二氧化碳捕集利用与封存技术国际研讨会，4月26日，2017

Fundamentals of CO_2 Safe Geological Storage and Efficient Utilization

二氧化碳地质封存与利用的基础研究

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Outline

1. **Background and Introduction**
2. **CO_2 Storage and Two-Phase Flow in Porous Media**
3. **CO_2 Enhanced Geothermal Systems and Heat Transfer in Fractures**
4. **CO_2 Enhanced Shale Gas and Mass Transfer in Nano Pores**
5. **Summary**

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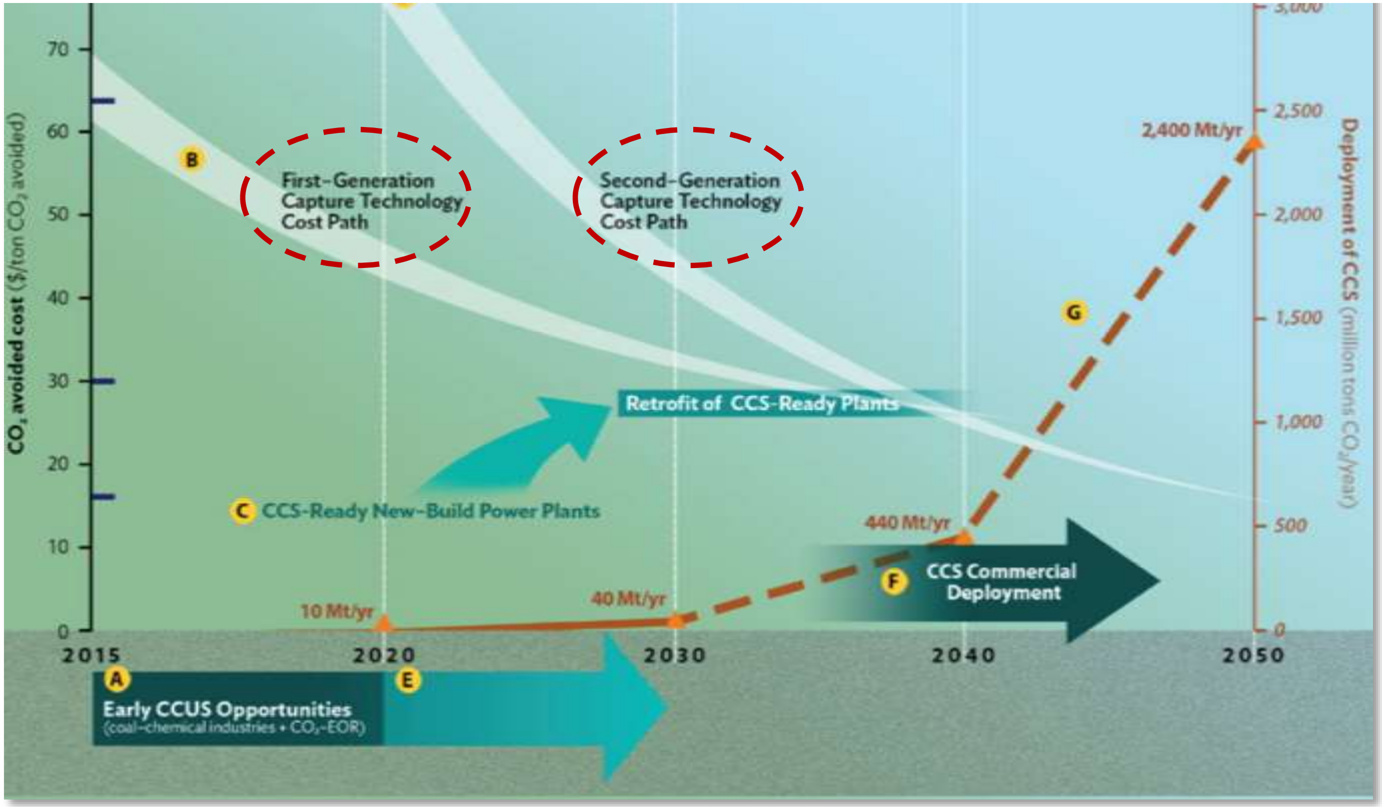
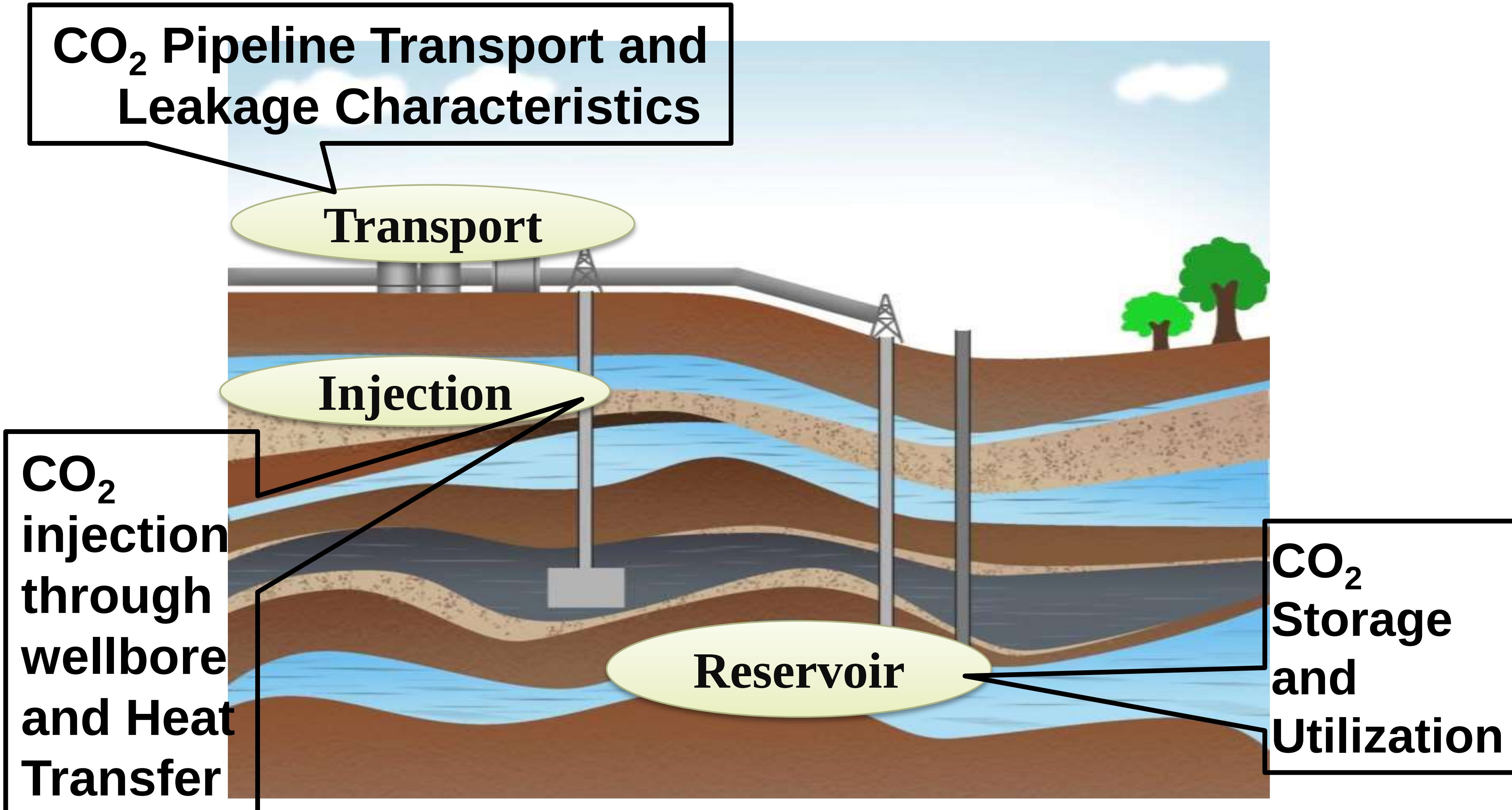
Background and Introduction

Roadmap for CCS Demonstration and Deployment in China, released on Climate Change Conference in Paris, 2015



- **New CO_2 capture technology with low energy consumption**
- **New CO_2 utilization and long-term safe storage**

Research Contents（CTUS）



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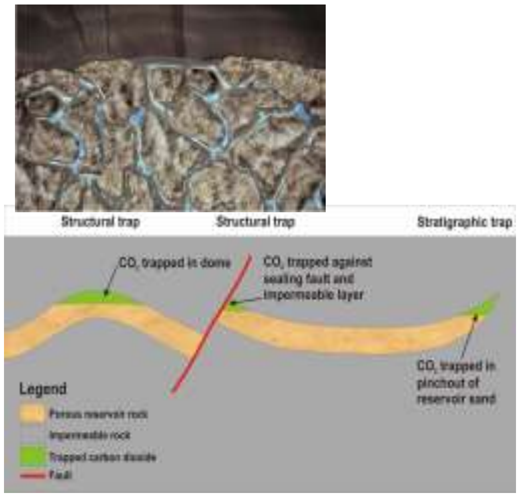
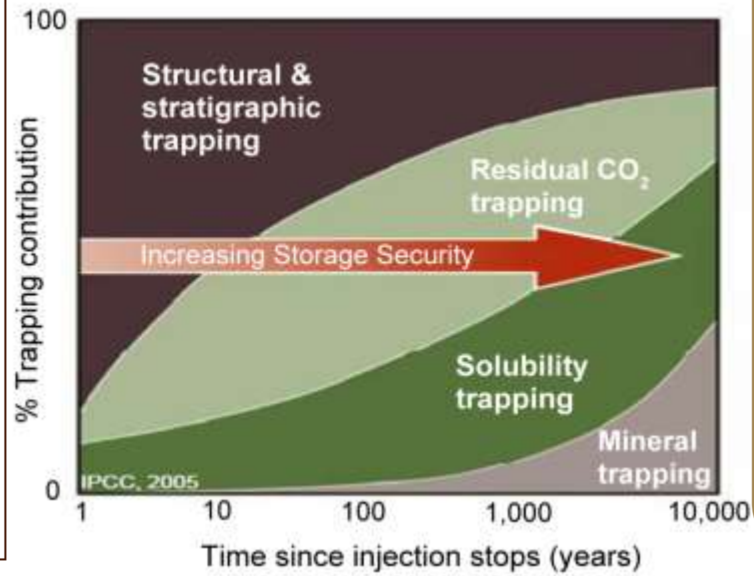
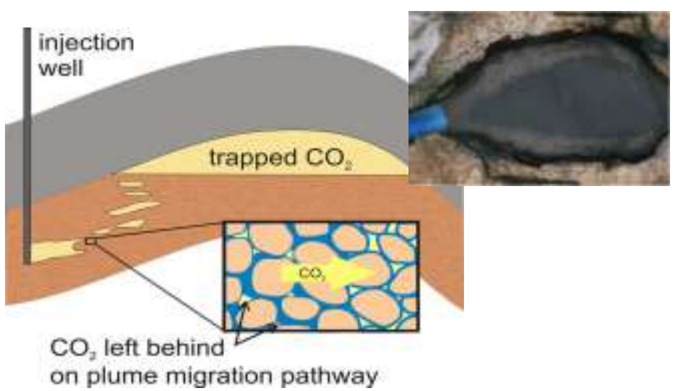
CO_2 Geological Storage



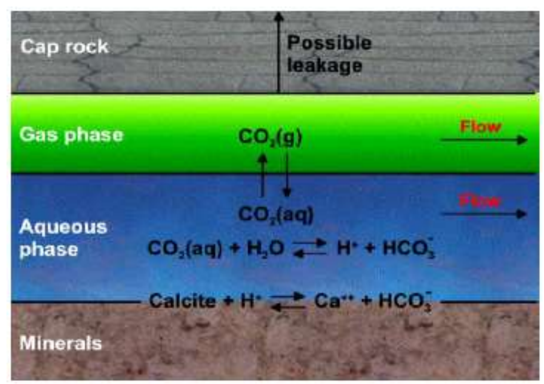
Structural Trapping

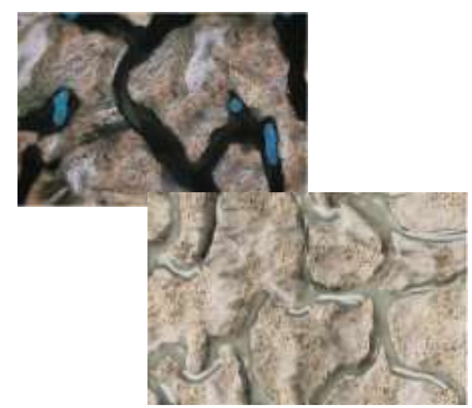


Trapping mechanism and **behavior** of SCP-CO_2 is a dynamic process and influences the fate and transport of CO_2



Residual Trapping





Solubility & Mineral Trapping

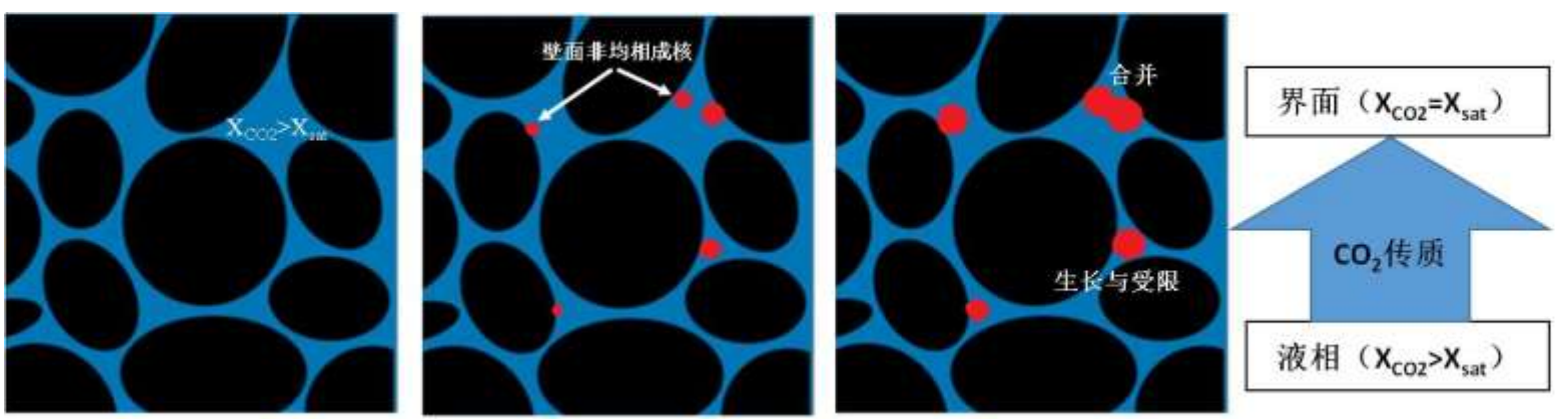
CO_2 Storage and Two-Phase Flow in Micro Porous Media

➢ Pore-scale

- **Micromodel experiments**
- **CT Scan & Reconstruction**
- **Numerical Simulation on**
  - **- Multi-particles by CFD code**
  - **- LBM**

