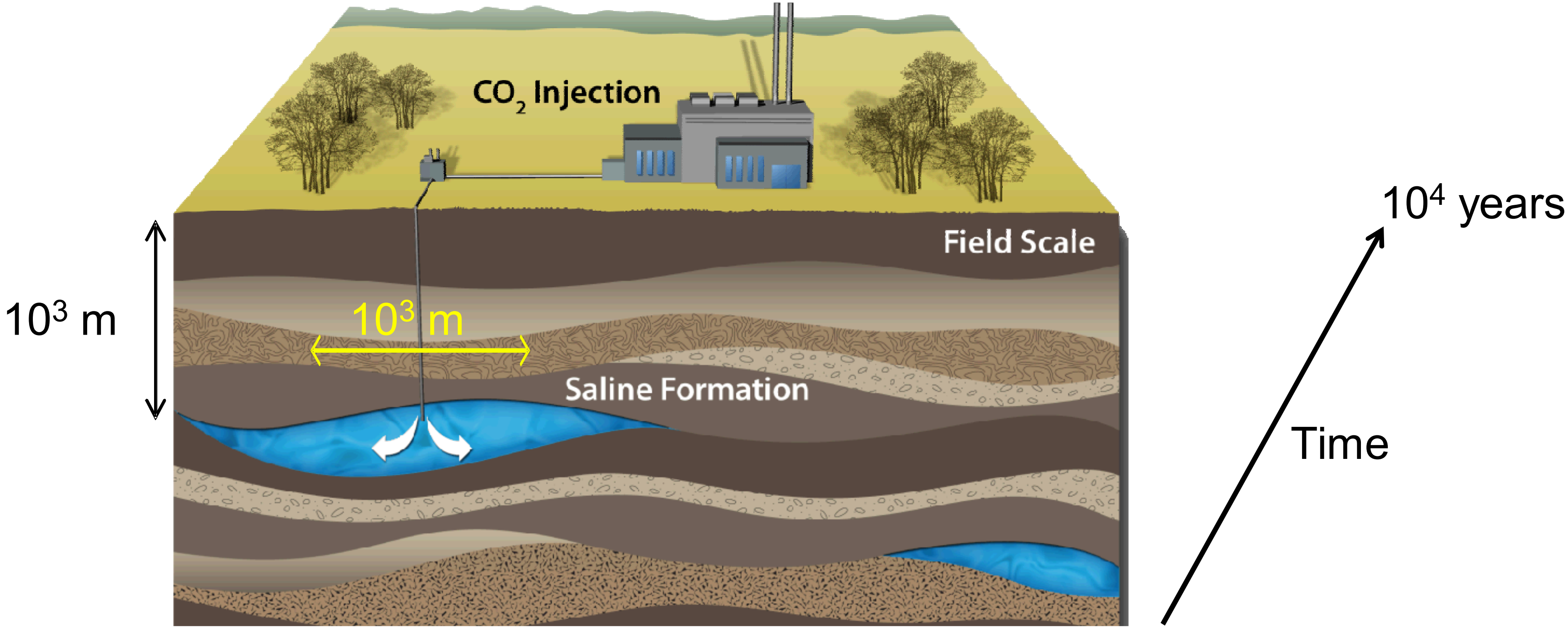
SAND2013-6721P

# Molecular Simulation of Carbon Dioxide, Brine, and Clay Mineral Interactions

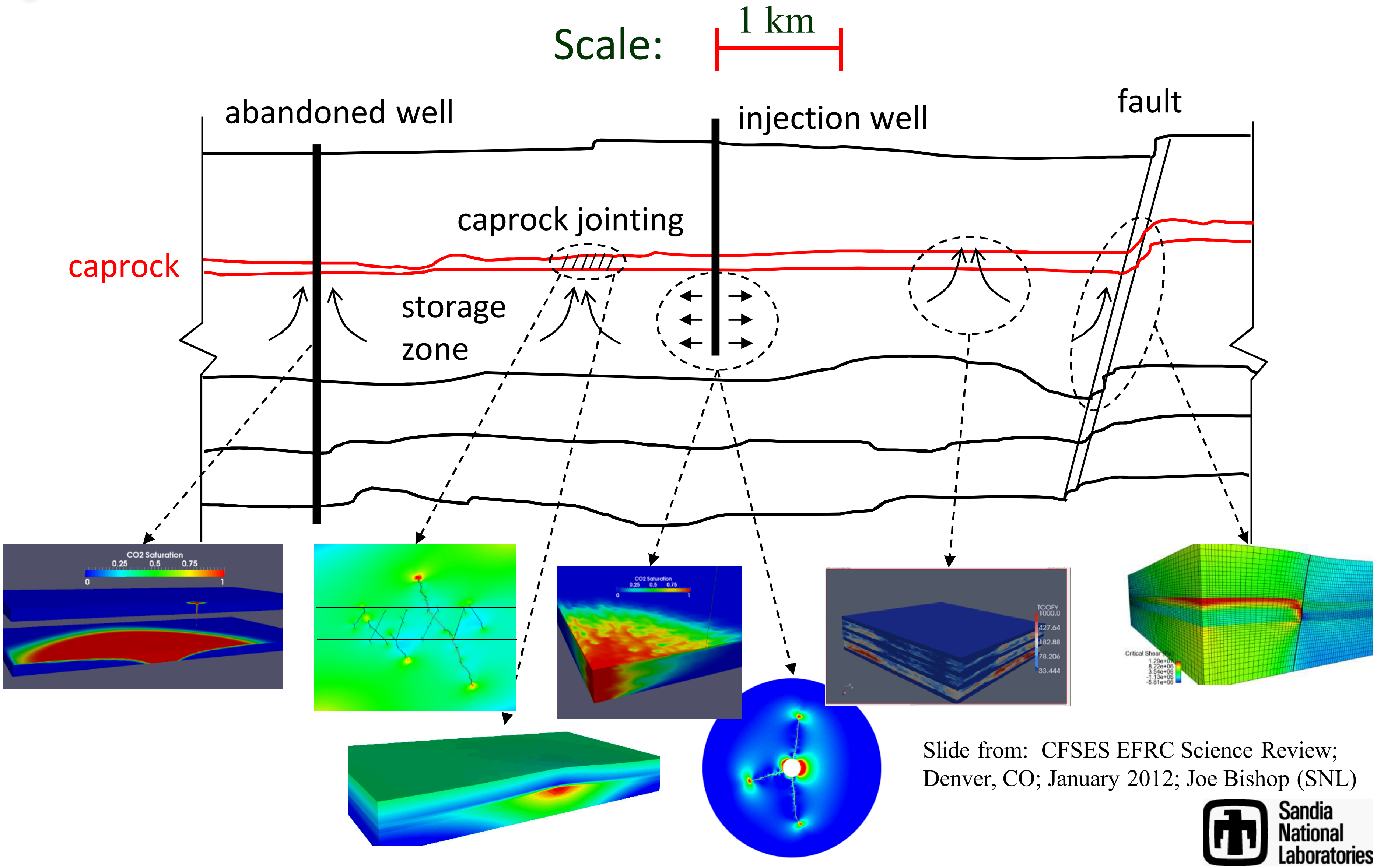
Craig M. Tenney and Randall T. Cygan

# Carbon capture and geological storage
# Big Picture



1. Capture $CO_2$
2. Inject it deep underground
3. Hope it stays there

# Field-scale modeling



Slide from: CFSES EFRC Science Review; Denver, CO; January 2012; Joe Bishop (SNL)

