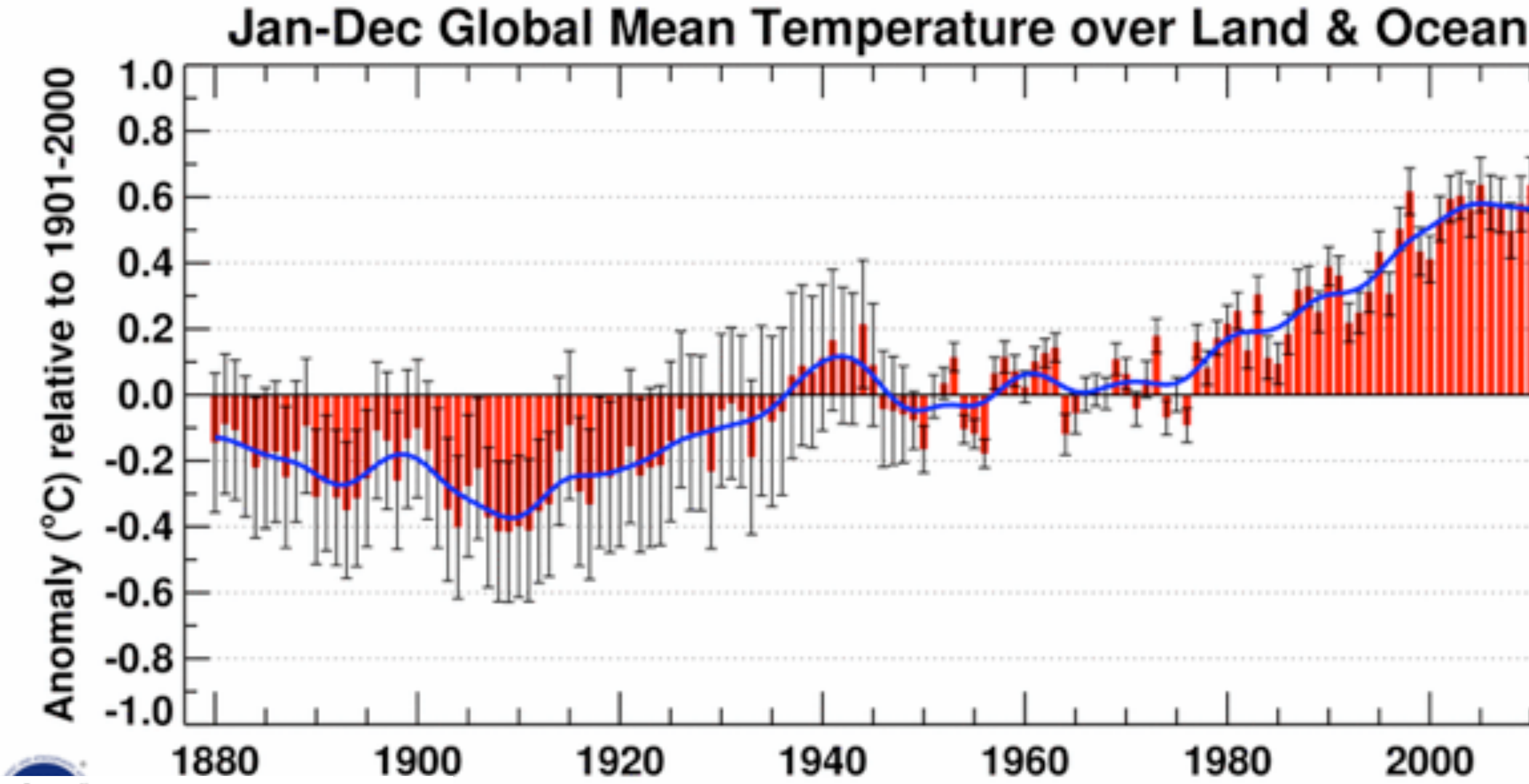
Berend Smit
UC Berkeley
Lawrence Berkeley National Laboratory

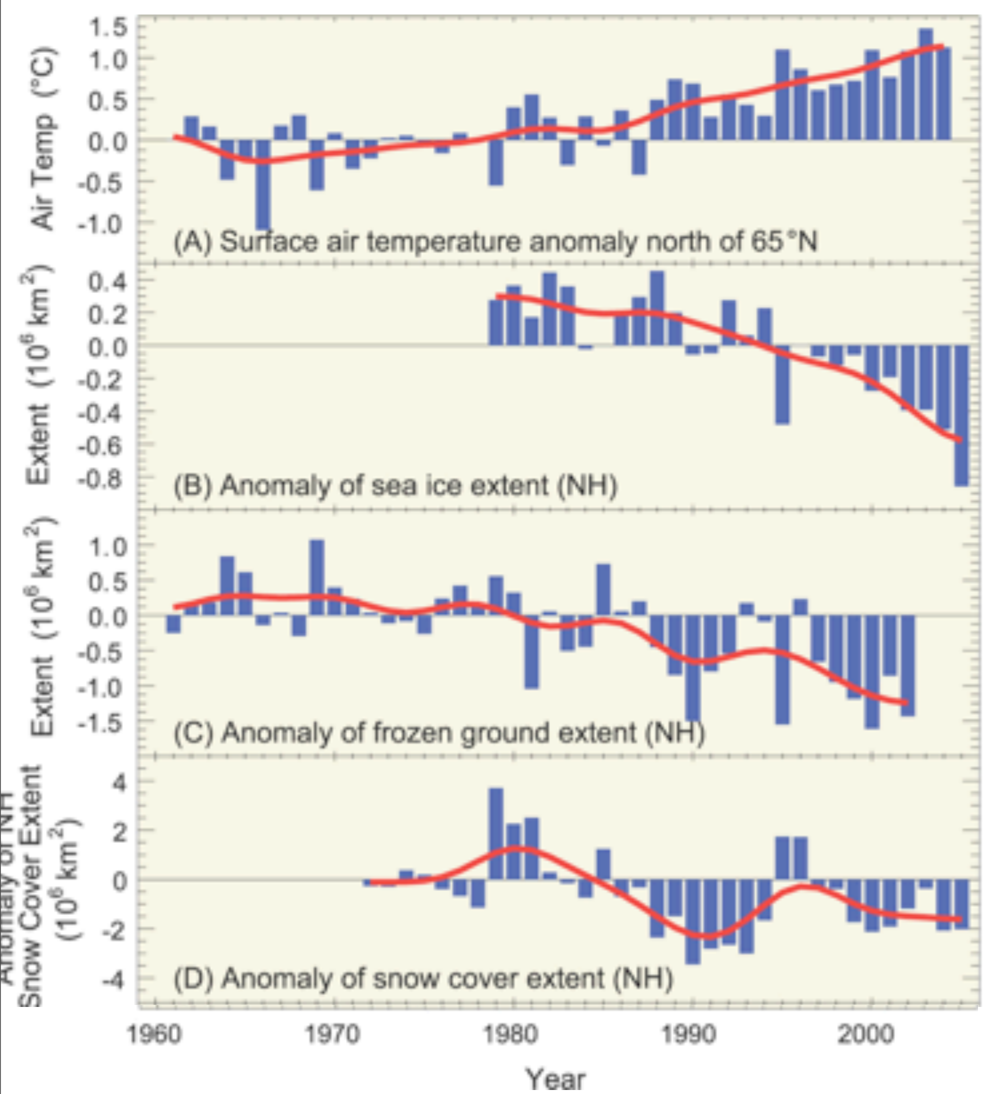
Carbon Capture and Sequestration

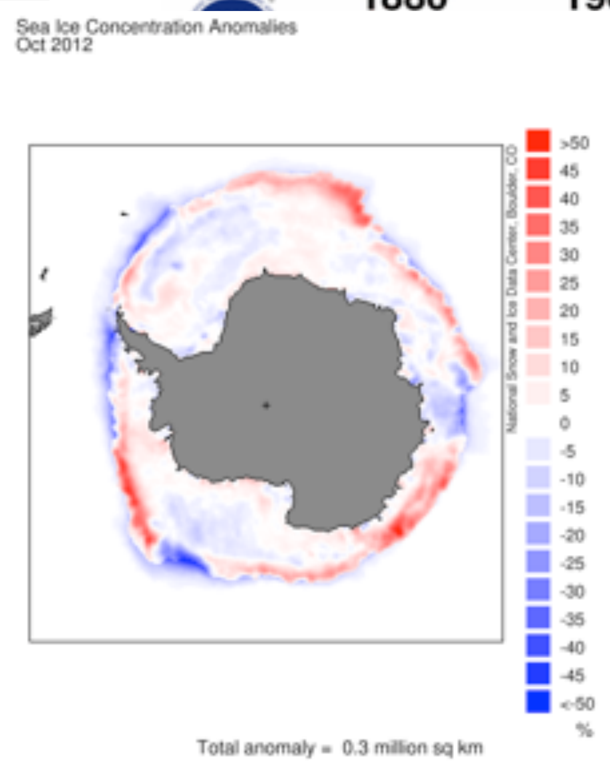


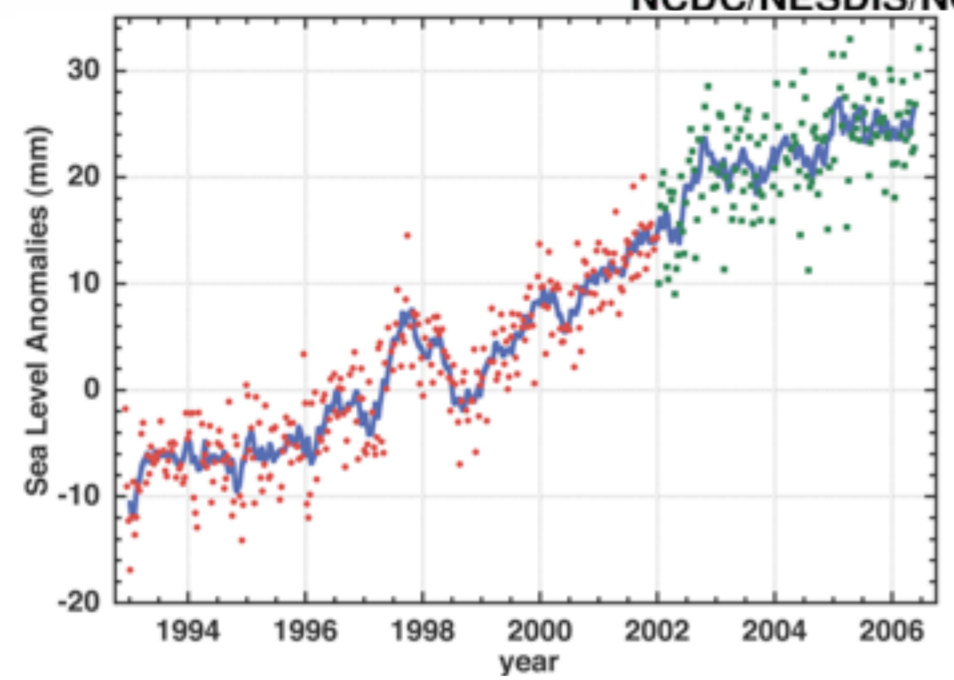

Decadal Land–Surface Average Temperature
10–year moving average of surface temperature over land
Gray band indicates 95% uncertainty interval
NASA GISS
NOAA / NCDC
Hadley / CRU
Berkeley Earth
Temperature Anomaly (°C)
1
0.5
0
−0.5
−1
−1.5
1750
1800
1850
1900
1950
2000


Decadal Land−Surface Average Temperature
10−year moving average of surface temperature over land
Gray band indicates 95% uncertainty interval
Temperature Anomaly (°C)
NASA GISS
NOAA / NCDC
Hadley / CRU
Berkeley Earth
1750
1800
1850
1900
1950
2000
1
0.5
0
−0.5
−1
−1.5


Jan-Dec Global Mean Temperature over Land & Ocean
Anomaly (°C) relative to 1901-2000
NCDC/NESDIS/NOAA
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
1880
1900
1920
1940
1960
1980
2000

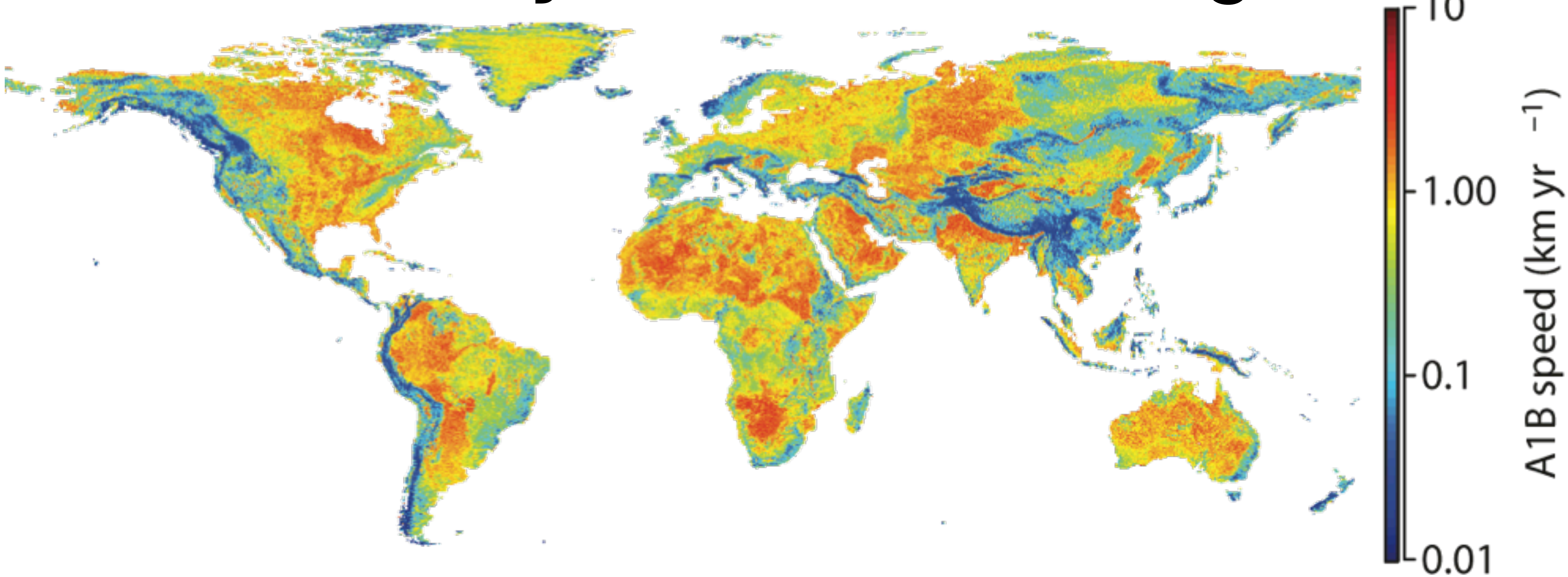

Air Temp (°C)
(A) Surface air temperature anomaly north of 65°N
Extent (10^6 km^2)
(B) Anomaly of sea ice extent (NH)
Extent (10^6 km^2)
(C) Anomaly of frozen ground extent (NH)
Anomaly of NH Snow Cover Extent (10^6 km^2)
(D) Anomaly of snow cover extent (NH)
1960
1970
1980
1990
2000
Year


Sea Ice Concentration Anomalies
Oct 2012
>50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
<-50
%
Total anomaly = 0.3 million sq km


Sea Level Anomalies (mm)
30
20
10
0
-10
-20
1994
1996
1998
2000
2002
2004
2006
year


2004

Consequences: velocity of climate change



- Historic rates: fastest 1 km/yr
- 28% of the surface > 1 km/yr

Figure 2.5.11 The velocity of climate change
Figure by Loarie et al. (2009)

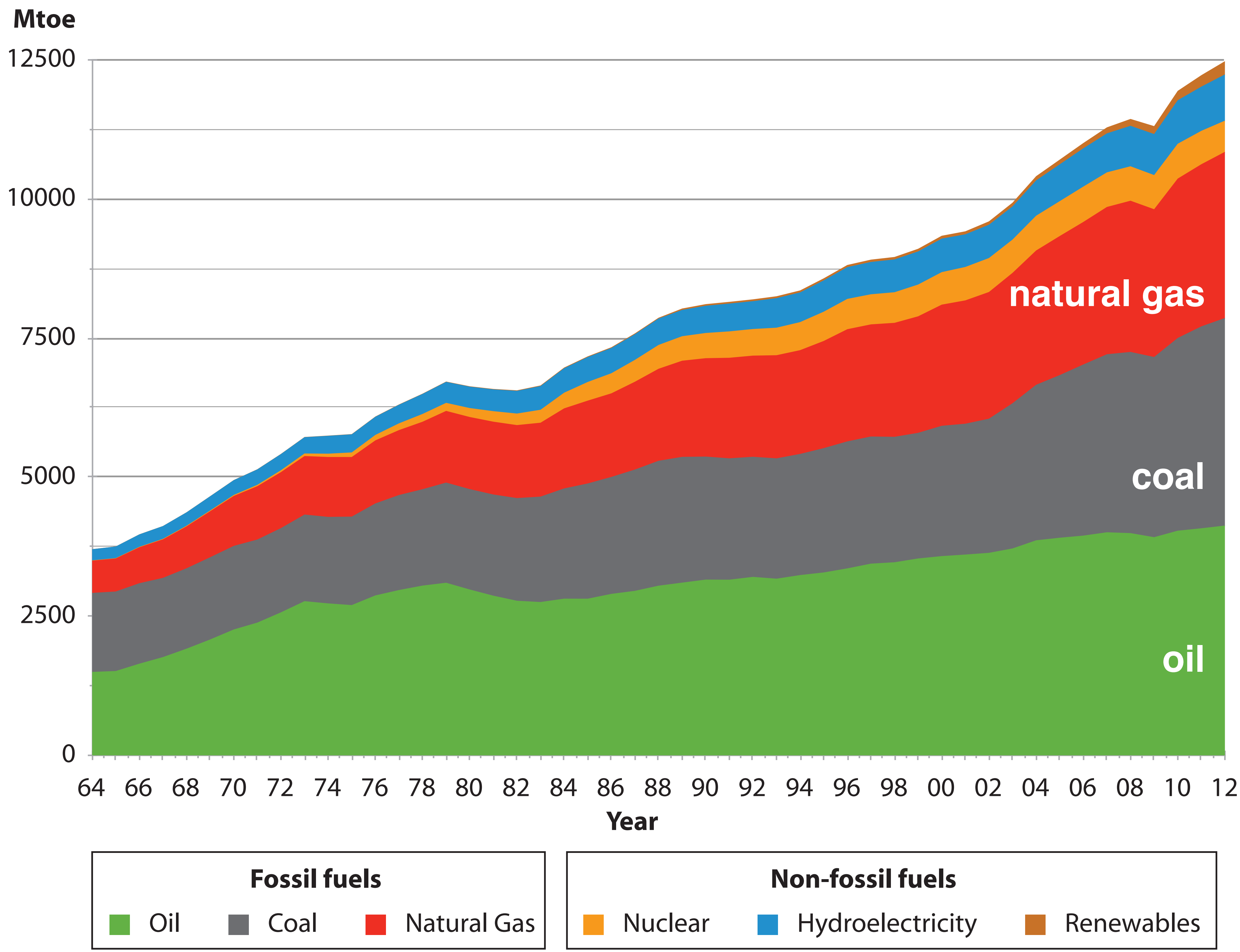
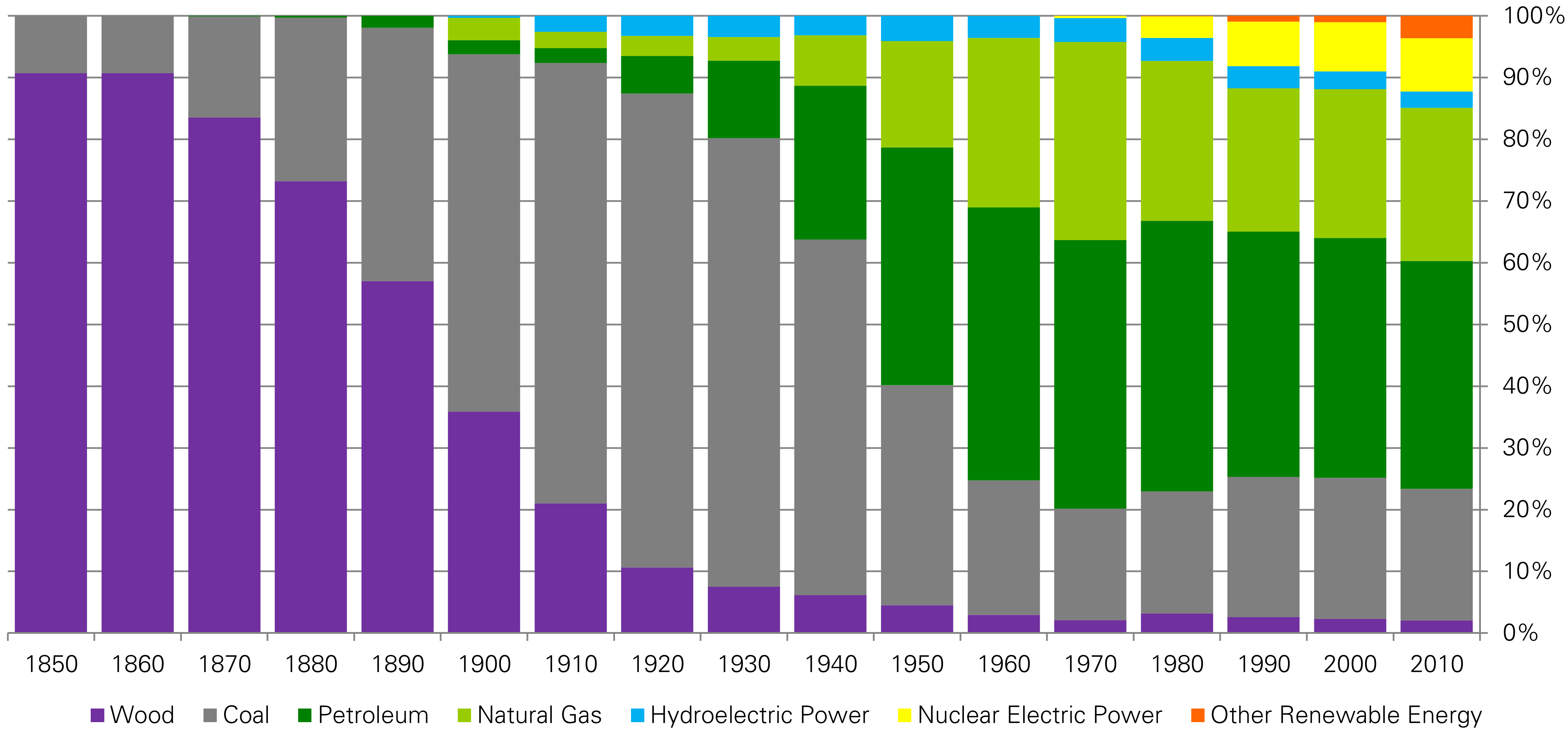


Figure 1.2.1 World energy consumption

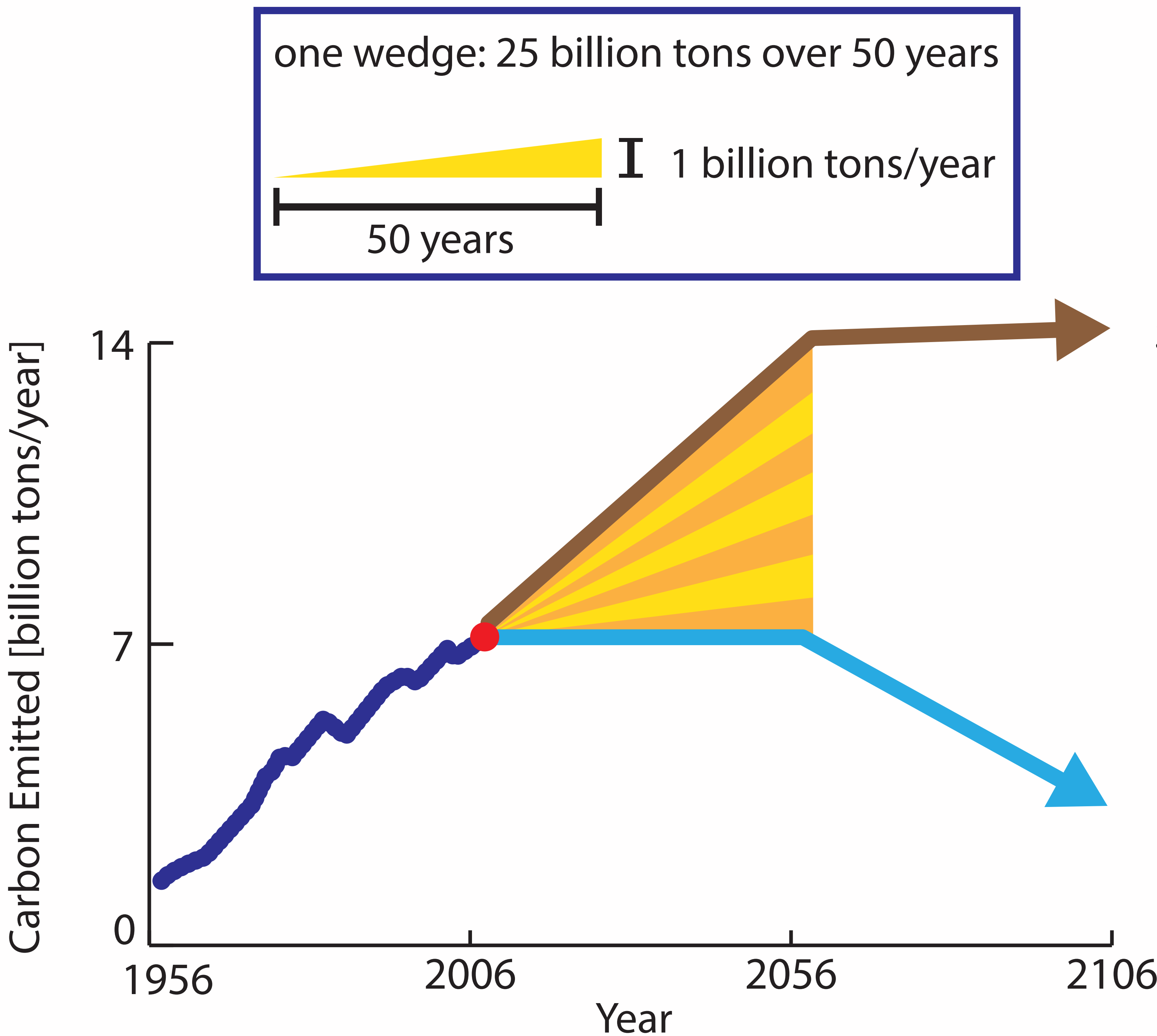
U.S. Primary Energy Consumption Estimates by Source, 1850-2010



3

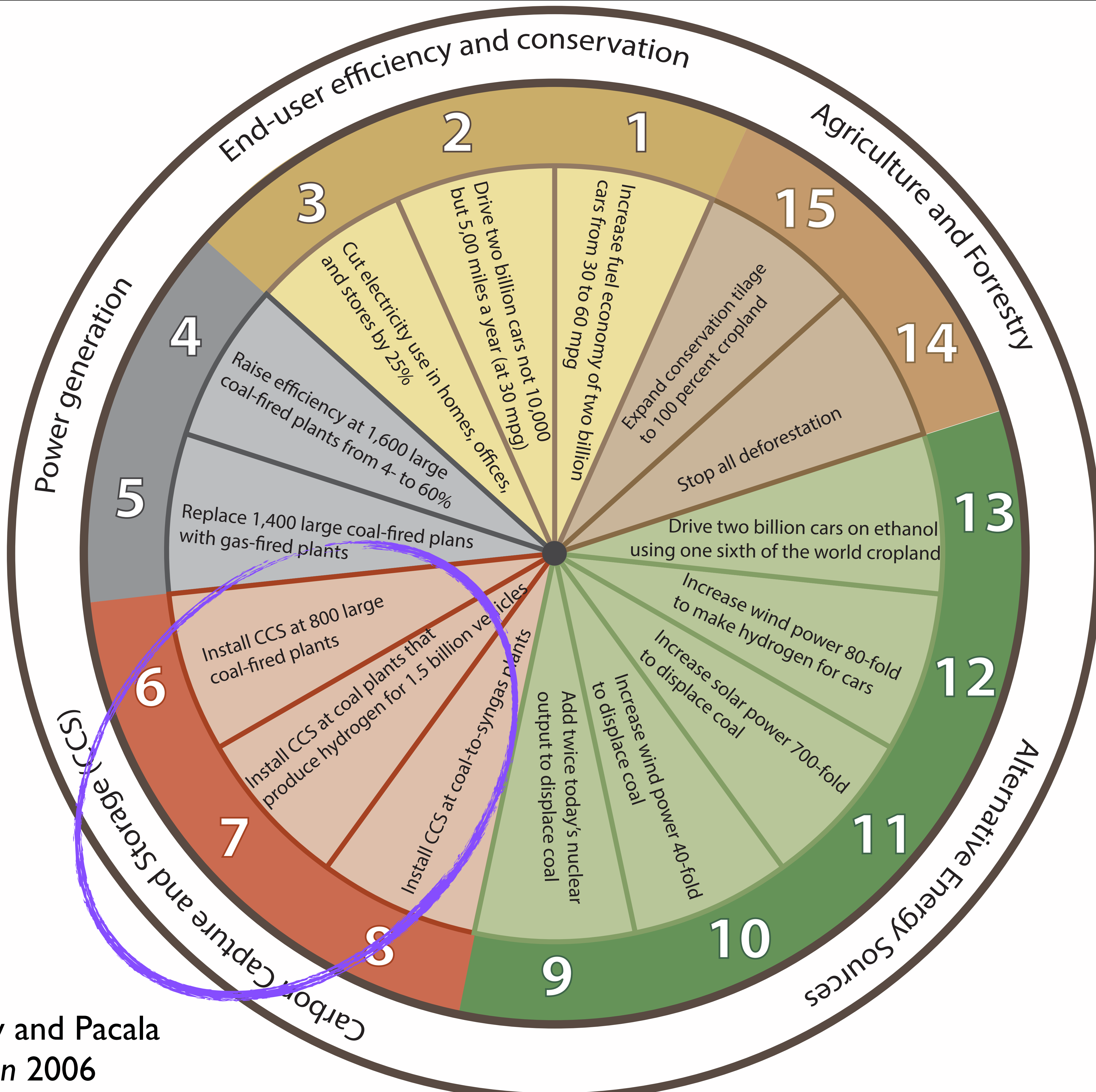
Source: U.S. Energy Information Administration Annual Energy Review, Tables 1.3, 10.1, and E1

“plan B”?



Solving the climate problem
for the next 50 years
with **current** technologies

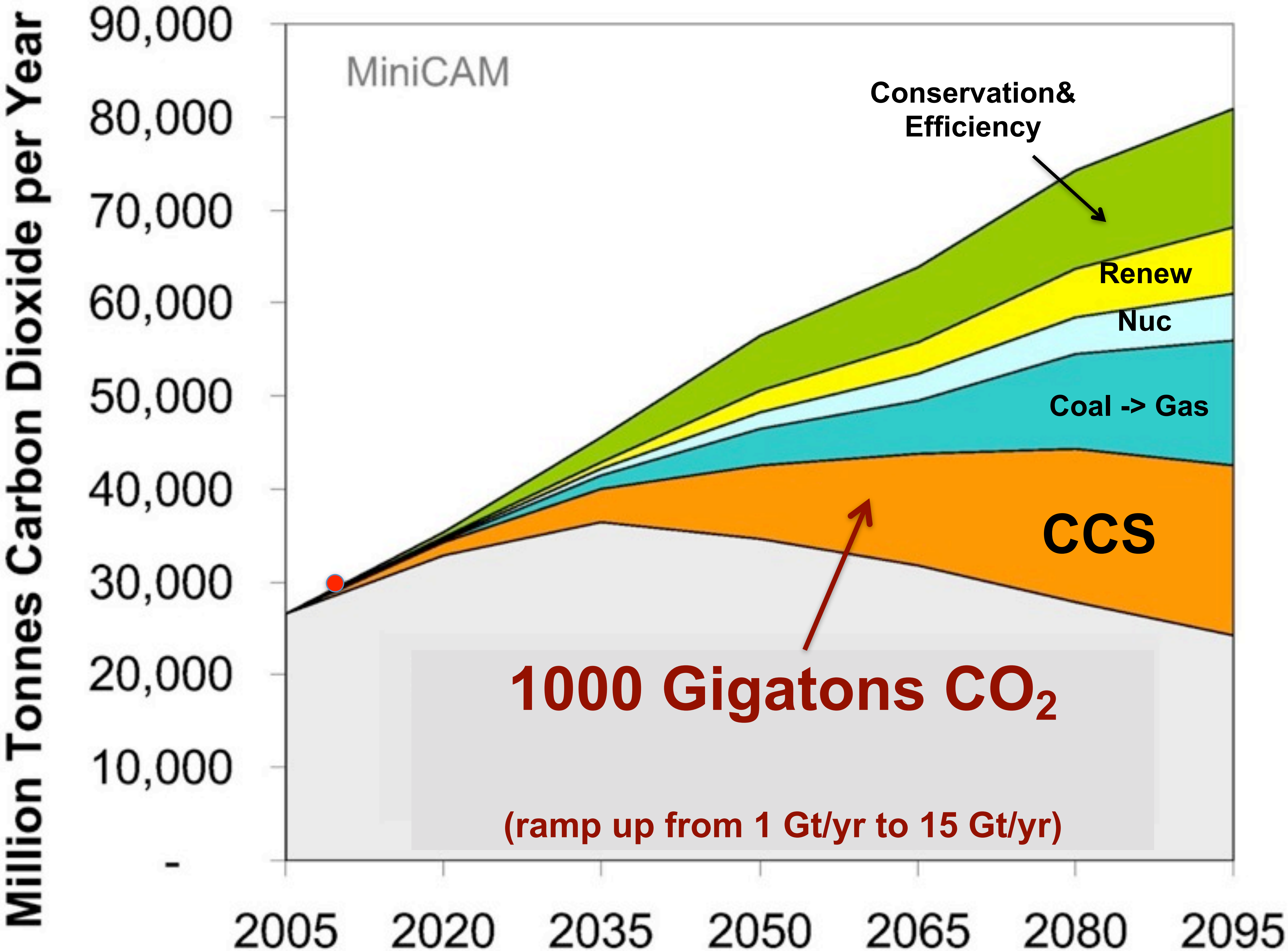
S. Pacala and R. Socolow,
*Stabilization wedges: Solving the climate problem for the next 50 years with **current** technologies*
Science **305** (5686), 968 (2004)



Source: Socolow and Pacala

Scientific American 2006

Different wedges



What to do with a GIGATON of CO_2?