➢ Core-scale

- **Visualization experimental investigations by MRI**
- **Volume average simulation**
  - **- By CFD code (Fluent)**
  - **- TOUGH**

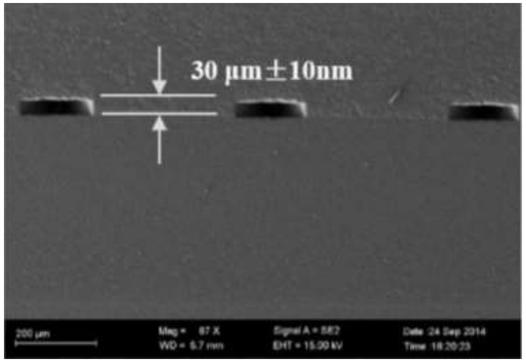


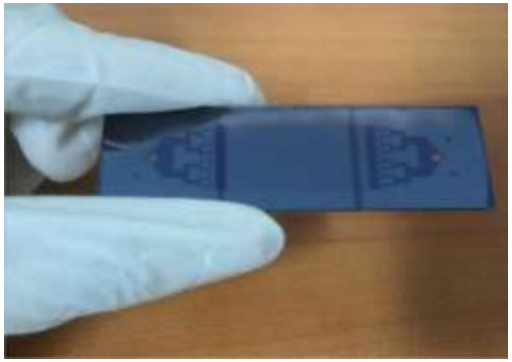
Coupling process: two-phase flow and exsolution/dissolution

Pore-Scale Experimental Setup

- The micromodel is visualized by an inverted microscope (Ti-E Nikon series, 800 nm resolution) with a fluorescence module.
- Sample holder: high pressure chamber up to 15 MPa, 50 ^{o}C
- Flow rate Range： 10^{-3} μL/min~10^{4} μL/min

Behavior of SCP-CO_2 under high pressure with high resolution

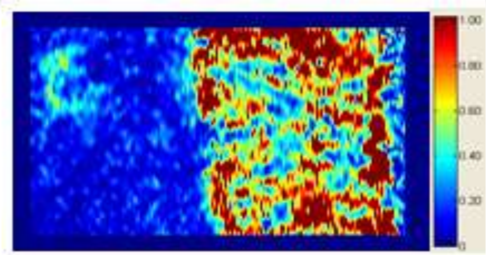


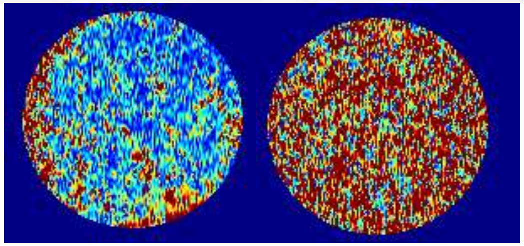


Core-Scale Experimental Setup

- NMR system has a magnetic field intensity of 0.5 T (21.3 MHz) and with a magnetic gradient of 0.03 T/m.
- Core holder: pressure up to 12MPa, temperature up to 80 ^{o}C

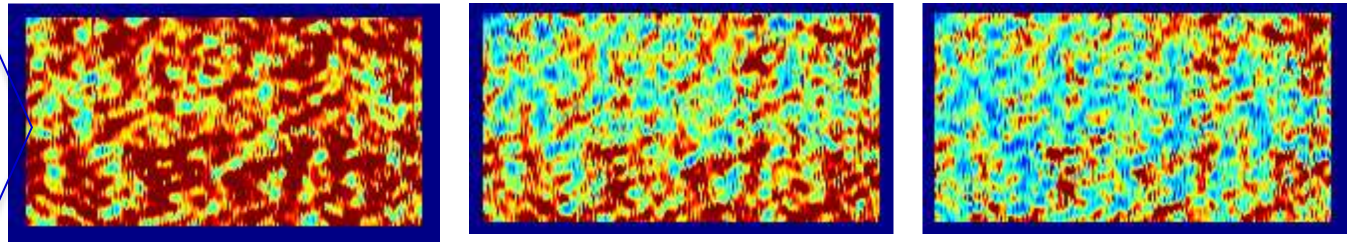
Quantitative online measurement with high accuracy





2.1 SCP-CO_2 displaced water: wettability effects

SCP-CO_2 Injection into Core

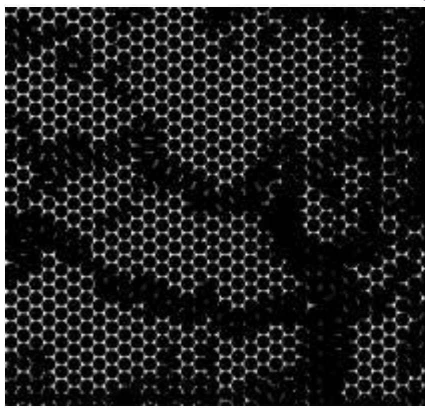


Red: Water
Blue: CO_2

SCP-CO_2 Injection into Micromodel

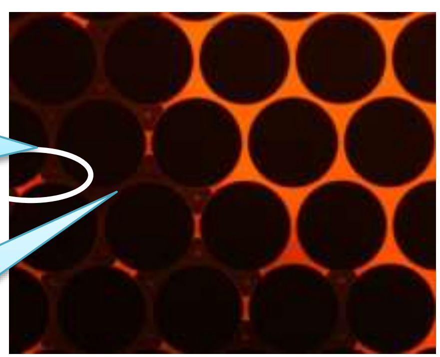
Hydrophilic

- Low sweep efficiency: Low viscosity of SCP-CO_2
- Fingering effect



Trapped water

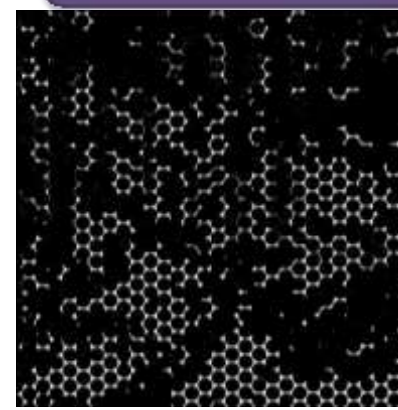
Liquid film



Red: Water

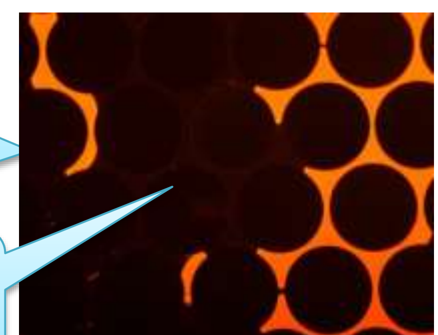
Hydrophobic

- Higher sweep efficiency
- Fingering effect



NO Trapped water

NO Liquid film

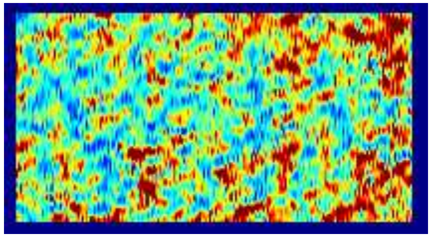


Red: Water

2.2 Water imbibition: wettability effects

（吸水）

SCP-CO_2 displaced water →



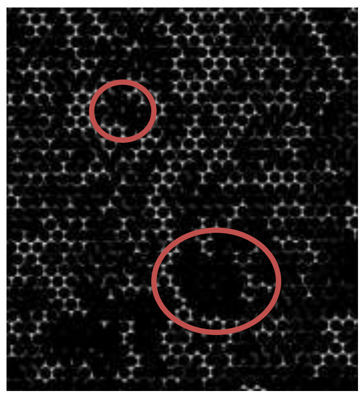
→ water imbibition →

Residual CO_2 — CO_2 trapped

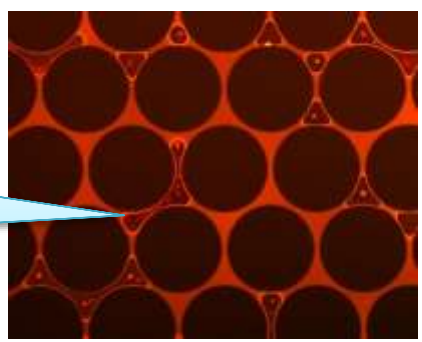
SCP-CO_2 Injection into Micromodel

Hydrophilic

Trapped CO_2
- separated
- low mobility



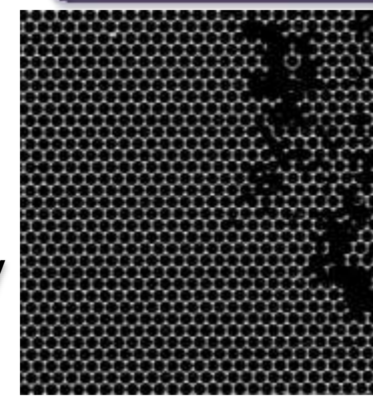
Trapped CO_2



Red: Water

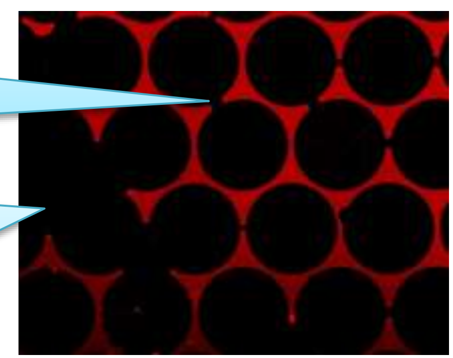
Hydrophobic

Trapped CO_2
- less
- higher mobility



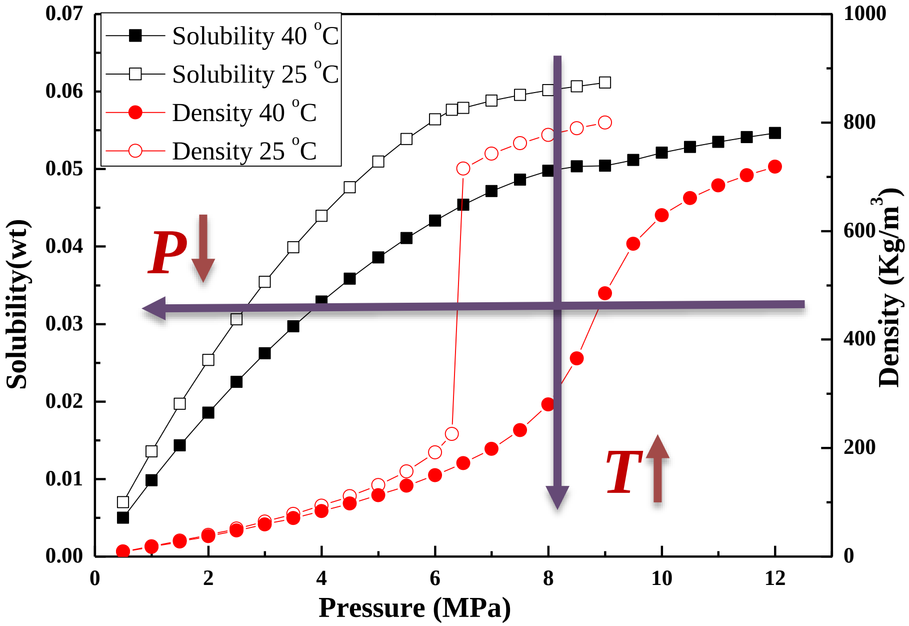
Trapped CO_2 in throats

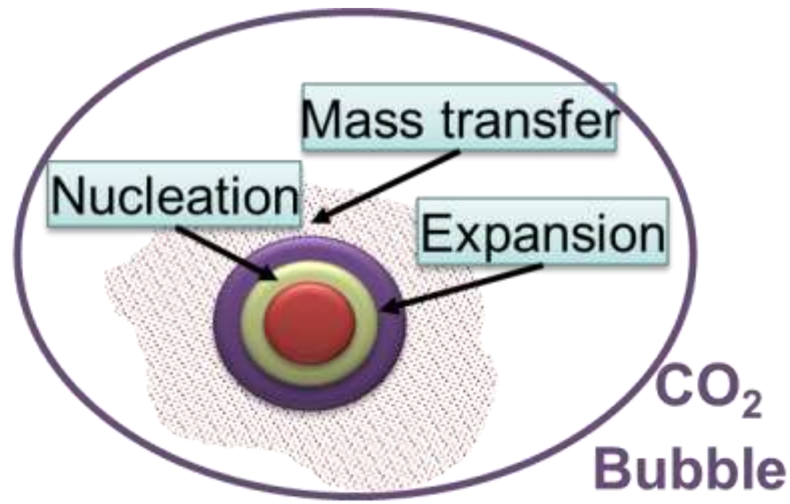
Trapped CO_2 linked

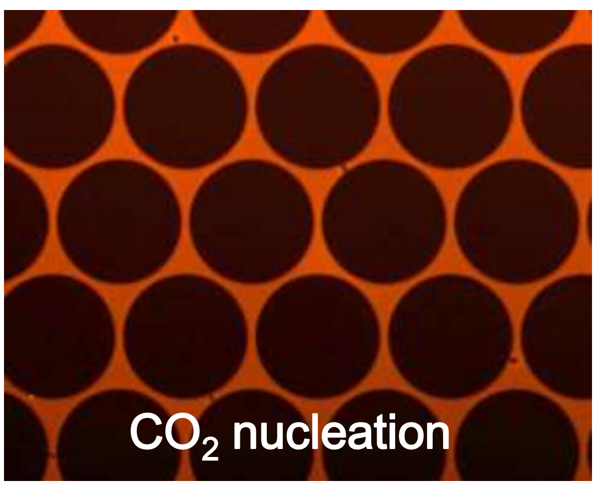


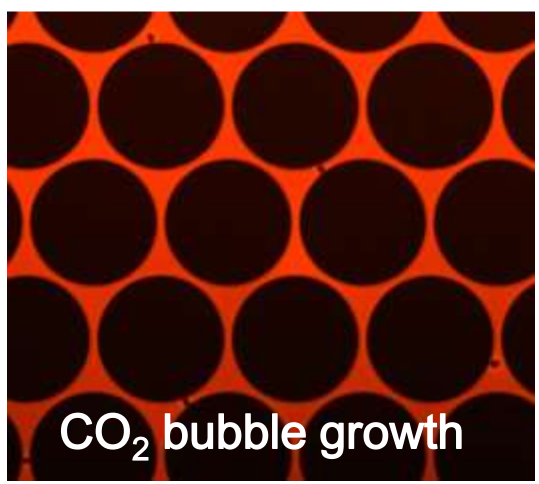
Red: Water

2.3 CO_2 Behavior: Exsolution





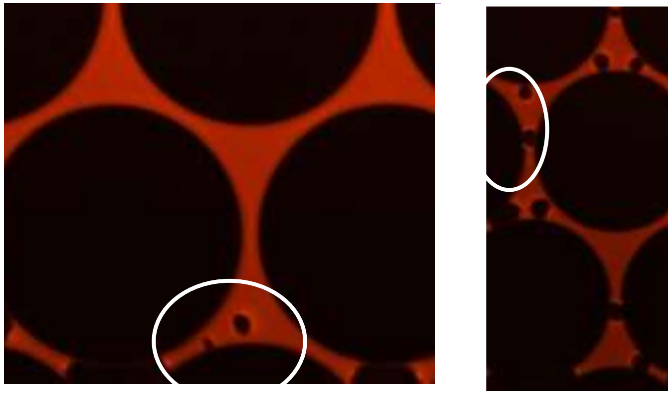




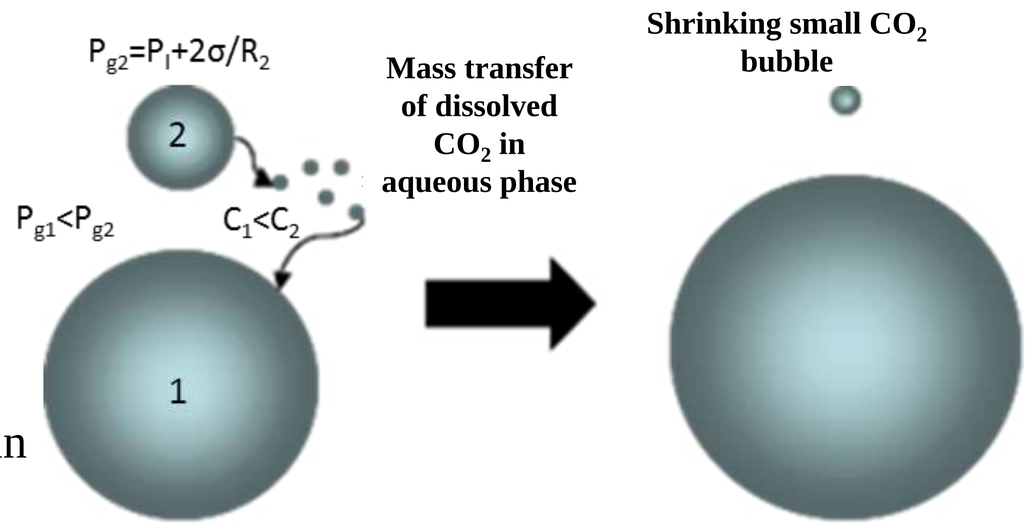
7.37-3.95MPa, 40℃ 40min(85.5KPa/min)