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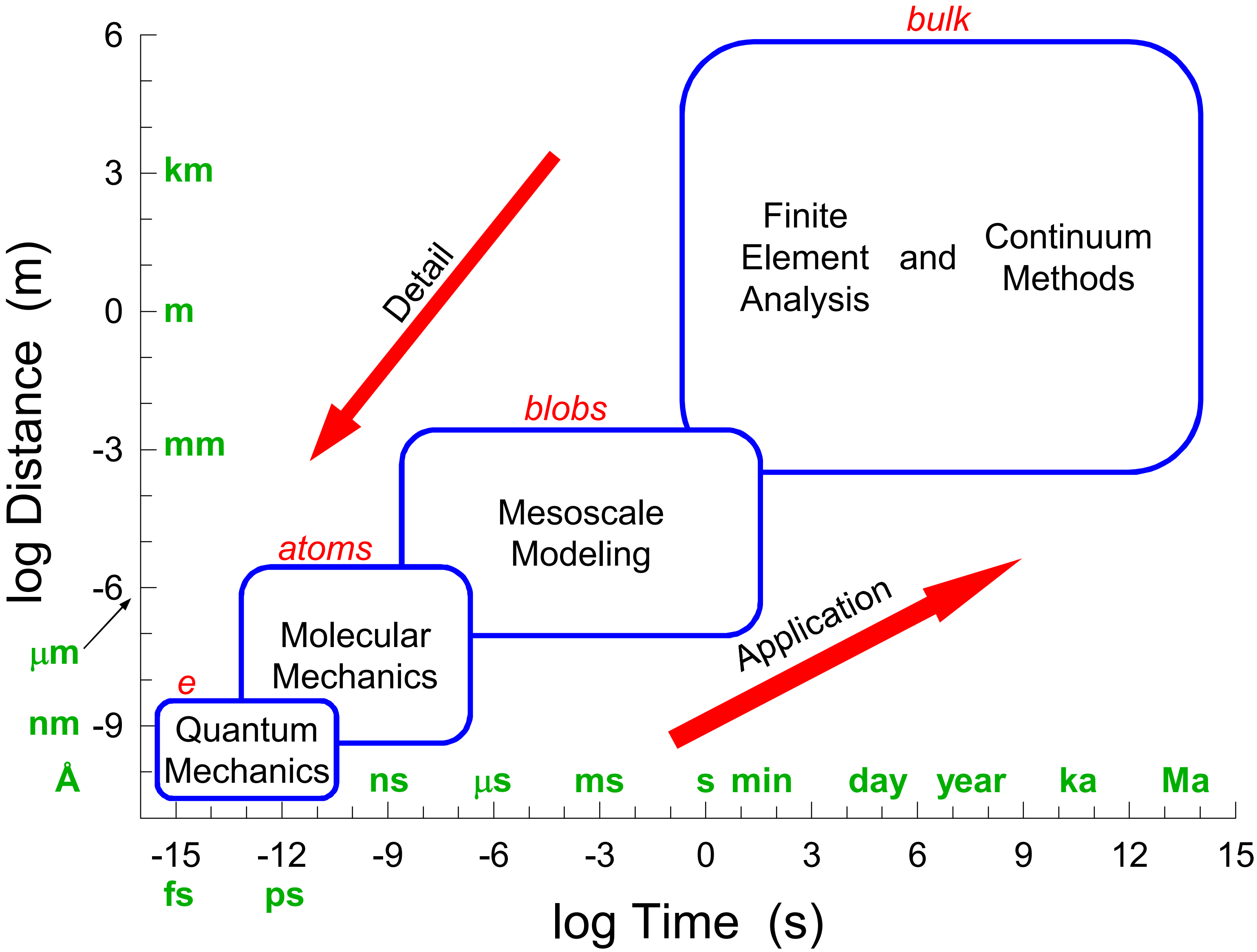
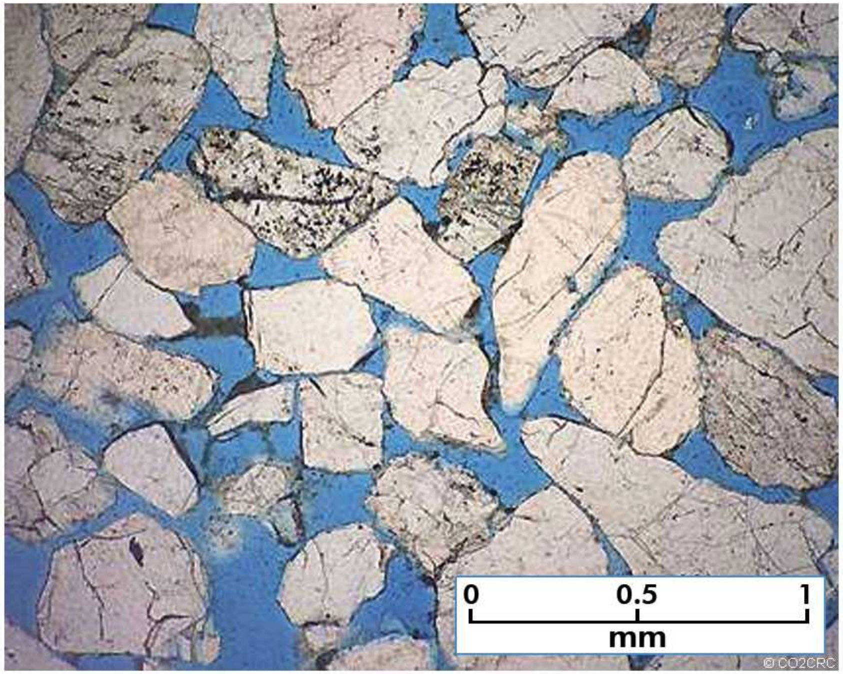
# Multiscale simulation