Let's convert CO_2 into "Dreamium™"

(in Berkeley we recycle everything!)

www.TwentyThousandMinusThreeAppsOfDreamium.com

Abhoyjit S. Bhown (EPRI):

		Estimated USA production			Estimated global production		
		Mt	Gmol	GWe-yr at 90% capture	Mt	Gmol	GWe-yr at 90% capture
1	Sulfuric acid	38.7	394	2.1	199.9	1879	10.0
2	Nitrogen	32.5	1159	6.2	139.6	4595	24.5
3	Ethylene	25.0	781	4.2	112.6	3243	17.3
4	Oxygen	23.3	829	4.4	100.0	3287	17.5
5	Lime	19.4	347	1.8	283.0	4653	24.8
6	Polyethylene	17.0	530	2.8	60.0	1729	9.2
7	Propylene	15.3	354	1.9	53.0	1134	6.0
8	Ammonia	13.9	818	4.4	153.9	8332	44.3
9	Chlorine	12.0	169	0.9	61.2	795	4.2
10	Phosphoric acid	11.4	116	0.6	22.0	207	1.1
...	...						
50	Nylon	1.9	8	0.0	2.3	8	0.0
	Total	**419**	**8,681**	**46**	**2,412**	**48,385**	**257**
2009 coal-fired generation GWe-yr				**200**			**>1000**
Approximate CO_2 emissions		**6,000**	**136,000**		**31,000**	**750,000**	

Table 1.3.1 Comparison of CO_2 production and the production of chemicals

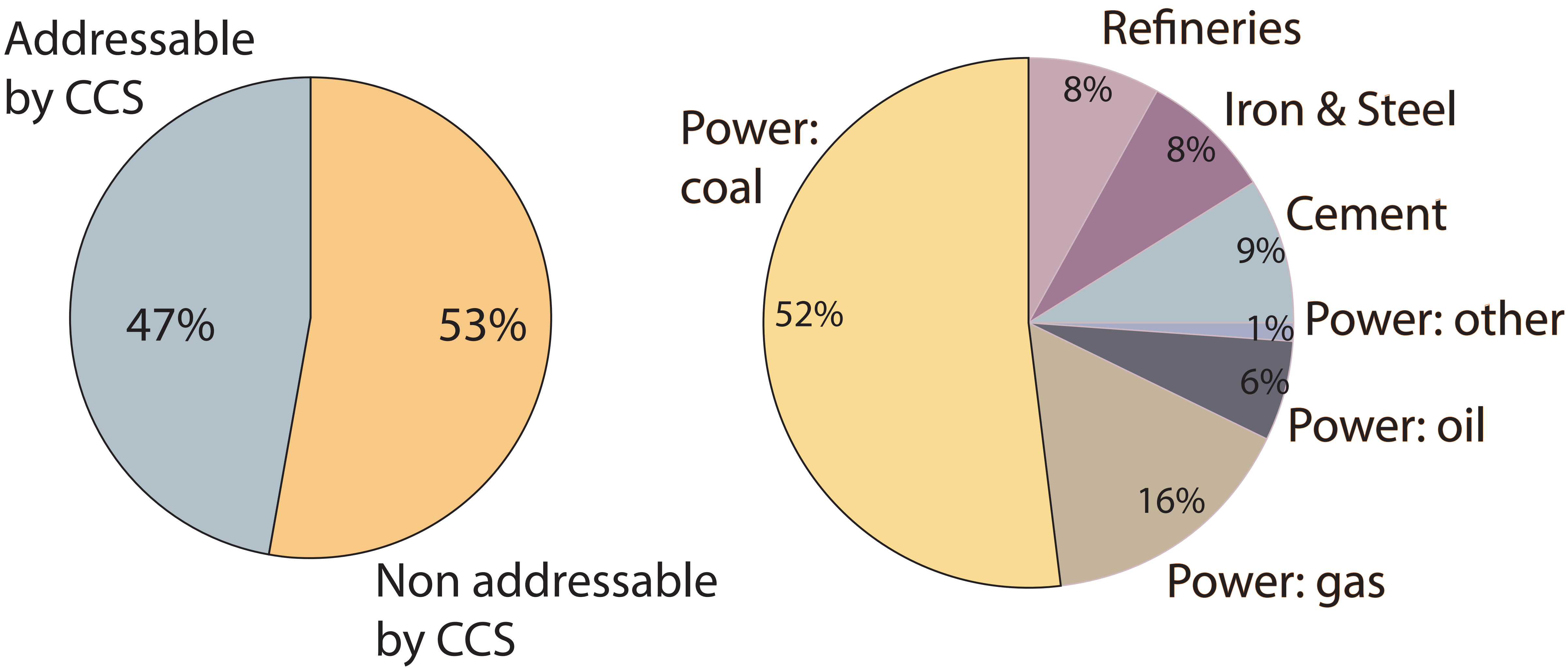
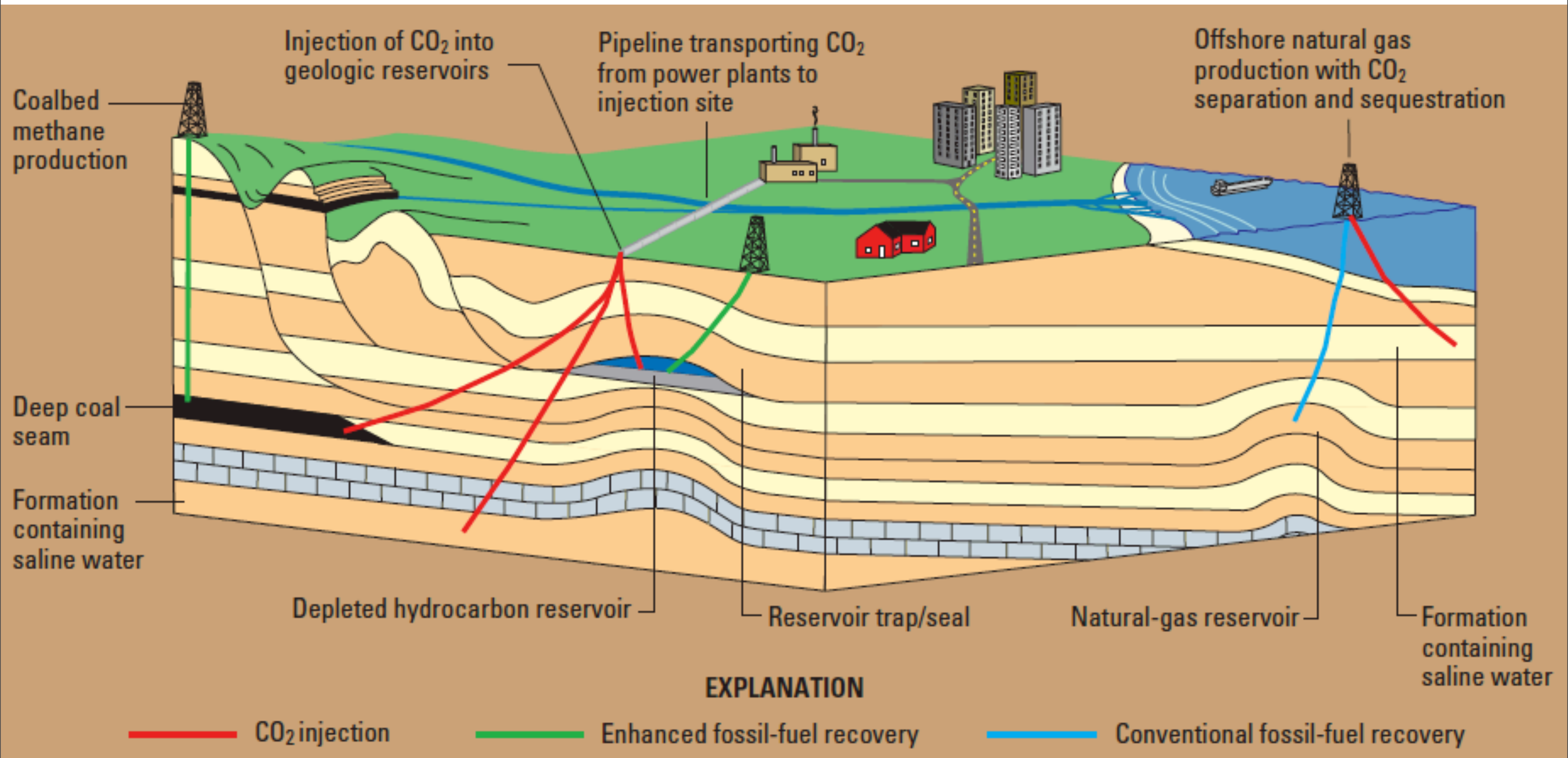


Figure 1.2.8 Distribution of (European) CO_2 emissions from different sources. *Redrawn from EEA GHG Emission Trends and Projects 2007 and IEA World Energy Outlook 2007*

Carbon Capture and Sequestration



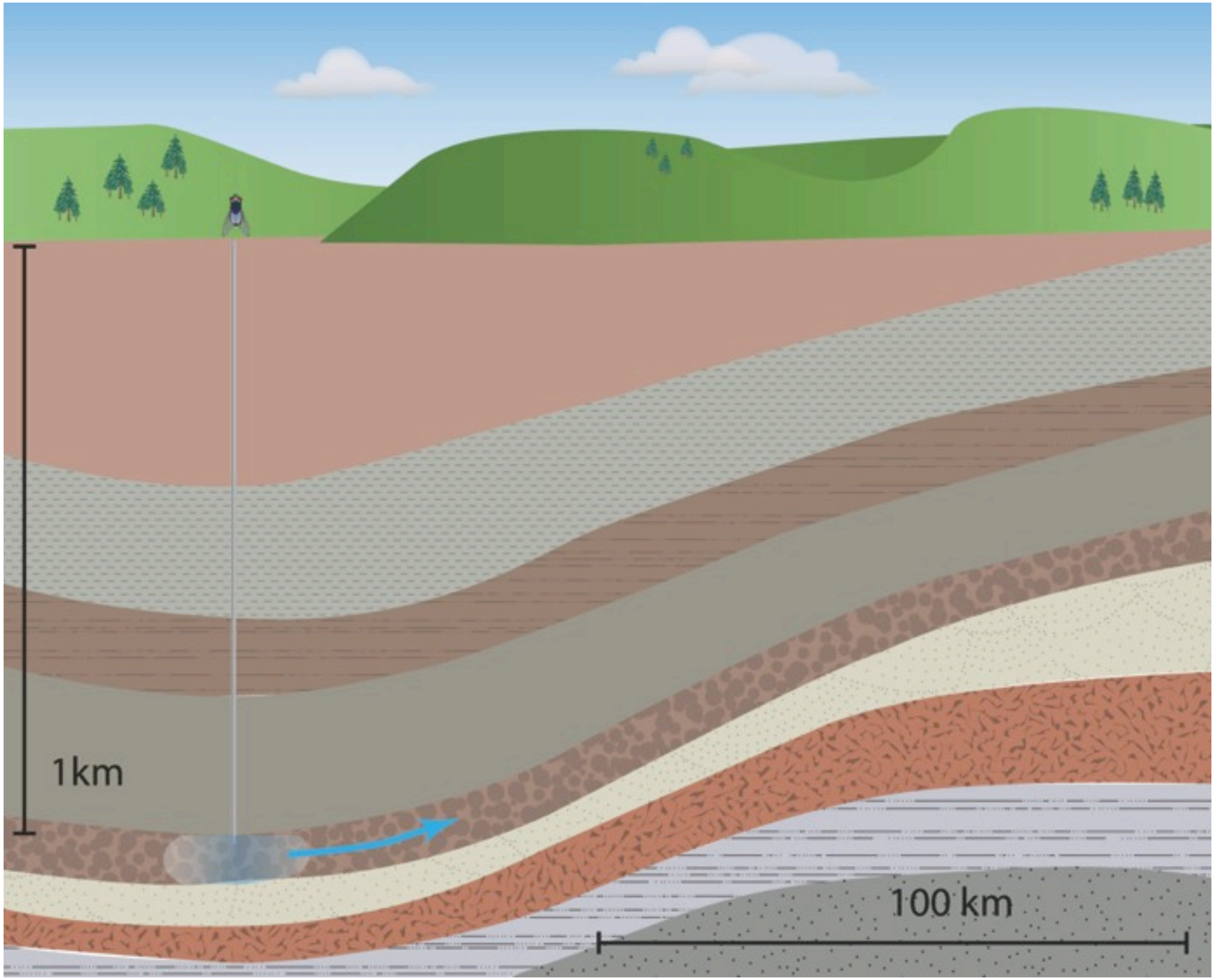


Figure 8.2.1 Injecting CO_2 below a caprock formation
(Figure based on information provided by CO2CRC)

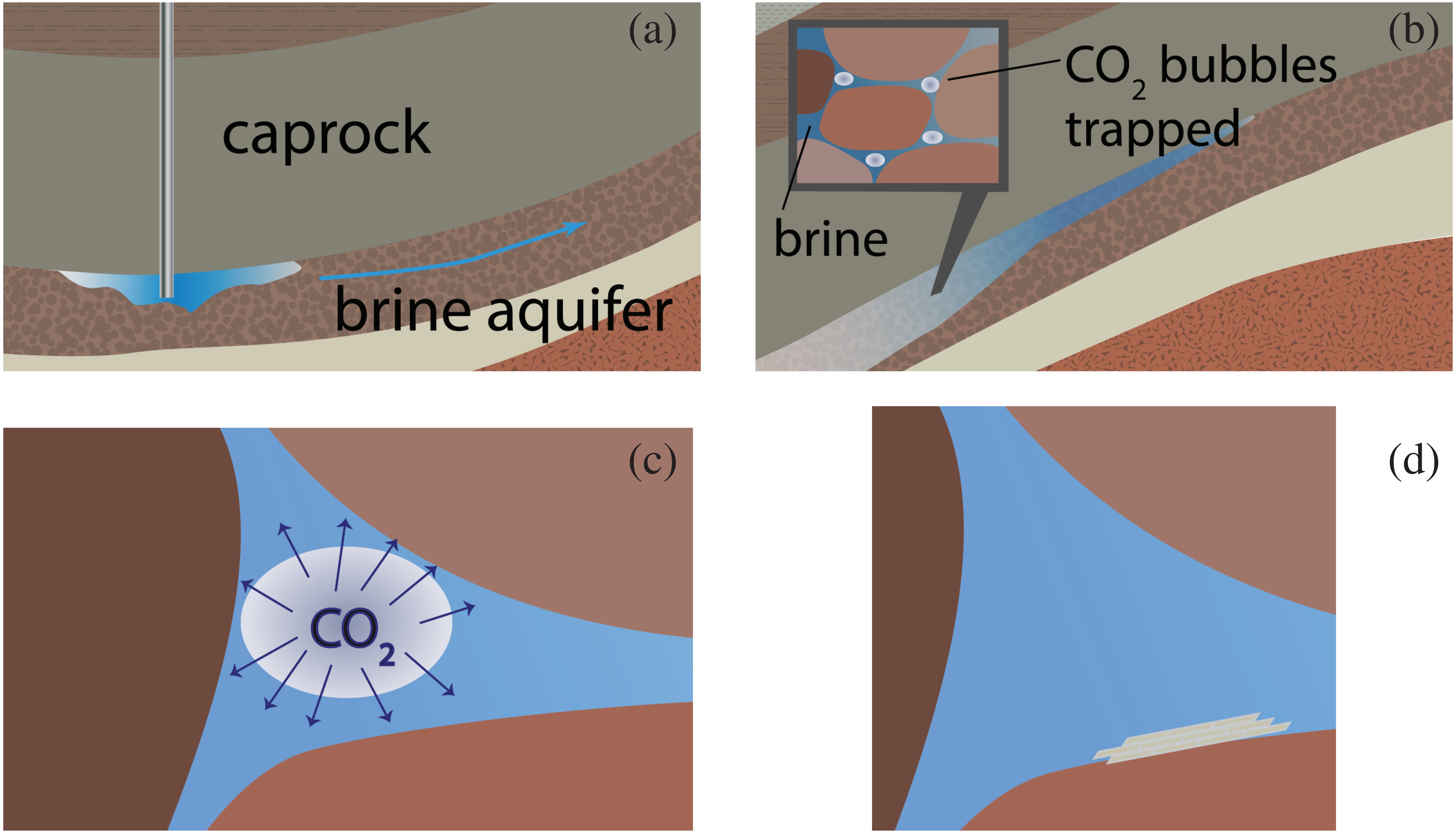


Figure 8.2.2 Mechanisms of CO_2 trapping

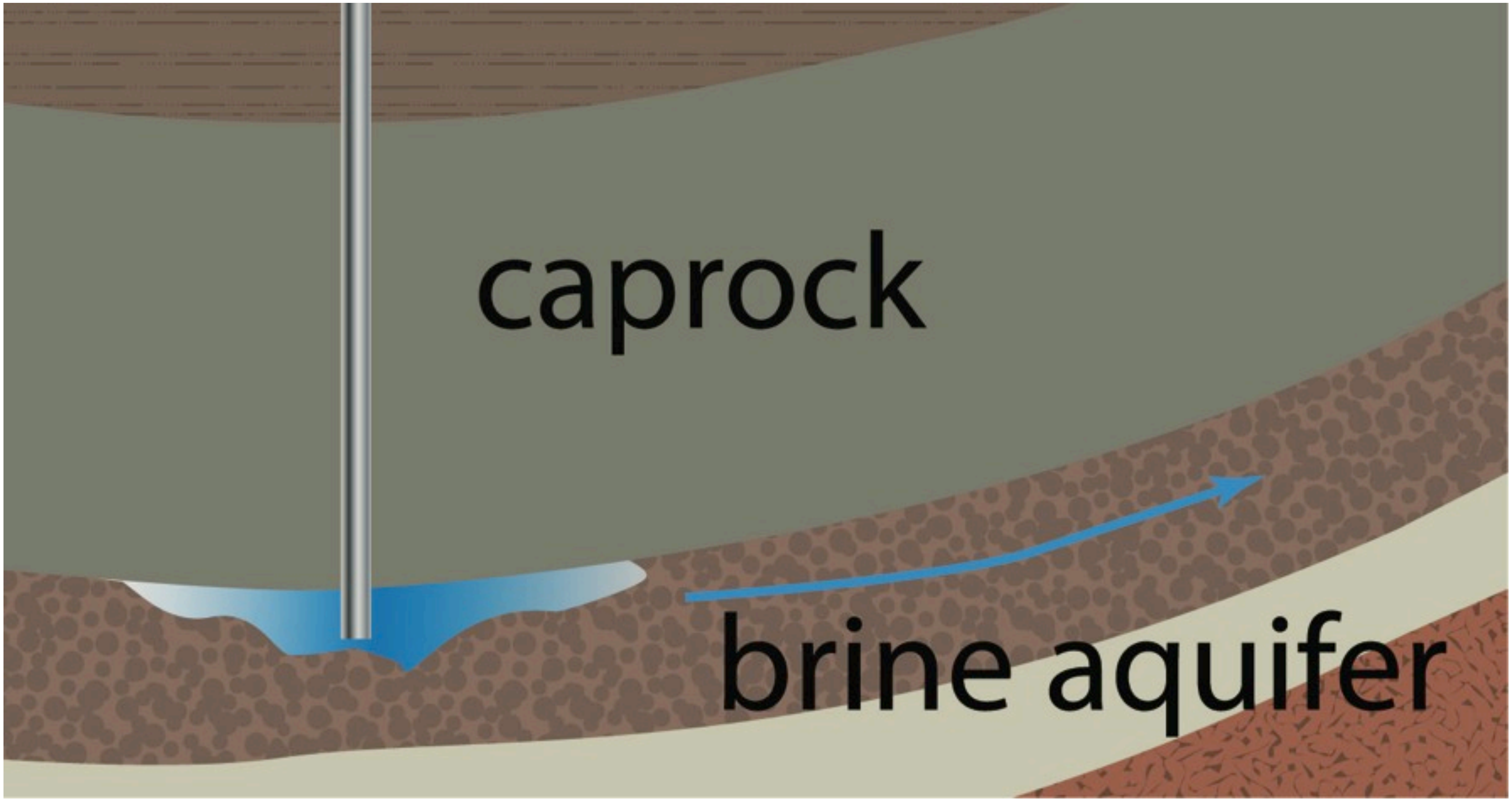


Figure 8.2.2 Mechanisms of CO_2 trapping
(a) Stratigraphic trapping

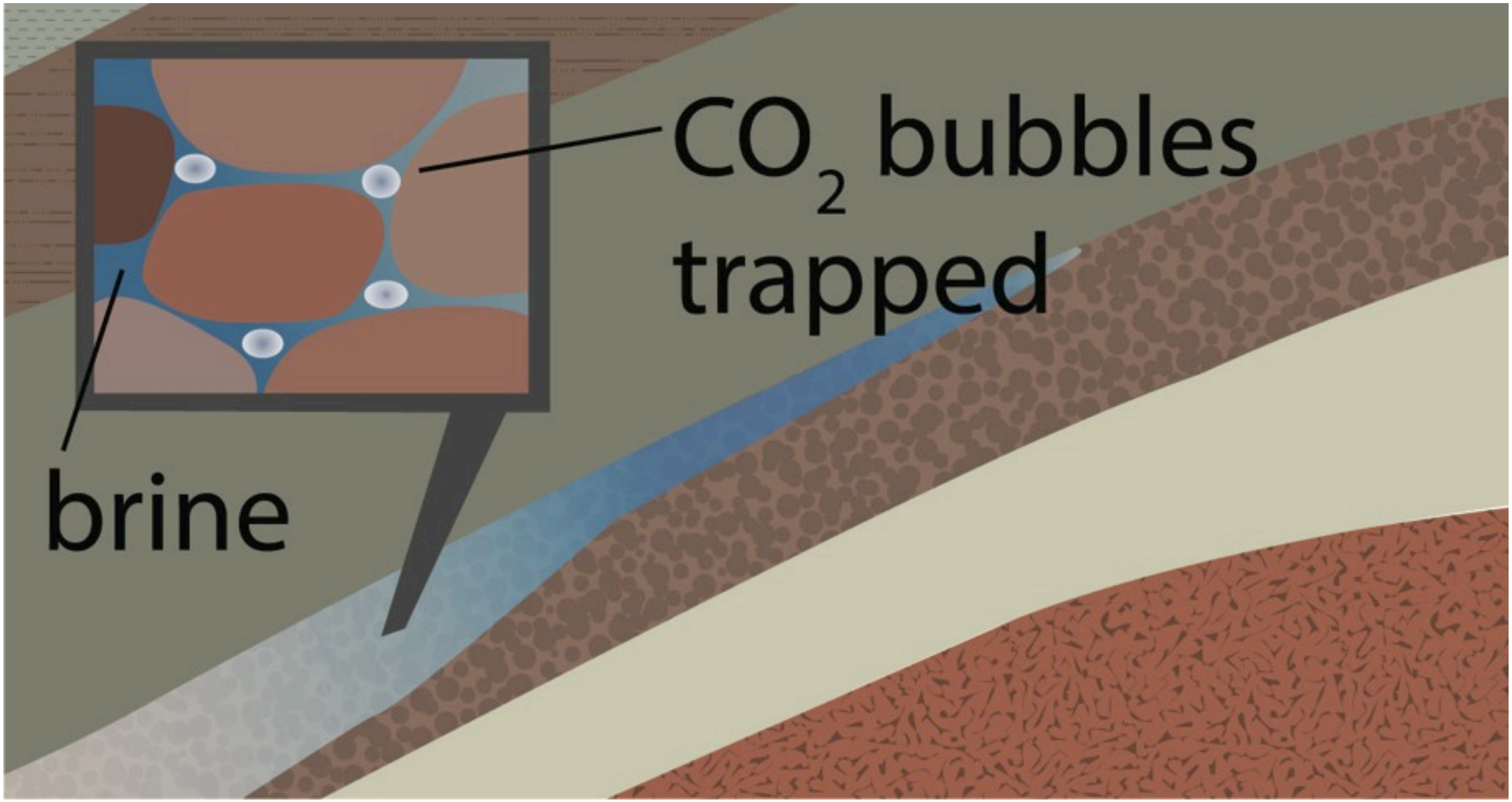


Figure 8.2.2 Mechanisms of CO_2 trapping
(b) Residual trapping

Movie 8.2.1 CO_2 residual trapping simulation
Movie from the CRC for Greenhouse Gas Technologies (CO2CRC)

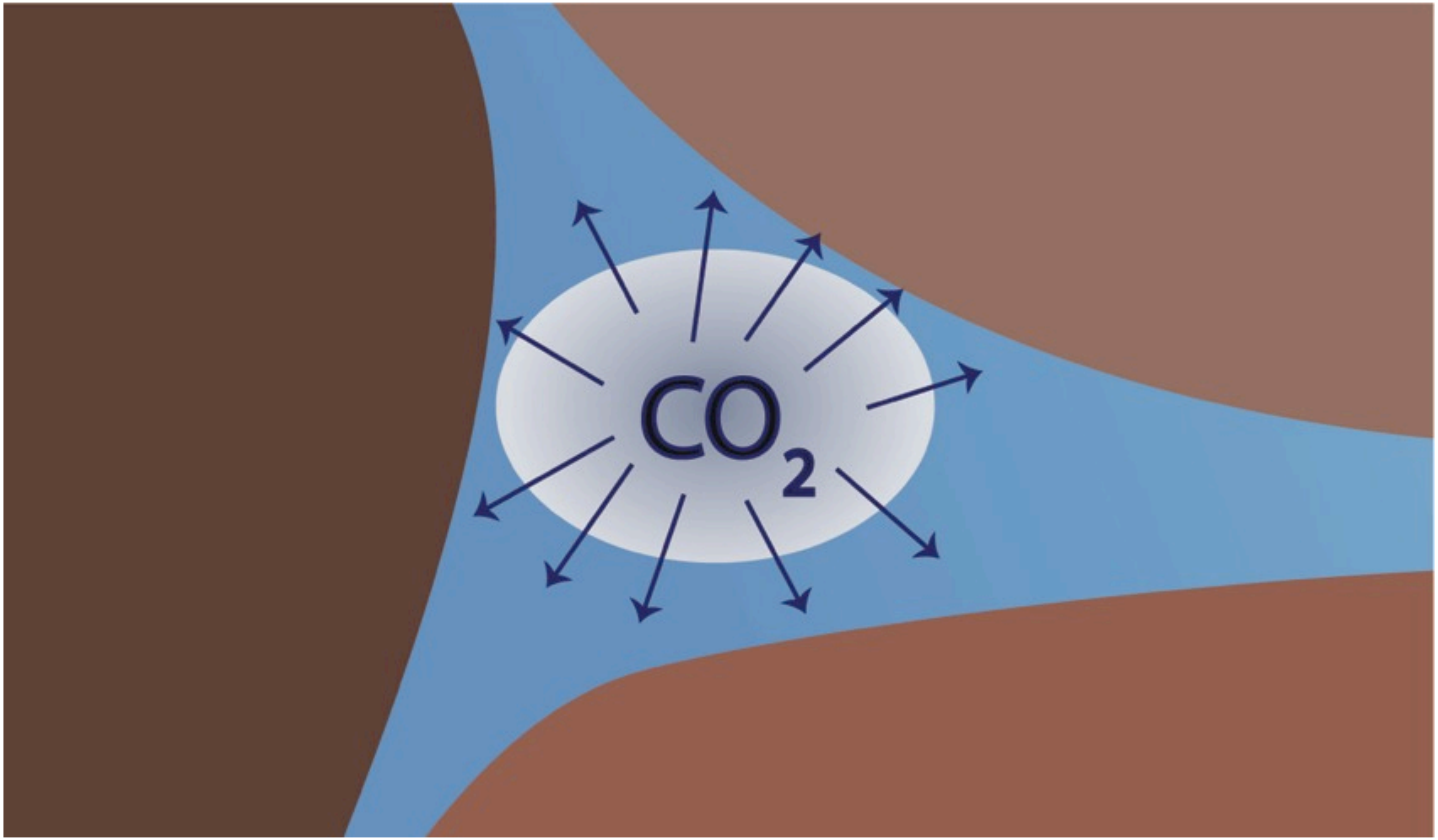


Figure 8.2.2 Mechanisms of CO_2 trapping
(c) Solubility trapping

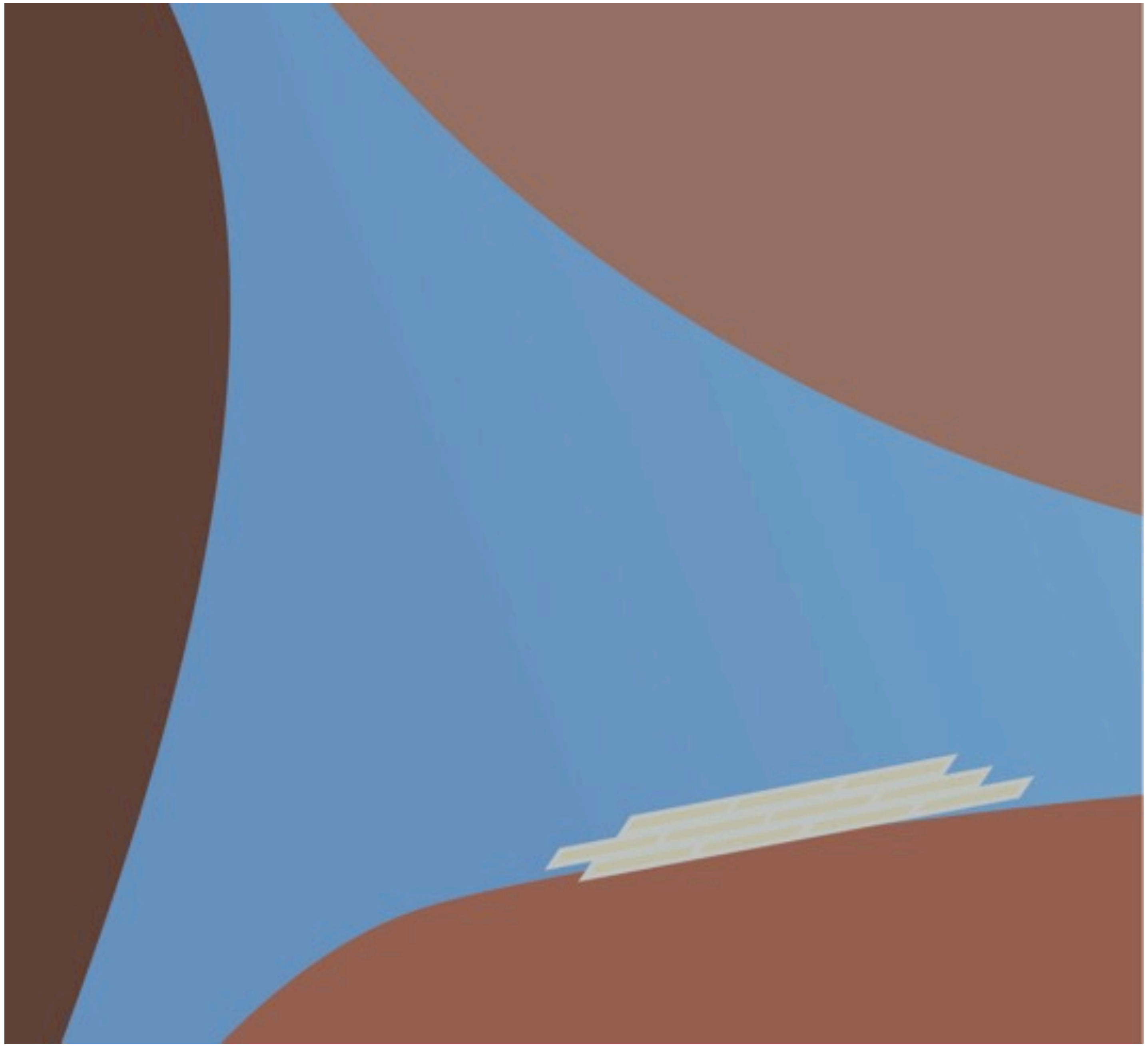


Figure 8.2.2 Mechanisms of CO_2 trapping
(d) Mineral trapping

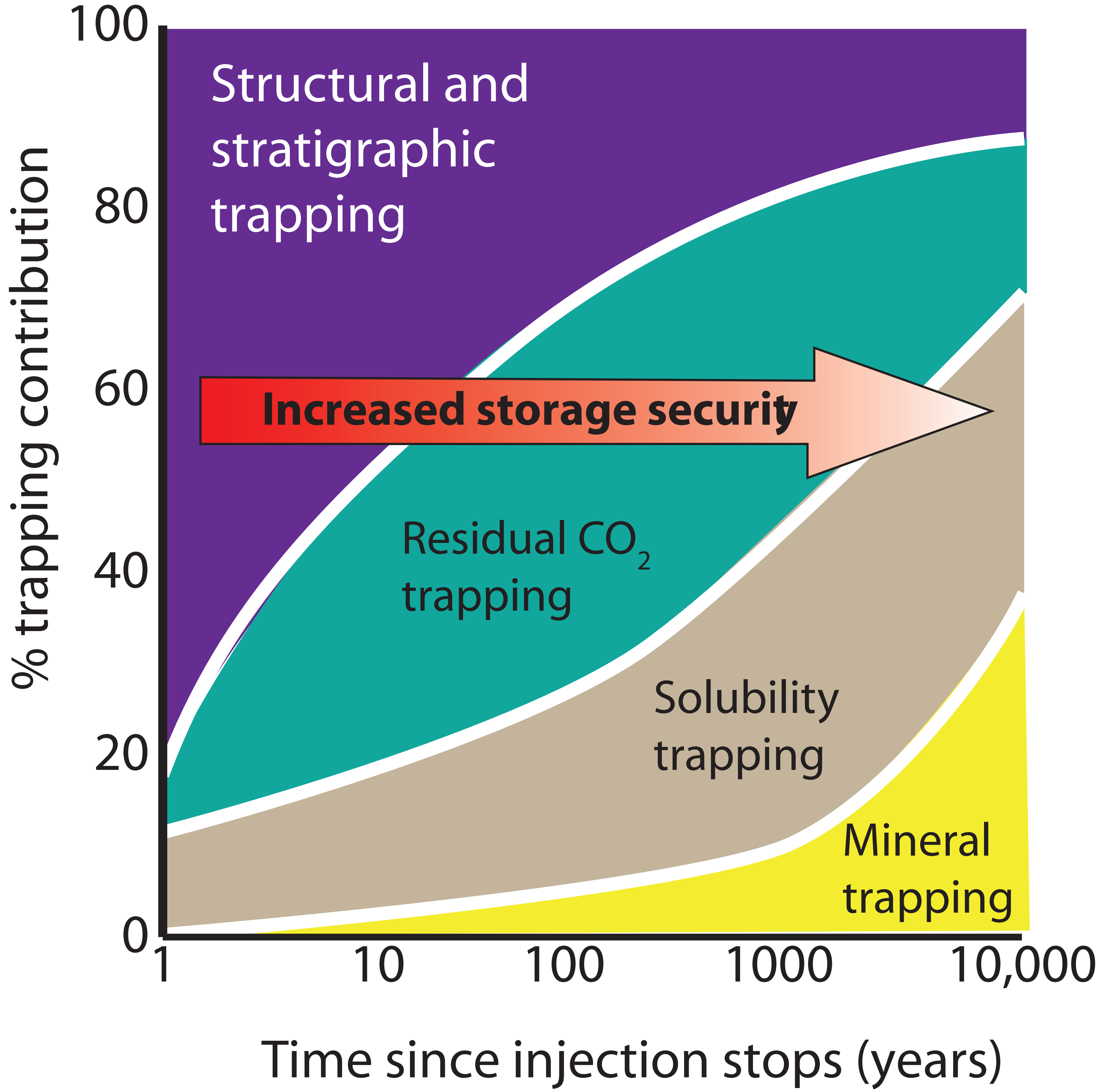


Figure 8.2.3 Trapping mechanisms as a function of time *(Figure adapted from Benson and Cole)*