- CO_2 nucleation sites are located at the surface of pore wall
- Bubbles grow up into the pore-body
- Exsolved phase shows low mobility

2.4 Ostwald Ripening



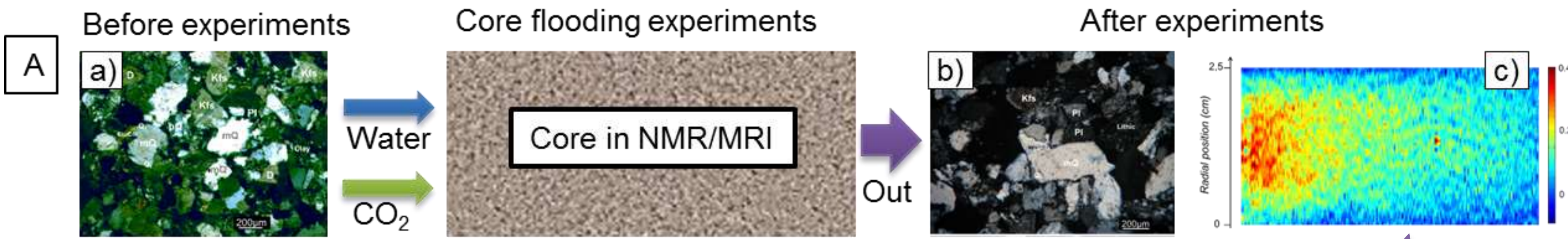
Constant pressure at 3.95 MPa for 4h in case 1 (25 ^oC)



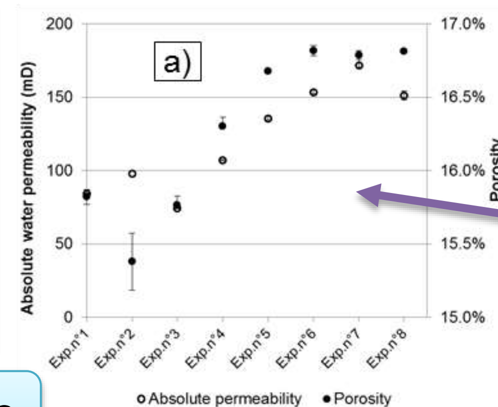
Bubble curvature → **Bubble pressure** → **CO_2 component concentration near the interface** → **CO_2 mass transfer in the aqueous phase**

> ➢ **Thermodynamic driving force: Reduction of surface free energy**

2.5 Effects of Chemical Reaction on Curves



Rock: **Mineral dissolution effects on the transport**: SCP-CO_2 / water with carbonate cement (碳酸盐水泥)：dolomite(白云石) (11%)

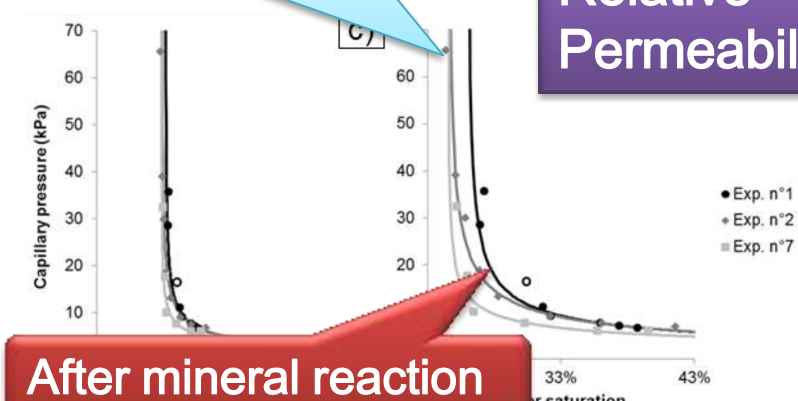


- Porosity increased
- Absolute permeability inceased

Initial core
After exp. n°1 and 2
After exp. n°3 and 4
After exp. n°5 and 6

Capillary Curve

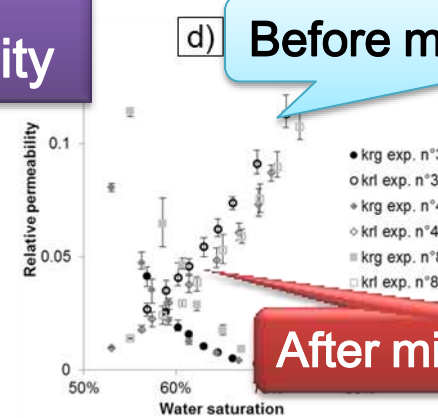
Before mineral reaction



After mineral reaction

Relative Permeability

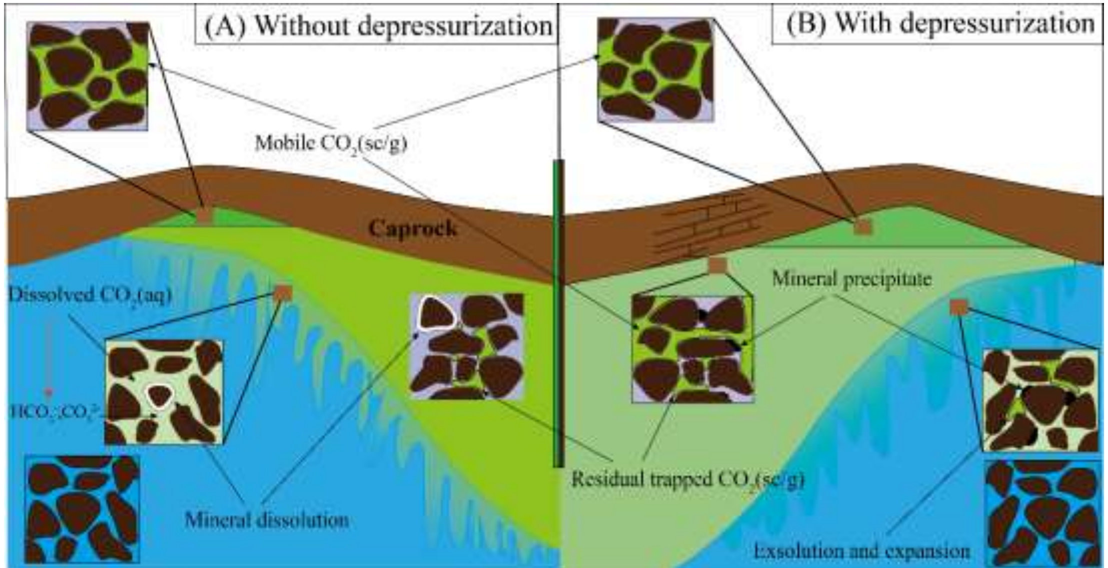
Before mineral reaction



After mineral reaction

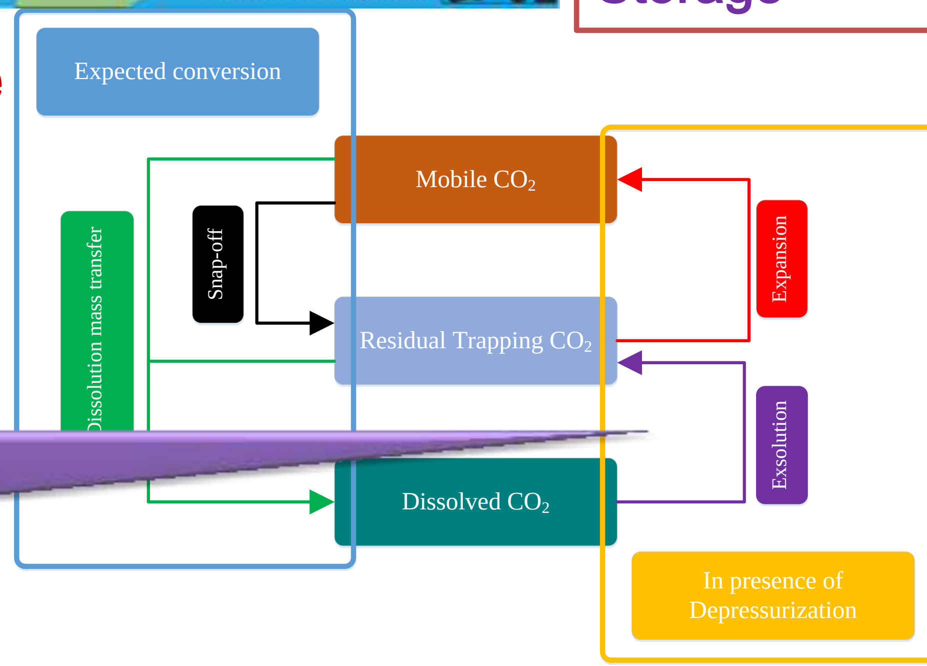
2.6 Effect of CO_2 Exsolution on CO_2 Storage

Potential leakage risk: **Pressure deceased** in storage sites



Invited paper by ***Accounts of Chemical Research***: Chemistry in Carbon Geological Storage

When pressure decreased, due to the CO_2 exsolution, water flow resistance increased, CO_2 has low mobility



Self-sealing mechanism that may reduce unfavorable CO_2 migration

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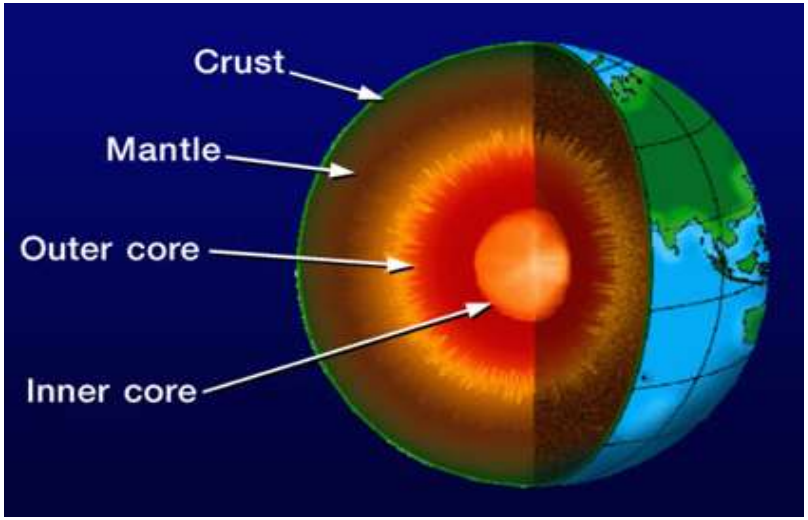
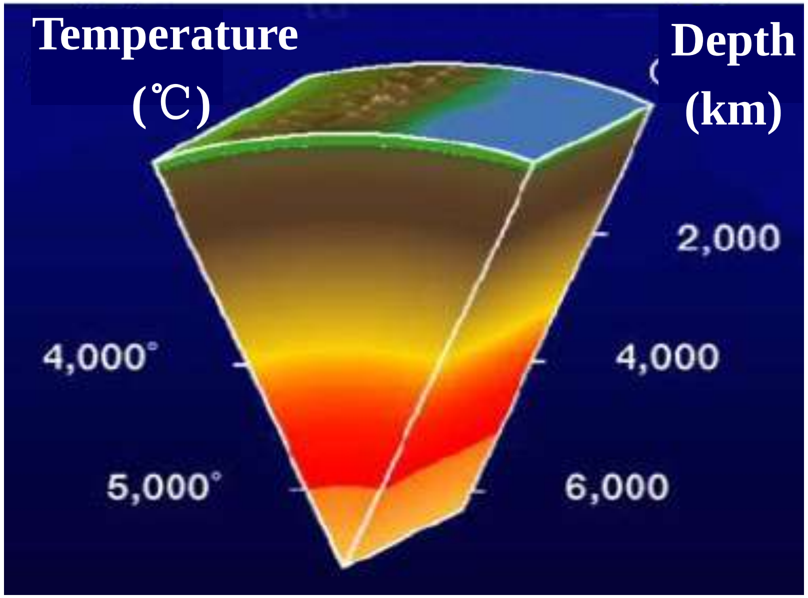
The Earth and geothermal energy