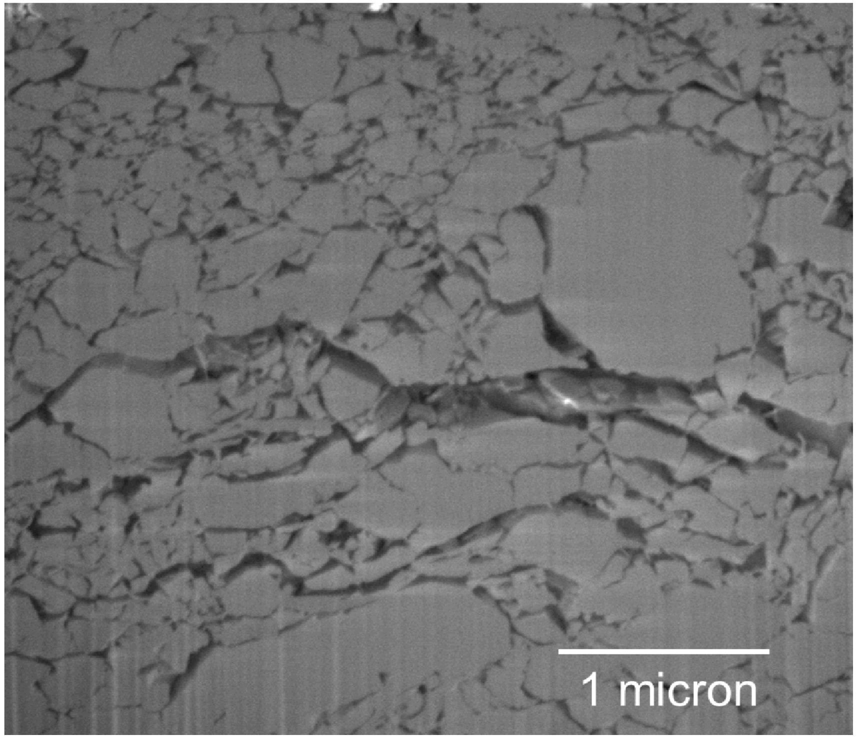
# Geological carbon storage
# Up Close

## reservoir rock



Source: Cooperative Research Centre
for Greenhouse Gas Technologies,
http://www.co2crc.com.au/

## cap rock

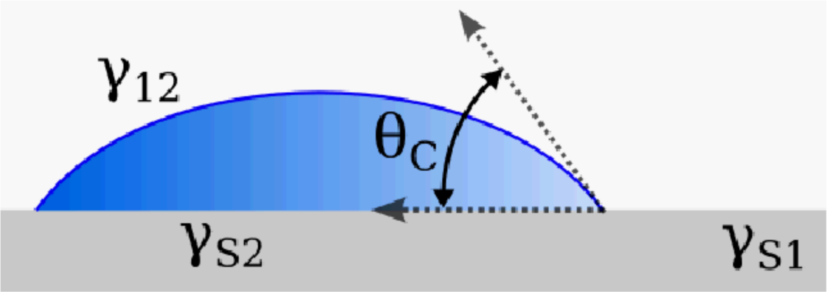


Source: Hongkyu Yoon (SNL)