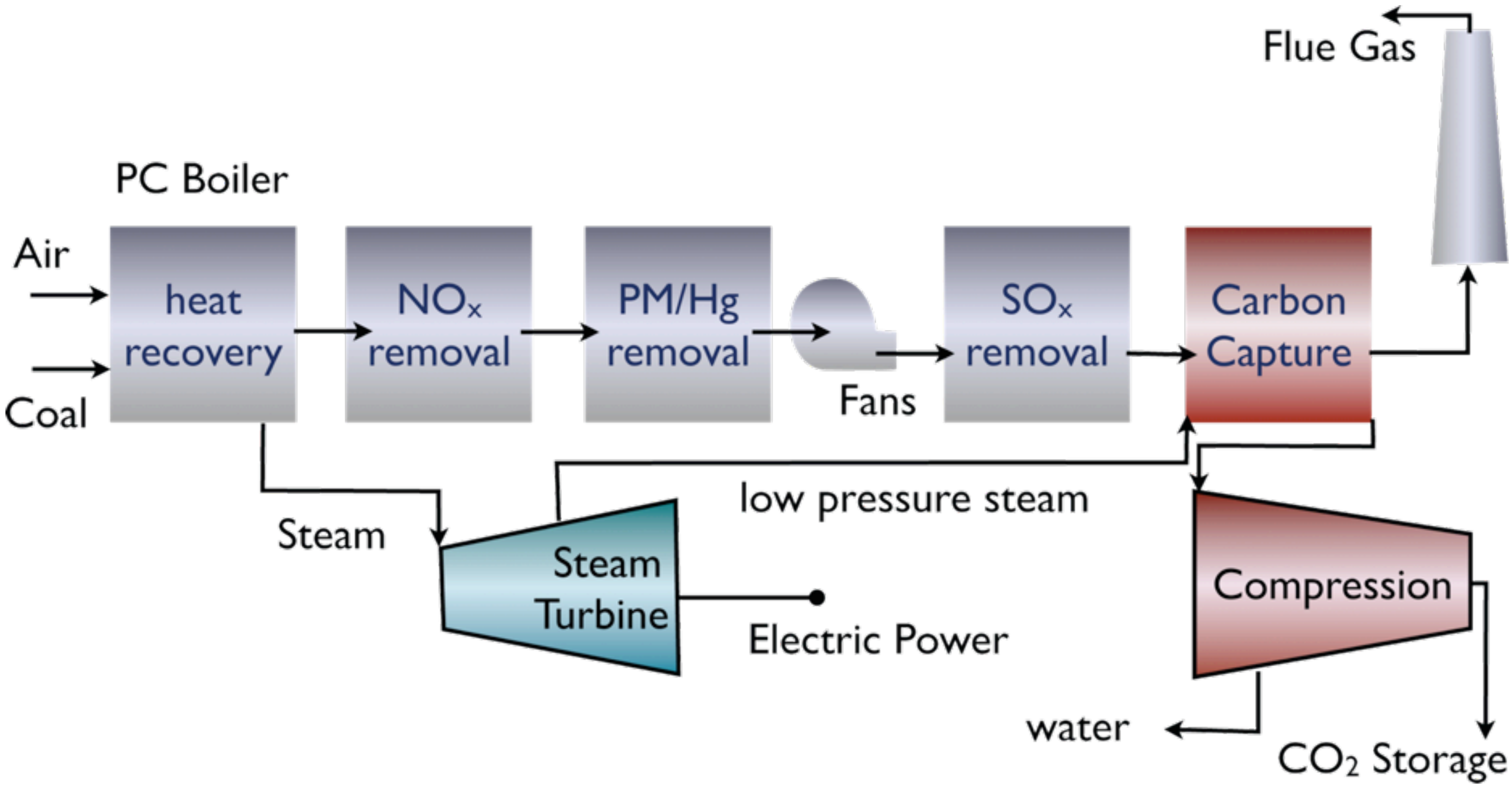
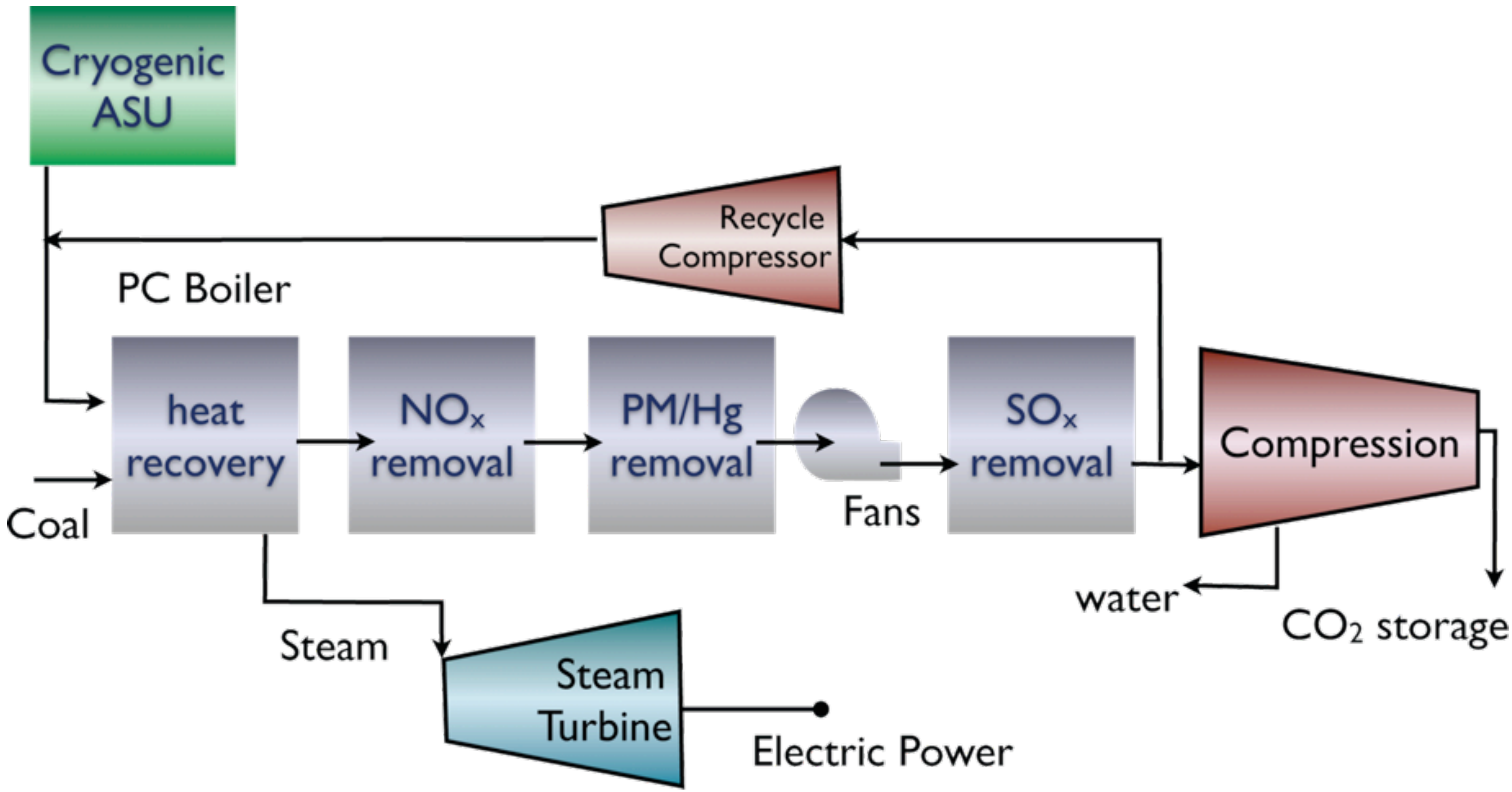
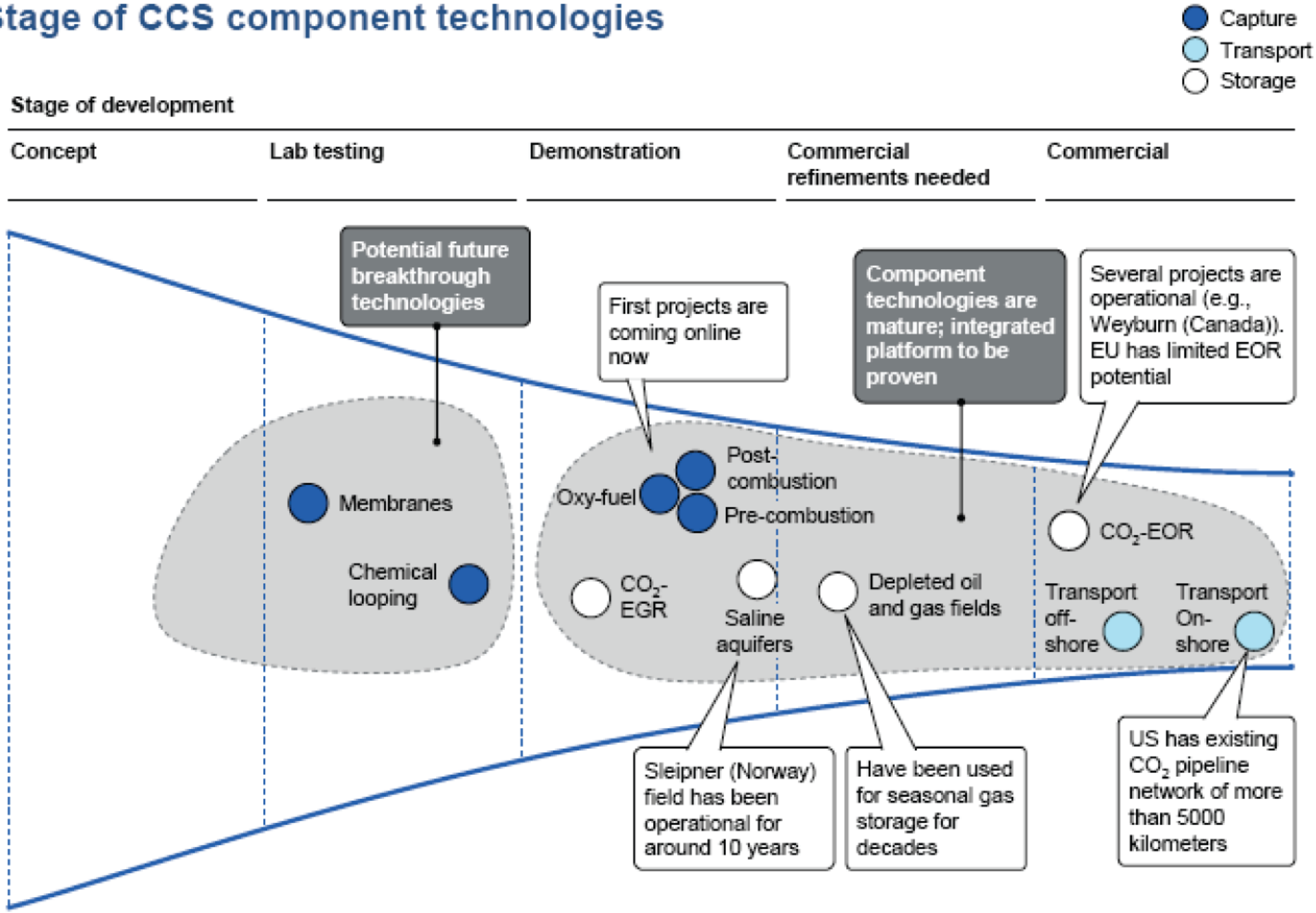


Figure 4.1.2 Coal-fired power plant with post-combustion carbon capture



Box 4.1.2 Oxycombustion (Pre-combustion carbon capture)

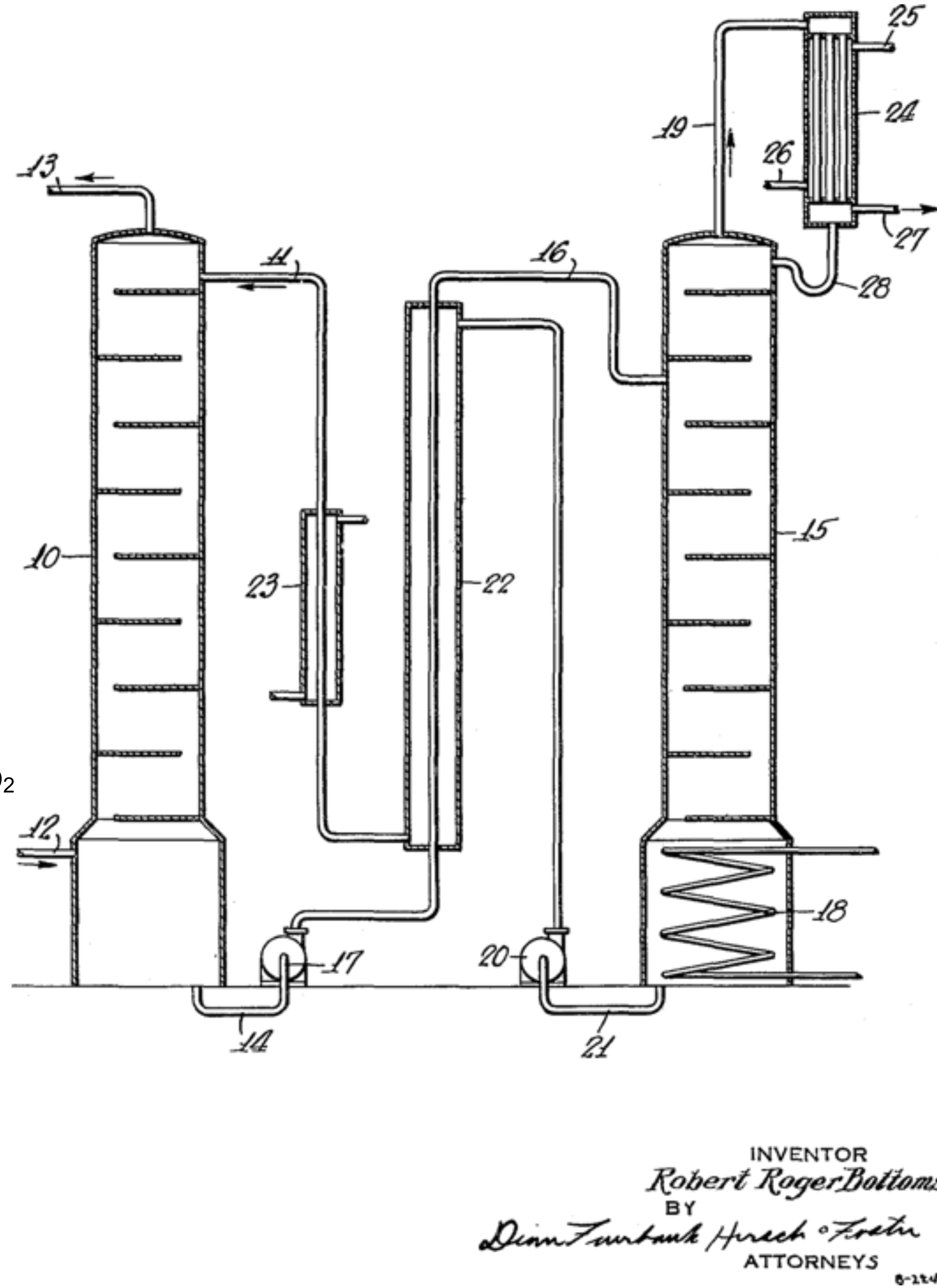
Stage of CCS component technologies



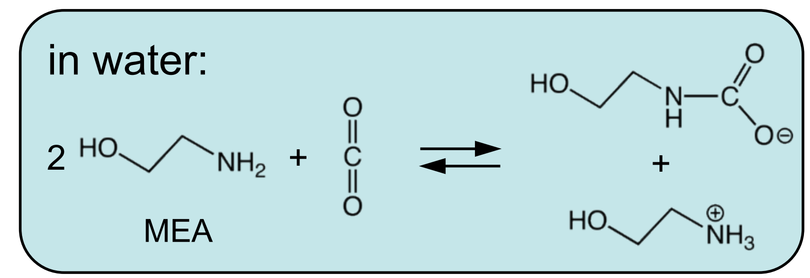
Source: Interviews; Team analysis

McKinsey & Company (2008)

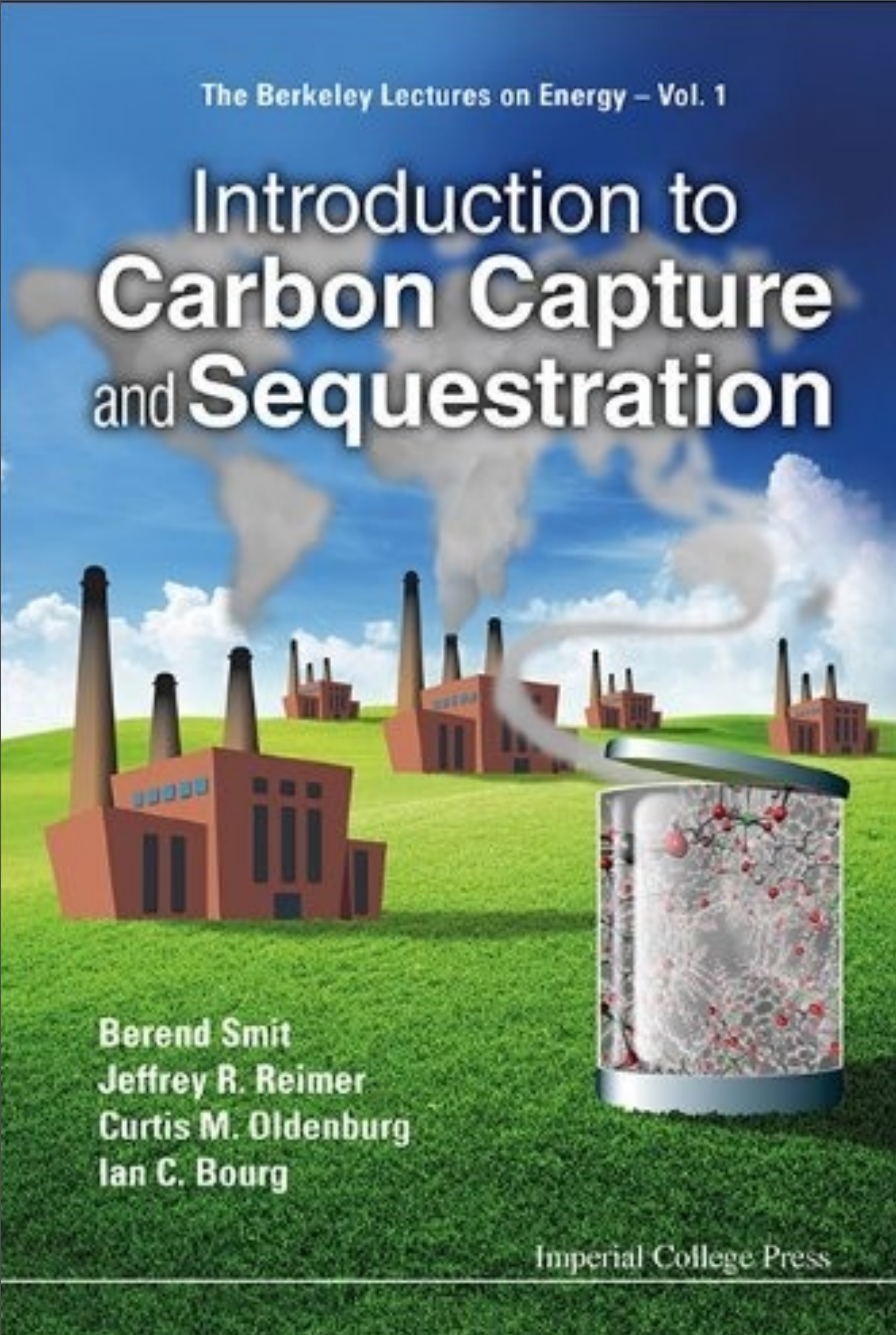
Amines



Flue gas:
0.7 bar N_2
0.1 bar CO_2



- Large amounts of pure water required
- ~30% energy penalty for regeneration

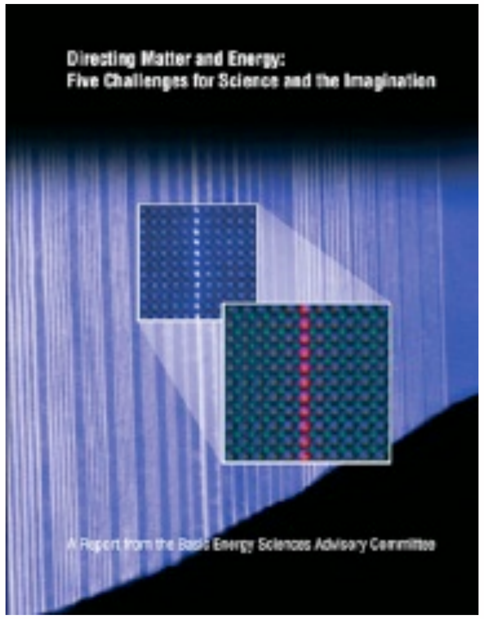


More on CCS

iBook version

B. Smit, J. R. Reimer, C. M. Oldenburg, I. C. Bourg, *Introduction to Carbon Capture and Sequestration*, Imperial College Press, London, **2014**.

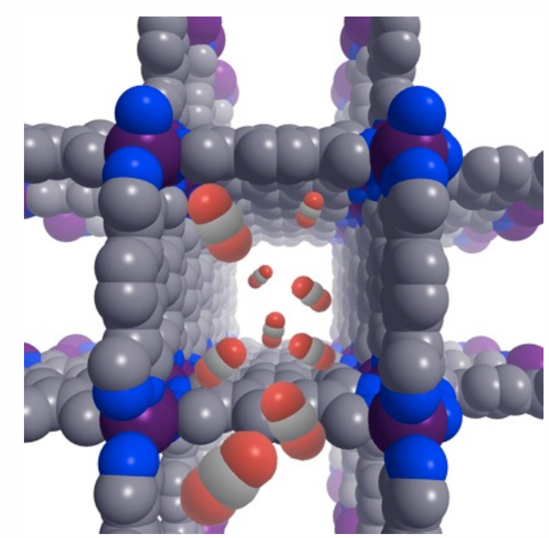
Carbon Capture



In the coming Control Age, scientists will be able to design and create entirely new materials and processes with desired properties and outcomes. With such capabilities, we should find solutions to some of the most vexing problems that civilization now faces, including energy, in all of its aspects, and changing global climate patterns.

EFRC - Carbon Capture

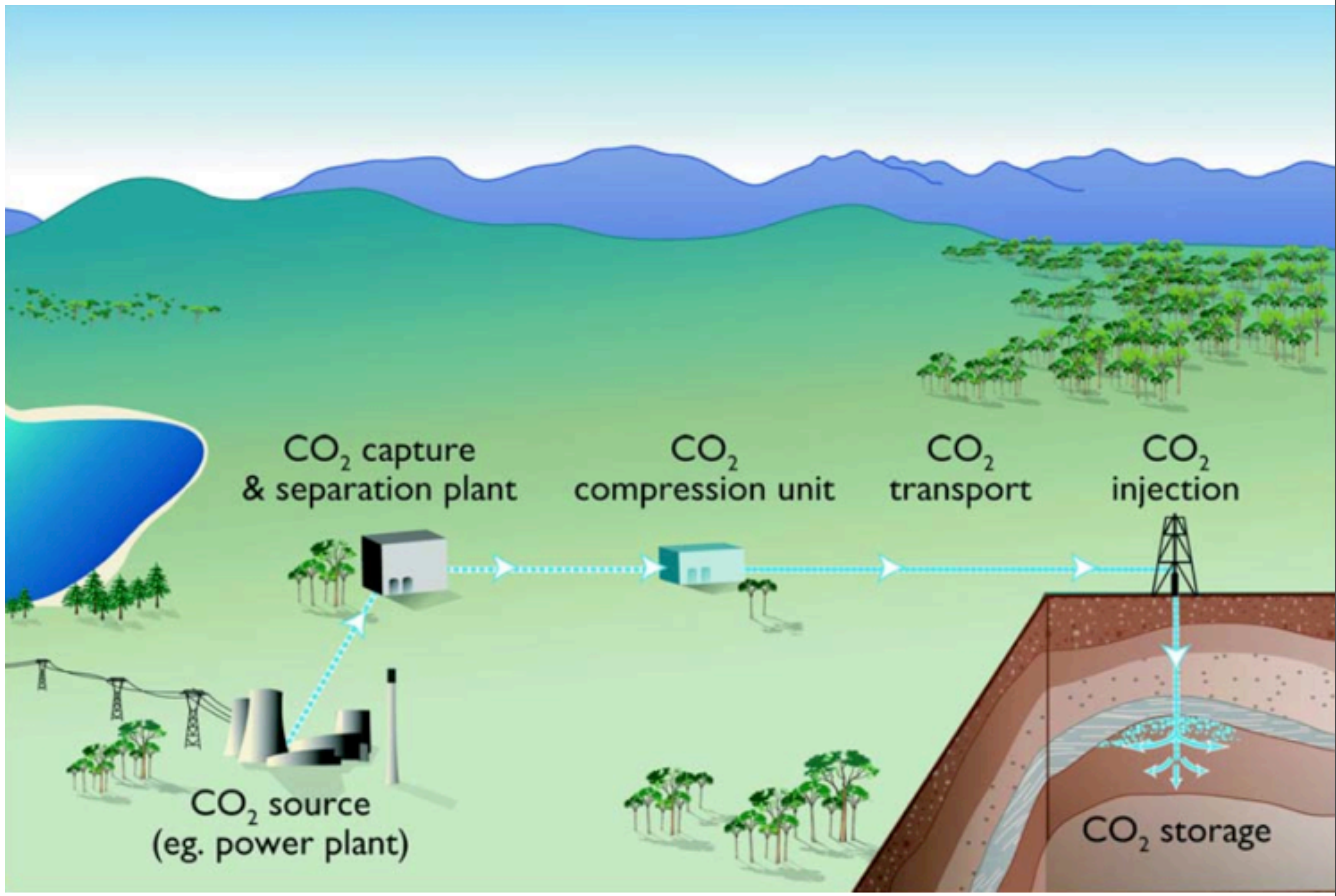
Capture of CO_2 from gas mixtures requires the molecular control offered by nanoscience to tailor-make those materials exhibiting exactly the right adsorption and diffusion selectivity to enable an economic separation process. Characterization methods and computational tools will be developed to guide and support this quest.



Carbon Capture and Sequestration Research

Capture is currently considered to be the most expensive part of CCS.

Geologic storage involves uncertainties and risks when considered at full scale.