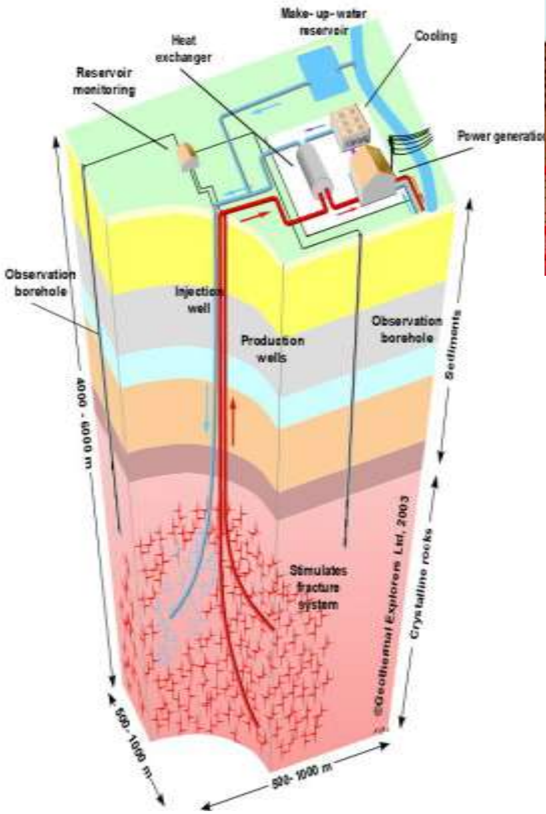


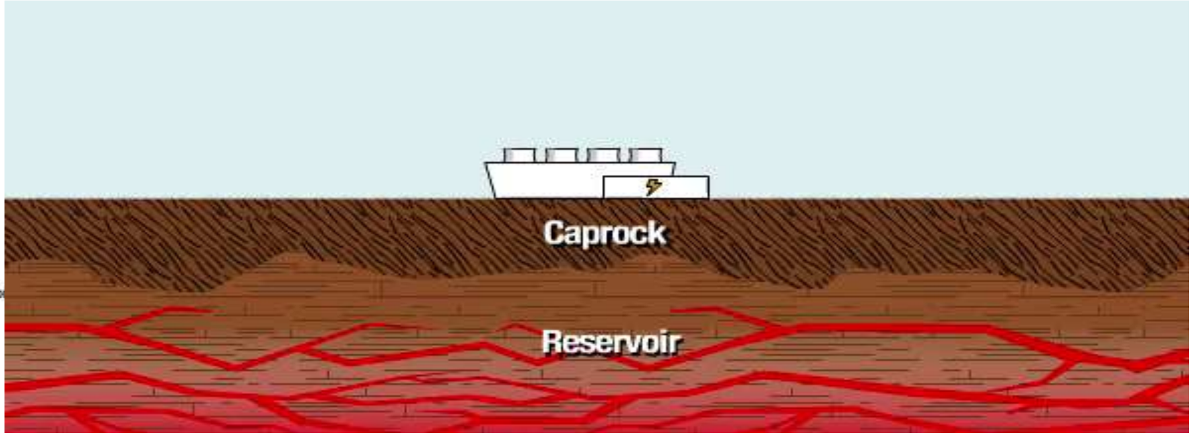
Depth	T(℃)
Surface: <0.2 km	Low: <90
Shallow: 0.2~3km	Middle: 90~150
Deep: >3 km	High: >150

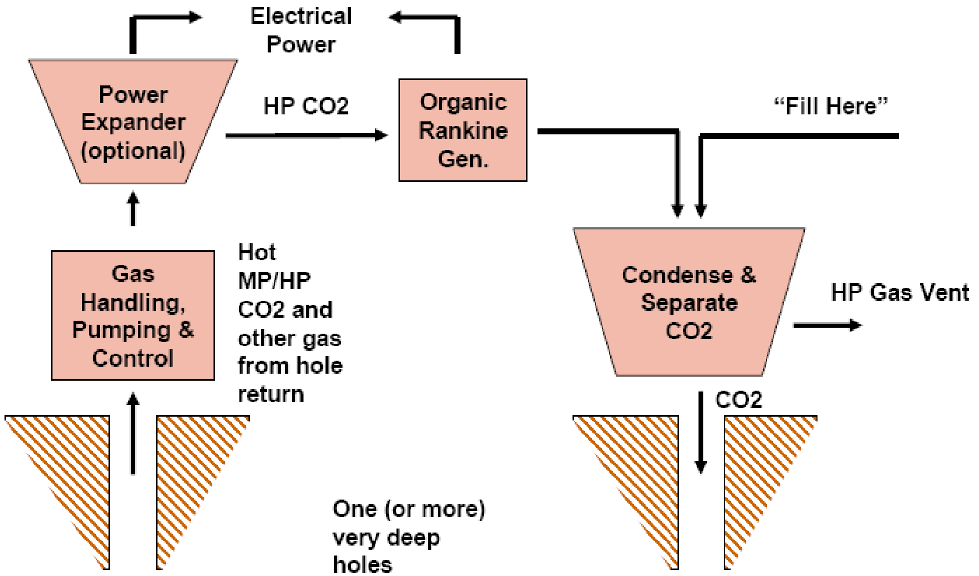
- **Geothermal resources in the deep earth is more than 90%!**

Enhanced Geothermal System – The future of geothermal energy

Enhanced Geothermal Systems (EGS)





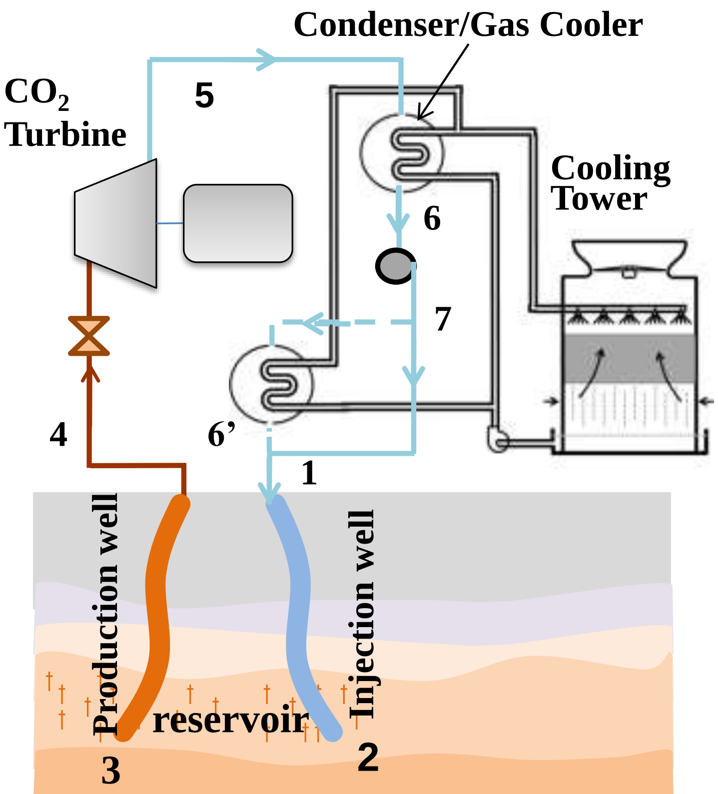


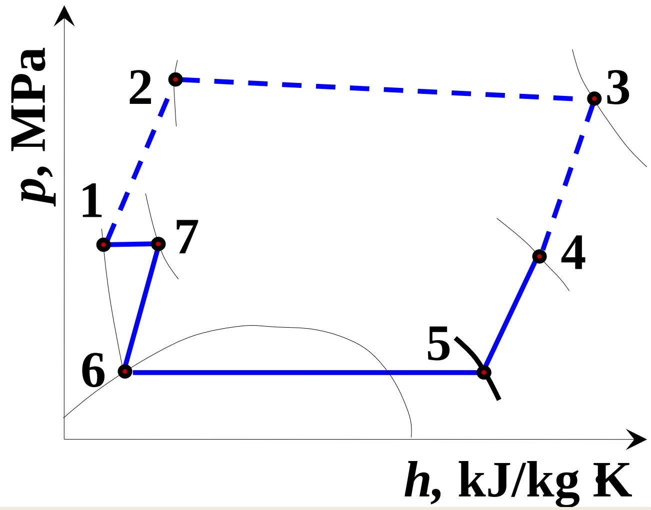
Challenges of EGS

- Small heat-recovery factors （小热回收系数）found in practice about 1-5% of the heat in the reservoir at depth is recovered at the wellhead
- Need the approaches toward creating sites for EGS, including science and engineering to enhance permeability and increase the energy recovery factor

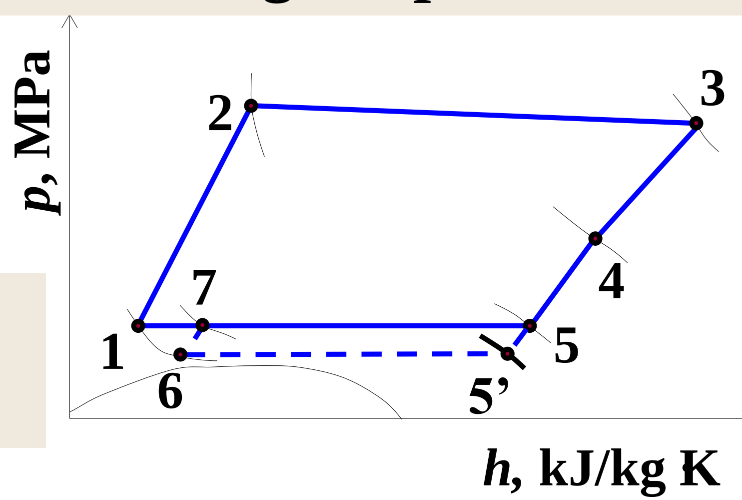
Characterize the heat transfer and heat conversion in EGS aim to improve the energy recovery factor

3.1 Working fluids selection





Power cycle of CO_2-EGS is transcritical for low surrounding temperature

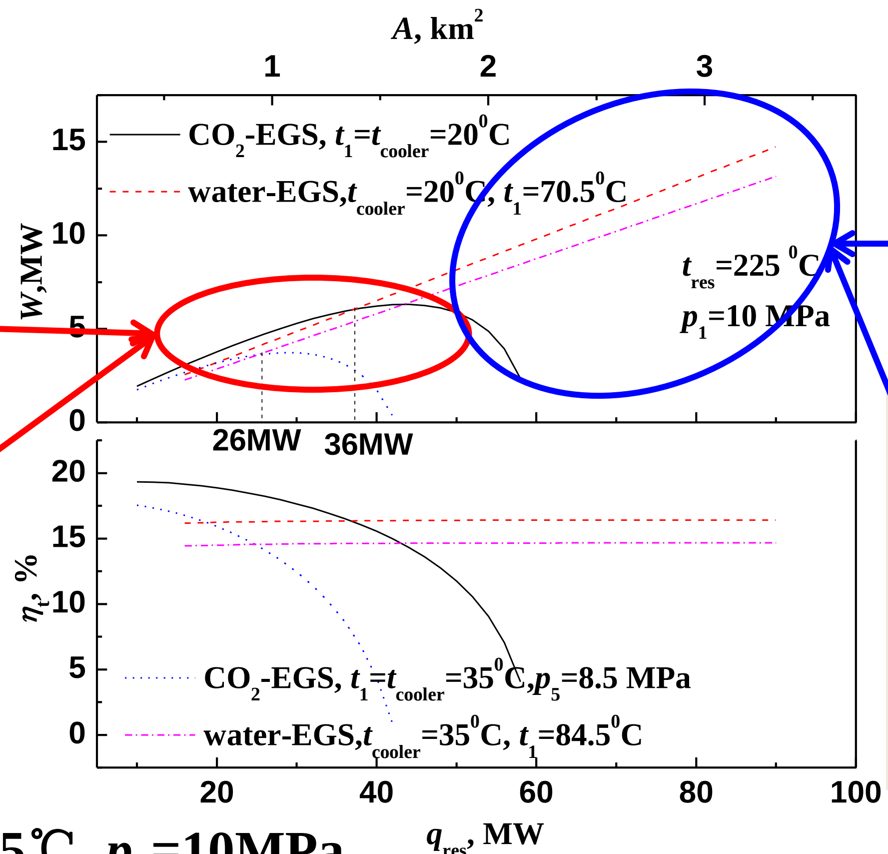


Supercritical for high surrounding temperature

Comparison between water/CO_2-EGS

for small stimulated fracture reservoir with lower q_{re}

CO_2-EGS will perform better than water-EGS does.



for large stimulated fracture reservoir with large q_{re}

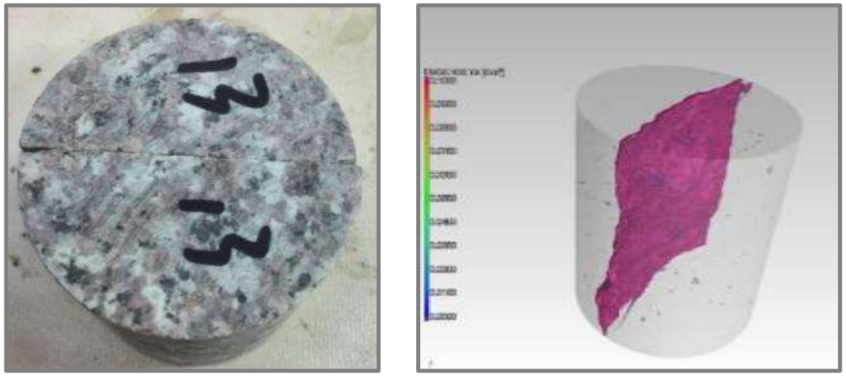
Water-EGS produces more power and has higher thermal efficiency than CO_2-EGS does

t_{res}=225℃, p_1=10MPa

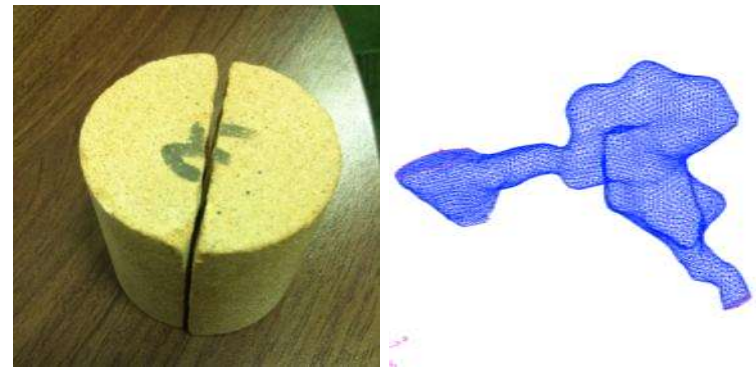
CO_2-EGS may be appropriate *for low recoverable heat energy*, but water-EGS perform *better for large recoverable heat energy* for given well diameter, number of injection and production well and surrounding temperature