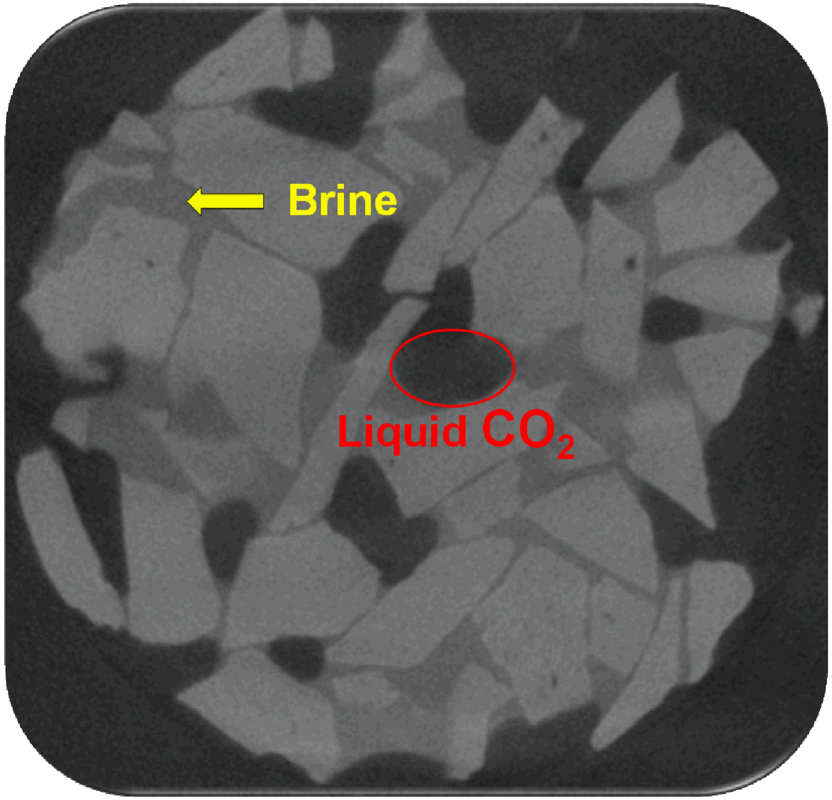
# Sub-pore scale

- **interfacial tension $\gamma_{12}$**
  - **surface free energy**

- **contact angle $\theta_C$**
  - **indication of wettability**



$$\gamma_{S1} - \gamma_{S2} = \gamma_{12} \cos\theta_C$$



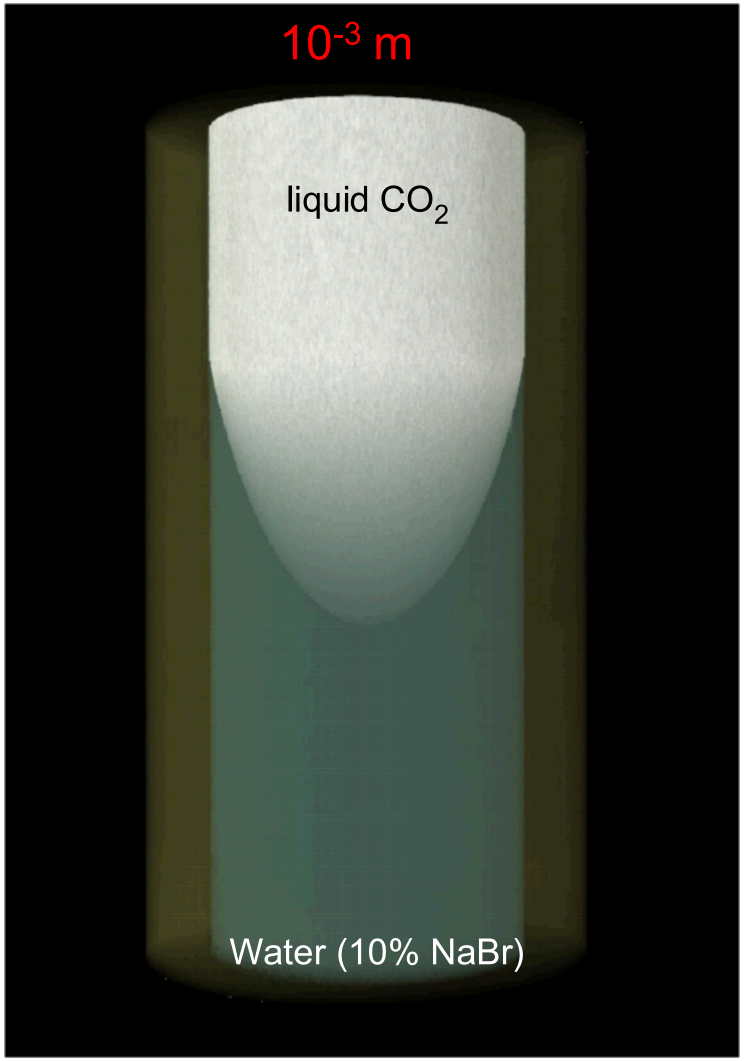
Source: Kuldeep Chaudhary (UT Austin)

# Pore- and field-scale

- **capillary pressure $p_c$**
  - **overpressure required to displace current fluid with new fluid**

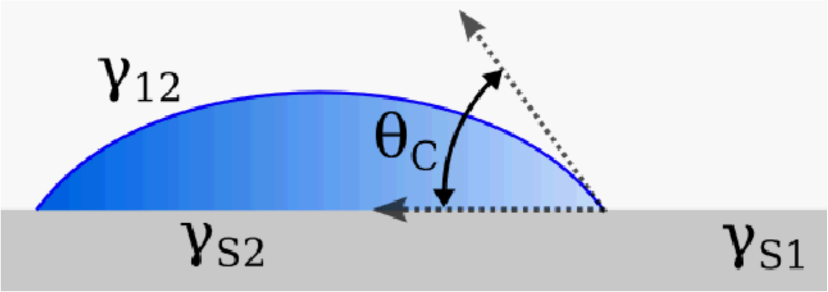
$$p_c = \frac{2\gamma_{12}\cos\theta_C}{r}$$

- **relative permeability**
  - **fractional permeability of a fluid in the presence of other fluid(s)**



Source: Kuldeep Chaudhary (UT Austin)

# Molecular simulation of aqueous and supercritical $CO_2$ nanodroplets

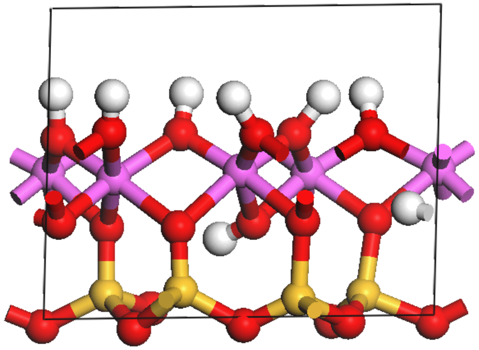


## kaolinite

gibbsite surface
(hydrophilic) →

siloxane surface
(hydrophobic) →

**H**
**Al**
**Si**
**O**



# Simulation details

- (20 x 20 x 17) nm
- 3 kaolinite layers
  (bottom two fixed)
- 330K, 20MPa
- 10-15 ns

- $CO_2$ in $H_2O$
  - 600k atoms
- $H_2O$ in $CO_2$
  - 300k atoms
- brine systems
  - 0.7 M NaCl
  - 0.2 M $CaCl_2$

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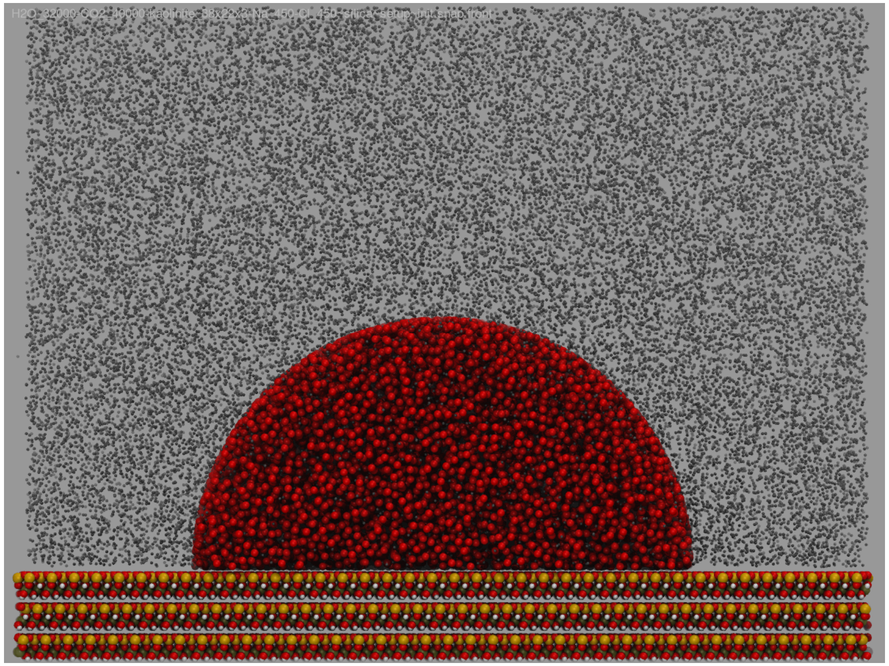
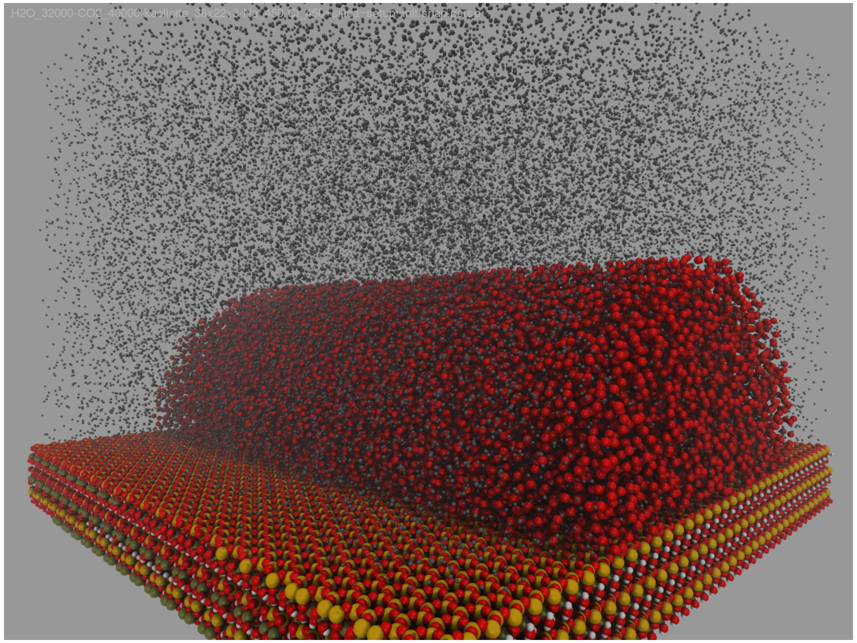
# siloxane (hydrophobic) surface
# 0.7M NaCl in $CO_2$ – initial configuration