Gas separations

Important CO_2 separations:

- Flue gasses (coal 12% CO_2; natural gas 4% CO_2)
  - "End of pipe" technology; low pressure
- Natural gas
  - High pressure form natural reservoirs
- CO_2 directly from air
  - Ultra low concentration of CO_2
- Oxygen from air:
  - Oxy-combustion

Jeffrey Long
UC Berkeley

Omar Yaghi
LNBL MF

Hong-Cai Zhou
Texas A&M

Maciej Haranczyk
LBNL

David Luebke
NETL

Blandine Jérôme
LBNL

Jeffrey Kortright
LBNL

Jeffrey Reimer
UC Berkeley

Simon Teat
LBNL

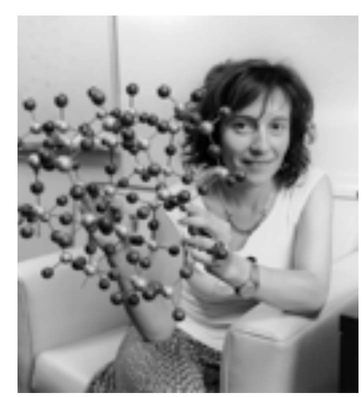
Jeffrey Neaton
LBNL-MF

Berend Smit
UC Berkeley

Frantisek Svec
LBNL-MF

Brett Helms
LBNL-MF

Ting Xu
UC Berkeley



Laura Gagliardi
U Minnesota

Giullia Galli
UC Davis

EFRC

Solid Adsorbents

- Jeffrey Long (UC Berkeley):
- Omar Yaghi (UC Berkeley)
- Hong-Cai Zhou (Texas A&M)

Polymer Membranes:

- Frantisek Svec and Jean Frechet (LBNL)
- Bret Helm and Ting Xu (LBNL)
- Dave Luebke (NETL)

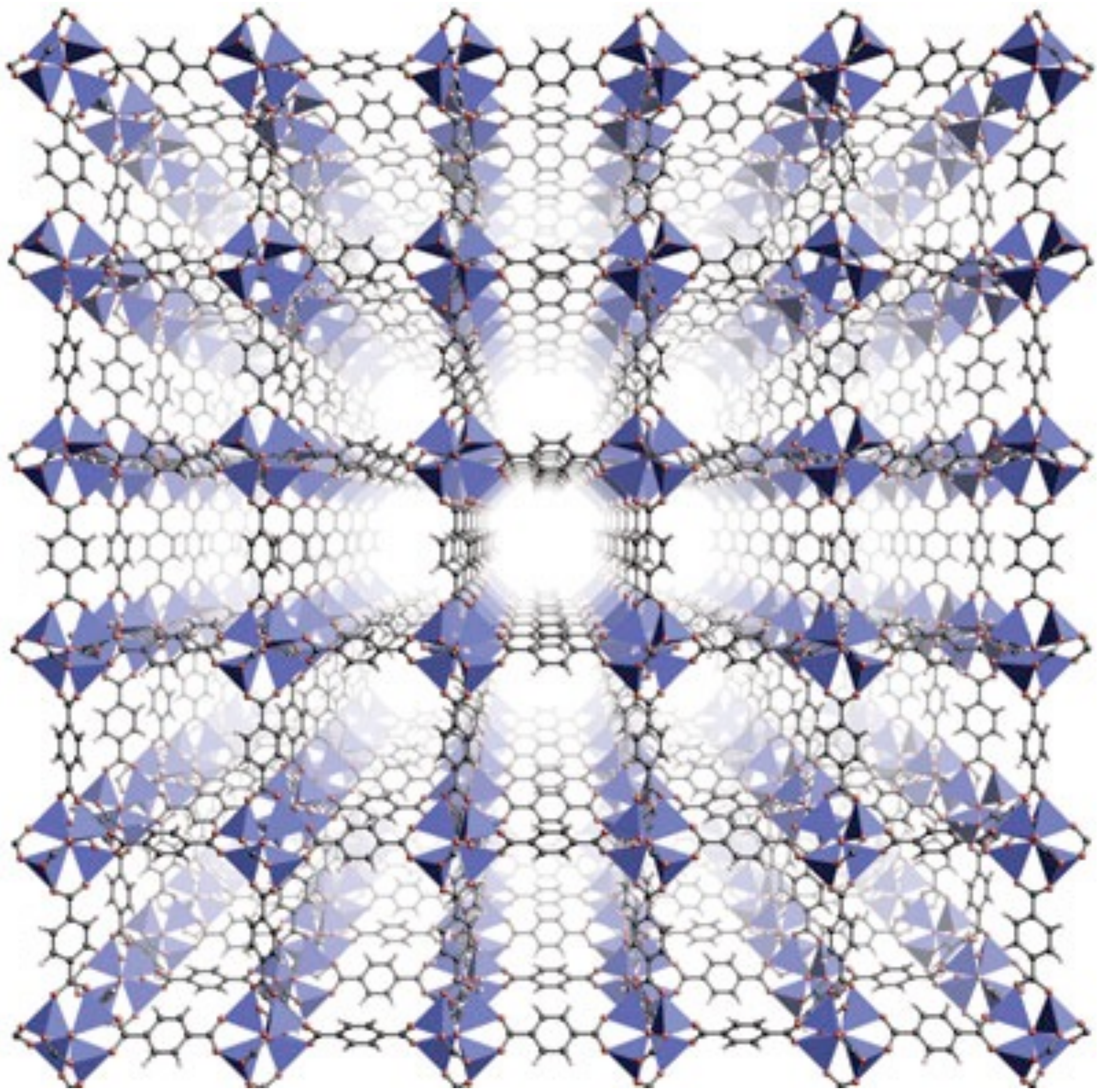
Characterization

- Resonance soft X-rays: Blandine Jerome and Jeff Kortright (LBNL)
- X-ray crystallography: Simon Teat (LBNL)
- NMR: Jeffrey Reimer (UC Berkeley)

Computation

- Adsorption and Diffusion: Berend Smit (UC Berkeley)
- Electronic Structure calculation: Jeff Neaton (LBNL) and Gullia Galli (UC Davis)
- Quantum calculations: Laura Gagliardi (U Minessota)
- Materials Screening: Maciej Haranczyk (LBNL)

Metal Organic Frameworks



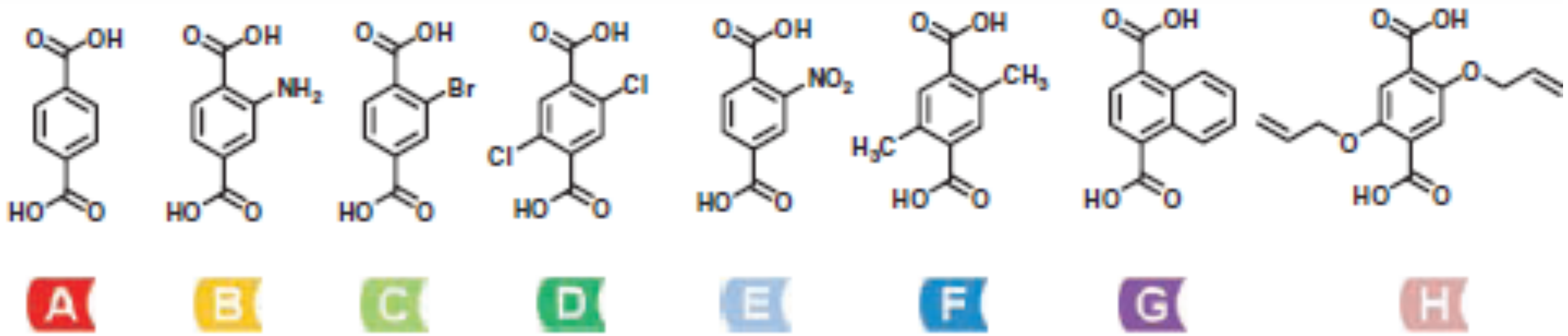
Zn_4O(1,4-benzenedicarboxylate)$_3$
MOF-5

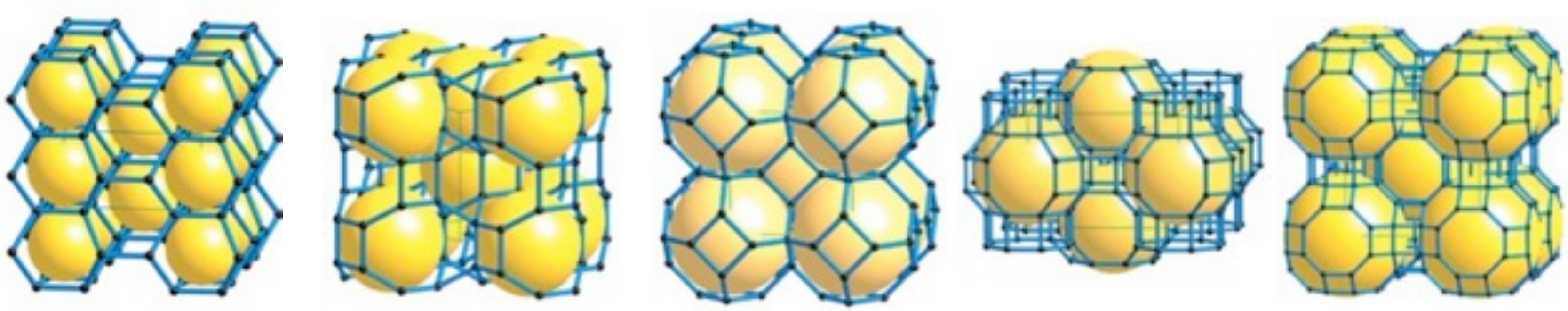
- BET surface areas up to 6200 m^2/g
- Density as low as 0.22 g/cm^3
- Tunable pore sizes up to 5 nm
- Channels connected in 1-, 2-, or 3-D
- Internal surface can be functionalized
- BASF production on ton scale

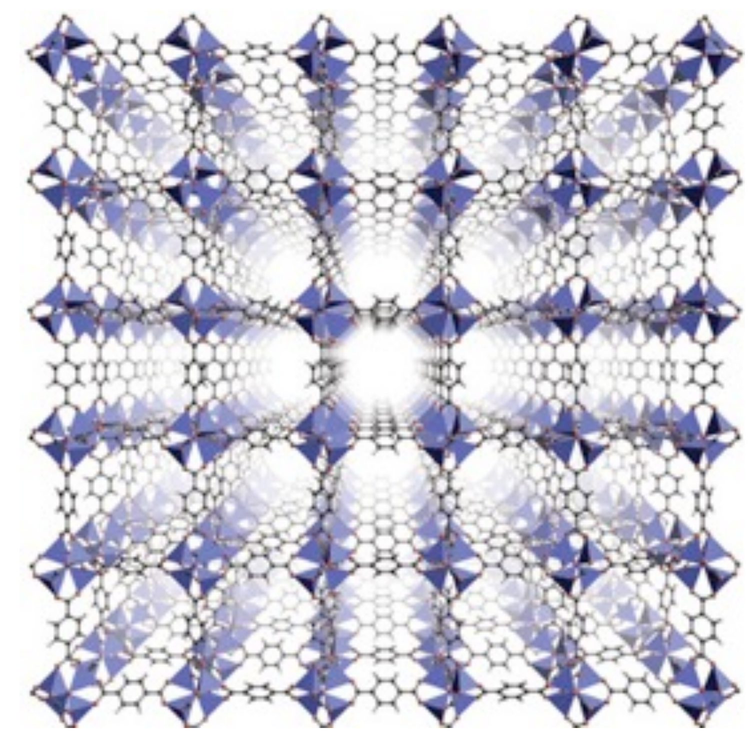
Computation Challenge

Chemical Flexibility of MOFs

- We can change the metal: Fe, Mg, Ca, Zn, Cu, etc
- We can change the linker
- We can change the pore topology



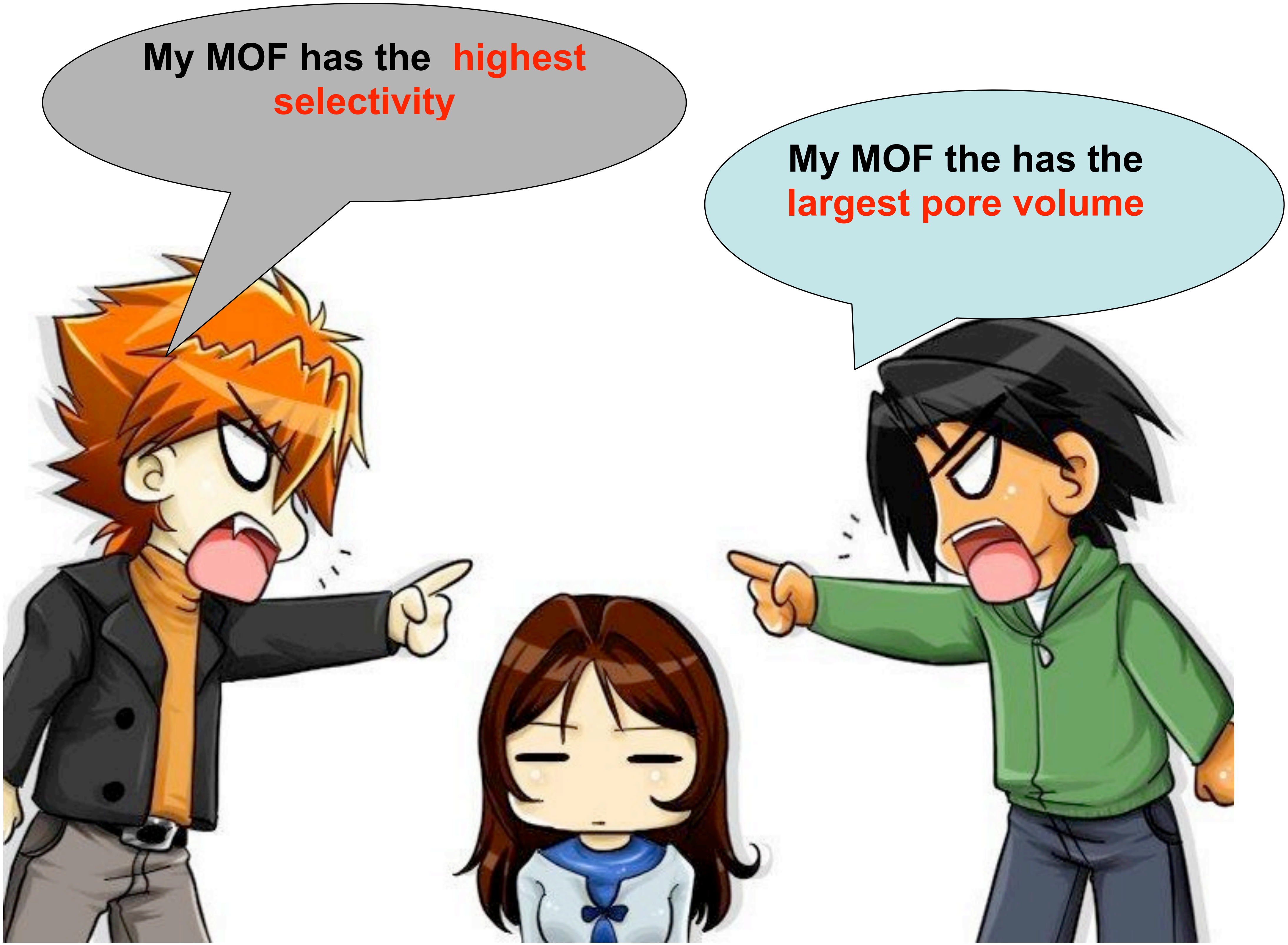




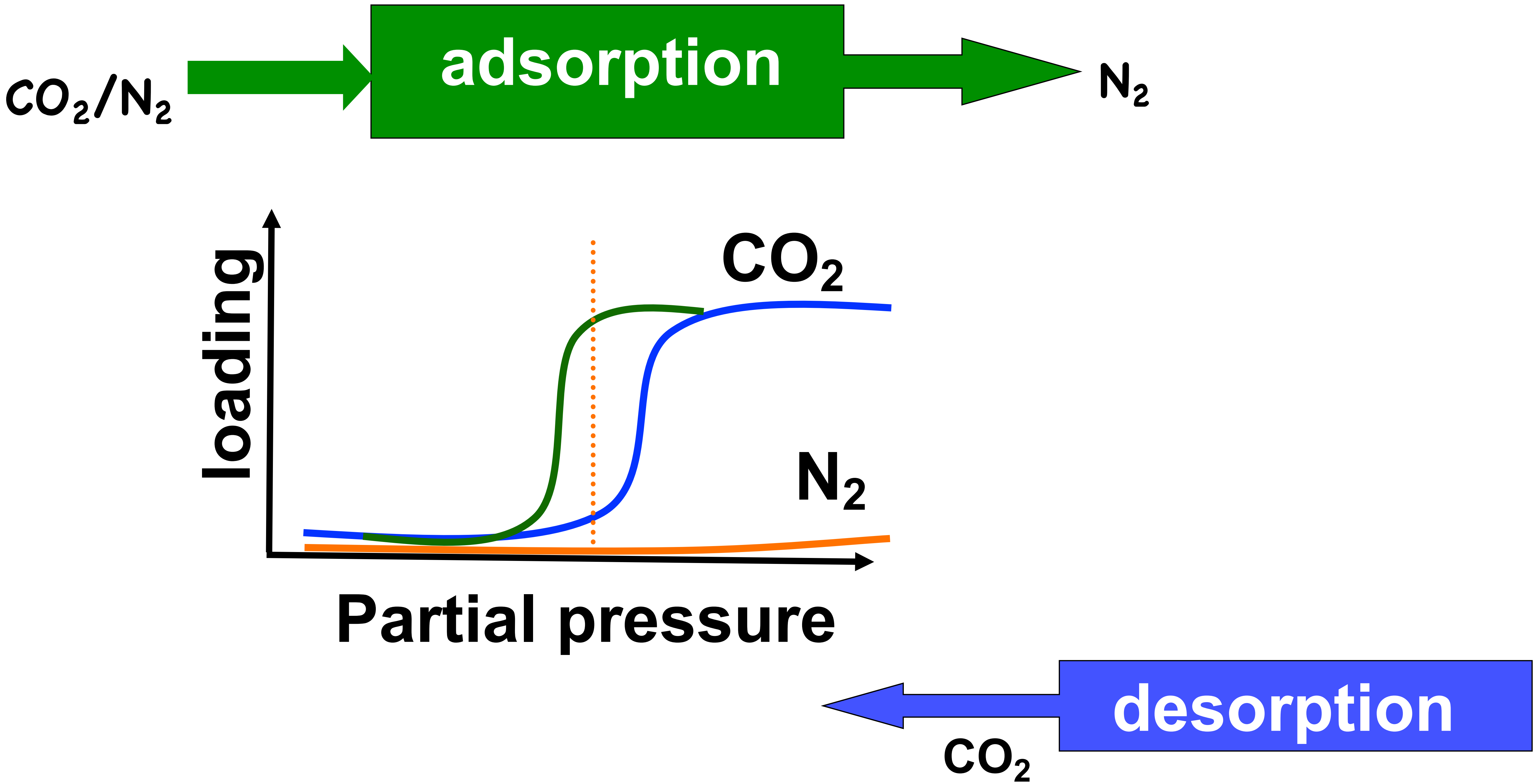
crb dft sod mer rho

Out of these many many millions of structures, which one is the best for Carbon Capture?

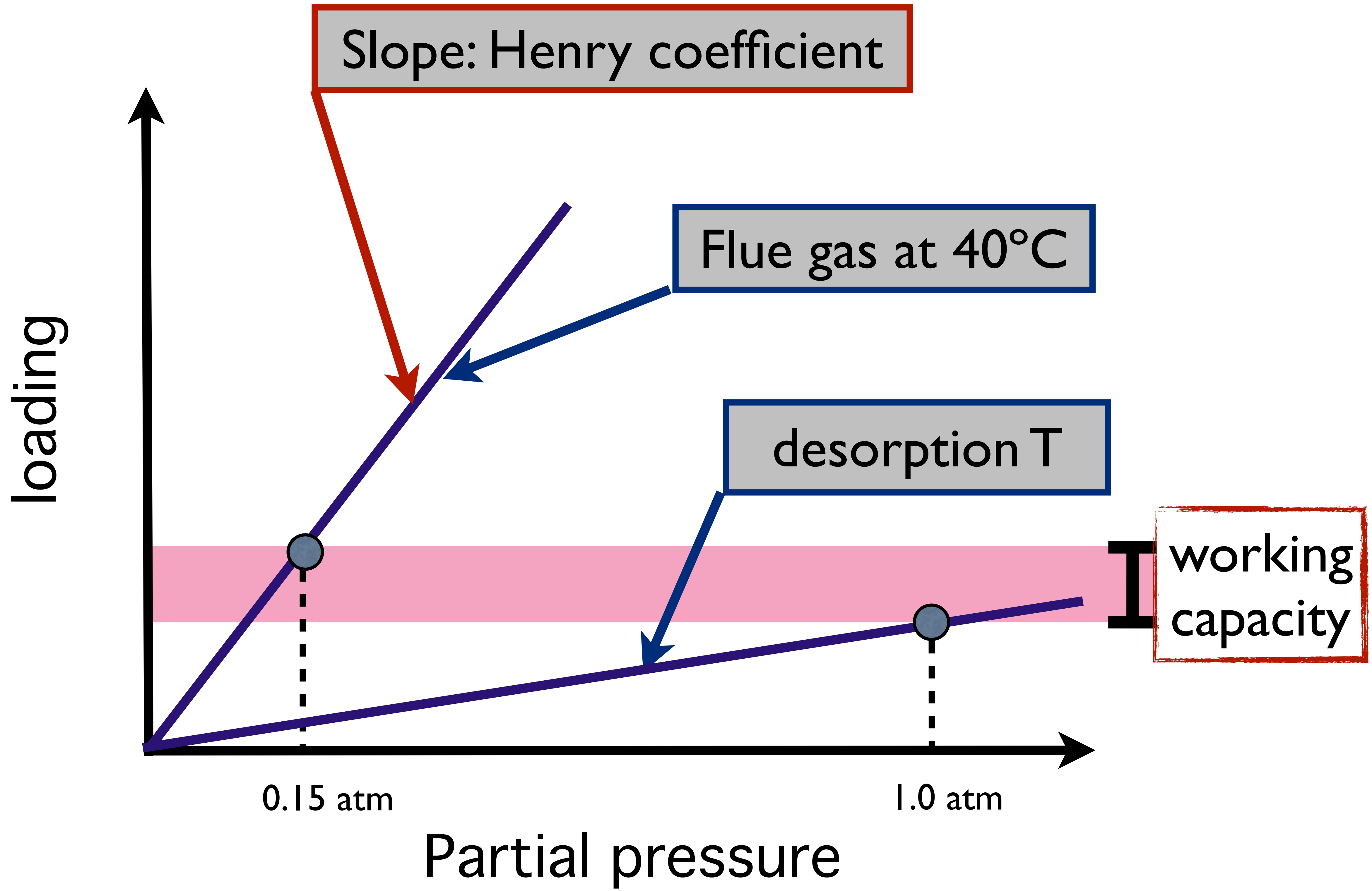
How to compare two MOFs



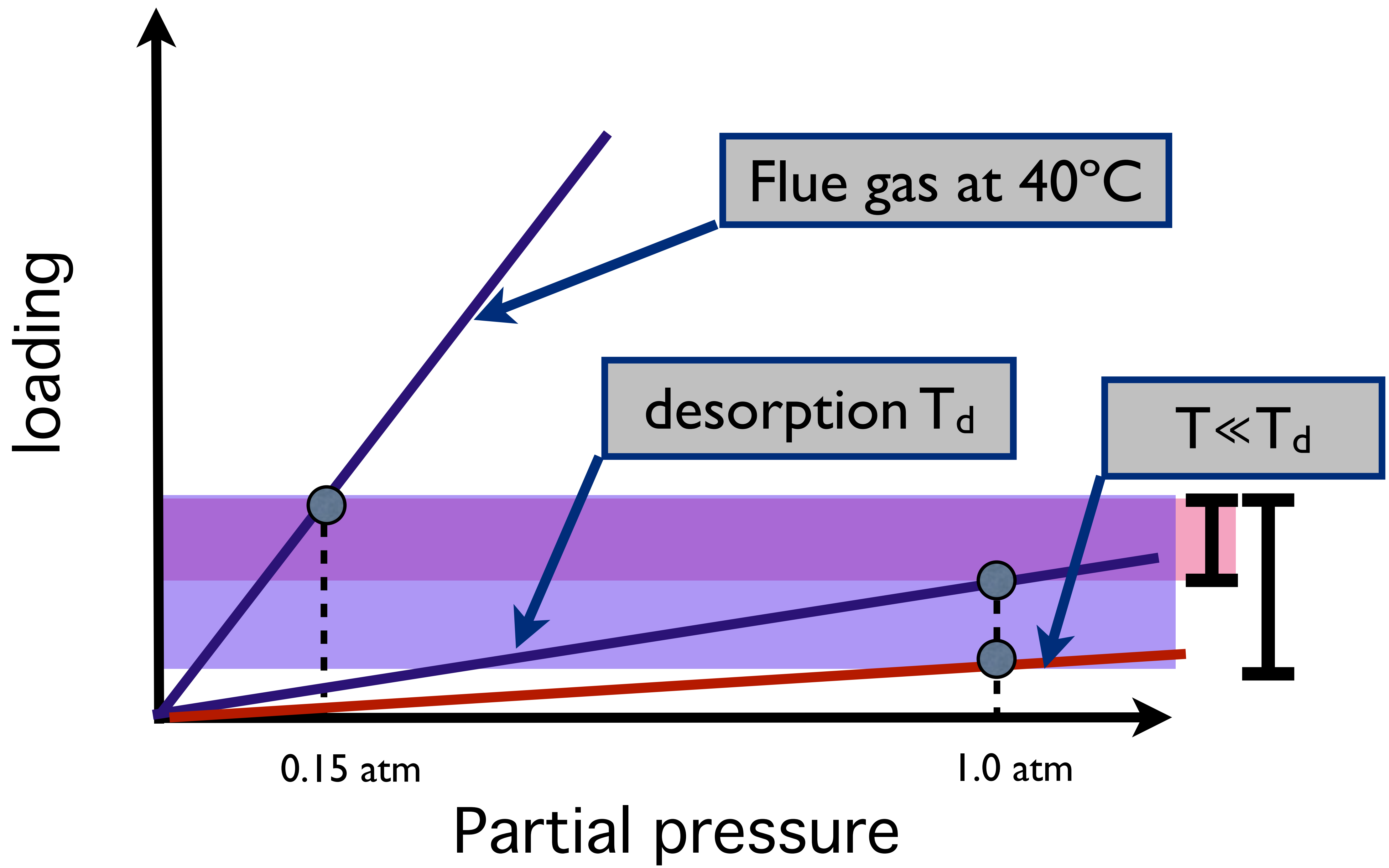
Separating CO_2



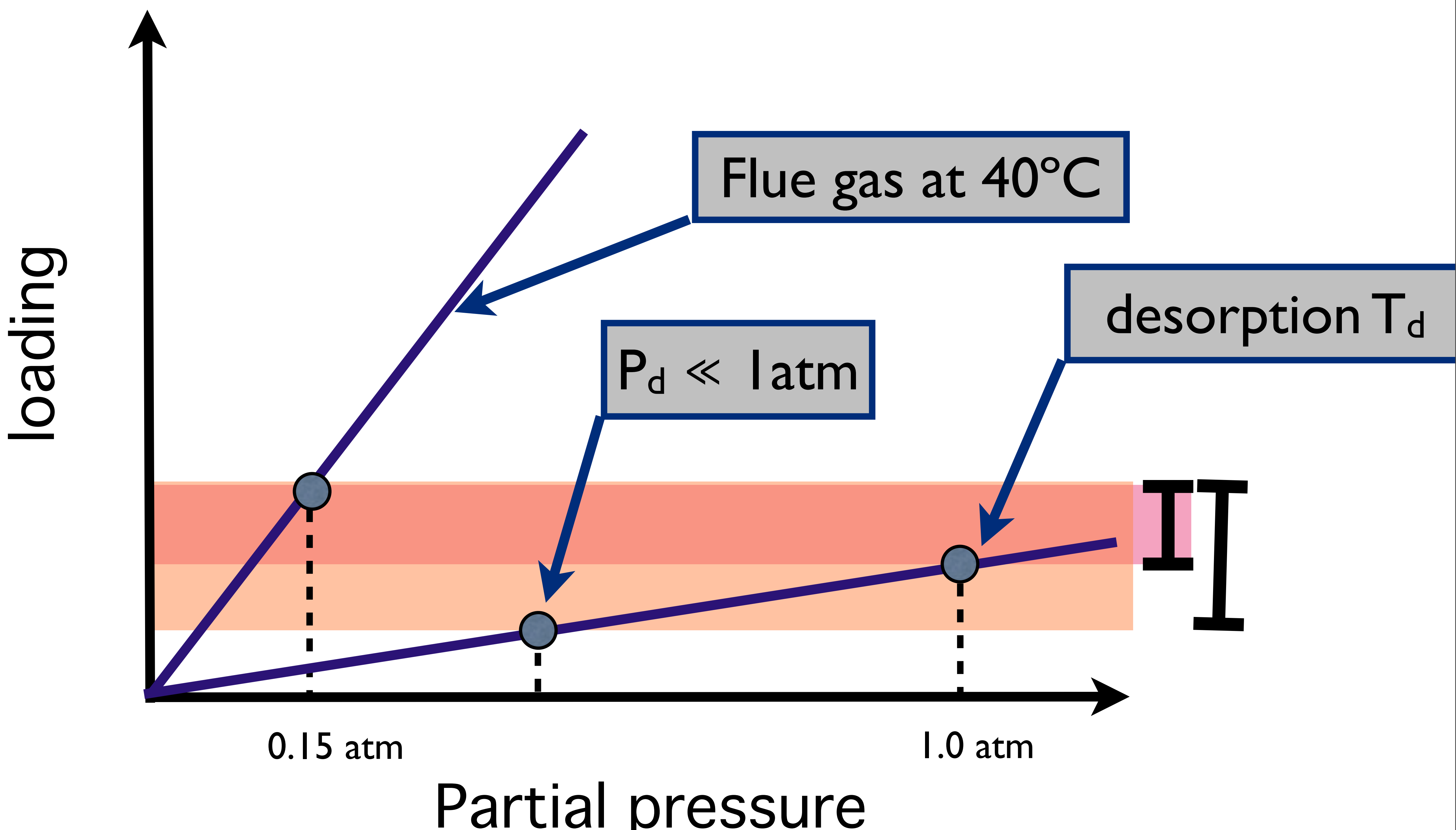
Working capacity & Henry coefficient



Increasing the working capacity: **temperature**



Increasing the working capacity: **pressure**

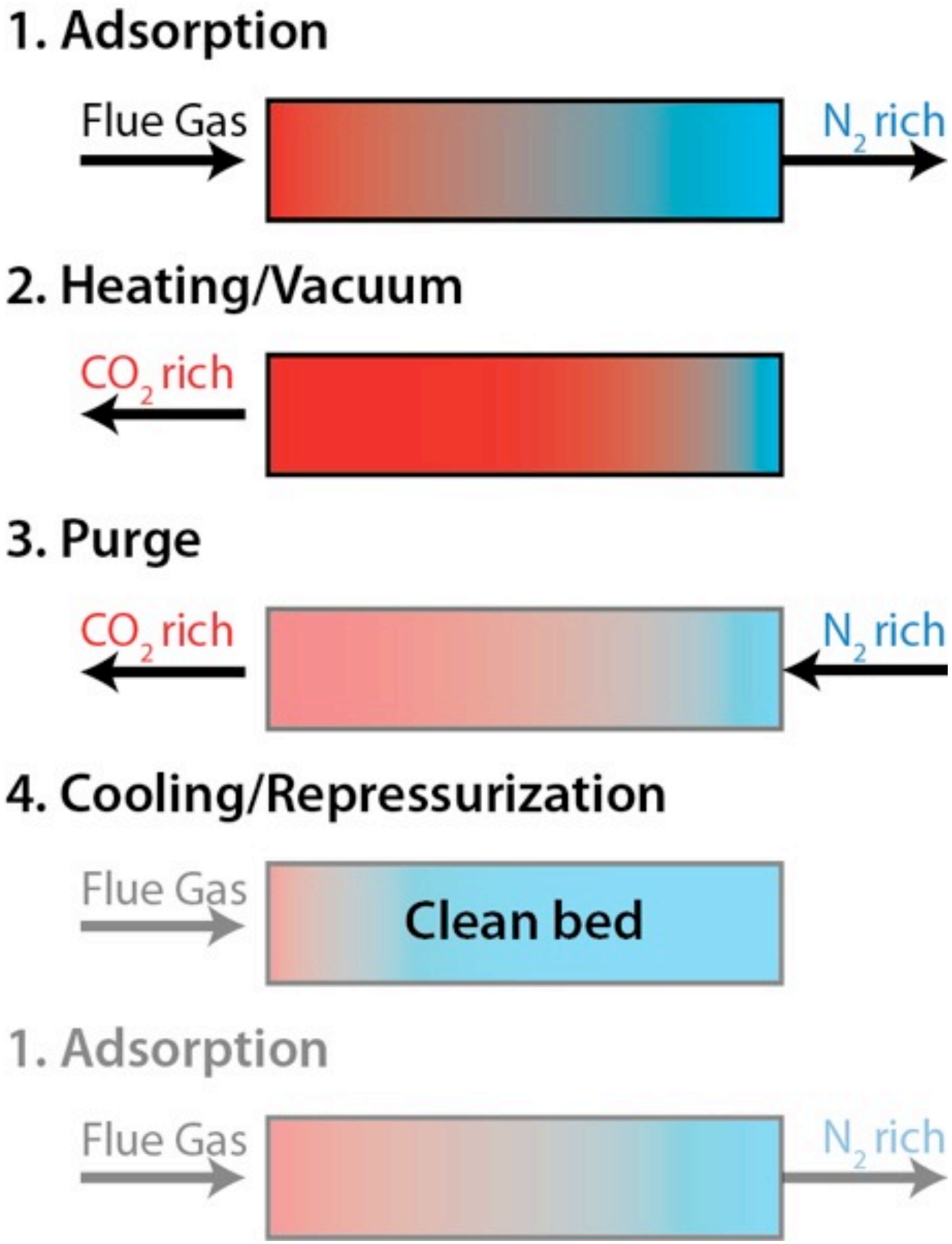


We can increase the working capacity, but at which cost?