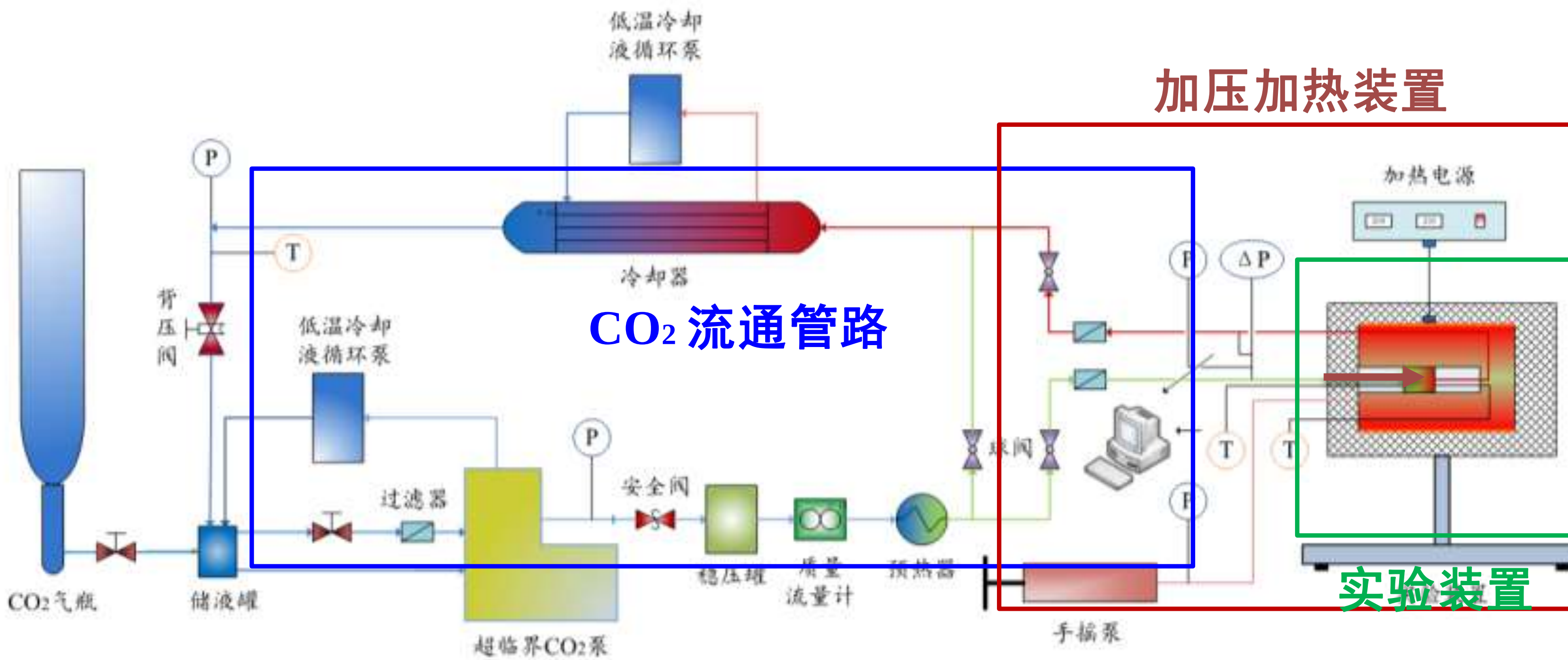
3.2 Heat transfer of SCP CO_2 in rock

Granite(花岗岩)

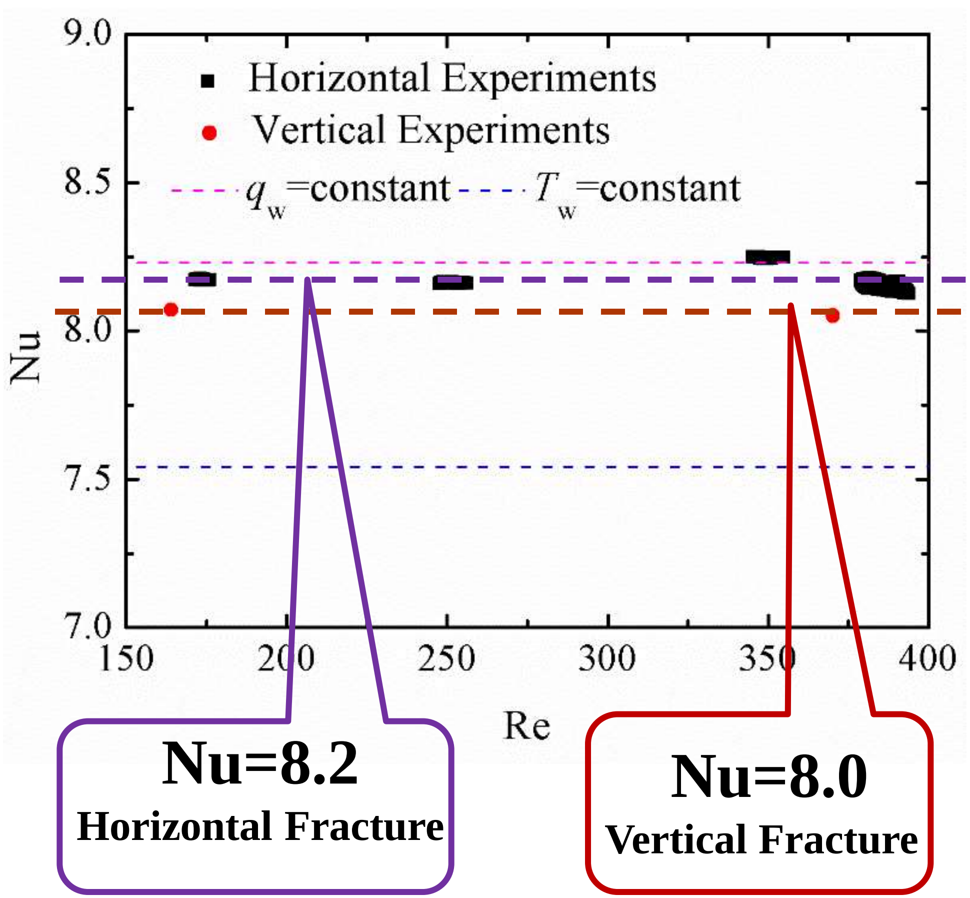


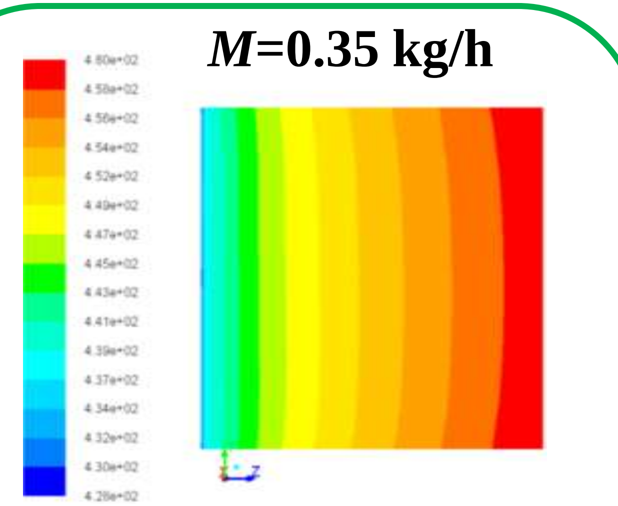
Sandstone（砂岩）

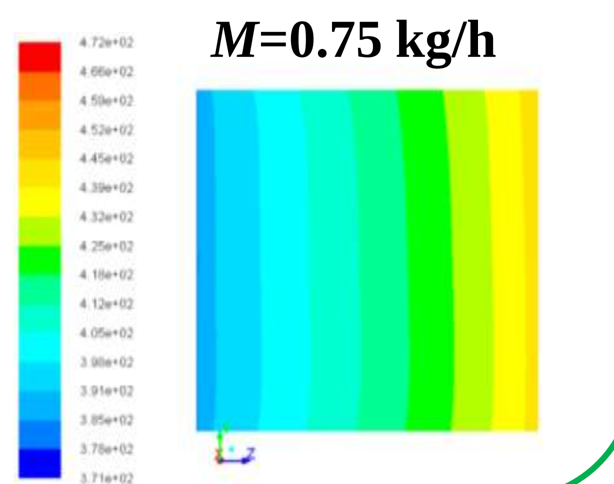




Heat transfer of SCP CO_2 in rock







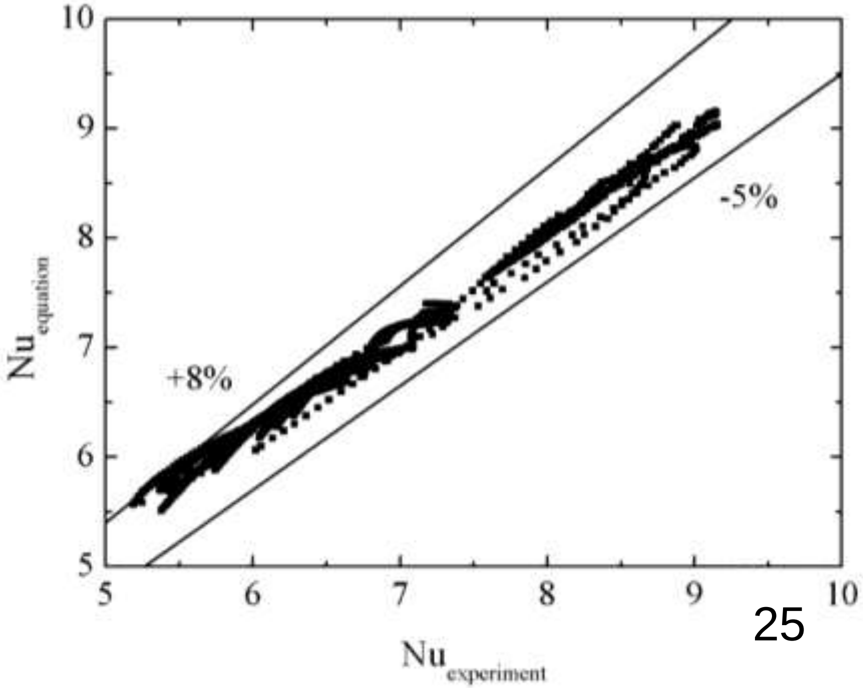
Heat transfer of SCP CO_2 in rock

$$\frac{\mathrm{Nu}}{\mathrm{Nu}_0}=\left(\frac{\overline{c_p}}{c_{pb}}\right)^n\left(\frac{\rho_w}{\rho_b}\right)^{-0.27}\left(\frac{\mathrm{Pr}_w}{\mathrm{Pr}_b}\right)^{0.043}$$

$$n=0.45 \qquad T_{\mathrm{b}}<T_{\mathrm{w}}<T_{\mathrm{pc}},1.2T_{\mathrm{pc}}<T_{\mathrm{b}}<T_{\mathrm{w}}$$

$$n=0.45+13.83\left(\frac{T_w}{T_{pc}}-1\right) \qquad T_{\mathrm{b}}<T_{\mathrm{pc}}<T_{\mathrm{w}}$$

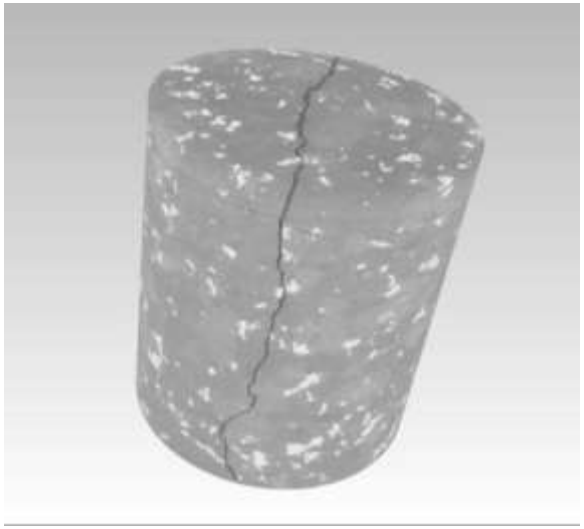
$$n=0.45+13.83\left(\frac{T_w}{T_{pc}}-1\right)\left[1-2.28\left(\frac{T_b}{T_{pc}}-1\right)\right] \quad T_{\mathrm{pc}}<T_{\mathrm{b}}\le 1.2T_{\mathrm{pc}}$$