**front view**

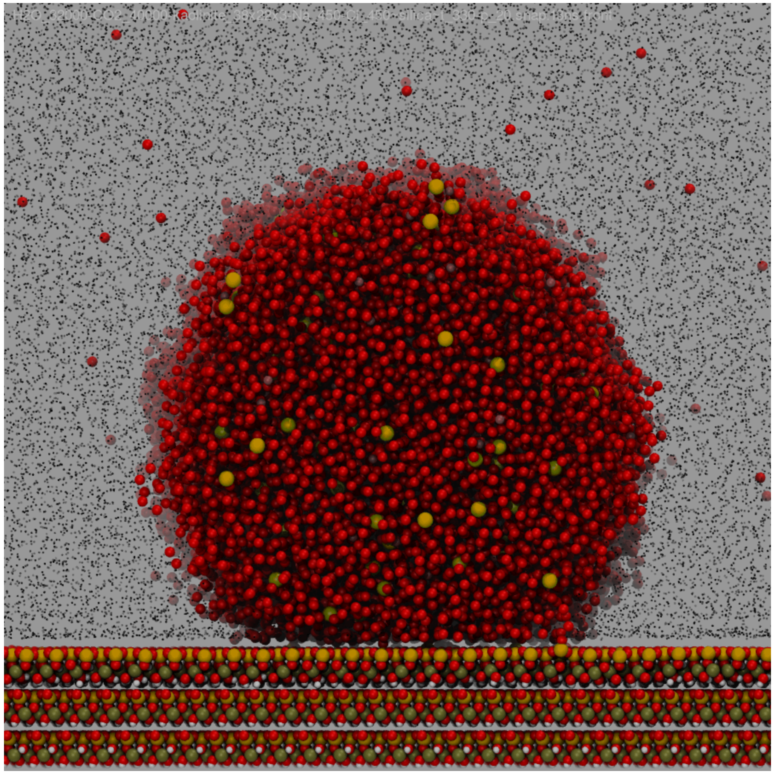


**oblique view**

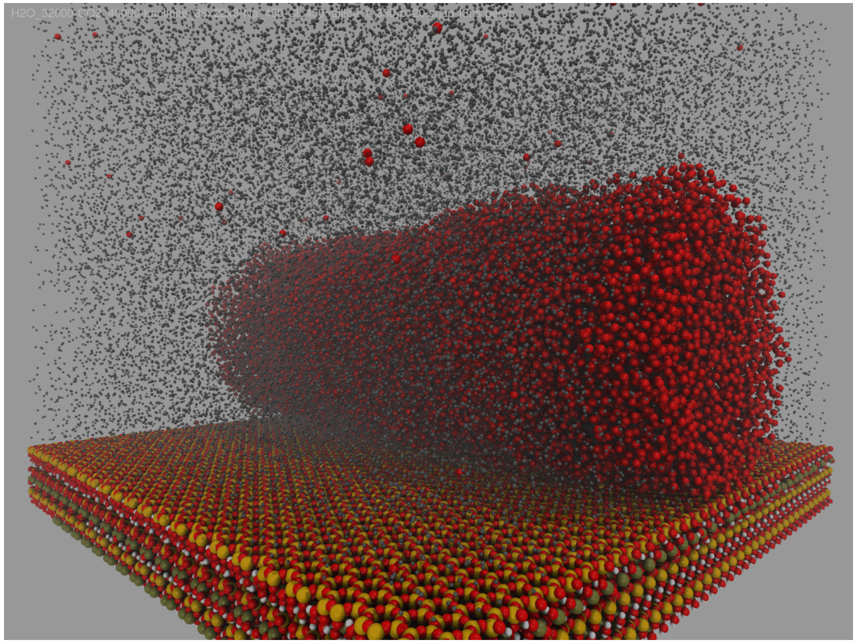


# siloxane (hydrophobic) surface
# 0.7M NaCl in $CO_2$ – final configuration

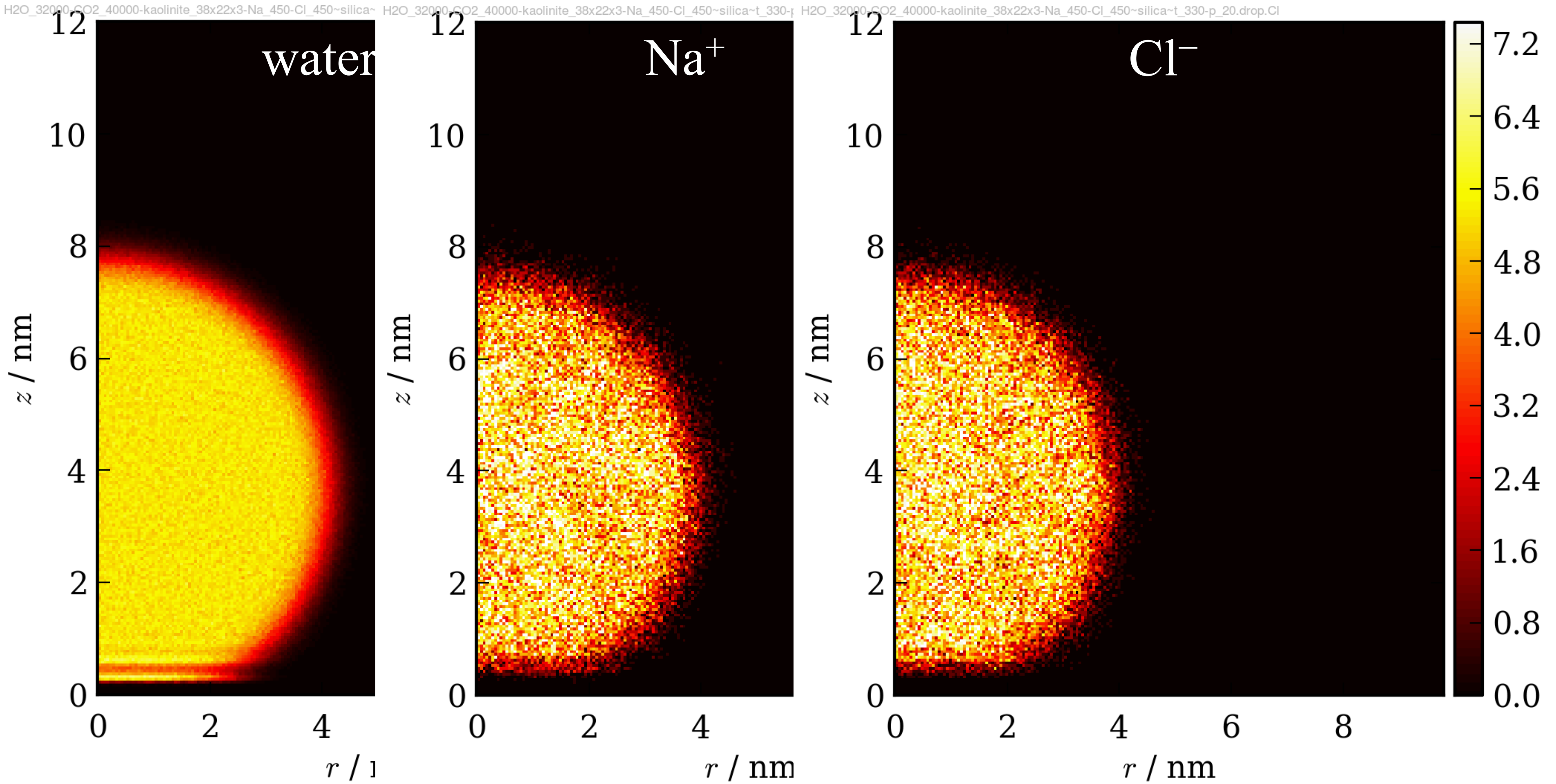
**front view**



**oblique view**

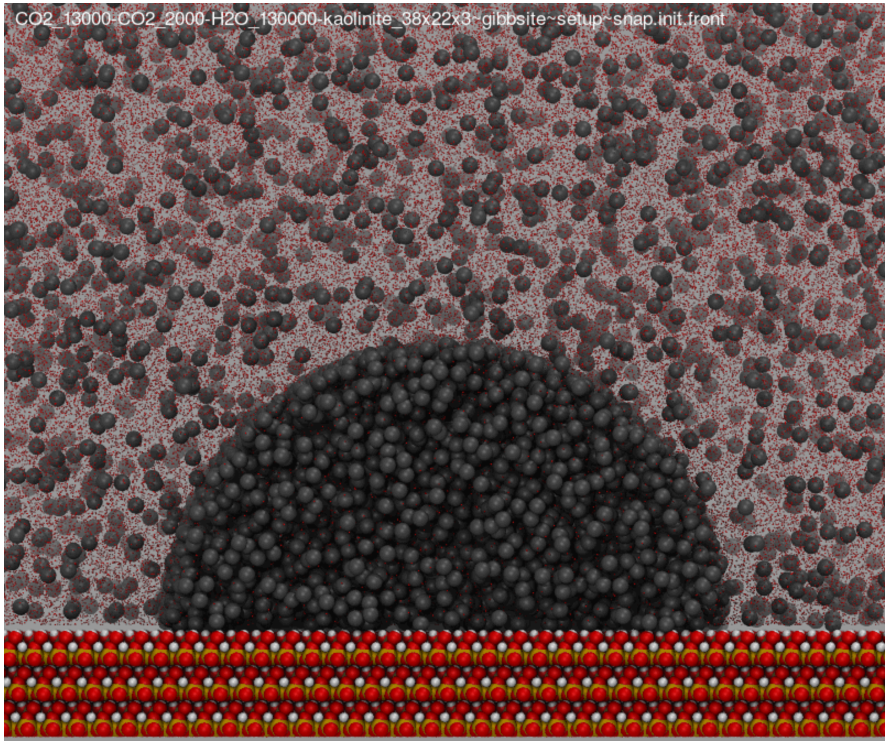