Model for Screening Materials

Calculate ***process independent performance*** characteristics of materials for CCS

- Fixed bed configuration
  - Temperature swing
  - Pressure swing
  - Hybrid processes
- Equilibrium model
  - No heat or mass transfer
  - Based on isotherms
- Uses difference in capacity between *adsorption / desorption* conditions



(Adam Berger and Abhoyit Bhown, EPRI)

Performance metric: parasitic energy

Energy penalty for Carbon Capture and Sequestration:

compression work and the **heating energy**:

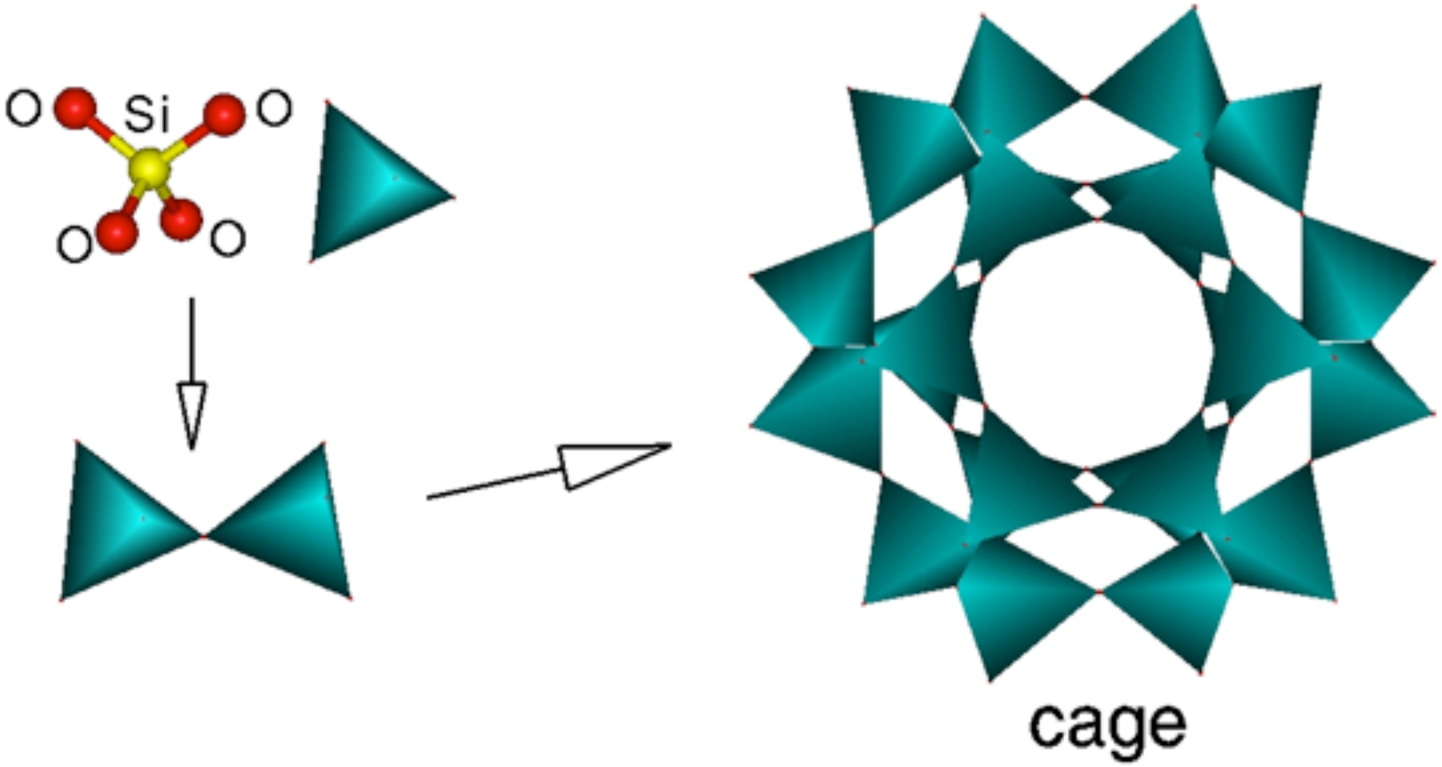
- Heating energy (Q): heat necessary to regenerate a given sorbent:
  - Sensible heat: heats and cools bed. Provides driving force to produce CO_2
  - Desorption heat: desorbs CO_2 (equal to heat of adsorption, Δh).

$$Q = \left(\underbrace{C_p \rho_{sorbent} \Delta T}_{\text{Sensible heat requirement}} + \underbrace{\Delta h_{CO2} \Delta q_{CO2} + \Delta h_{N2} \Delta q_{N2}}_{\text{Desorption heat requirement}} \right) \Big/ CO_{2\,\mathrm{Pr}oduced}$$

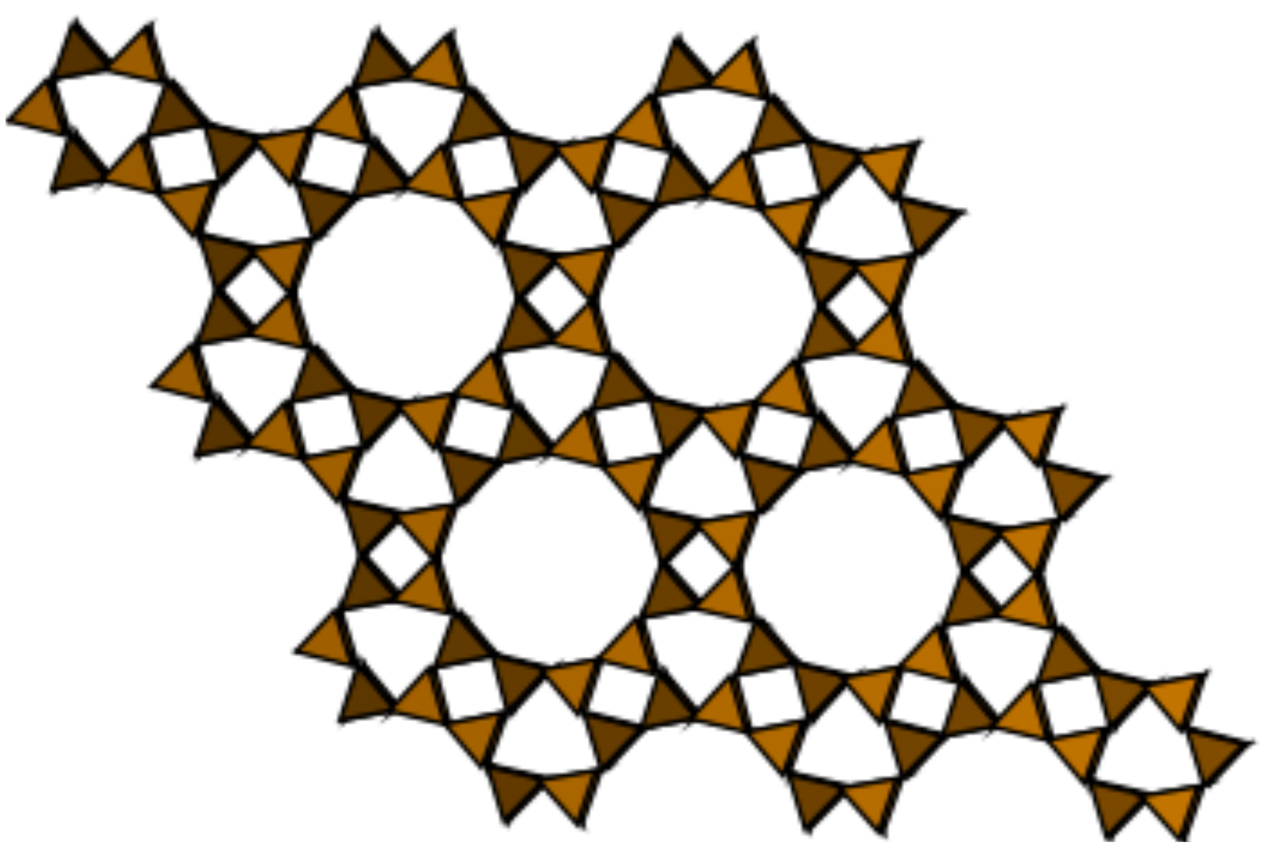
- Compressor work (W_{comp}): Work to compress CO_2 to 150 bar (for transport)

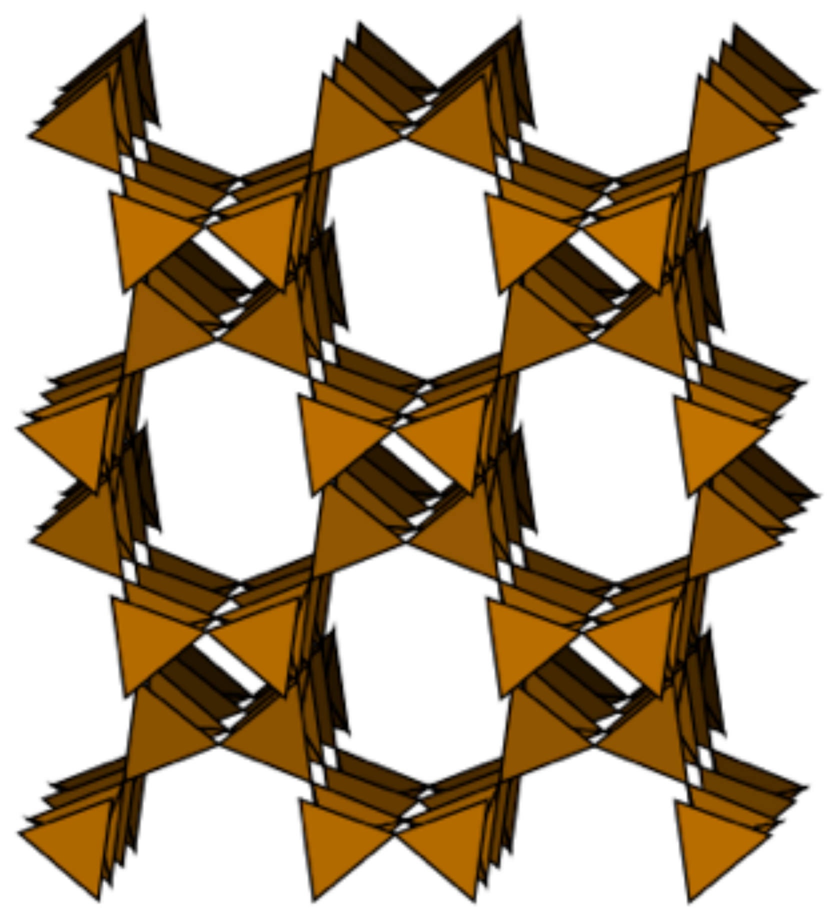
$$W_{eq} = \left(0.75 Q \cdot \eta_{carnot} + W_{comp} \right)$$

- Parasitic energy calculated by discounting the heat requirement by the Carnot efficiency to simulate the effect of taking steam from a steam cycle



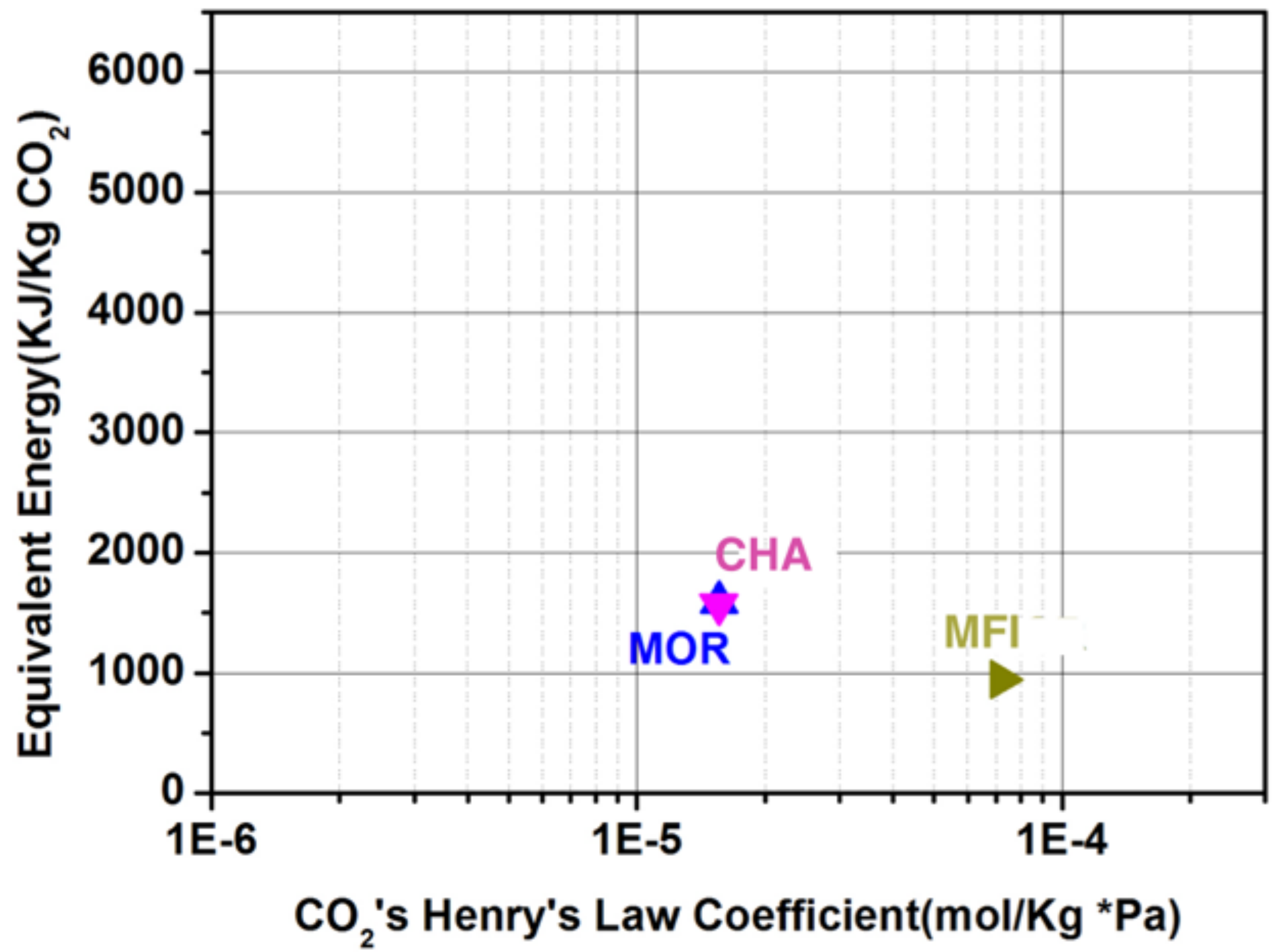
- 180 Known structures
- >3.000,000 hypothetical structures
- **Which is the best for carbon capture?**





Zeolites for Carbon Capture

Equivalent Energy for those all silica structures with experimental data

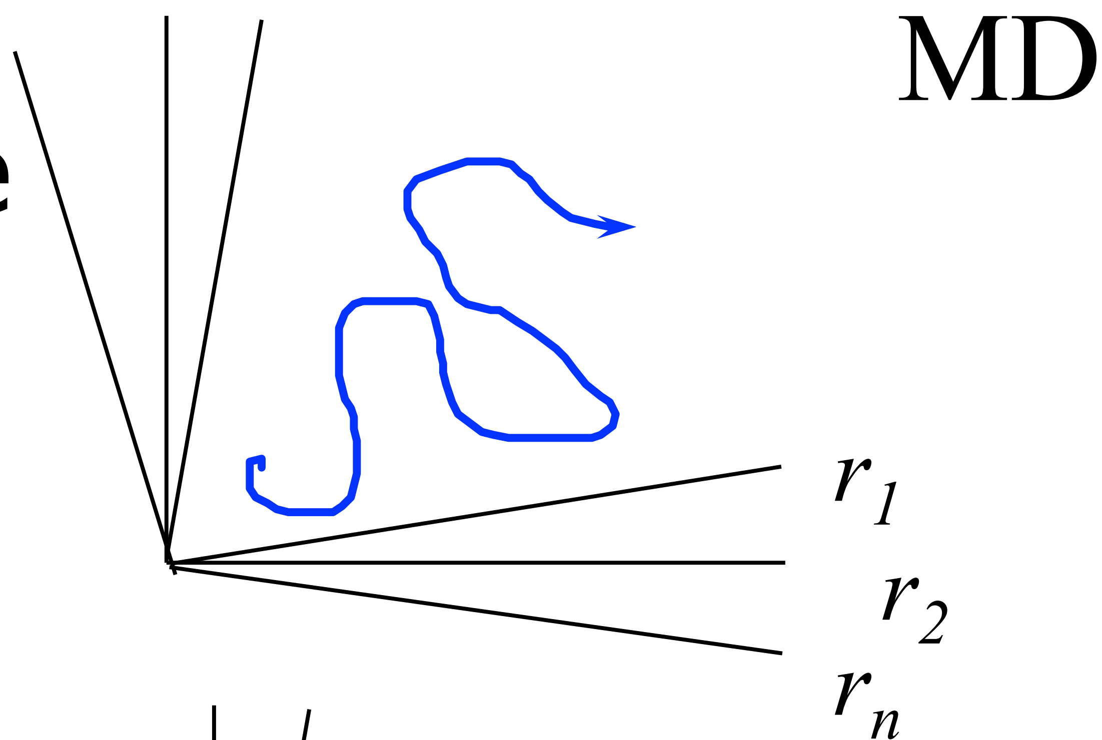


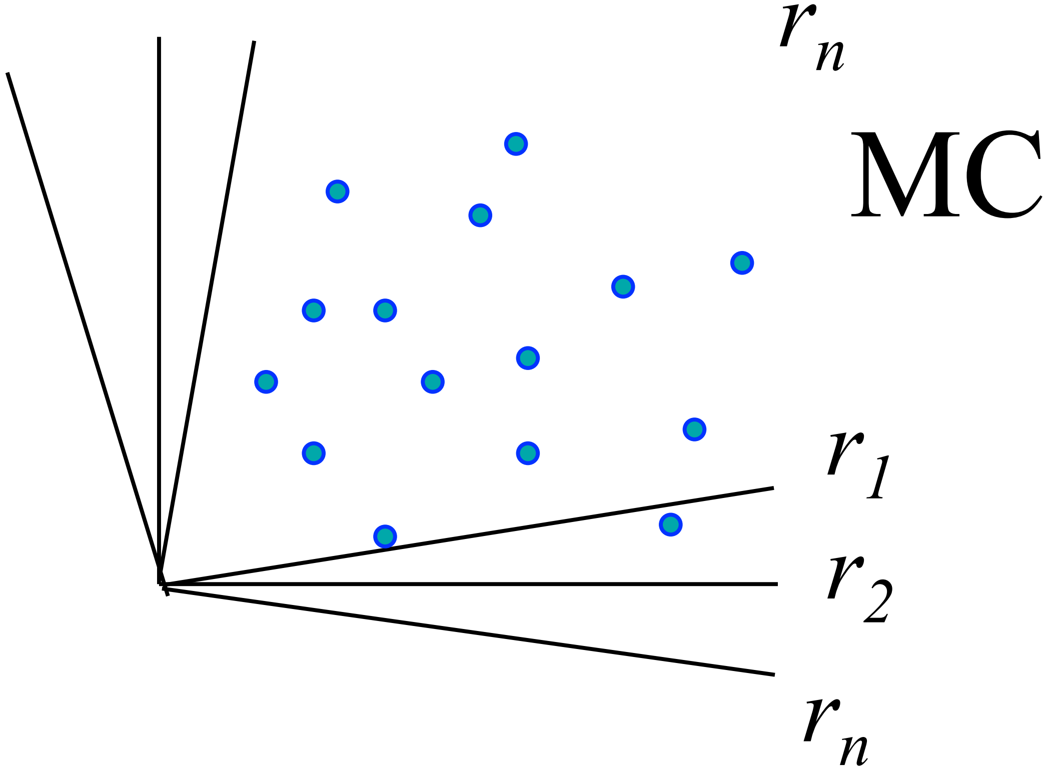
What is the best structure?

What is the lowest energy?

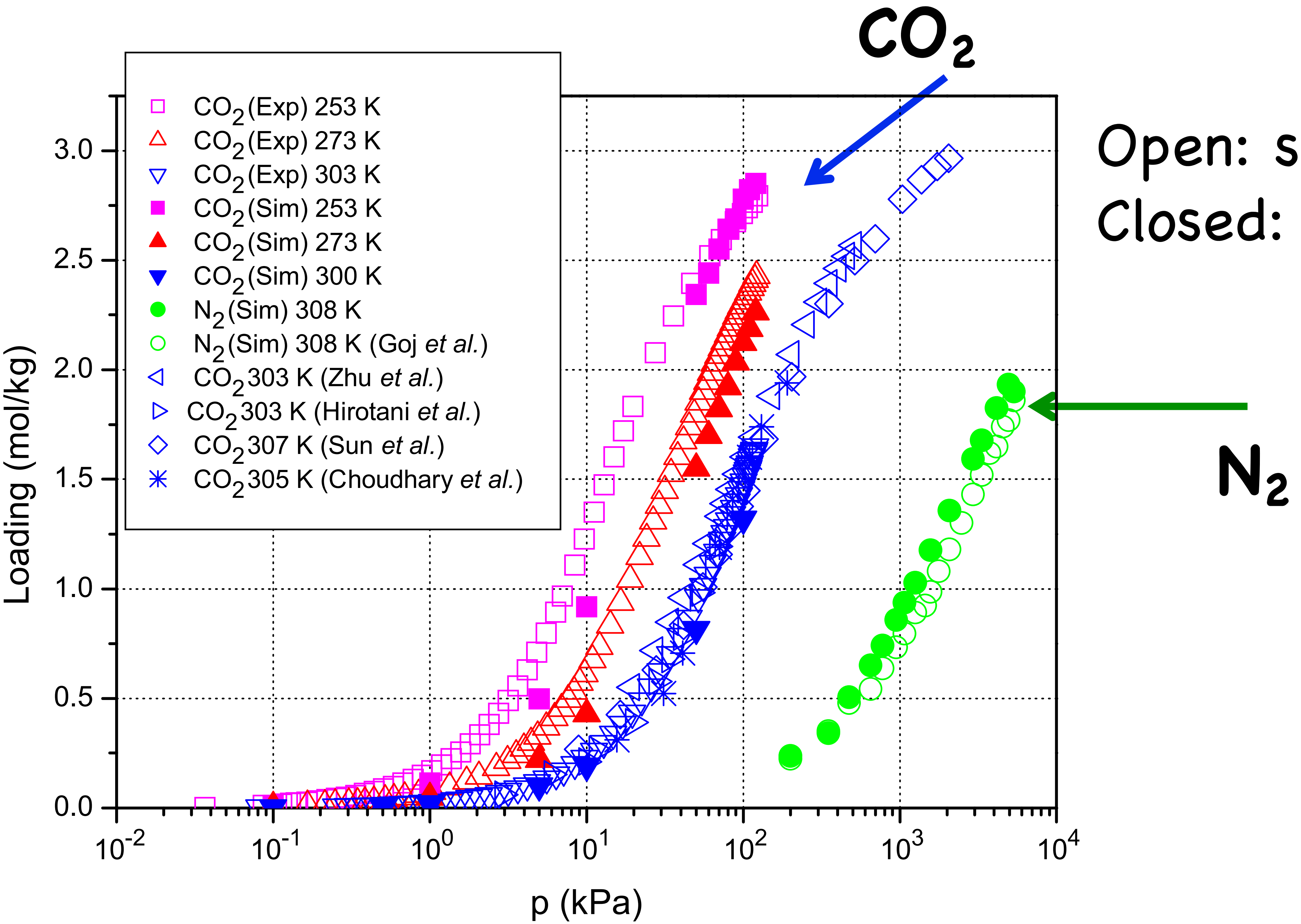
Molecular Simulations

- Molecular dynamics: solve equations of motion
- Monte Carlo: importance sampling
- ➡ calculate thermodynamic and transport properties for a given intermolecular potential





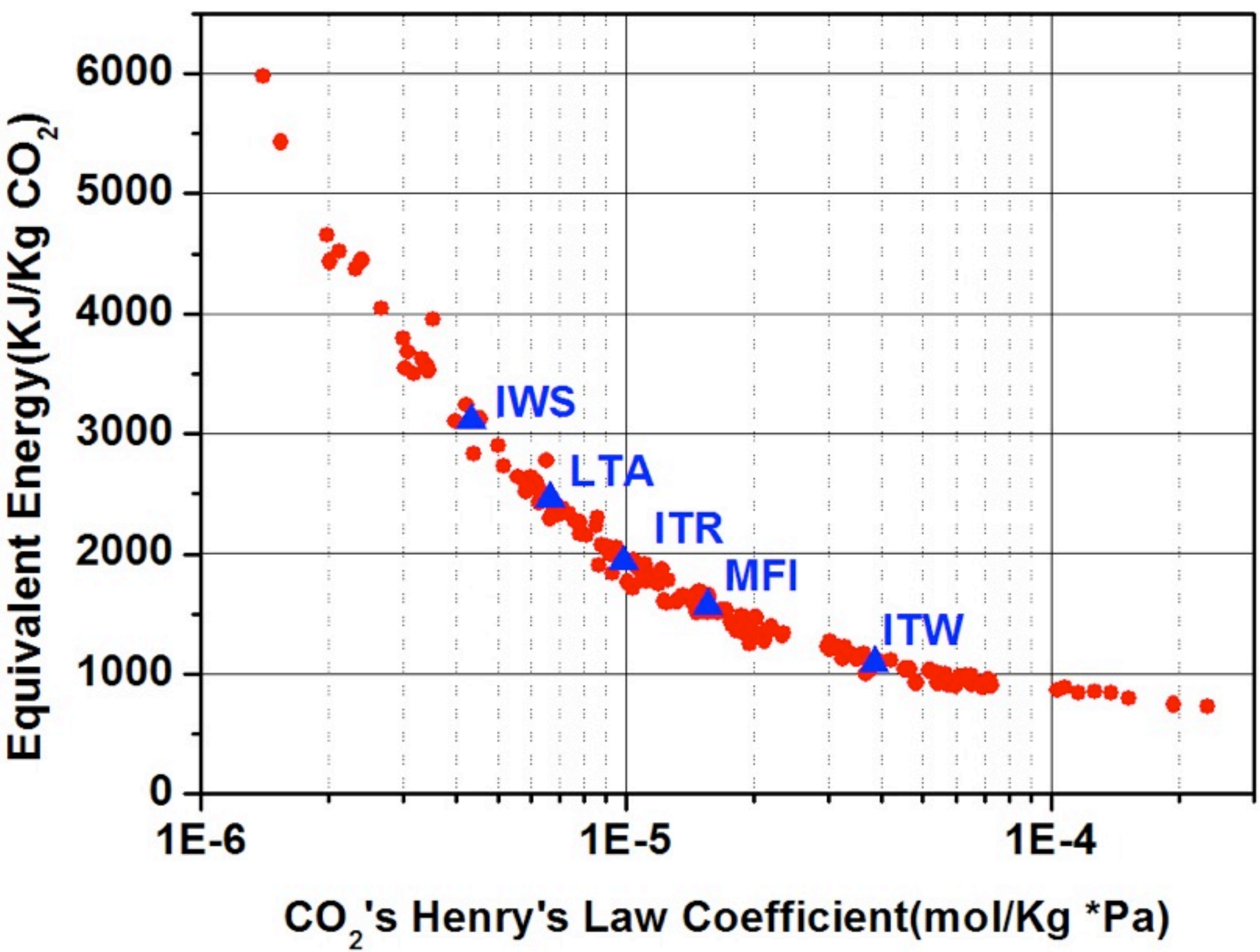
Zeolites (MFI)



Open: simulations
Closed: experiments

(E. García-Pérez et al. Adsorption (2007) 13: 469-476)

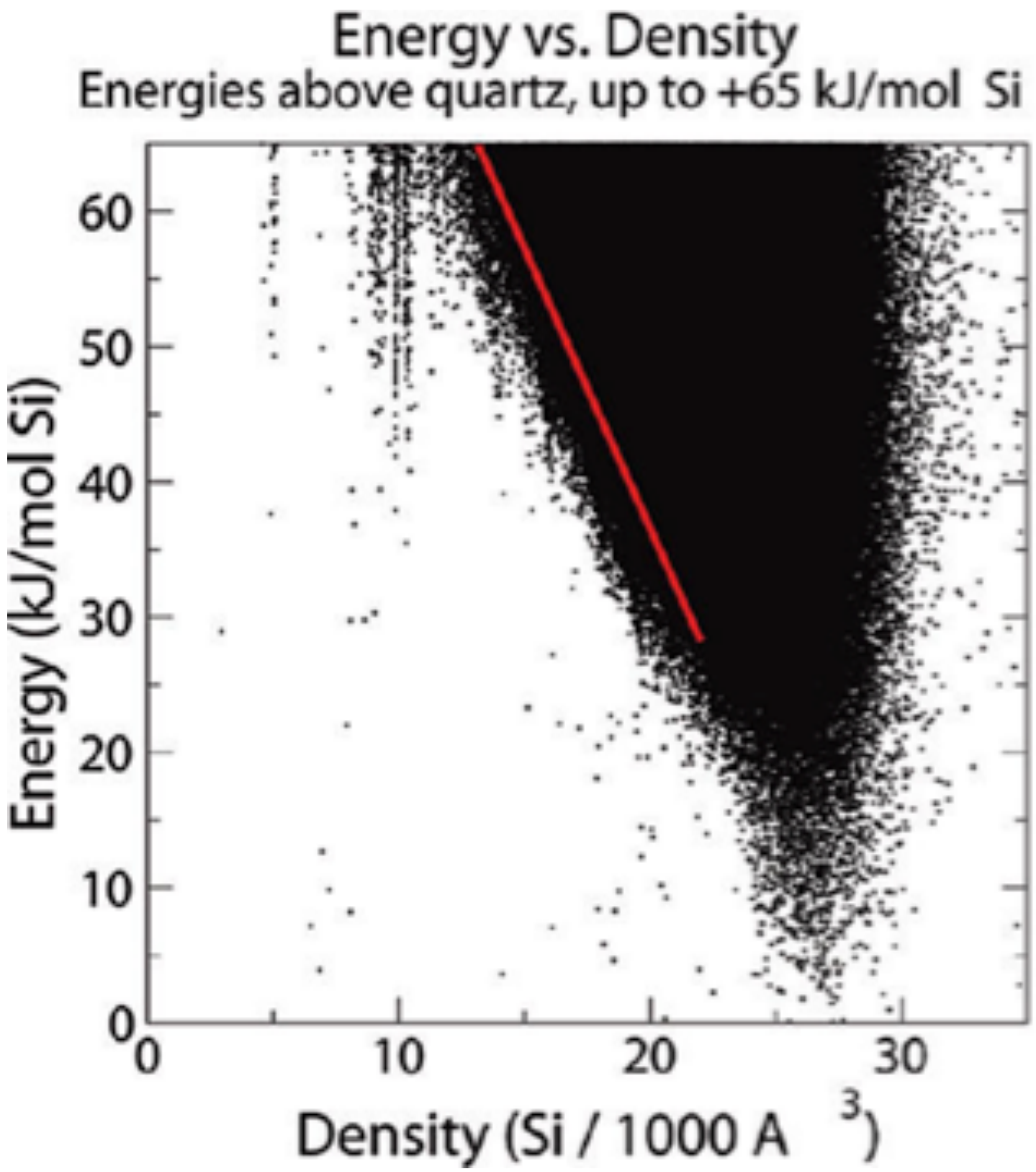
All known zeolites

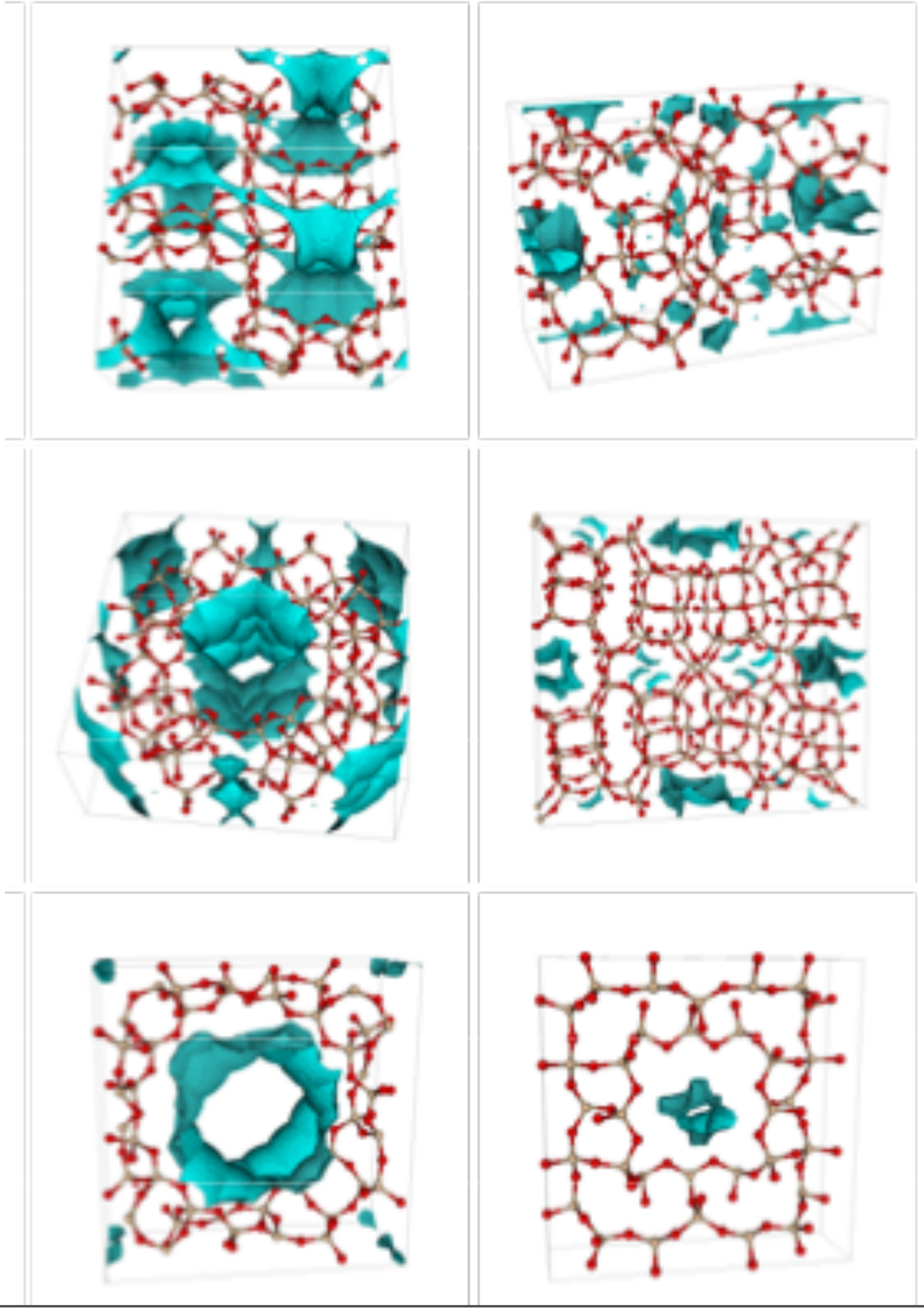


What is the best zeolite structure? (Materials Genome)

Hypothetical zeolites

*~**2.7 10^6 unique structures** were enumerated, with roughly 10% within the +30 kJ/mol Si energetic band above R-quartz in which the known zeolites lie*



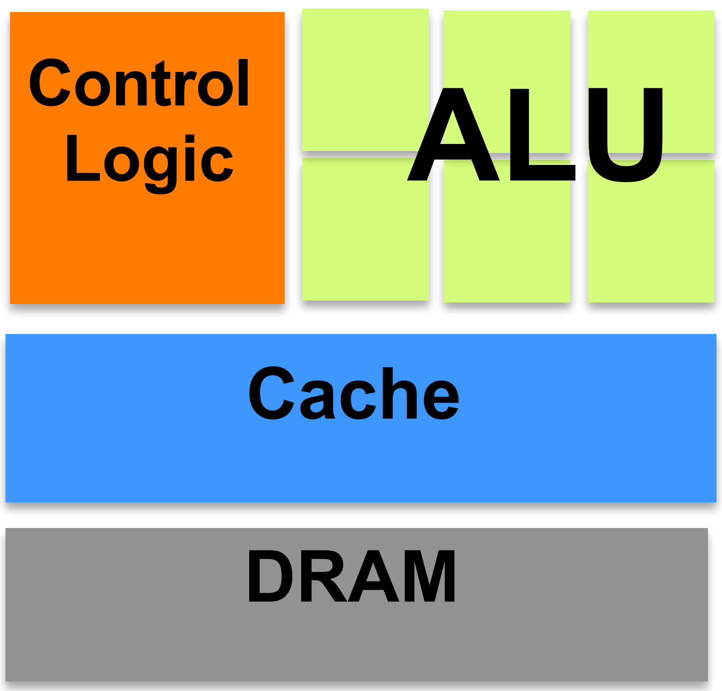


Deem et al. *J. Phys. Chem. C* 2009, *113*, 21353.