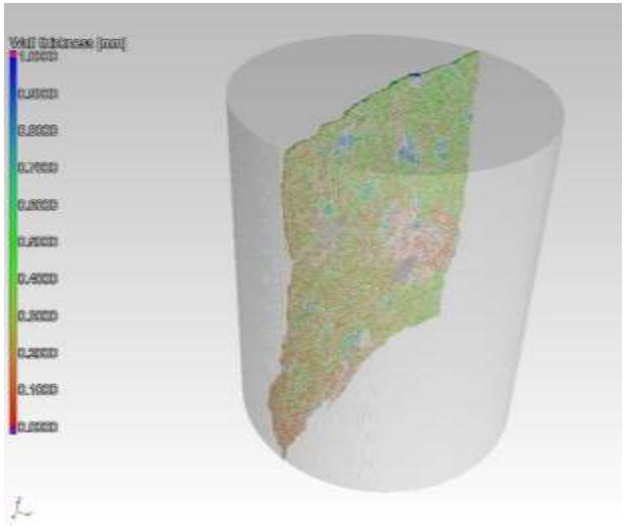


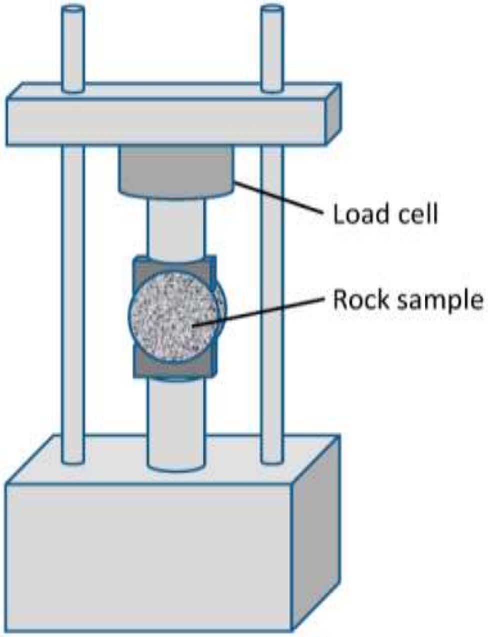
Coarse Rock fracture

Coarse granite fracture

CT scan and reconstruction



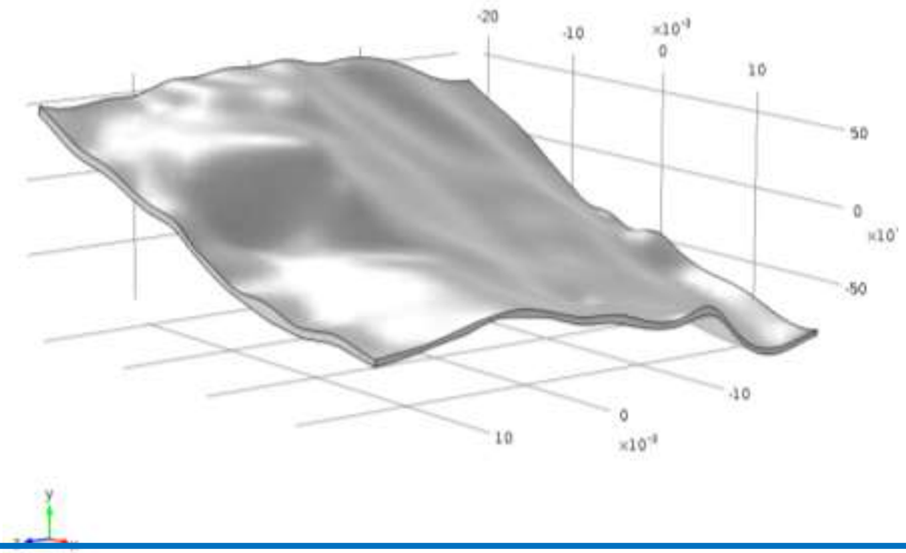


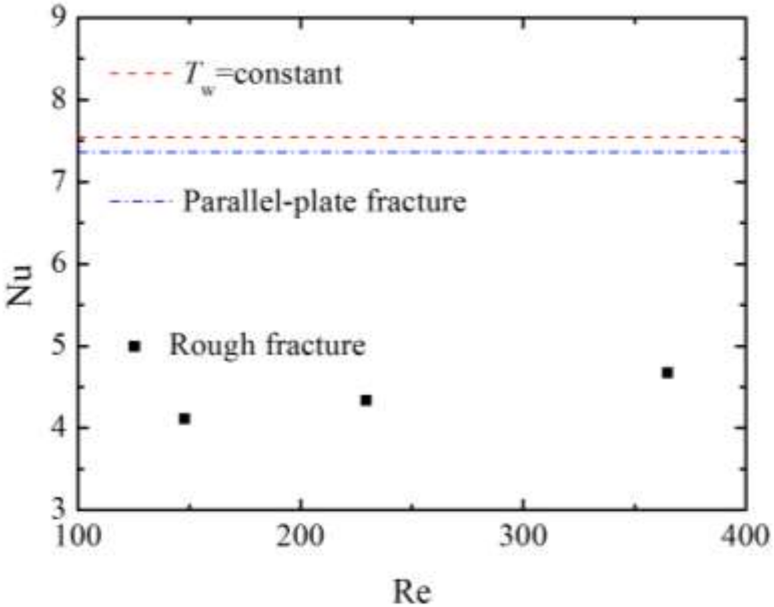


Brazilian test

Coarse Rock fracture

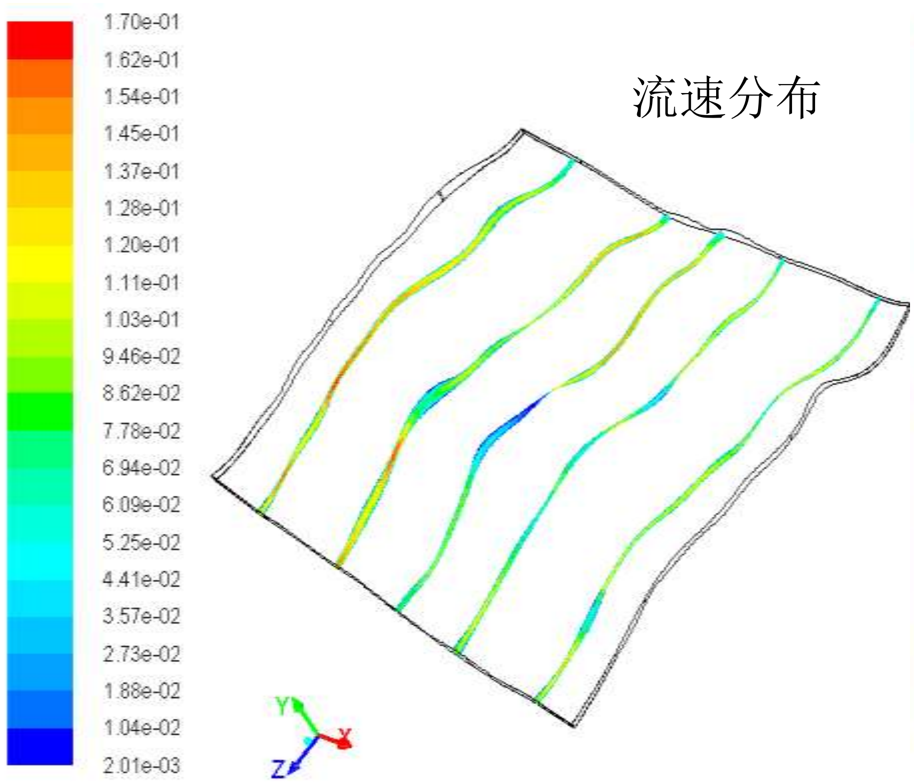
Reconstruction simulation model

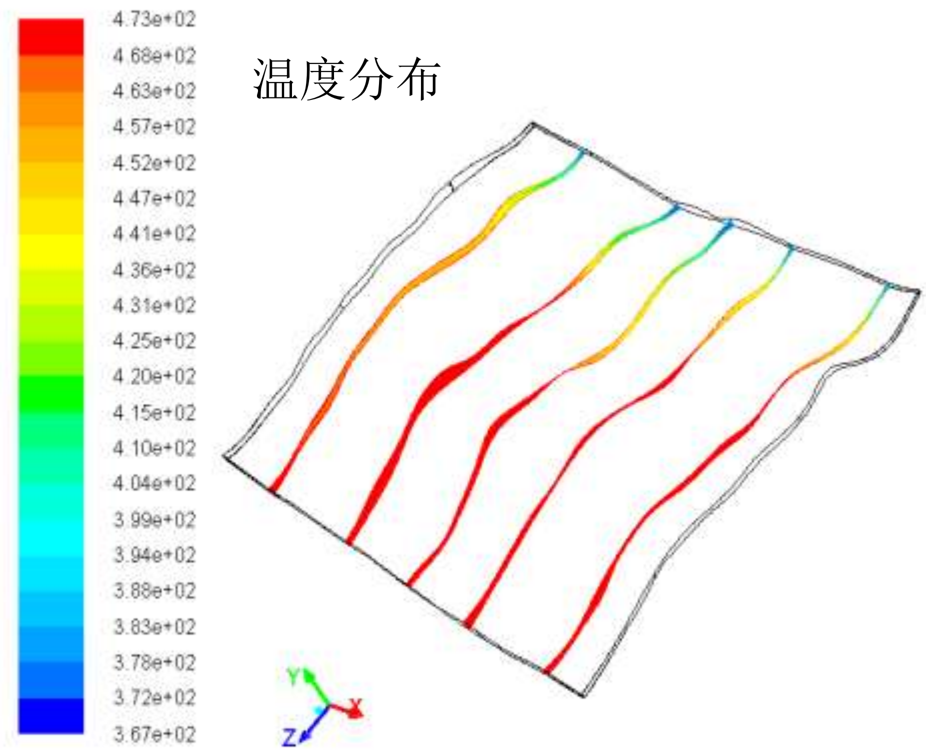




- The effect of enhanced heat transfer at developing region on the overall heat transfer characteristic is more significant at larger mass flow rates in a rough fracture
- The overall heat transfer performance in a rough fracture is an integrated effect of channeling effect and disturbance effect by the tortuous flow path

Coarse Rock fracture





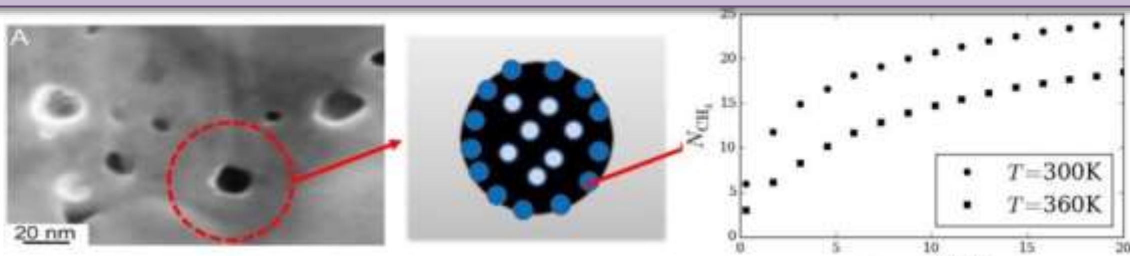
- Heat exchange is less efficient in a rough fracture compared to flat fractures with equivalent permeability due to the caused channeling effect

Outline

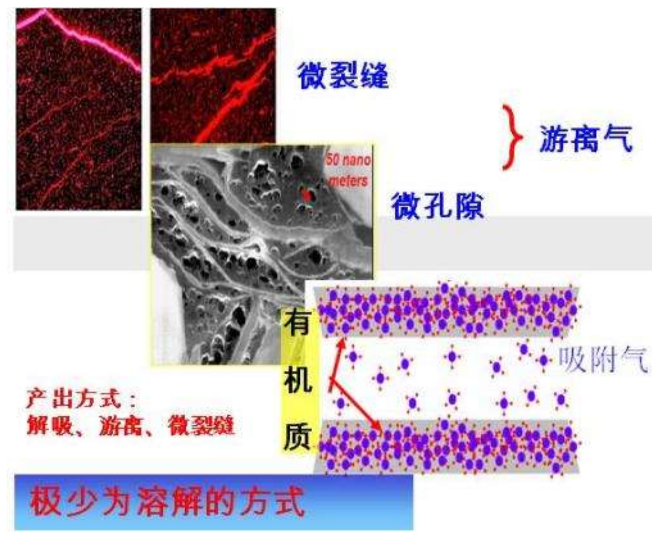
1. **Background and Introduction**
2. **CO_2 Storage and Two-Phase Flow in Porous Media**
3. **CO_2 Enhanced Geothermal Systems and Heat Transfer in Fractures**
4. **CO_2 Enhanced Shale Gas and Mass Transfer in Nano Pores**
5. **Summary**

CO_2页岩气开发中关键热质传递基础问题
—Transport phenomenon in micro-/nano-pores in CO_2-Shale gas exploitation

纳米孔隙中的超临界流体**吸附、输运机理**是深入认识页岩气赋存方式及提高采收效率的基础



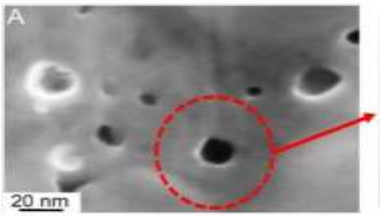
对页岩基质的化学分析、重构　　对等温吸附过程的分子模拟　　获得等温吸附线



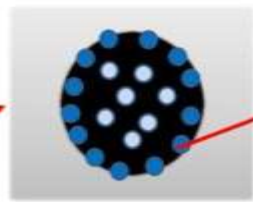
- ➢ CO_2是否能够用于页岩气增产以及效果如何？
  ——超临界压力CO_2与CH_4的竞争吸附规律
- ➢ Effects of CO_2 enhanced shale gas recovery: competition adsorption between CO_2/CH_4

4.1 超临界压力CO_2在纳米孔隙中吸附

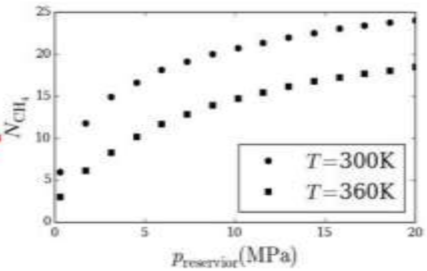
Adsorption of supercritical CO_2 in nanopores



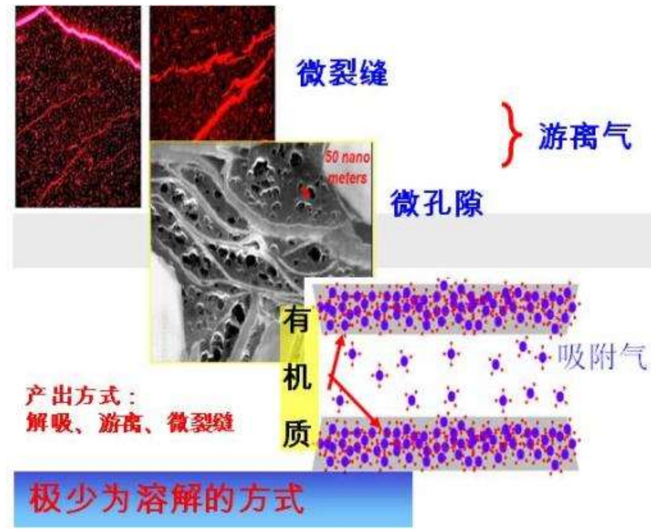
对页岩基质的化学分析、重构



对等温吸附过程的分子模拟



获得等温吸附线



MD模拟＋拓扑重构 ⟹ 页岩实验测量

⟹ 理论和数值模型

MD＋Molecular Reconstruction ⟹ Shale core experiment

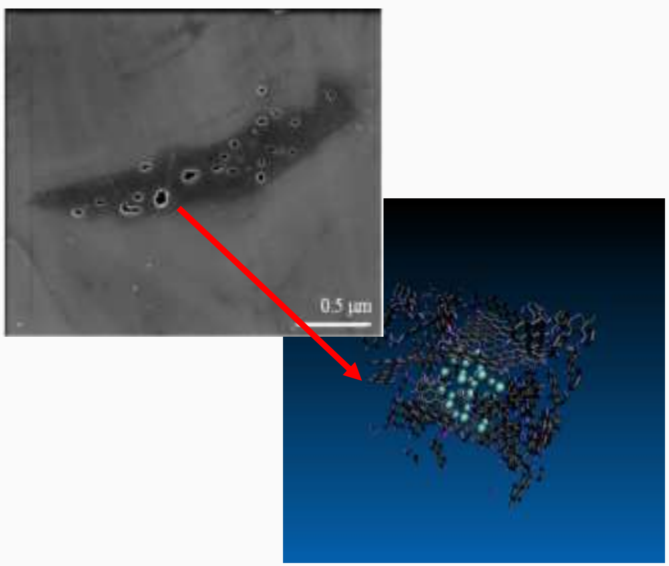
孔隙分子结构使得超临界甲烷在有机质微孔中的吸附出现差异

Molecular structure of the nano-pore of shale decides the methane adsorption behavior

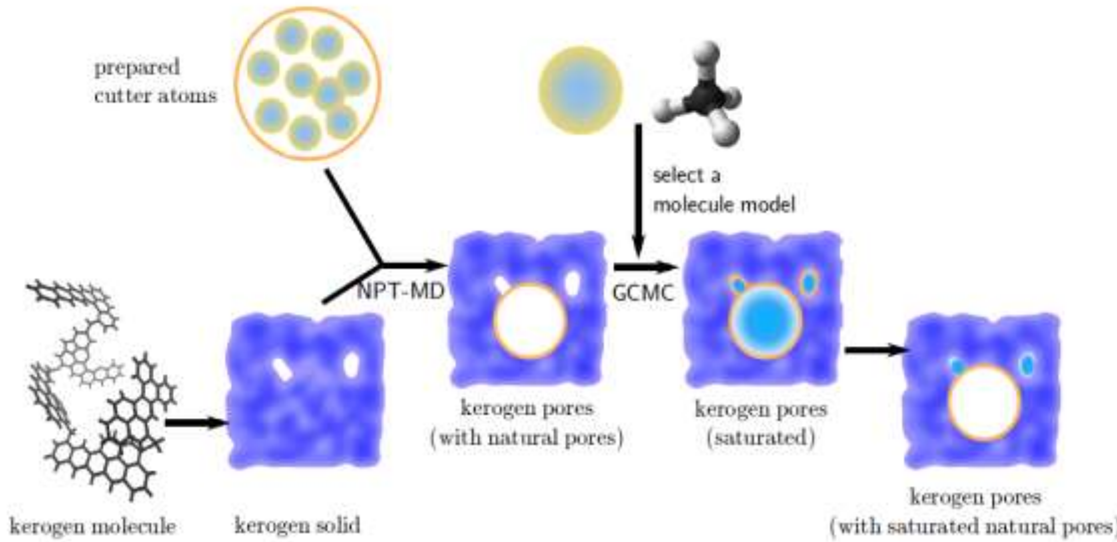
4.2 干酪根单孔吸附模拟

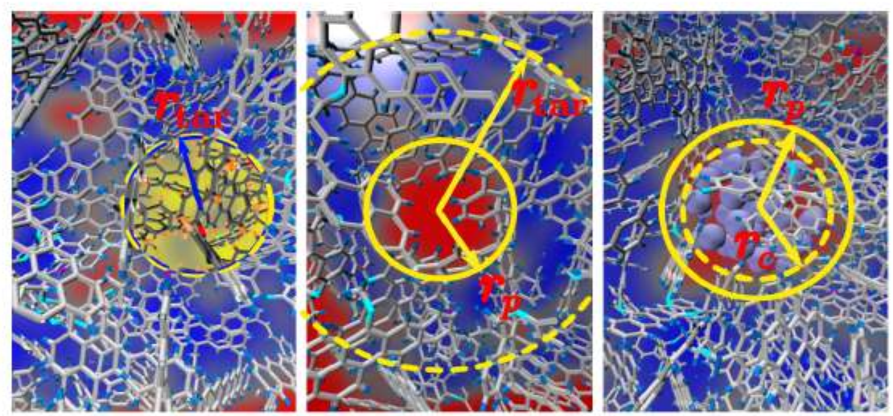
Simulation of adsorption in a single kerogen pore

- 基于元素分析的干酪根分子/固体重构
  Reconstruction of kerogen solid/pore based on chemistry element/group analysis



- **基于官能团谱、复杂拓扑的干酪根分子重构**

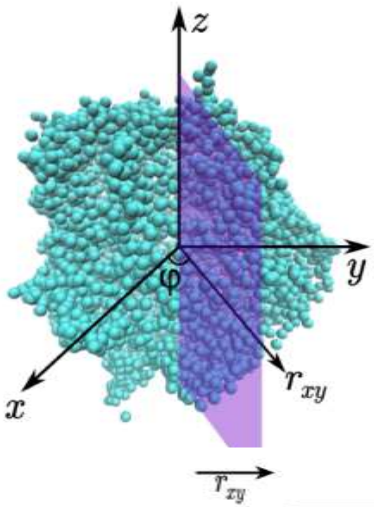


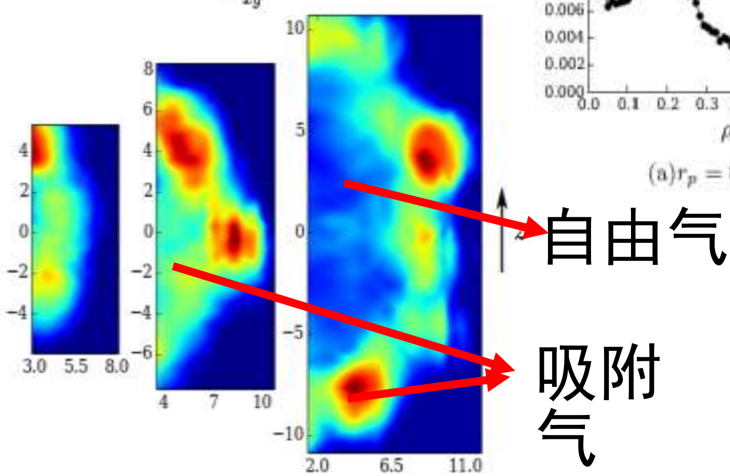


(a) (b) (c)

4.3 干酪根纳米孔隙吸附/游离态

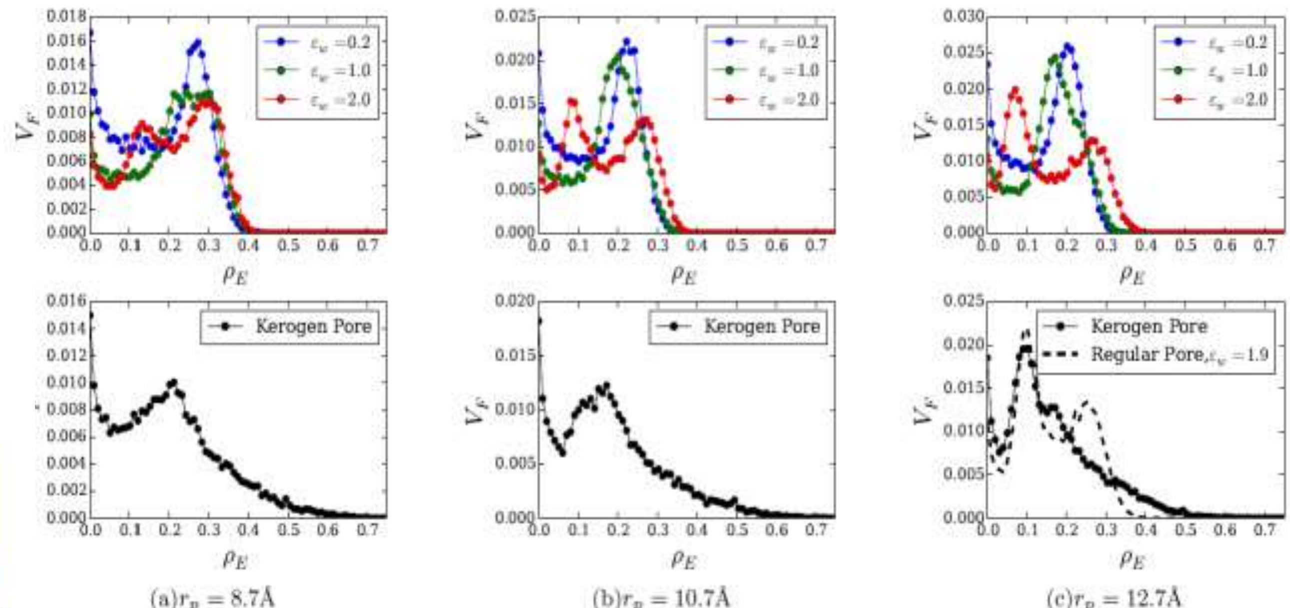
Adsorbed and Free gas states in kerogen nanopores





干酪根纳米孔中的甲烷密度场

Density fields of methane adsorption

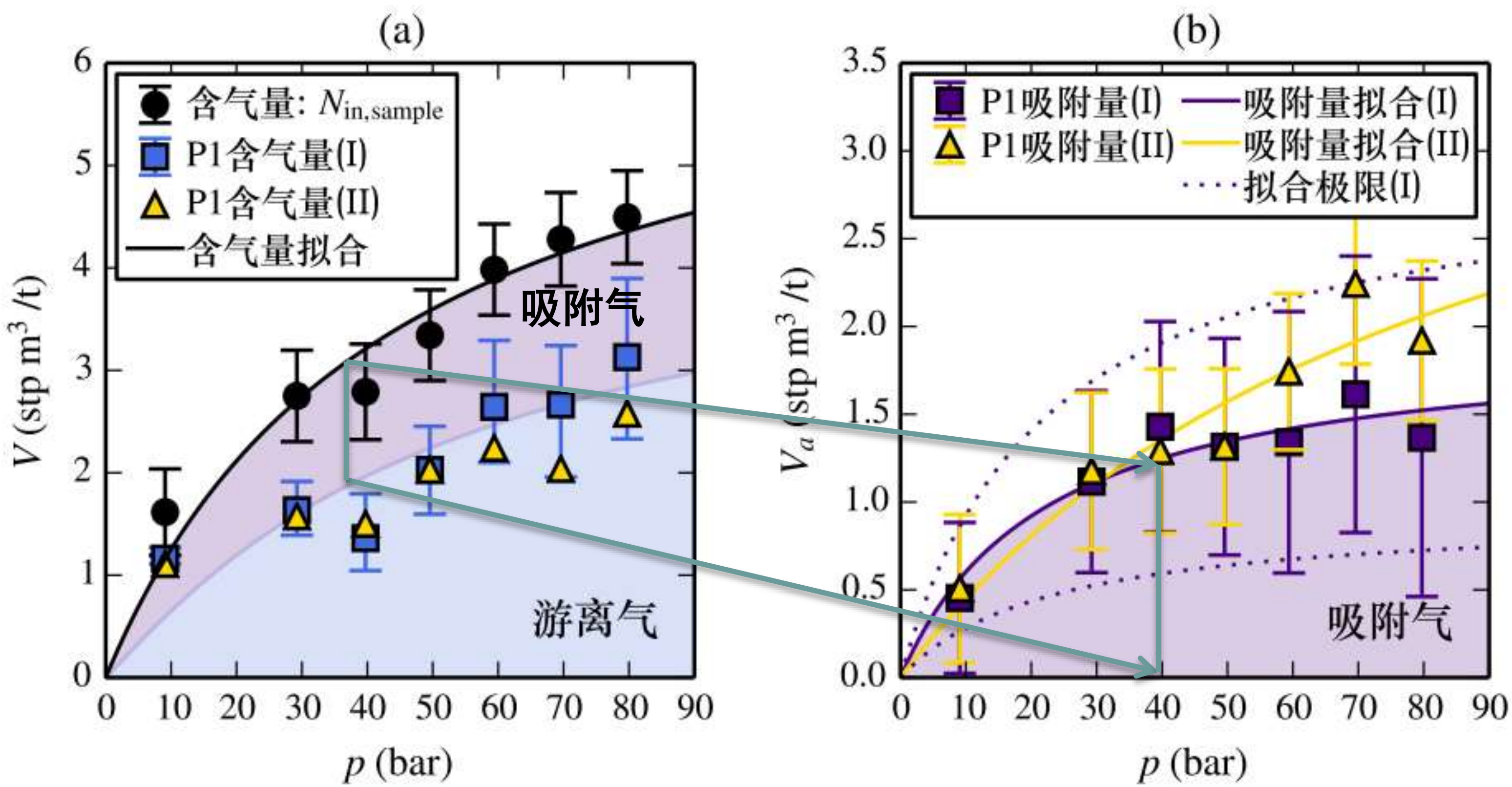


$$\rho_E(x) = \lim_{N\to\infty} \lim_{r'\to 0} \frac{1}{N} \frac{\left| \left(\bigcup_{n\leq N} X_{s,n} \right) \bigcap B_{\text{sphere}}(x, r') \right|}{4/3\pi r'^3}$$

Zhou B, Xu RN, Jiang PX. Fuel, 2016

4.4 页岩纳米孔的吸附气比例

Adsorbed gas ratio in shale nanopores

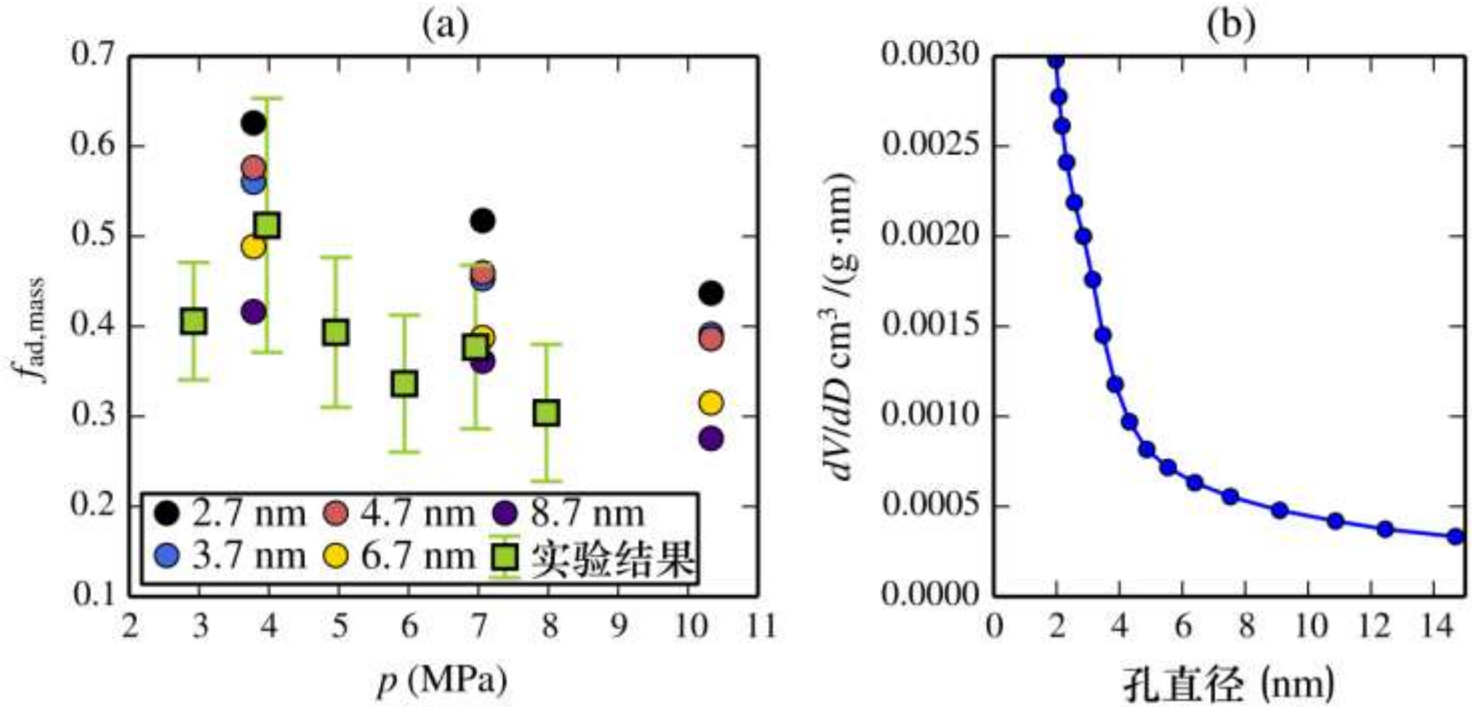


页岩中甲烷含气量和吸附量的核磁共振实验测量结果

Nuclear Magnetic Resonance (NMR) experiments results for gas content and adsorption in gas (CH_4) bearing shale

4.4 页岩纳米孔的吸附气比例

Adsorbed gas ratio in shale nanopores



干酪根孔中吸附气比例的分子模拟结果
与页岩核磁共振实验结果

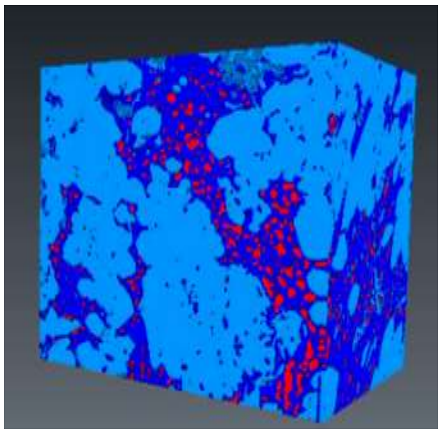
实验样品的BET孔径
分布表征结果

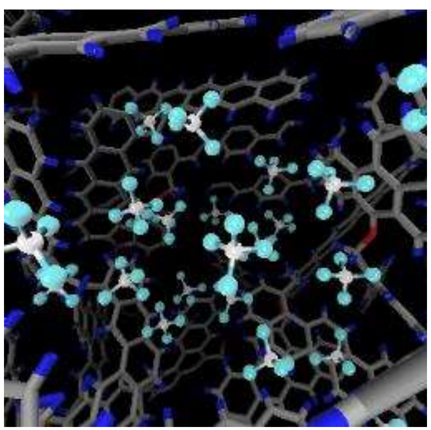
Molecular simulation and NMR experiments results for adsorbed gas ratio in kerogen nanopores and shale