How to predict 1 million isotherms?

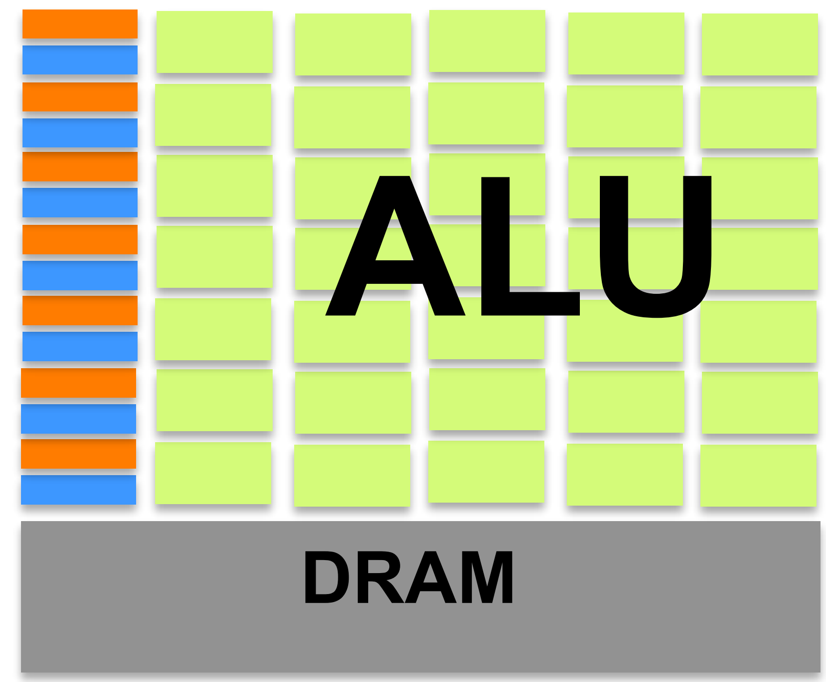
CPU: one isotherm **5-10 days**

CPU



- Less than 20 cores
- Designed for general programming

GPU



- More than 500 cores
- Optimized for SIMD (same-instruction-multiple-data) problems

GPU

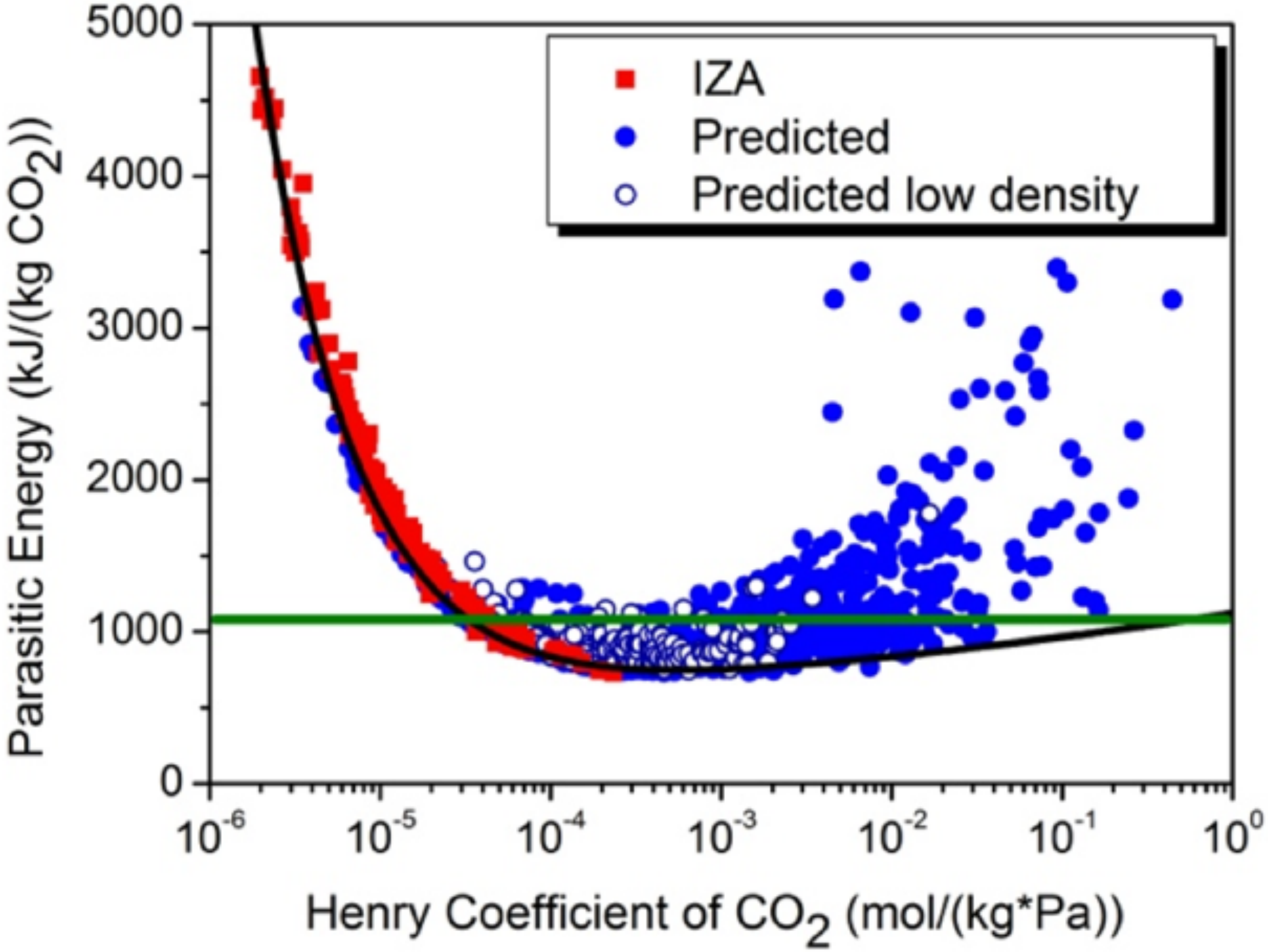
trade-off between memory, # threads, and work load

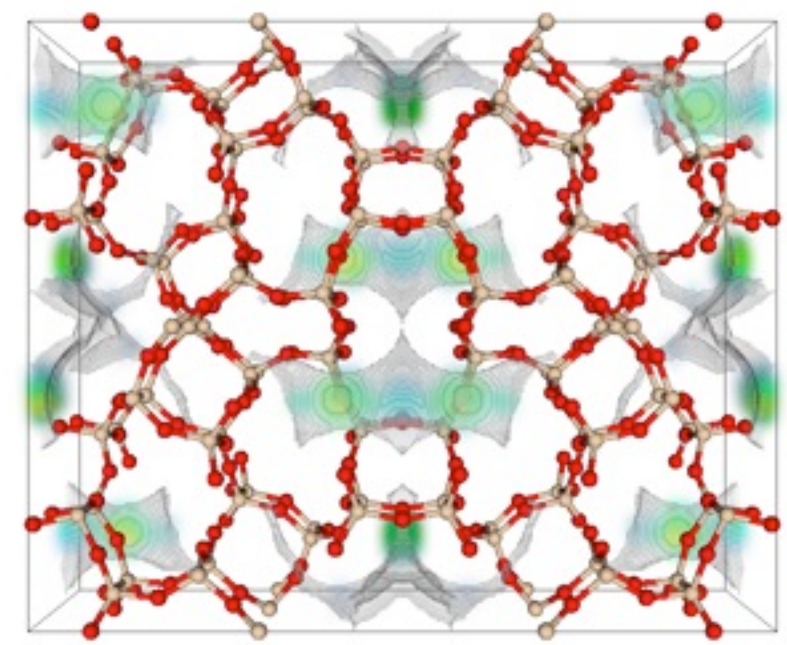
- Energy calculation in parallel
- Monte Carlo in parallel for different pressures

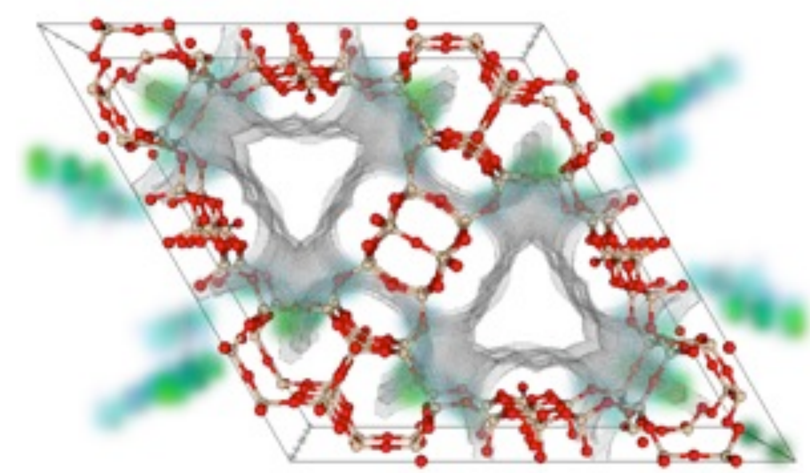
J. Kim and B. Smit, J. Chem. Theory Comput. **8** (7), 2336 (2012)

GPU: one isotherm in **1 minute**

Screening: zeolites

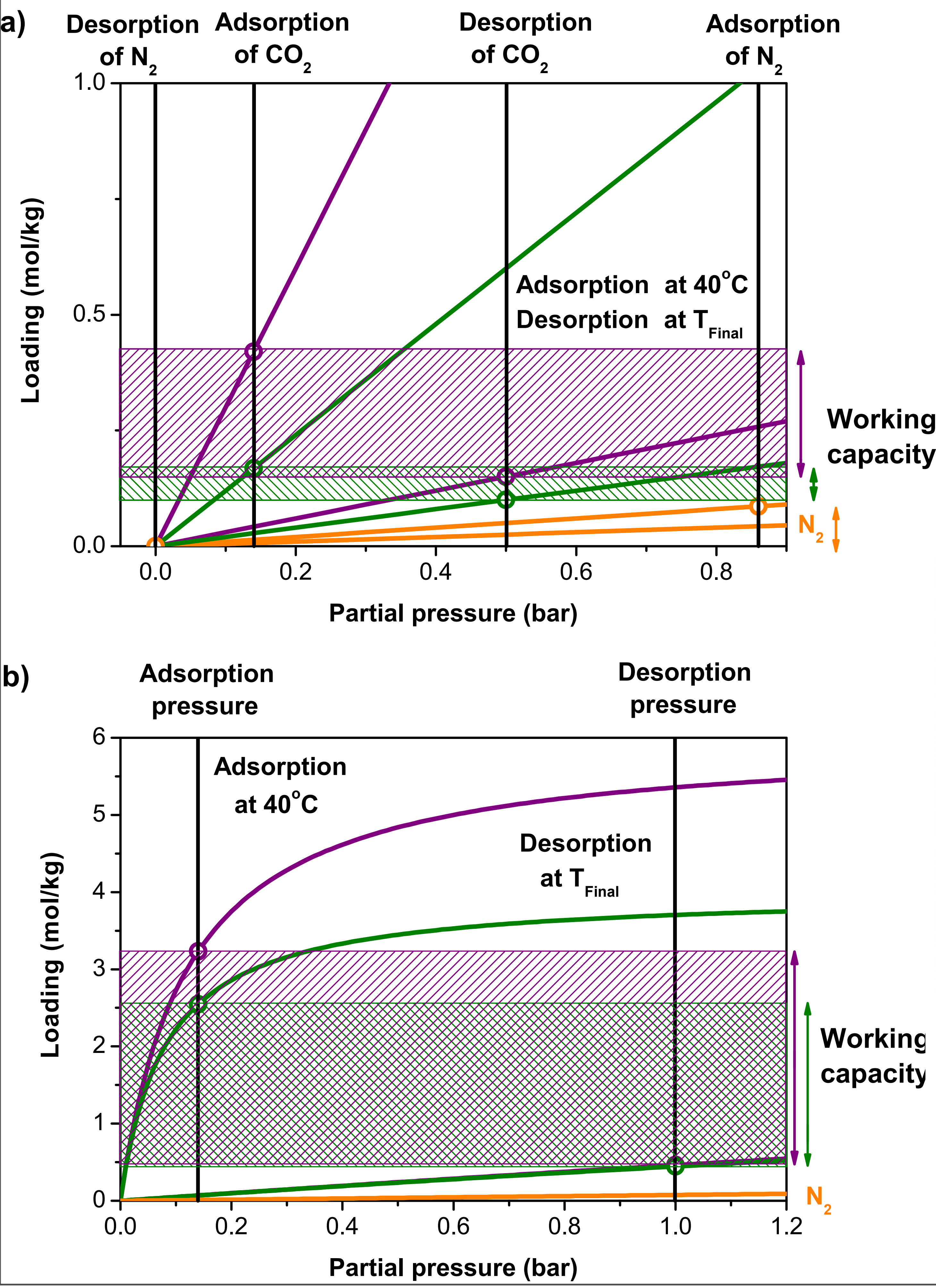


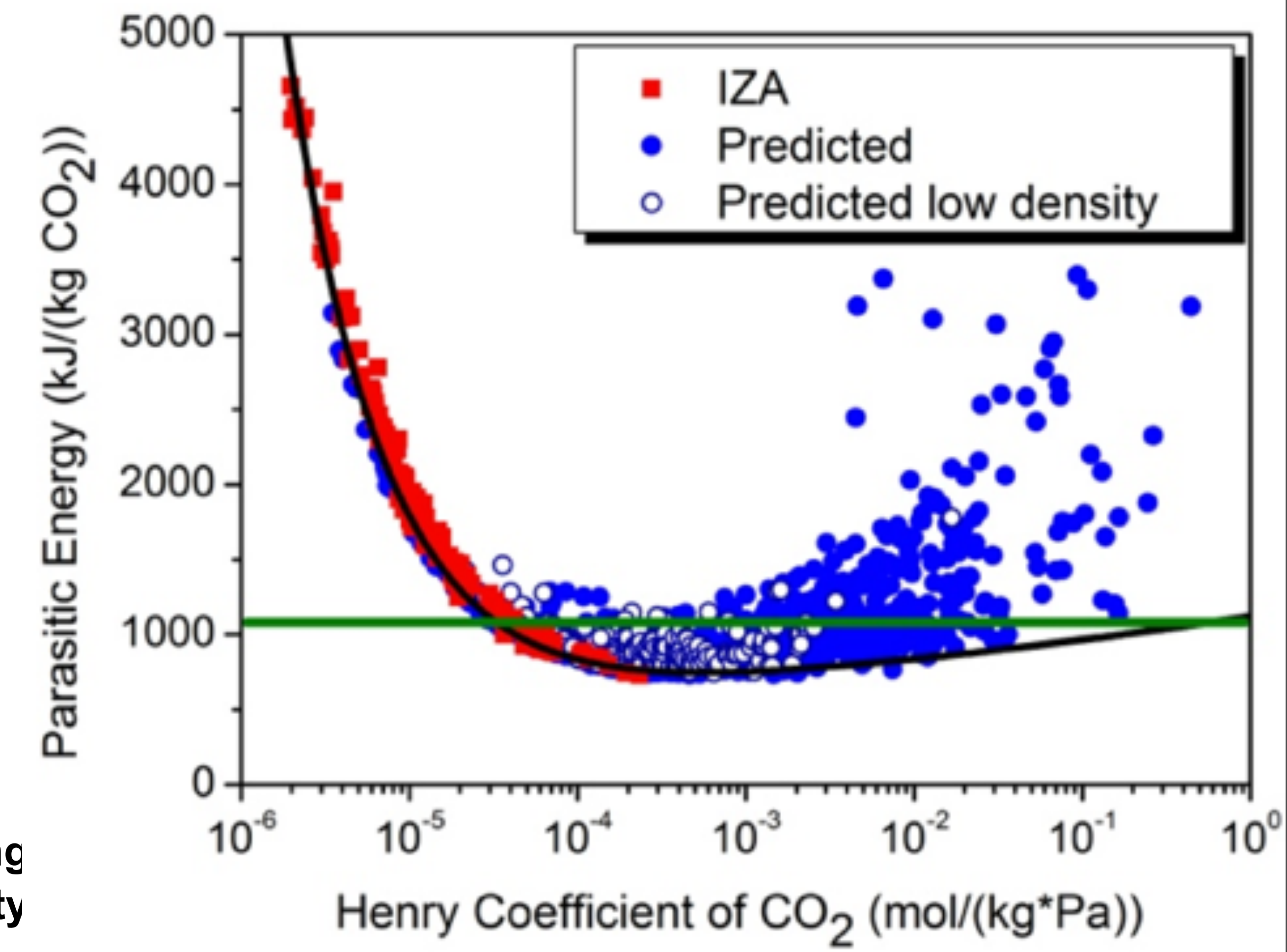




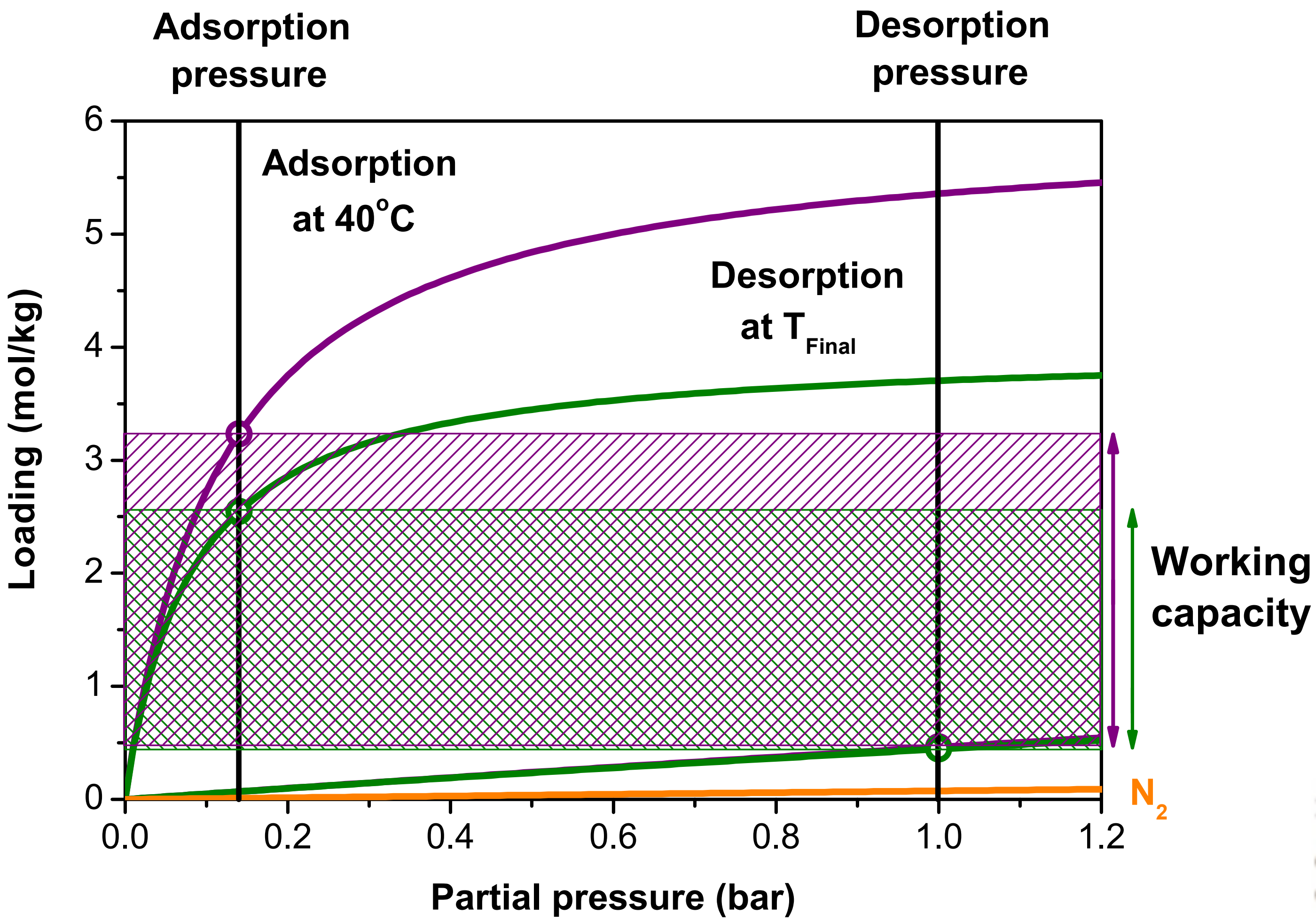
Screening: > 300,000 structures
Identified many structures with a significantly lower parasitic energy compared to the current technology

L.-C. Lin, et al, *In silico screening of carbon-capture materials* Nat Mater **11** (7), 633 (2012)


a)
Desorption of N_2
Adsorption of CO_2
Desorption of CO_2
Adsorption of N_2
Adsorption at 40°C
Desorption at T_{Final}
Working capacity
N_2
Loading (mol/kg)
Partial pressure (bar)
b)
Adsorption pressure
Desorption pressure
Adsorption at 40°C
Desorption at T_{Final}
Working capacity
N_2
Loading (mol/kg)
Partial pressure (bar)

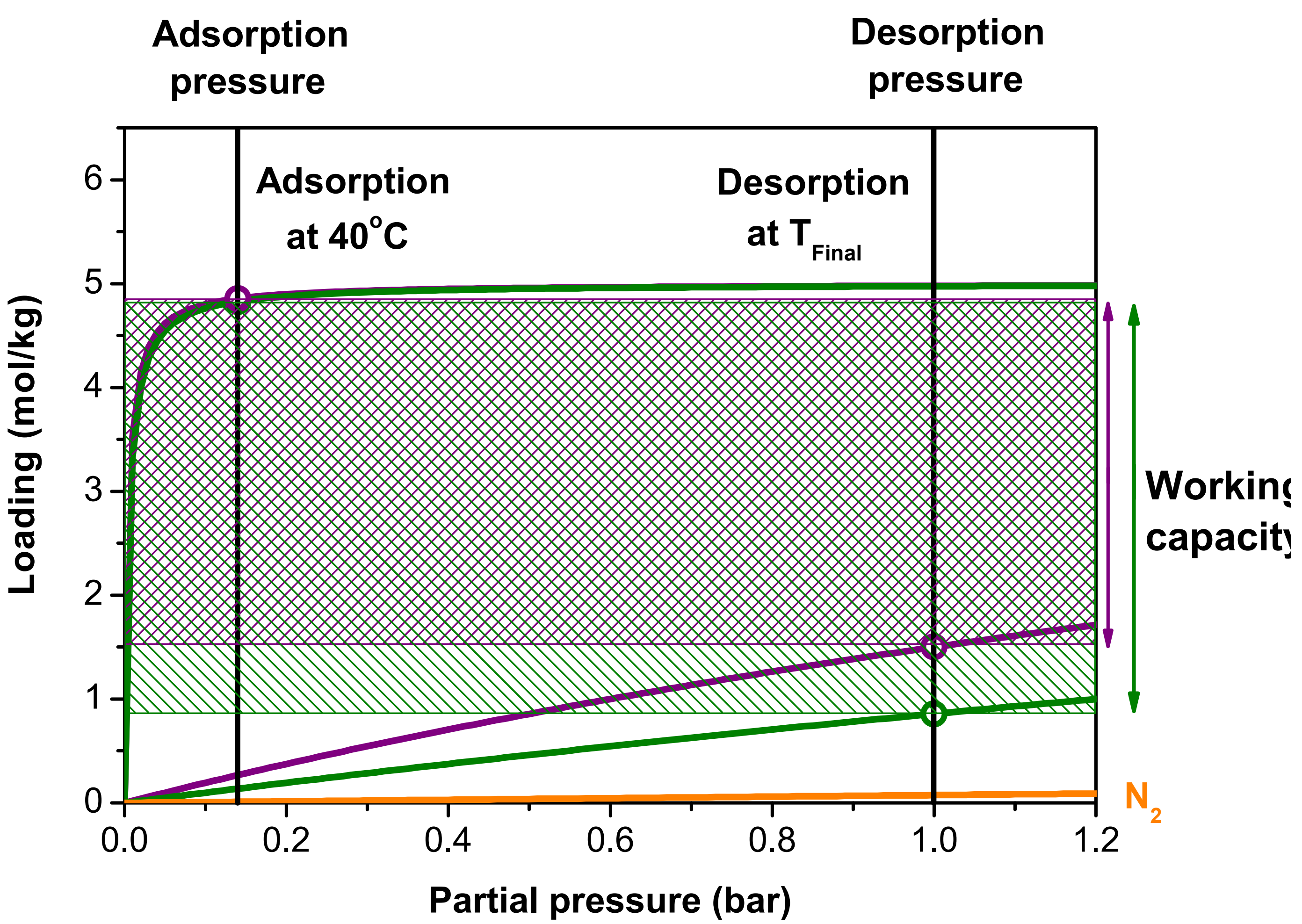

IZA
Predicted
Predicted low density
Parasitic Energy (kJ/(kg CO_2))
Henry Coefficient of CO_2 (mol/(kg*Pa))

(b)

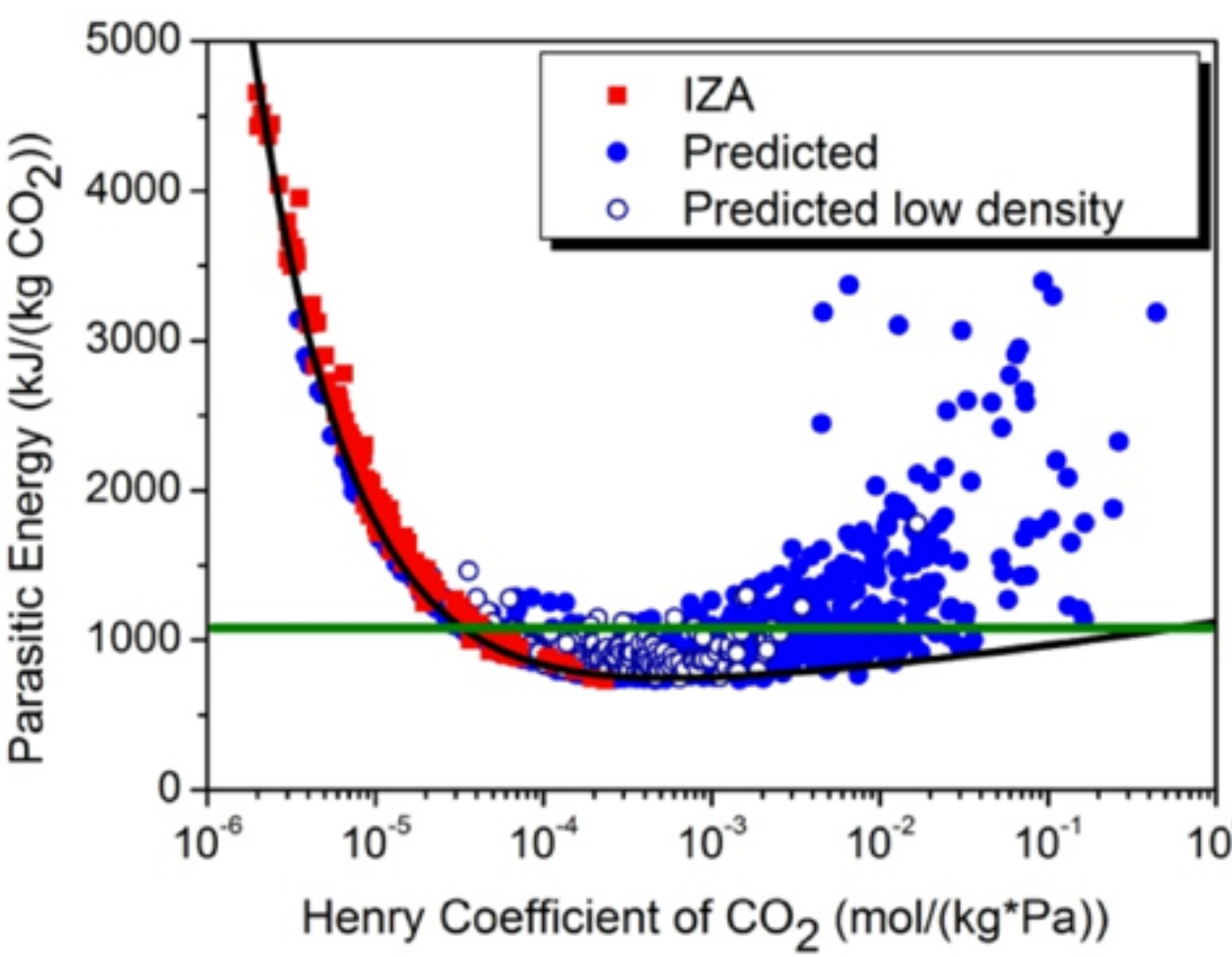


Adsorption pressure
Desorption pressure
Adsorption at 40°C
Desorption at T Final
Working capacity
N2
Loading (mol/kg)
Partial pressure (bar)

(c)