BET pore size characterization results for shale

4.5 页岩纳米孔隙CO_2竞争吸附

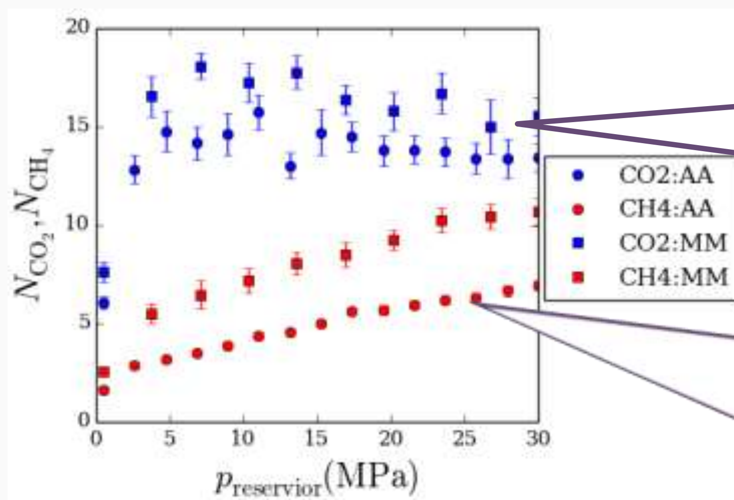
Competition adsorption between CO_2/CH_4 in kerogen nano-pores





高压甲烷吸附

- 单孔CH_4-CO_2混合物吸附解吸
- CH_4/CO_2 mixture adsorption in a single pore



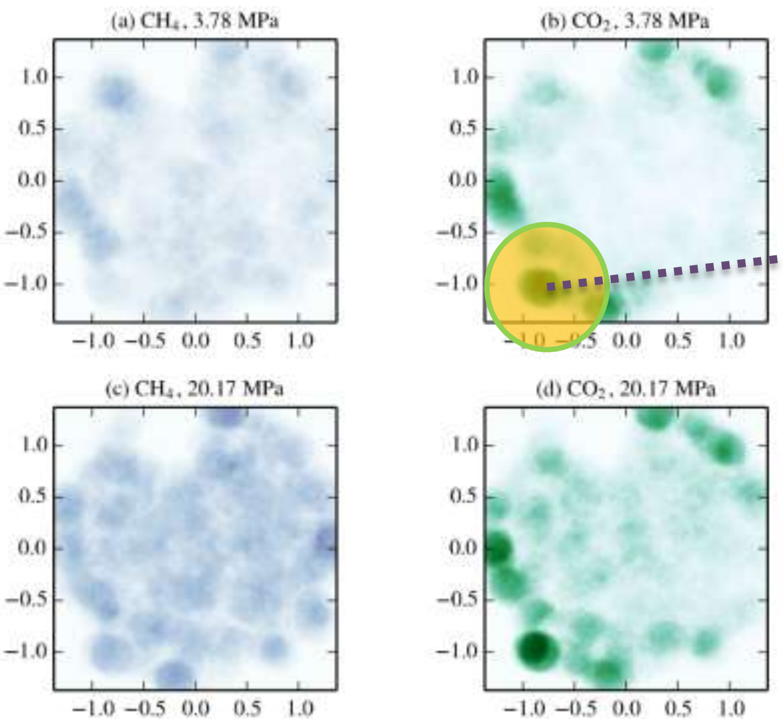
CO_2比甲烷更易于吸附在纳米孔中

CO_2 owns a higher adsorption affinity than CH_4

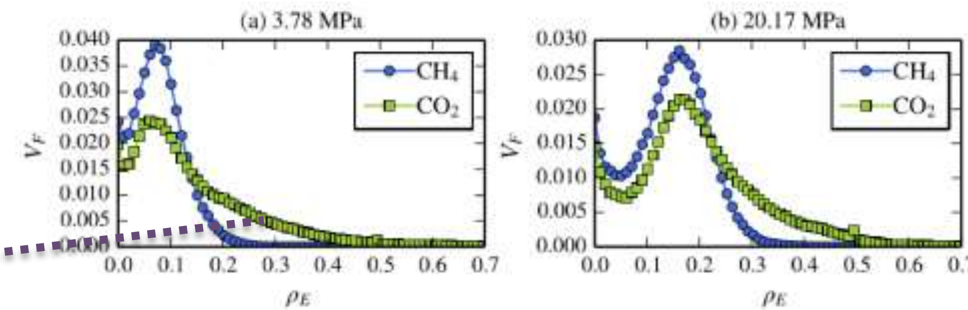
4.5 干酪根纳米孔隙CO_2竞争吸附

Competition adsorption between CO_2/CH_4 in kerogen nano-pores

CH_4-CO_2混合气体的系综密度分布



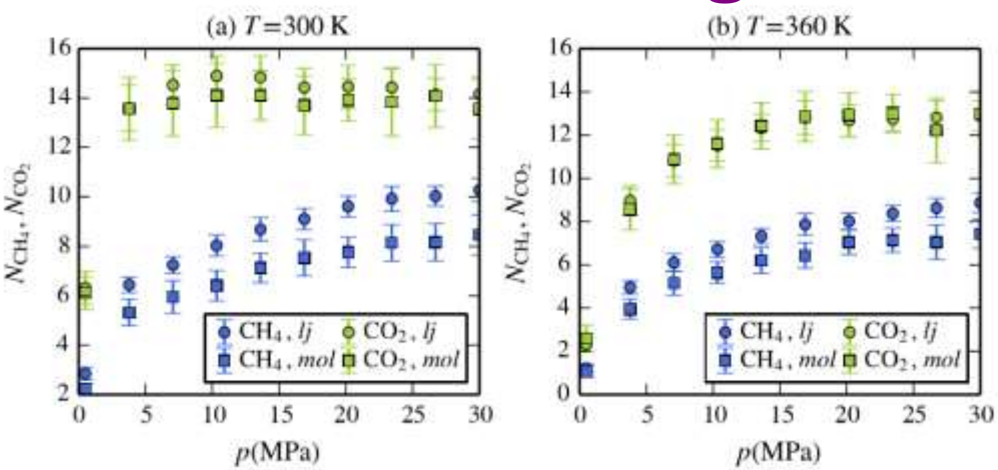
CH_4-CO_2混合气体的系综密度谱



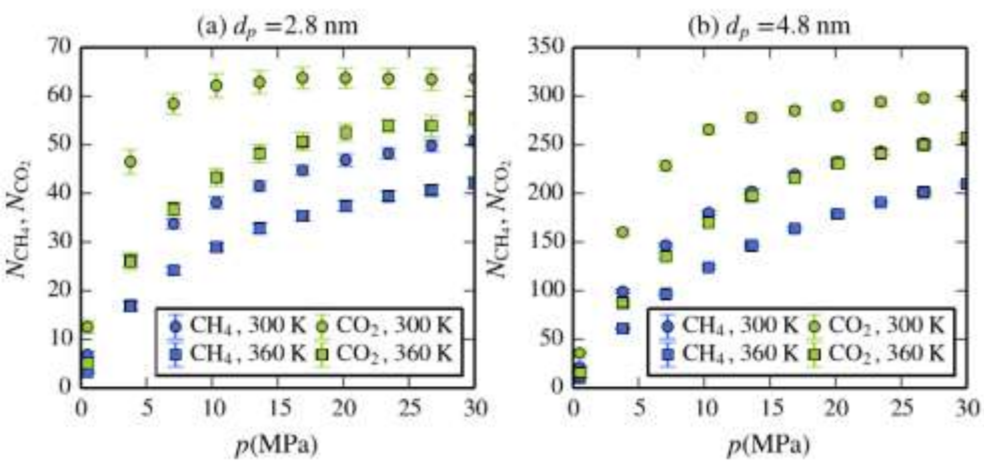
- 竞争吸附条件下，CH_4 难以在页岩纳米孔隙表面形成吸附态。**CO_2 具有显著的置换CH_4的效果**
- With competition of CO_2 , CH_4 can hardly form adsorbed layers on nano-pore surfaces.

4.5干酪根纳米孔隙CO_2竞争吸附

Competition adsorption between CO_2/CH_4 in kerogen nano-pores



1.8 nm干酪根孔的混合气体等温含气线



2.8和4.8 nm干酪根孔的混合气体等温含气线

- **随着压力增加**，吸附态中的CO_2分子总数逐渐增加至饱和，**游离态中CO_2的浓度逐渐提高并趋近于块体值**
- **随着孔直径的增加**，孔表面的**竞争吸附效应对孔隙总含气量的影响逐渐降低**

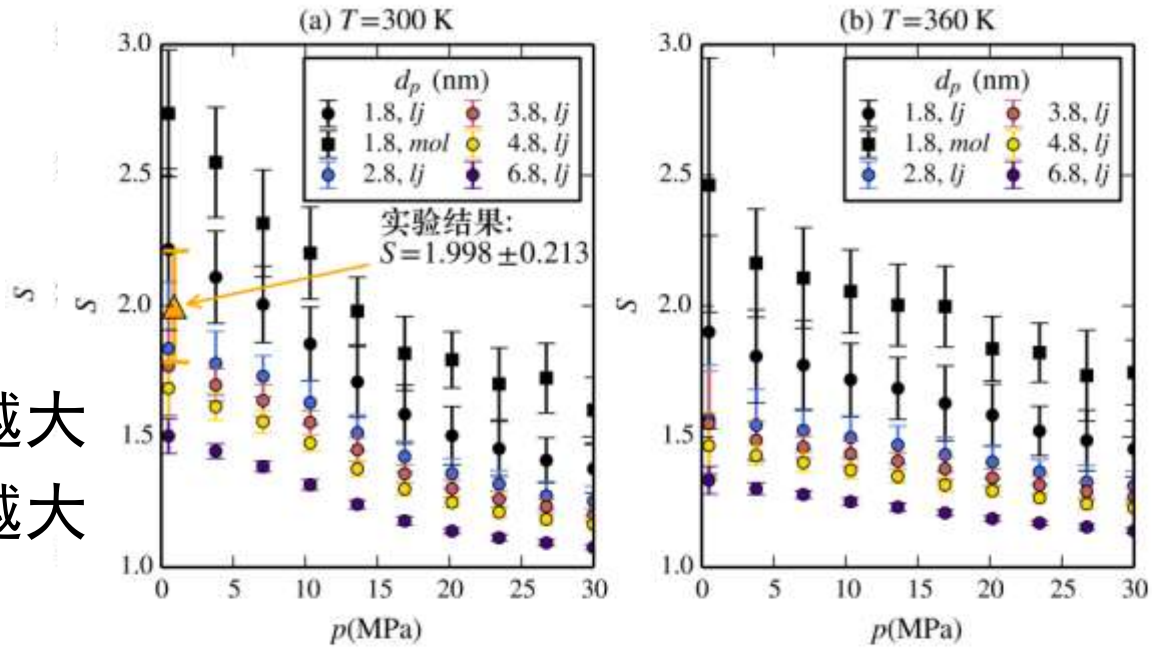
4.5干酪根纳米孔隙CO_2竞争吸附

Competition adsorption between CO_2/CH_4 in kerogen nano-pores

定义置换比S为：

$$S = \frac{N_{CO_2}/N_{CH_4}}{x_{CO_2}/x_{CH_4}}$$

- **孔径越小**，置换比S越大
- **压力越低**，置换比S越大



- 从热力学角度来看，CO_2置换驱技术是适用于**开采晚期、储层压力较低或基质孔径较小**的页岩气井的增产手段。

4.6 页岩纳米孔隙吸附规律

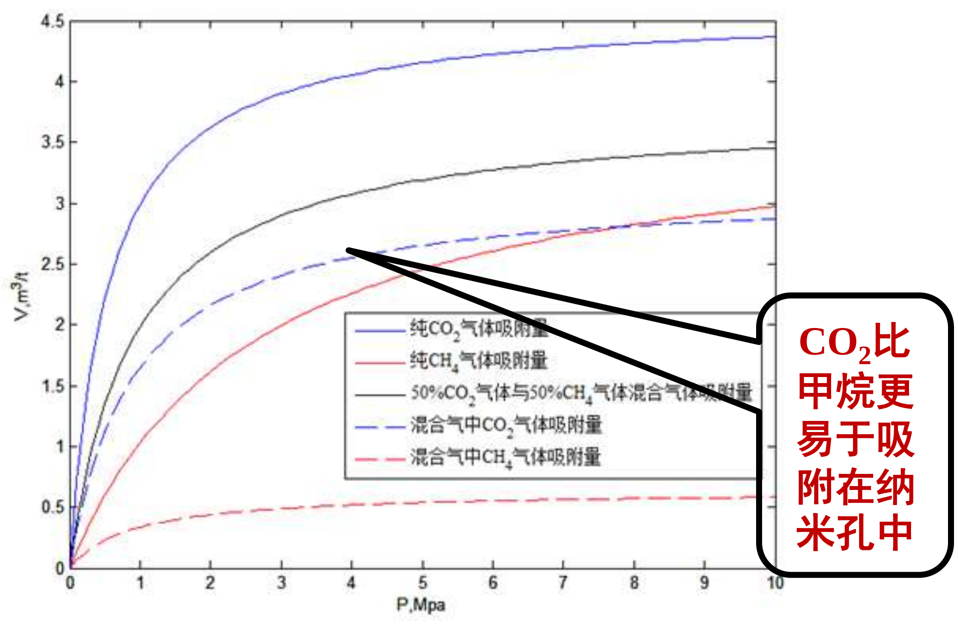
Adsorption isotherms of shale samples

龙马溪组（中石化主力产气层）、山西组高粘土页岩样品：

- 页岩对CH_4（CO_2）的等温吸附实验
- 页岩对CH_4、CO_2和N_2的等温吸附对比实验
- 30℃、77 ℃和116 ℃下，页岩对CH_4、CO_2的等温吸附实验

Shale samples form Lungmachi Formation（The major shale gas productive reservoir of Sinopec）、Shanxi Formation (with high clay contents)

- Experimental adsorption isotherms of CH_4（CO_2）at 30℃, 77 ℃ and 116 ℃
- Experimental adsorption isotherms for mixtures of CH_4, CO_2 and N_2



Outline

1. **Background and Introduction**
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5. **Summary**

Summary

- **CO_2 Storage and Two-Phase Flow in Micro Porous Media**
- **CO_2 Utilization and Heat Mass Transfer in Fractures and Nano Pores (CO_2-EGS and Enhanced shale gas recovery)**

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- Tsinghua University

Thank you for your attention!