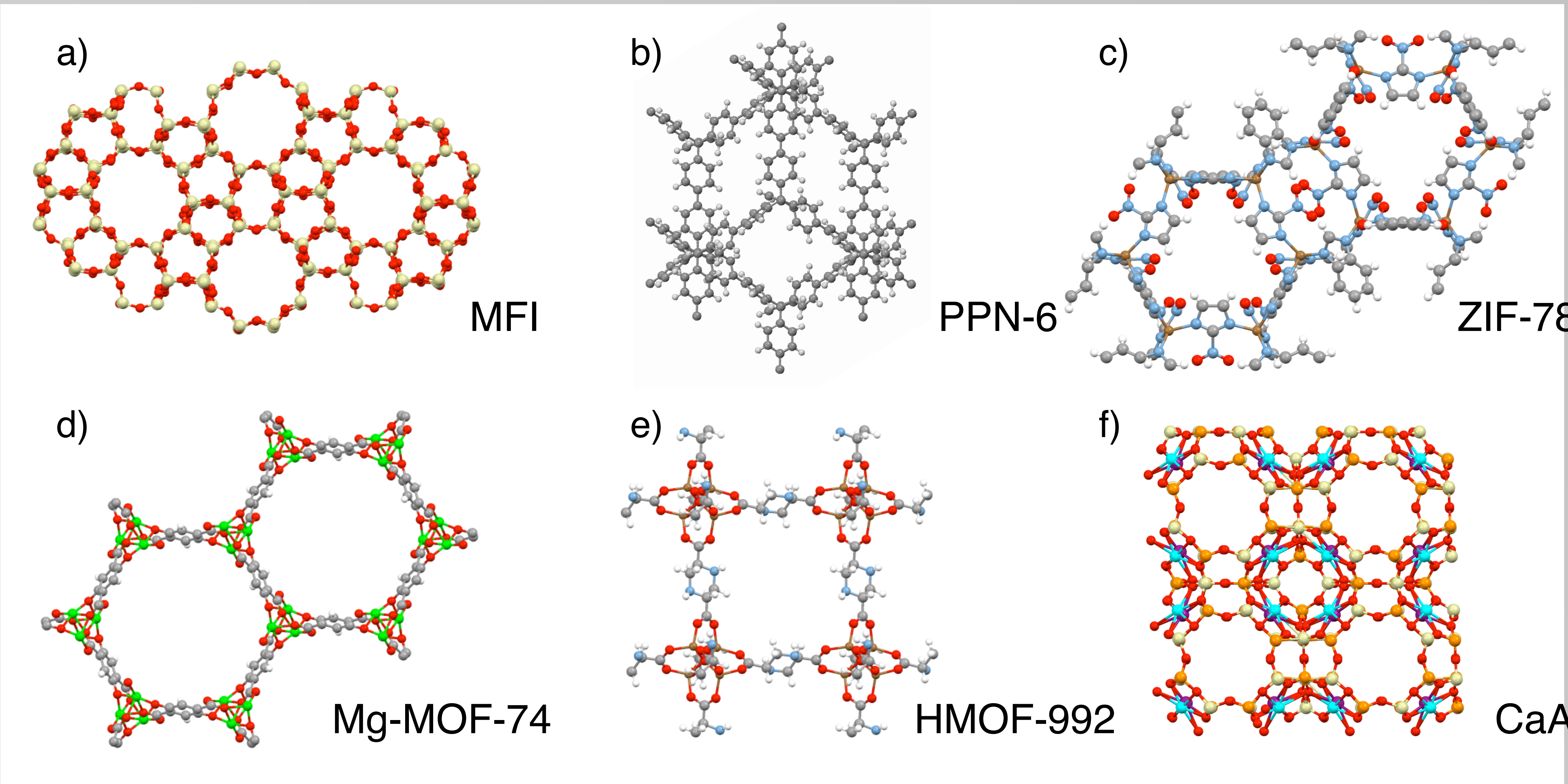
Adsorption pressure
Desorption pressure
Adsorption at 40°C
Desorption at T Final
Working capacity
N2
Loading (mol/kg)
Partial pressure (bar)

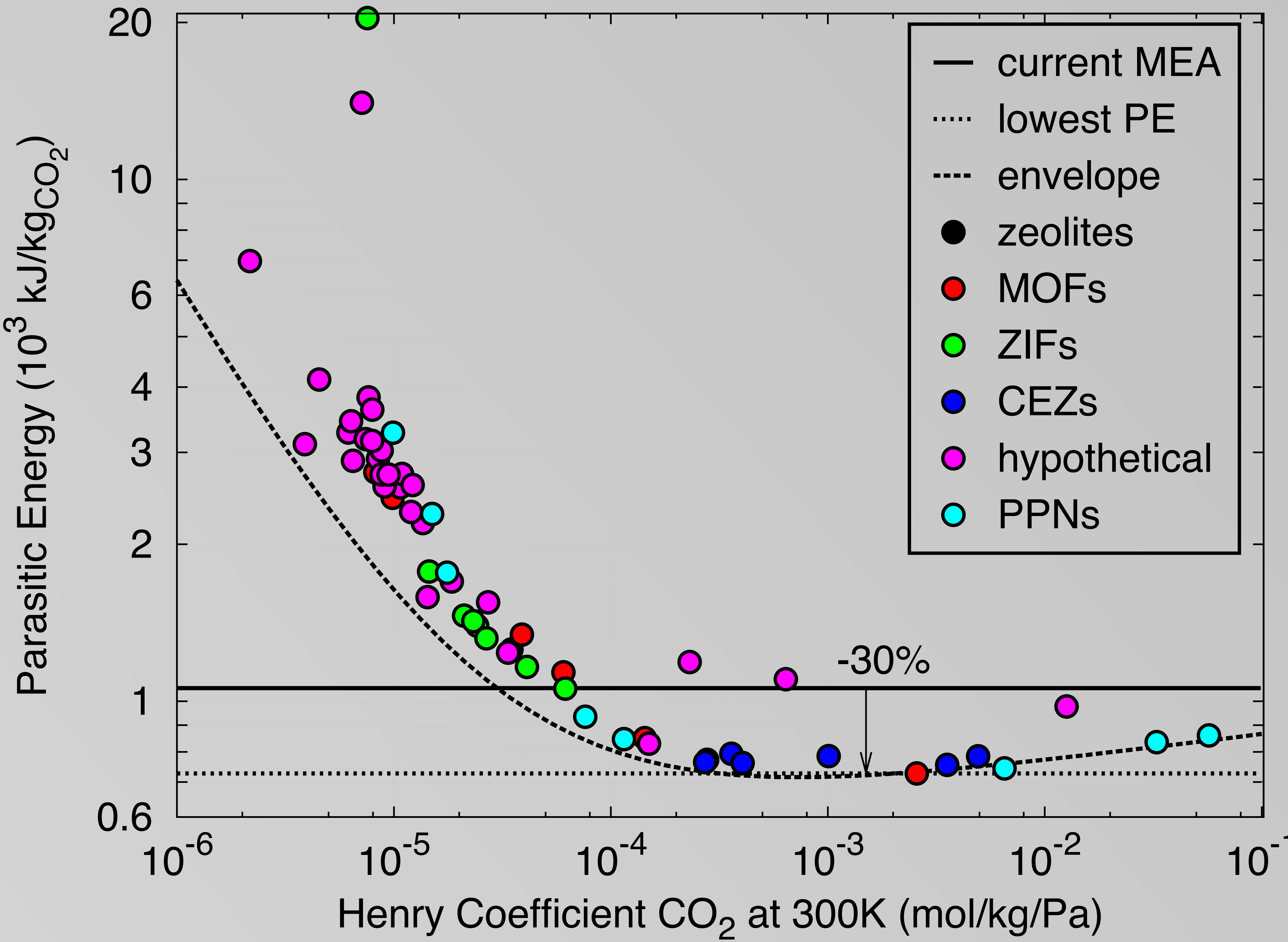


IZA
Predicted
Predicted low density
Parasitic Energy (kJ/(kg CO2))
Henry Coefficient of CO2 (mol/(kg*Pa))

…. and now MOFs

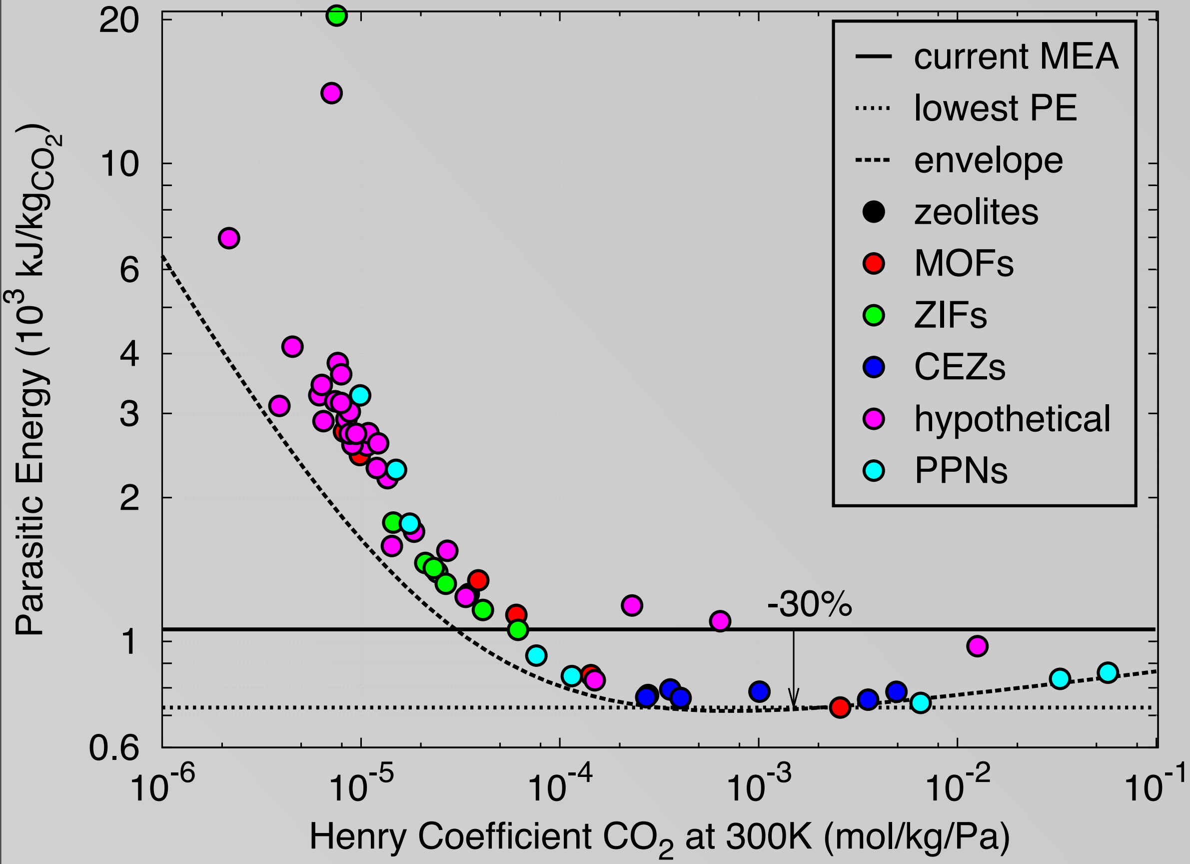
Materials synthesized in EFRC

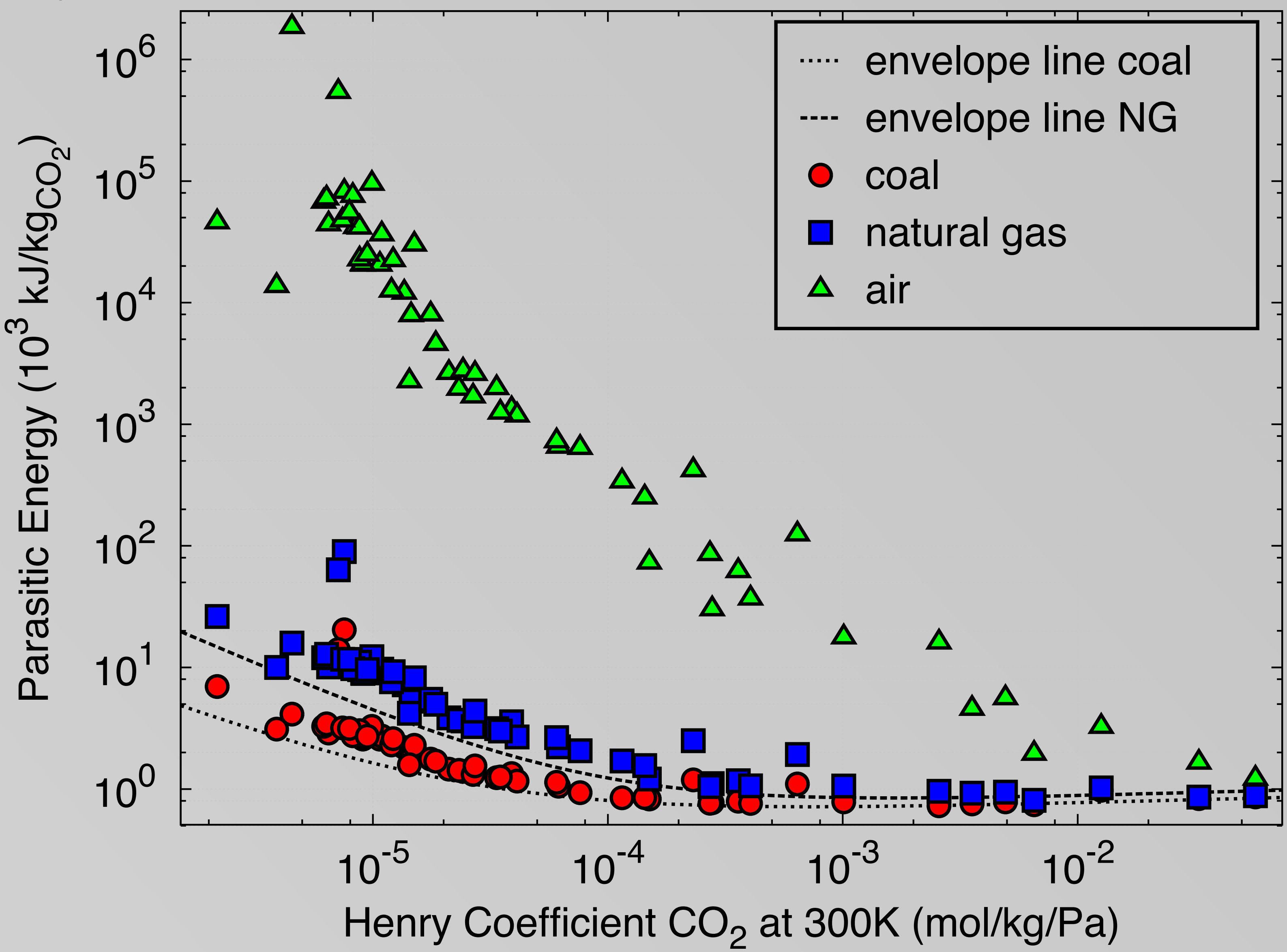




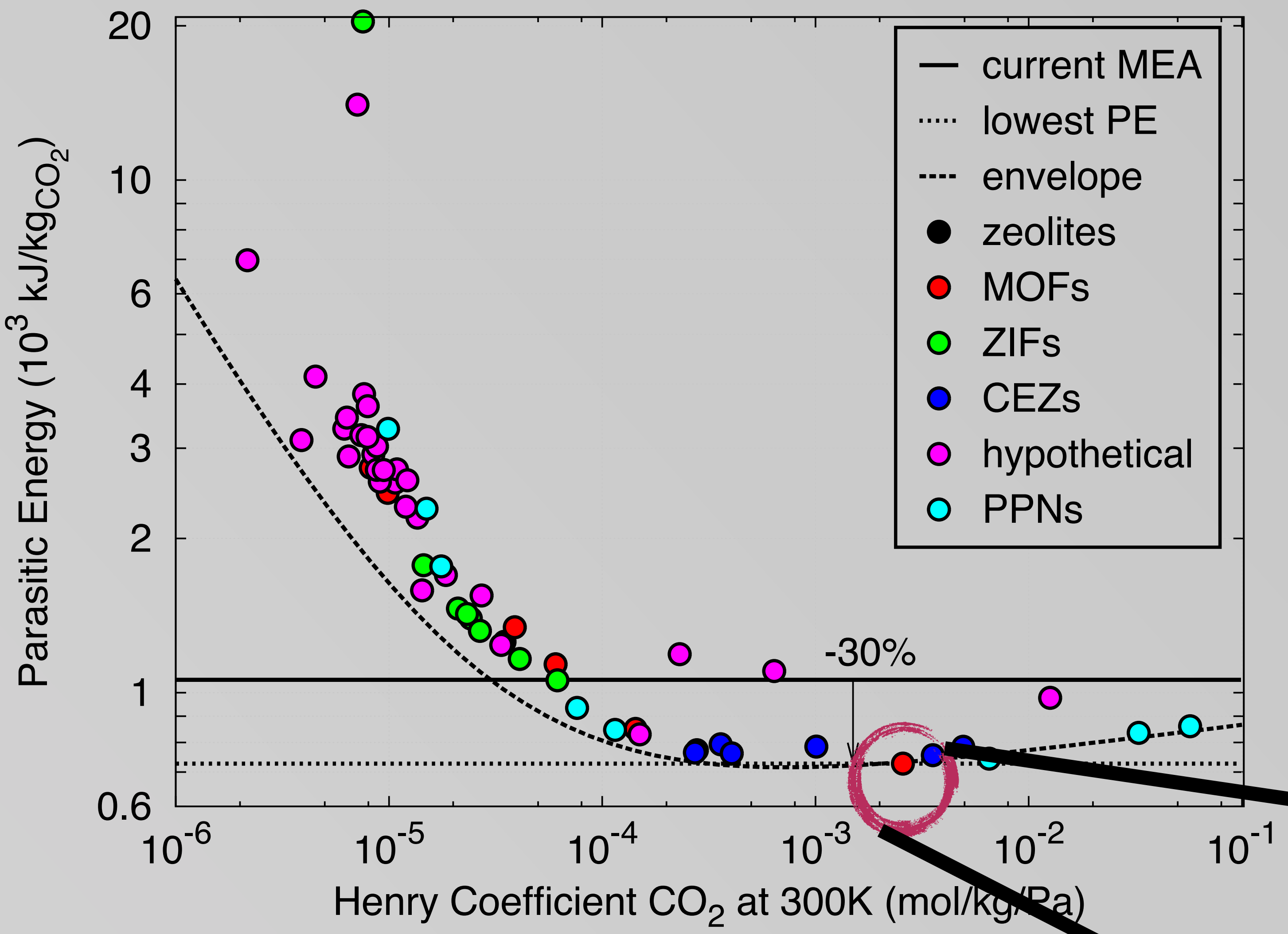
Parasitic Energy (10^3 kJ/kg_{CO_2})
20
10
6
4
3
2
1
0.6
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
Henry Coefficient CO_2 at 300K (mol/kg/Pa)
current MEA
lowest PE
envelope
zeolites
MOFs
ZIFs
CEZs
hypothetical
PPNs
-30%

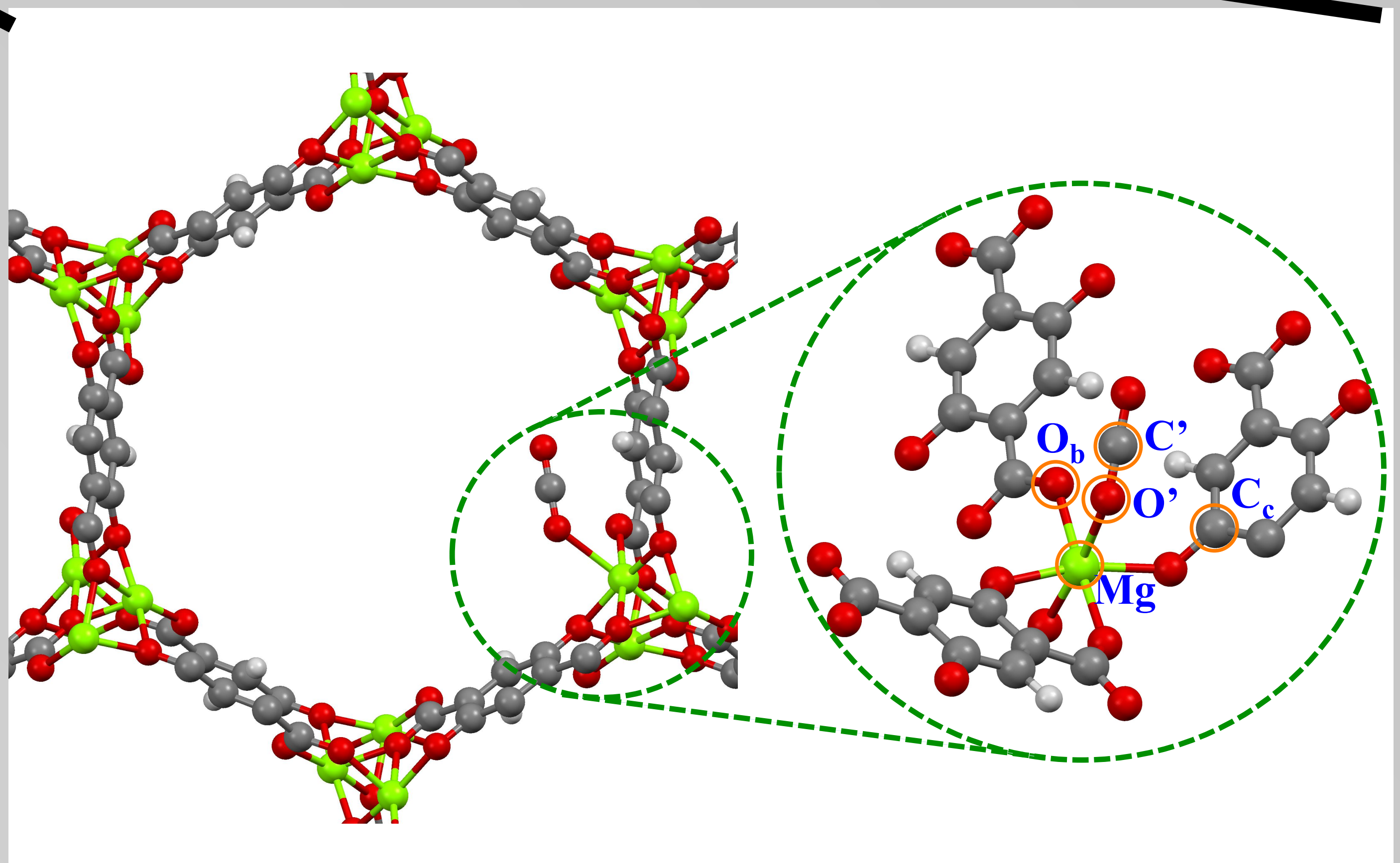
Coal, natural gas , and air



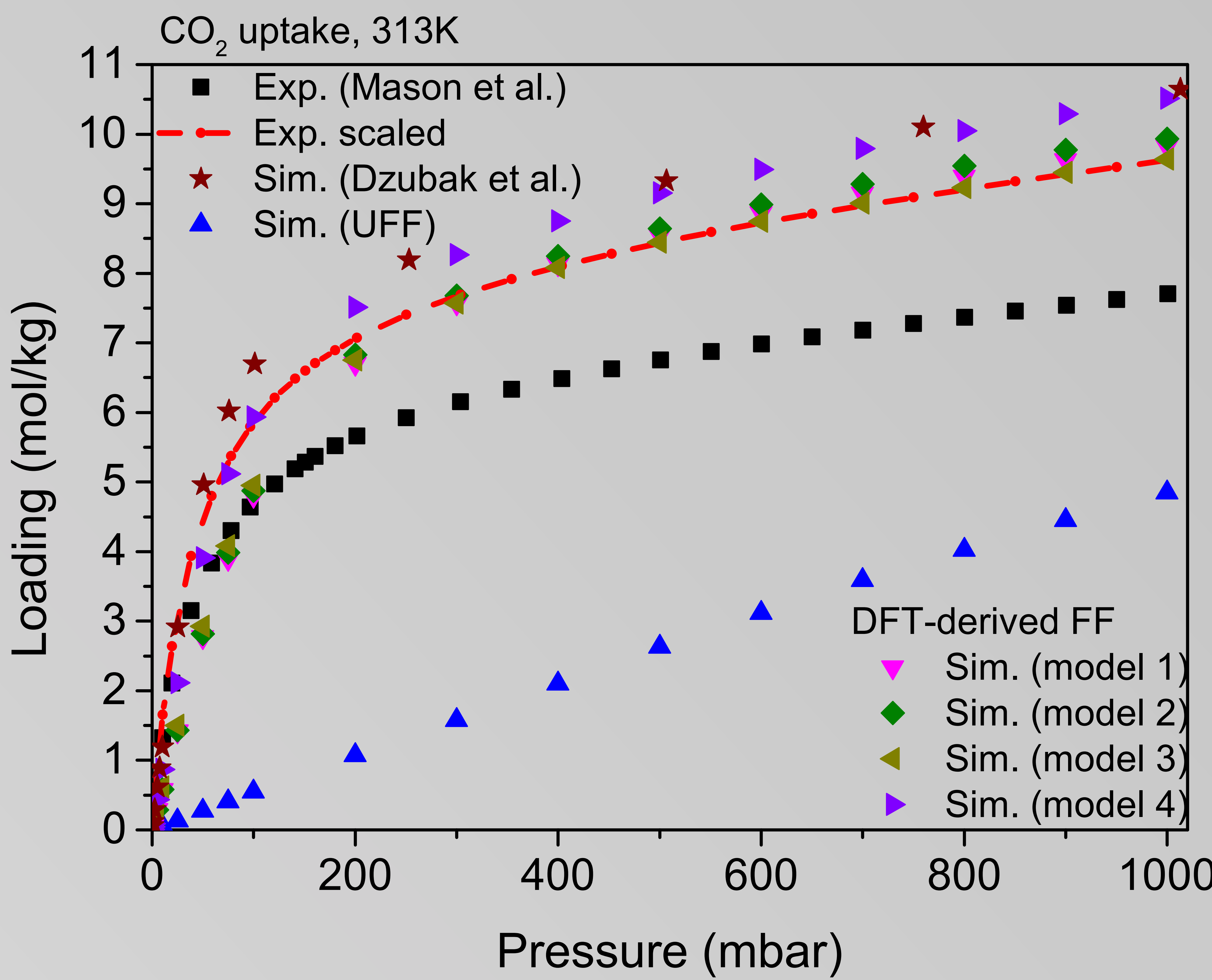


Open Metal Sites



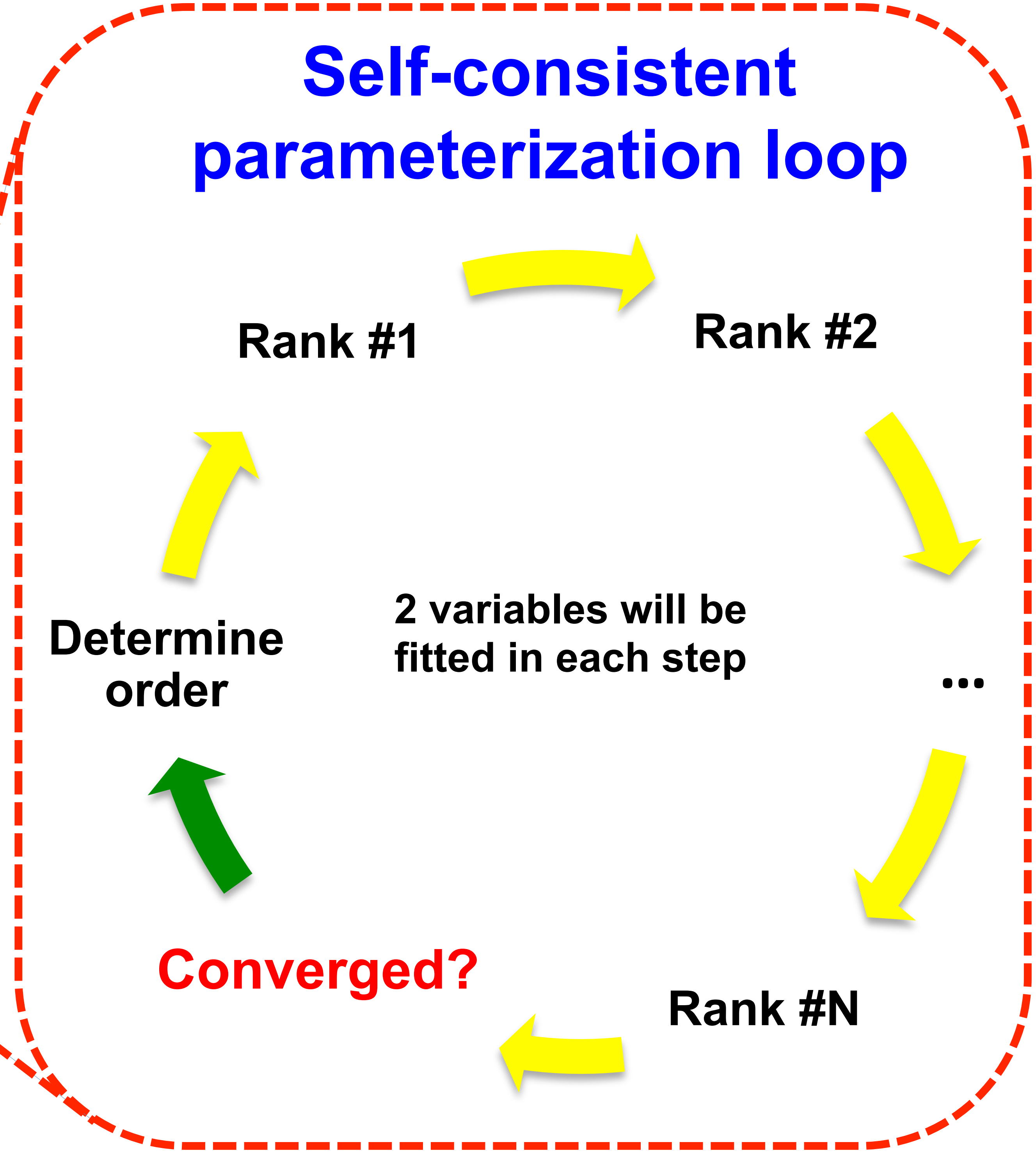


CO_2 adsorption



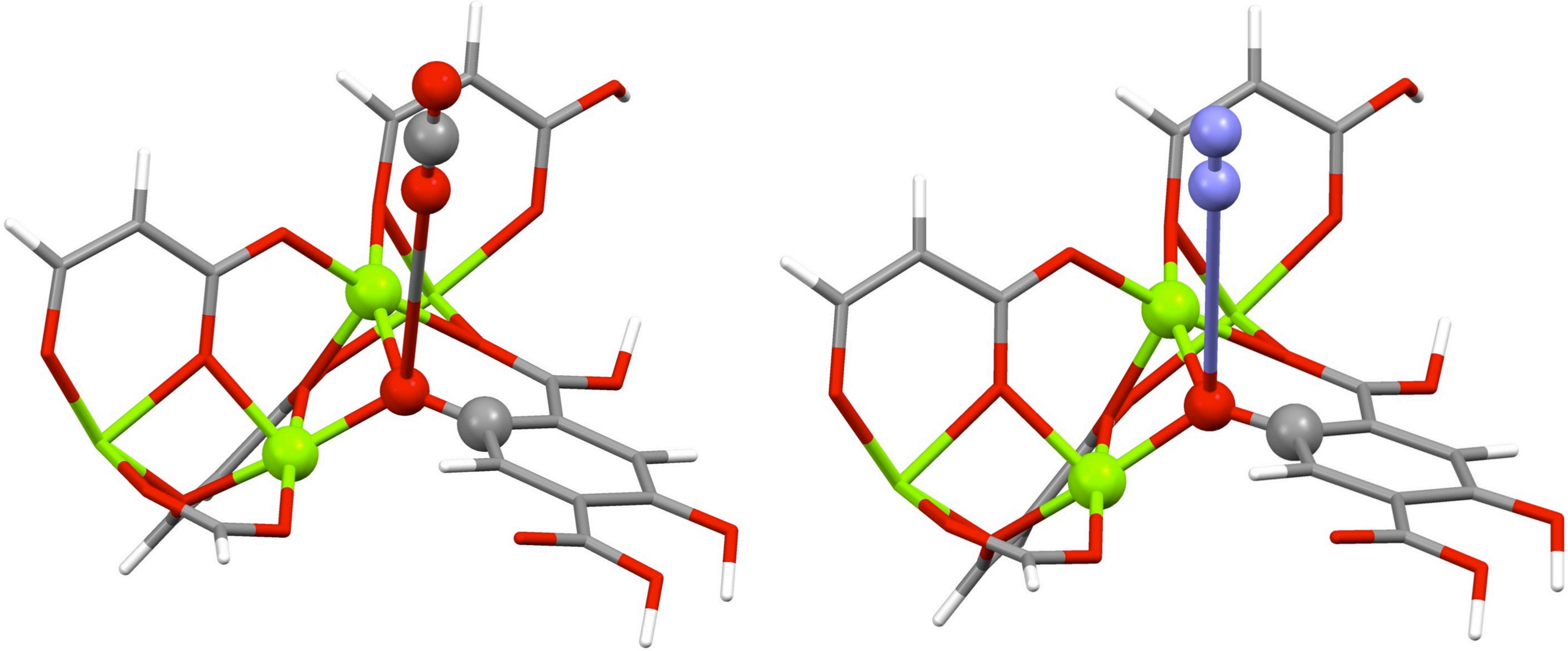
Force-field

- **Structure optimization (DFT)**
- ↓
- **Atom-types identification**
- ↓
- **Approaching paths determination**
- ↓
- **Interaction energy calculations (DFT)**
- ↓
- **Energy decomposition**
- ↓
- **Force-field parameterization (S_g, Repulsion)**
- ↓
- **Classical molecular simulation (MC/MD)**



Force Fields

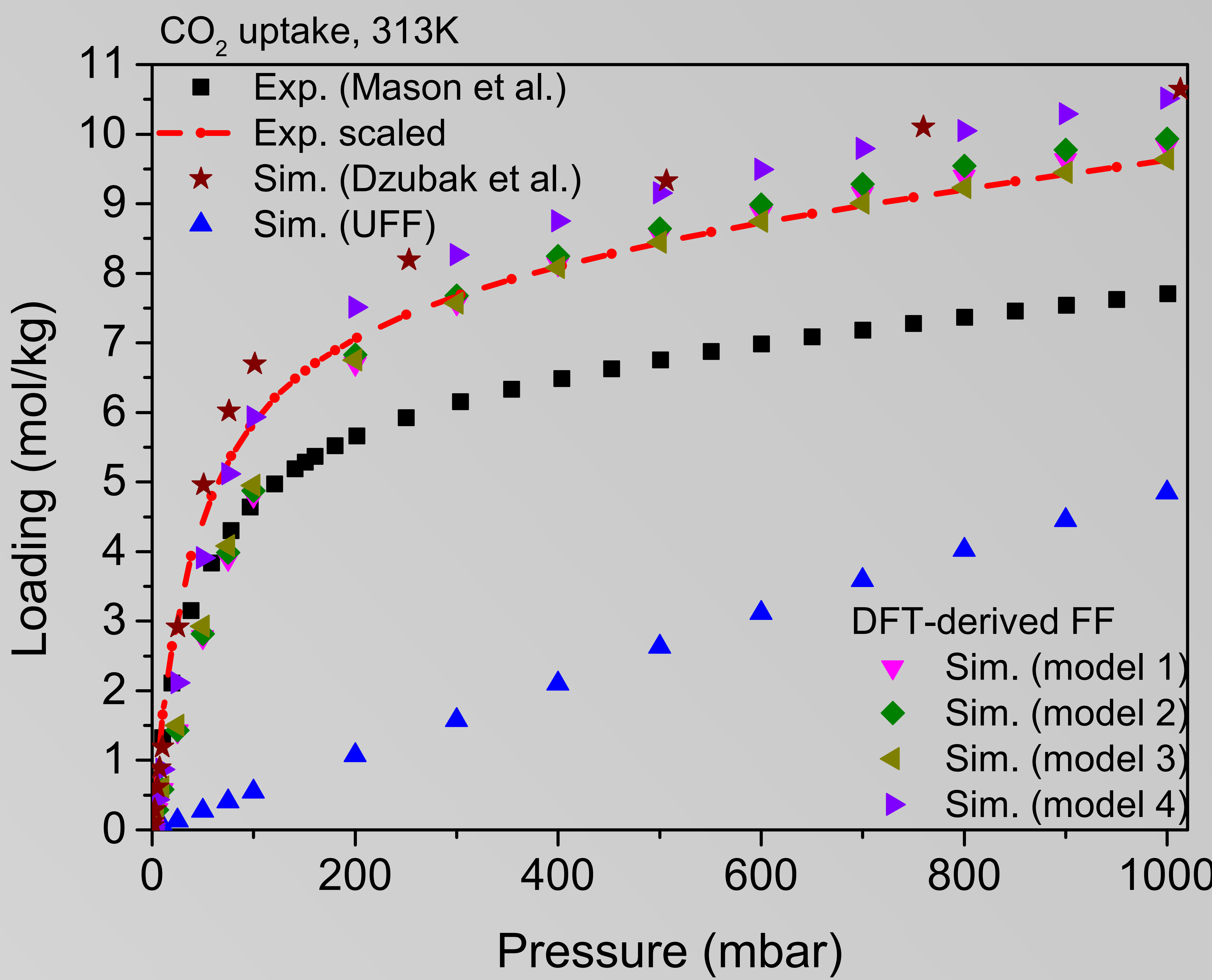
Quantum calculations (MP2) +
NEMO decomposition

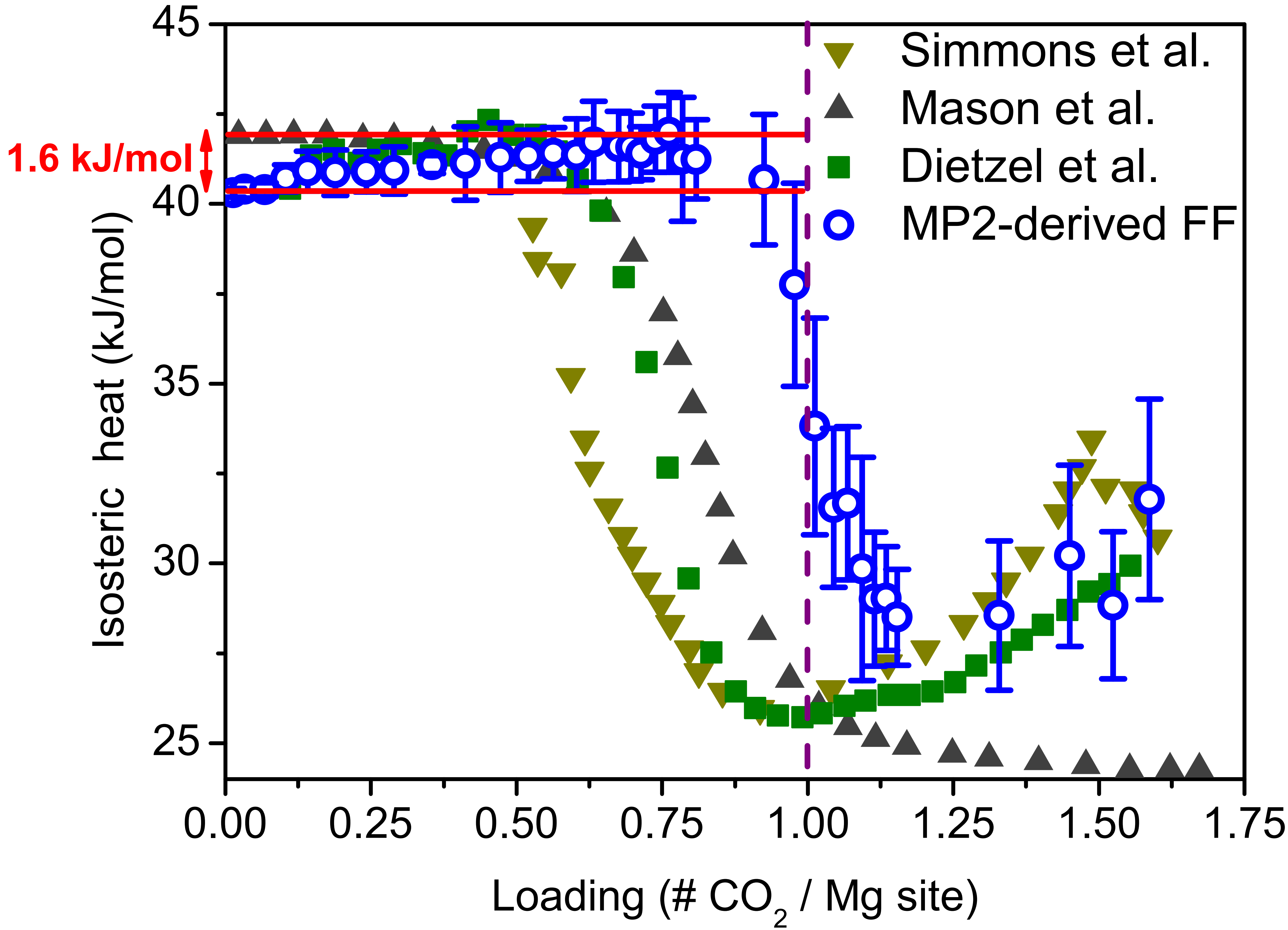


with Laura Gagliardi (U Minnesota)

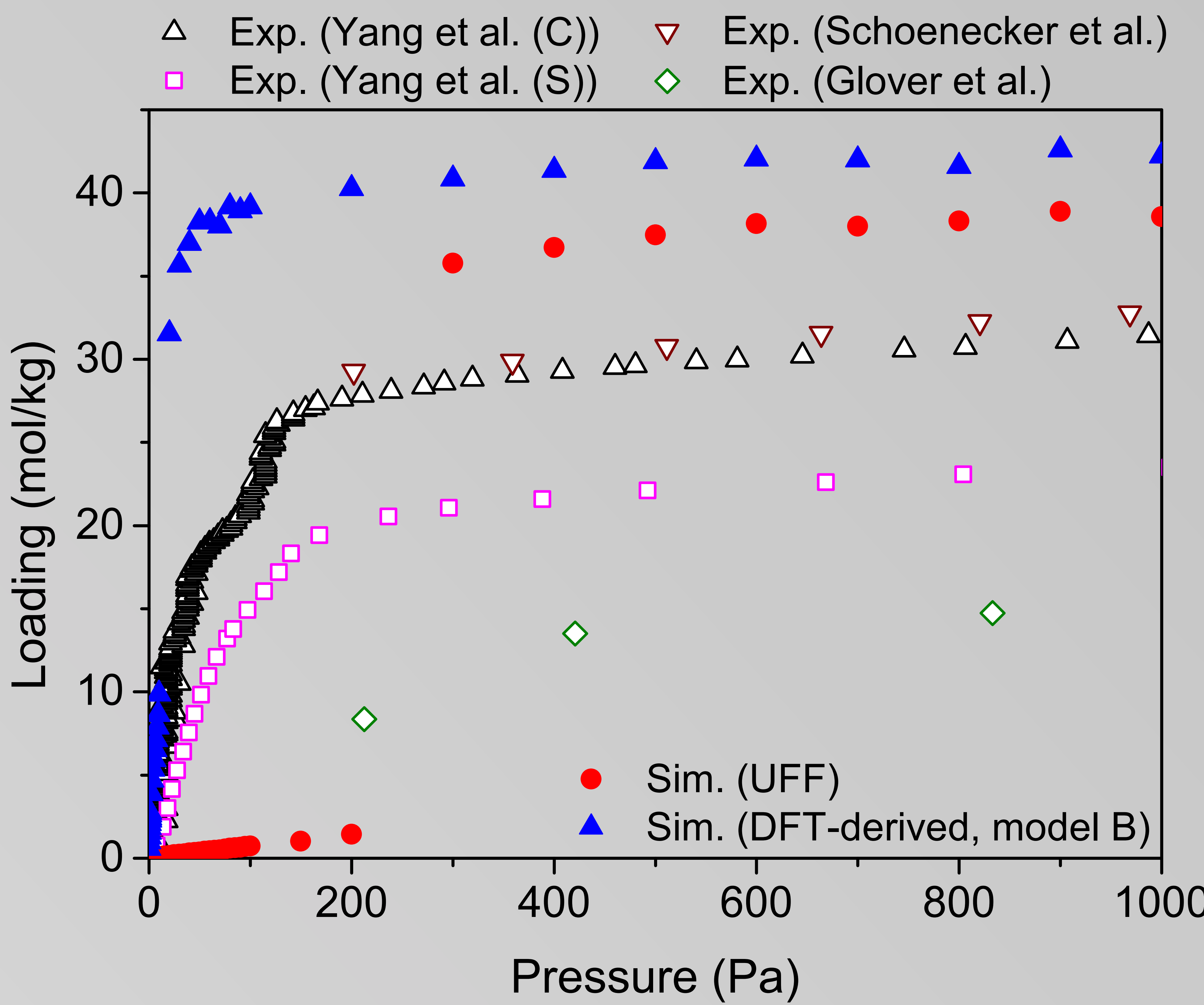
A. Dzubak, et al, Ab-initio Carbon Capture in Open-Site Metal Organic Frameworks Nat Chem (2012) http://dx.doi.org/0.1038/NCHEM.1432

CO_2 adsorption



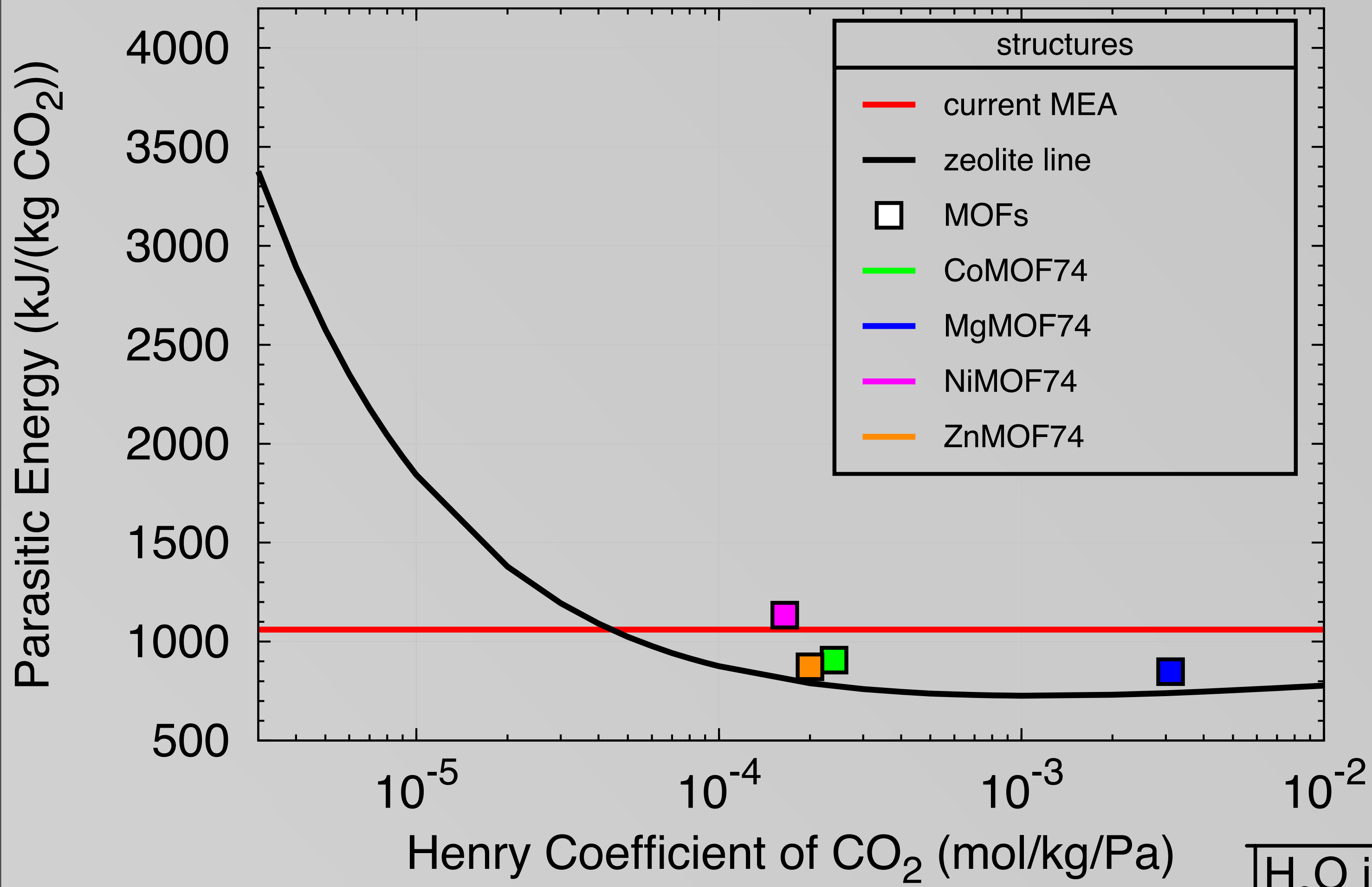

1.6 kJ/mol
Simmons et al.
Mason et al.
Dietzel et al.
MP2-derived FF
Isosteric heat (kJ/mol)
Loading (# CO2 / Mg site)
45
40
35
30
25
0.00
0.25
0.50
0.75
1.00
1.25
1.50
1.75

Water isotherms?

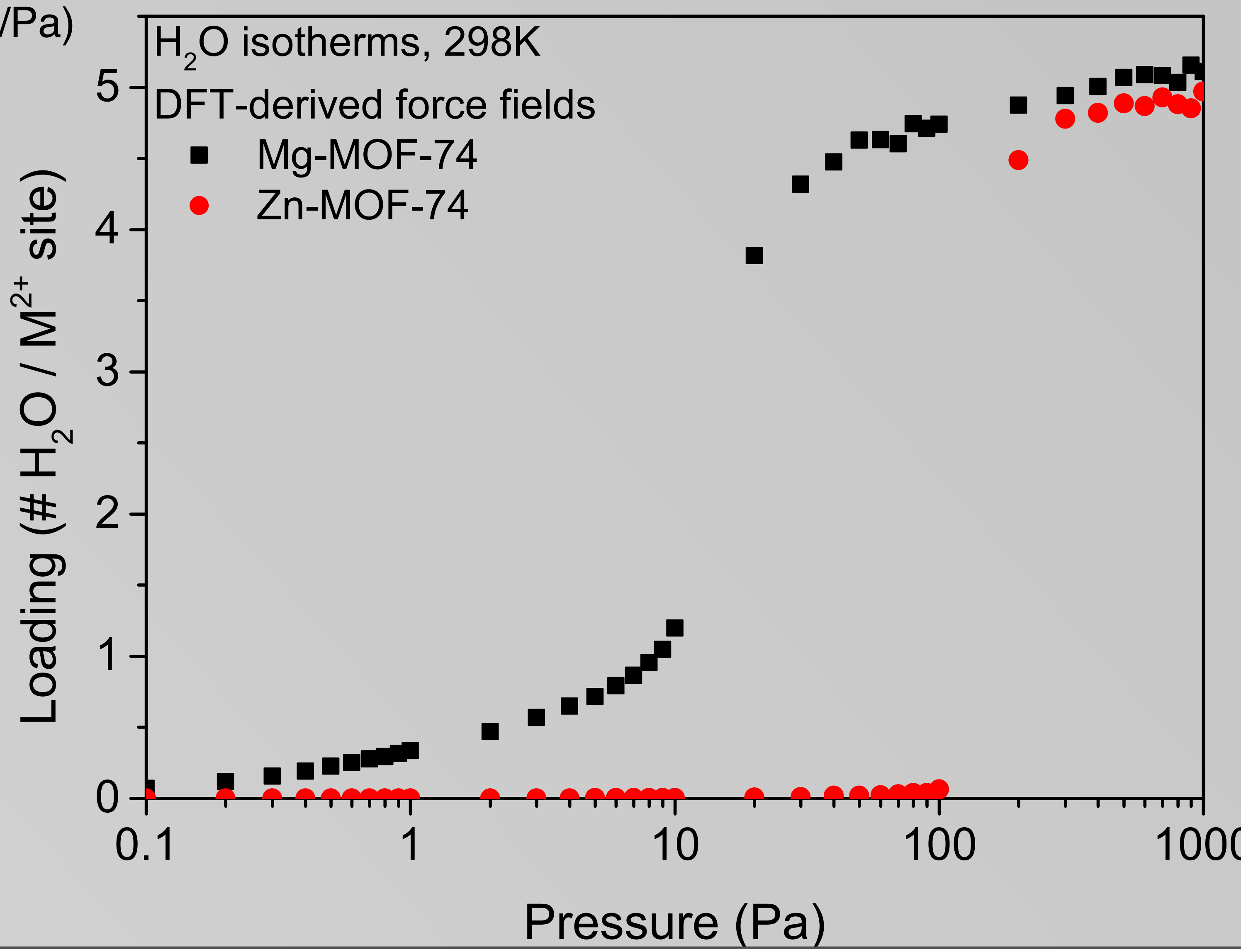


L.-C. Lin, K. Lee, L. Gagliardi, J. B. Neaton, B. Smit, *J. Chem. Theory Comput.* **2014**.

Mg versus Zn

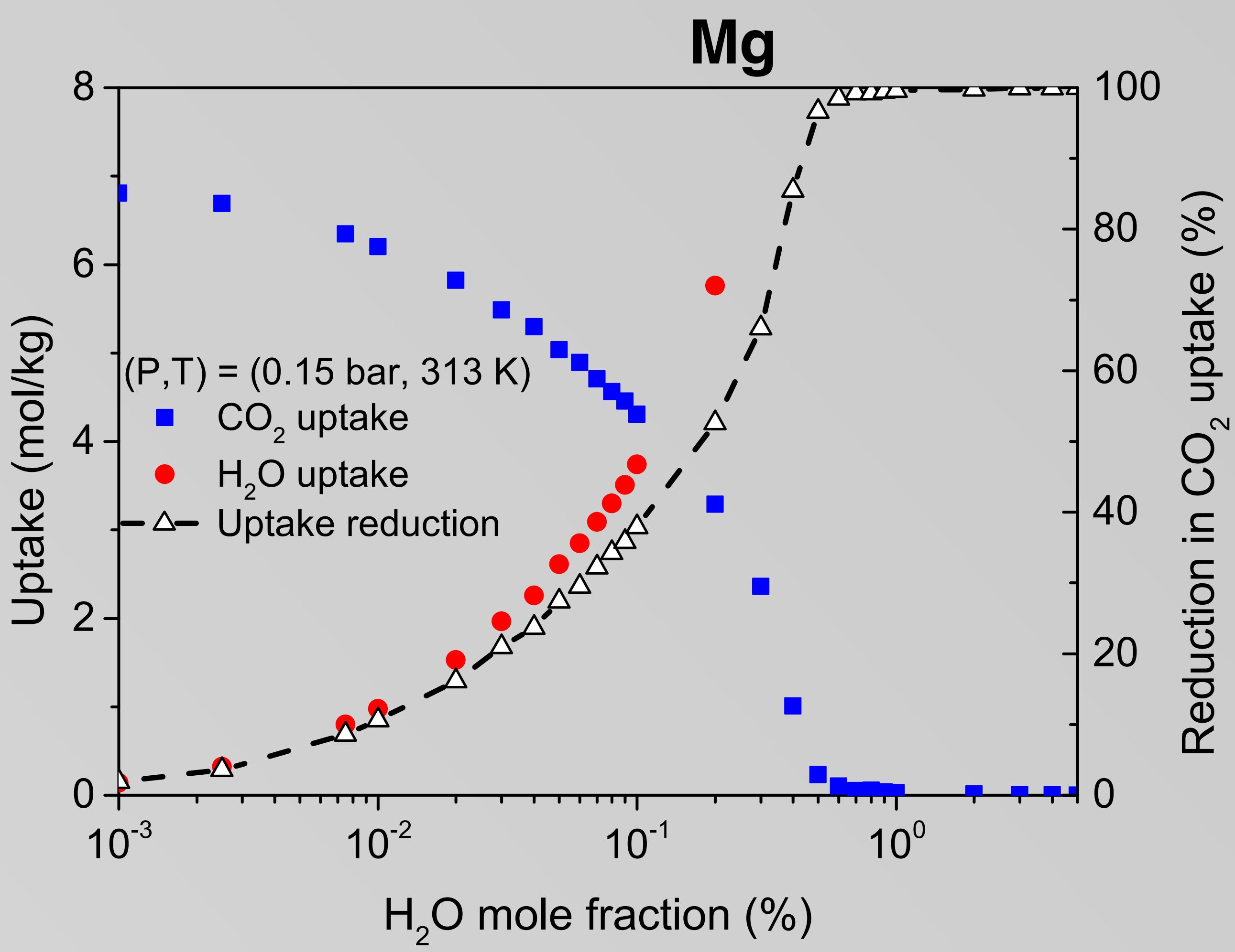


structures
current MEA
zeolite line
MOFs
CoMOF74
MgMOF74
NiMOF74
ZnMOF74
Parasitic Energy (kJ/(kg CO_2))
Henry Coefficient of CO_2 (mol/kg/Pa)
4000
3500
3000
2500
2000
1500
1000
500
10^{-5}
10^{-4}
10^{-3}
10^{-2}

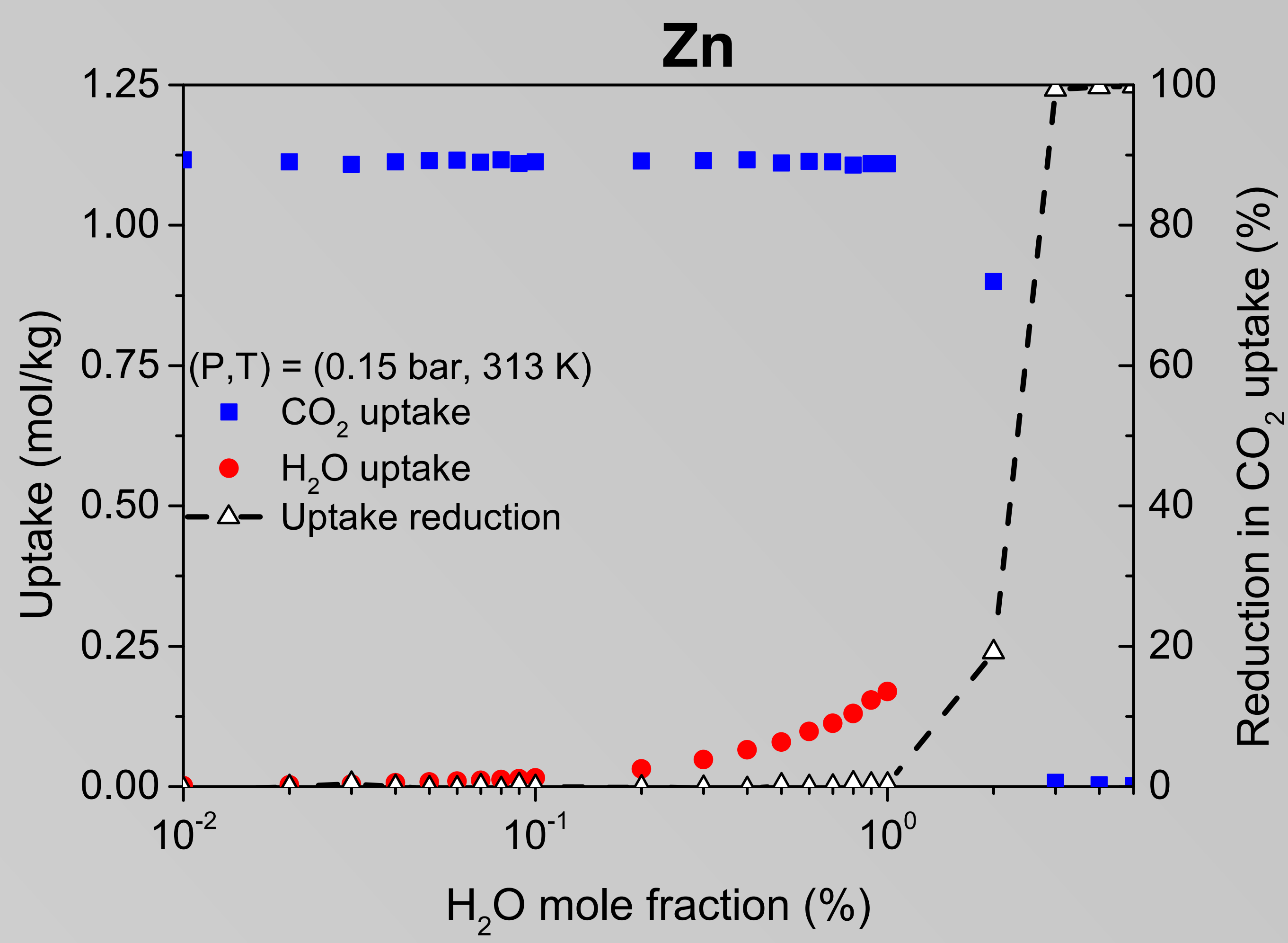


H_2O isotherms, 298K
DFT-derived force fields
Mg-MOF-74
Zn-MOF-74
Loading (# H_2O / M^{2+} site)
Pressure (Pa)
0
1
2
3
4
5
0.1
1
10
100
1000

Water-CO_2



Mg
(P,T) = (0.15 bar, 313 K)
CO2 uptake
H2O uptake
Uptake reduction
Uptake (mol/kg)
Reduction in CO2 uptake (%)
H2O mole fraction (%)
0
2
4
6
8
0
20
40
60
80
100
10-3
10-2
10-1
100



Zn
(P,T) = (0.15 bar, 313 K)
CO2 uptake
H2O uptake
Uptake reduction
Uptake (mol/kg)
Reduction in CO2 uptake (%)
H2O mole fraction (%)
0.00
0.25
0.50
0.75
1.00
1.25
0
20
40
60
80
100
10-2
10-1
100

Conclusions

- Parasitic energy is a useful concept to rank materials
  - best material adsorption not to strong/not to weak
  - Natural gas: higher adsorption is better
- EFRC: we can tailor make the best adsorbent if flue gasses where mixtures of N_2/CO_2
- Open metal sites
  - Very interesting chemistry: conventional force fields do not work
  - Systematic methods to develop force fields
  - Effect of water
- Materials Genome:
  - Intelligence versus brute force ....
  - Screening for best materials: what can be obtained

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frontiers of science

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Defining the Frontiers

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Easton, MA

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Berend Smit

Vice Chair:
Ah-Hyung (Alissa) Park

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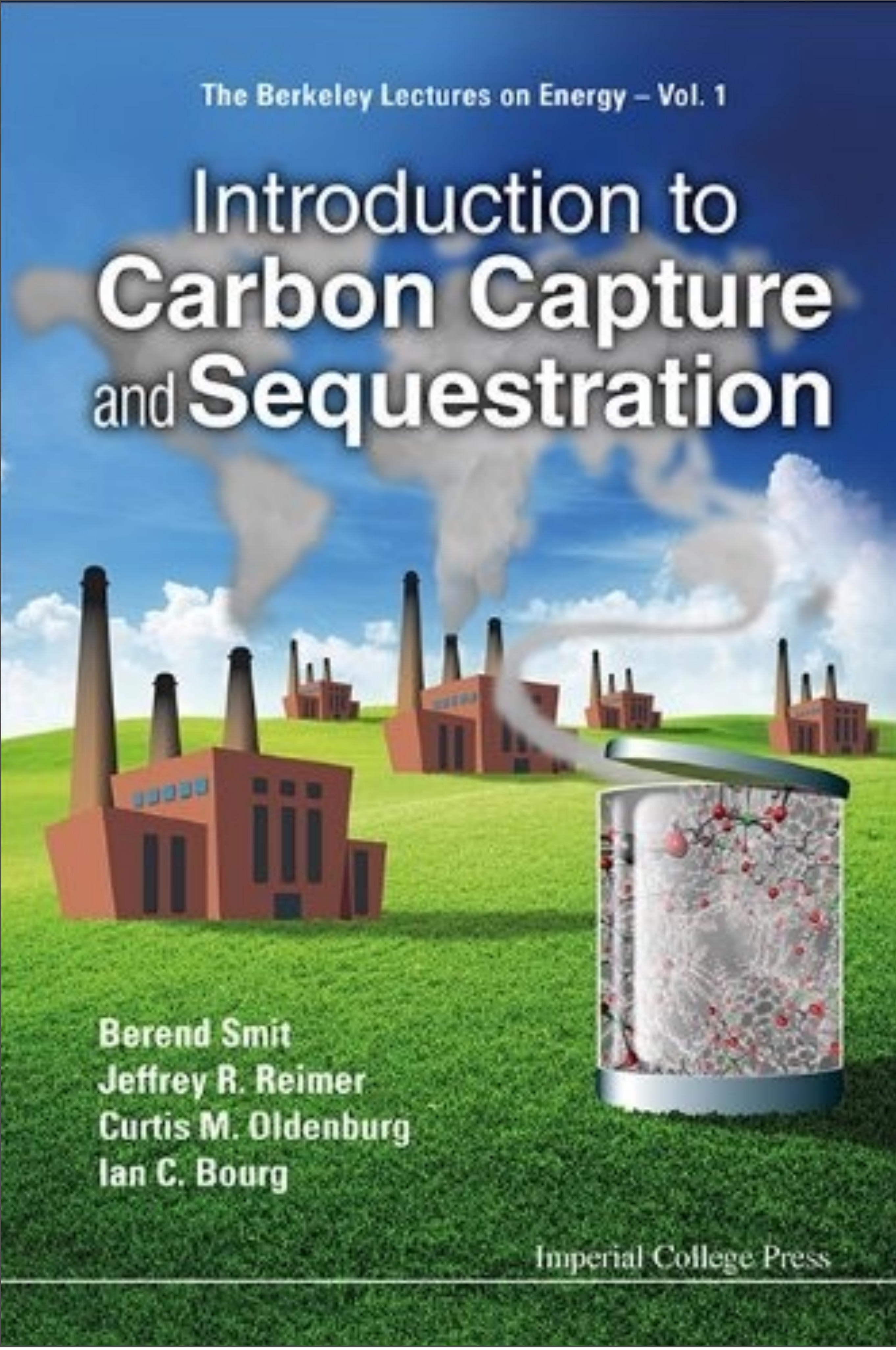
May 31 – June 5, 2015



Buy the book!

B. Smit, J. R. Reimer, C. M. Oldenburg, I. C. Bourg, *Introduction to Carbon Capture and Sequestration*, Imperial College Press, London, **2014**.

Thanks!

- Jihan Kim, Li-Chiang Lin, Joe Swisher, Roberta Poloni, Adam Berger, Allison Dzubak, Richard Martin

- Jeff Long (UC Berkeley)
- Jeff Neaton (LBNL)
- Jeff Reimer (UC Berkeley)
- Maciej Haranczyk (LBNL)
- Mike Deem (Rice)
- Laura Gagliardi (U Minessota)
- Abhoyjit Bhown (EPRI)

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