# siloxane (hydrophobic) surface
# 0.7M NaCl in $CO_2$ – final configuration

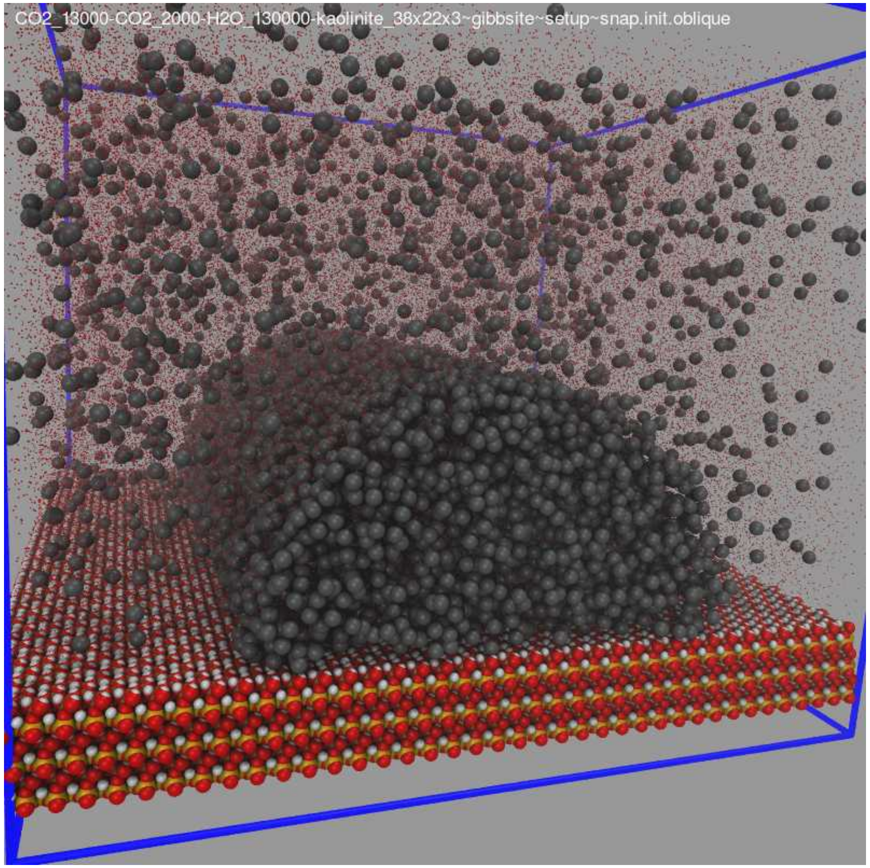


# gibbsite (hydrophilic) surface
# $CO_2$ in $H_2O$ – initial configuration

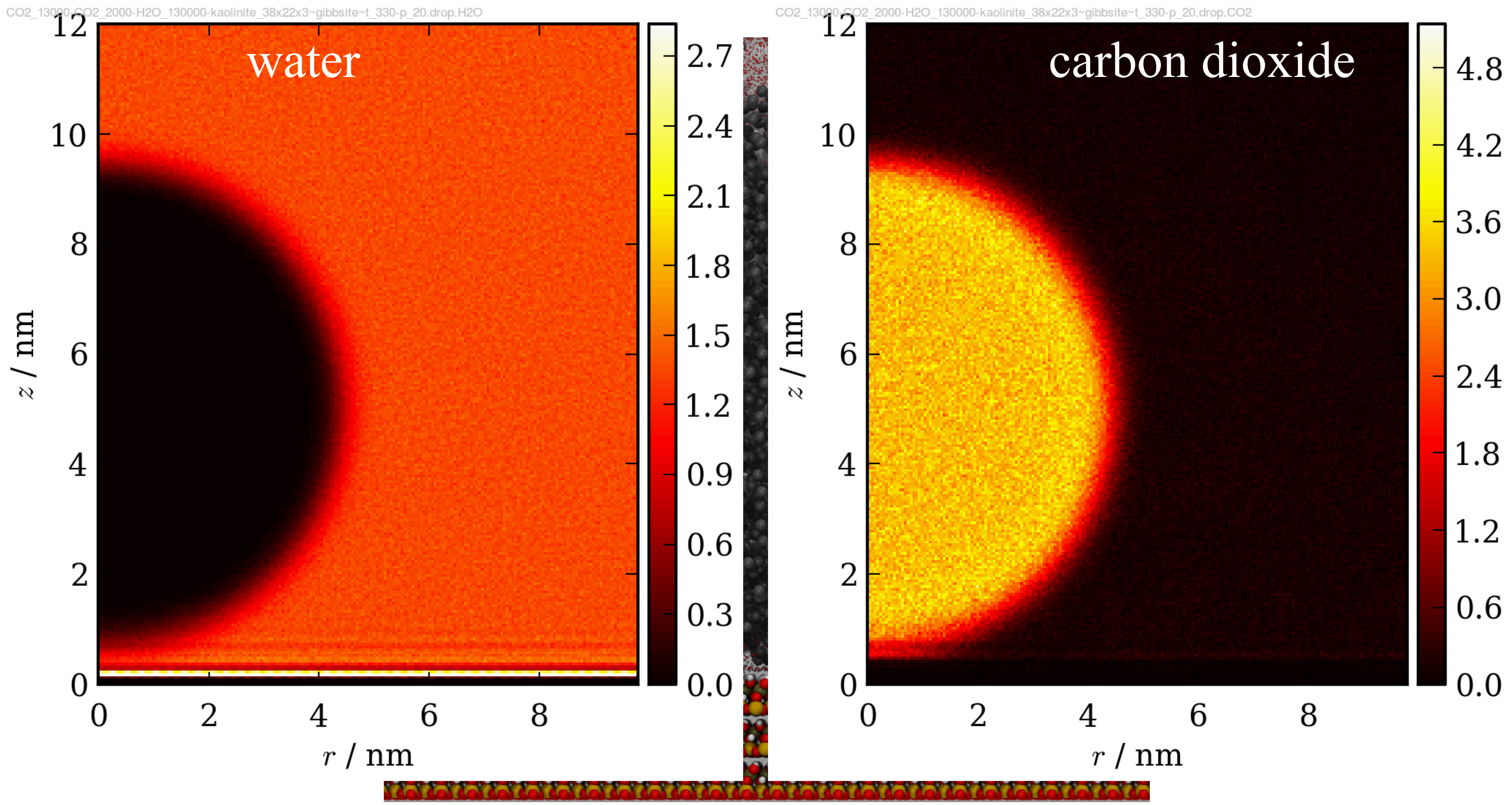
**front view**



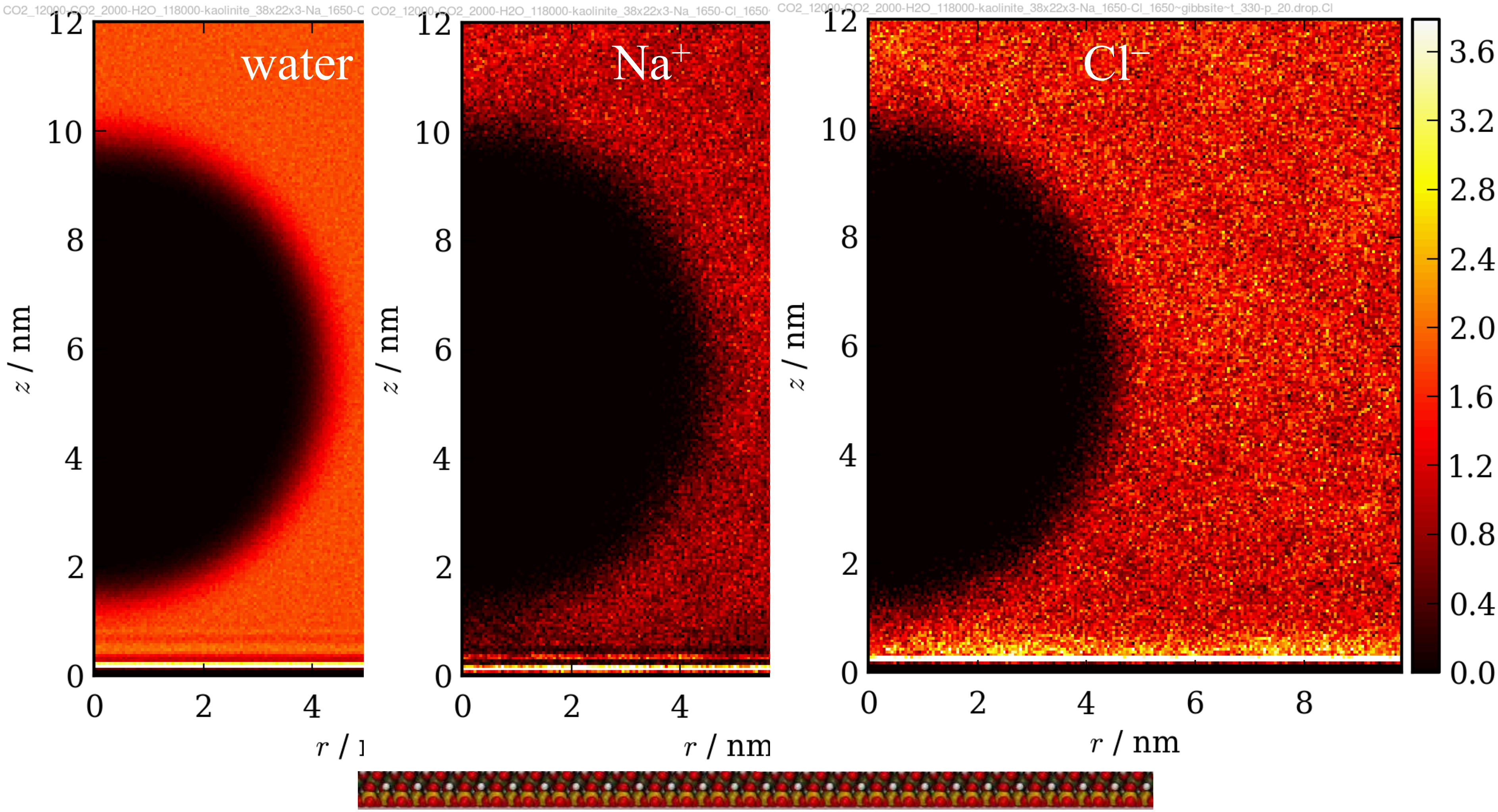
**oblique view**



# gibbsite (hydrophilic) surface
# $CO_2$ in $H_2O$ – final configuration



# gibbsite (hydrophilic) surface
# $CO_2$ in 0.7M NaCl – final configuration



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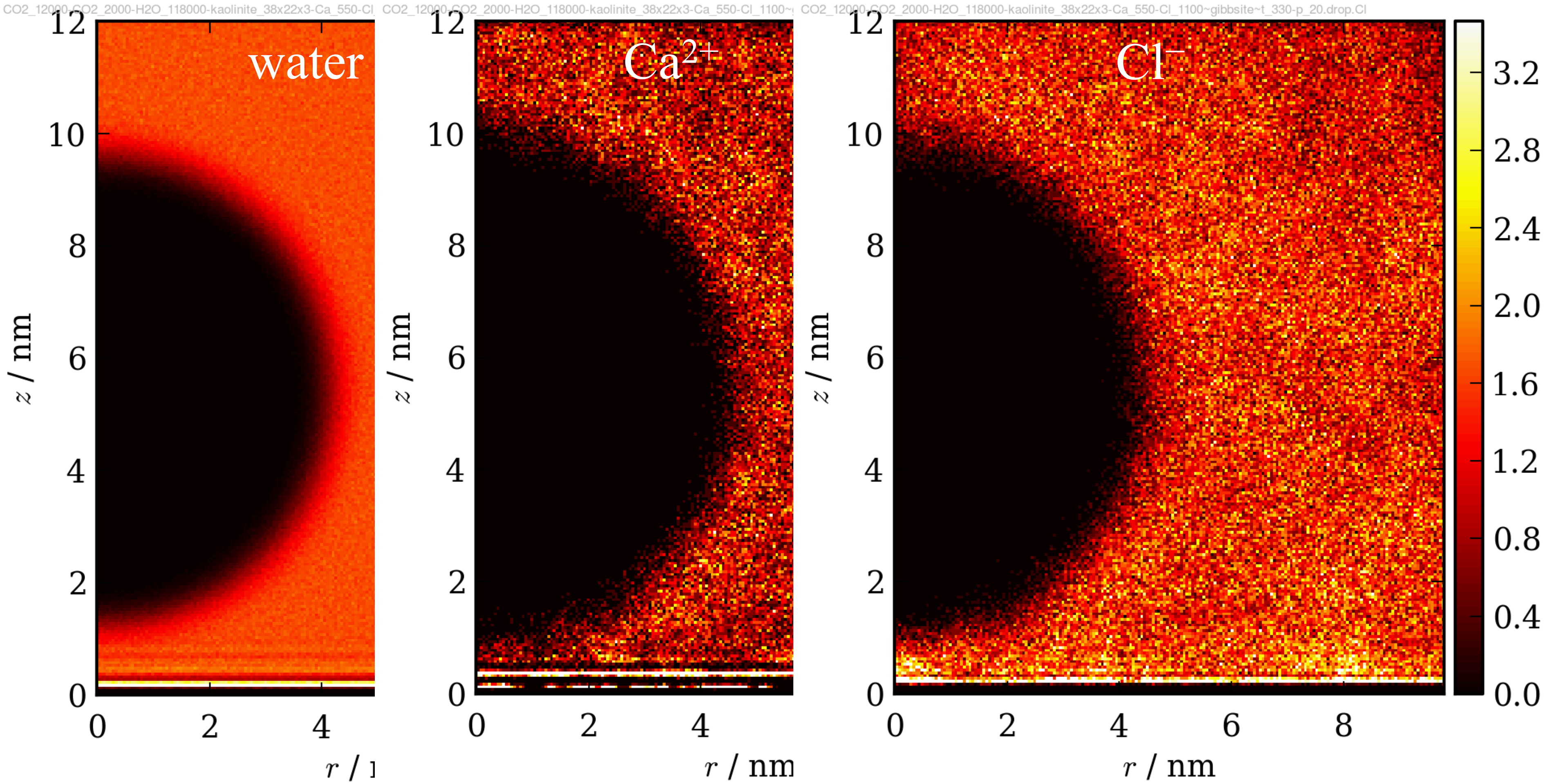
# gibbsite (hydrophilic) surface
# $CO_2$ in 0.2M $CaCl_2$ – final configuration



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# Summary

- **Simulation shows realistic behavior for $CO_2$, $H_2O$, and ions on hydrophilic and hydrophobic basal surfaces of kaolinite.**

- **Possible future application: rational design of surfactants, coatings, enhanced oil or gas recovery**

# Acknowledgments

- Simulation development aided by discussions with
  - Louise Criscenti (SNL)
  - Ian Bourg (LBNL)

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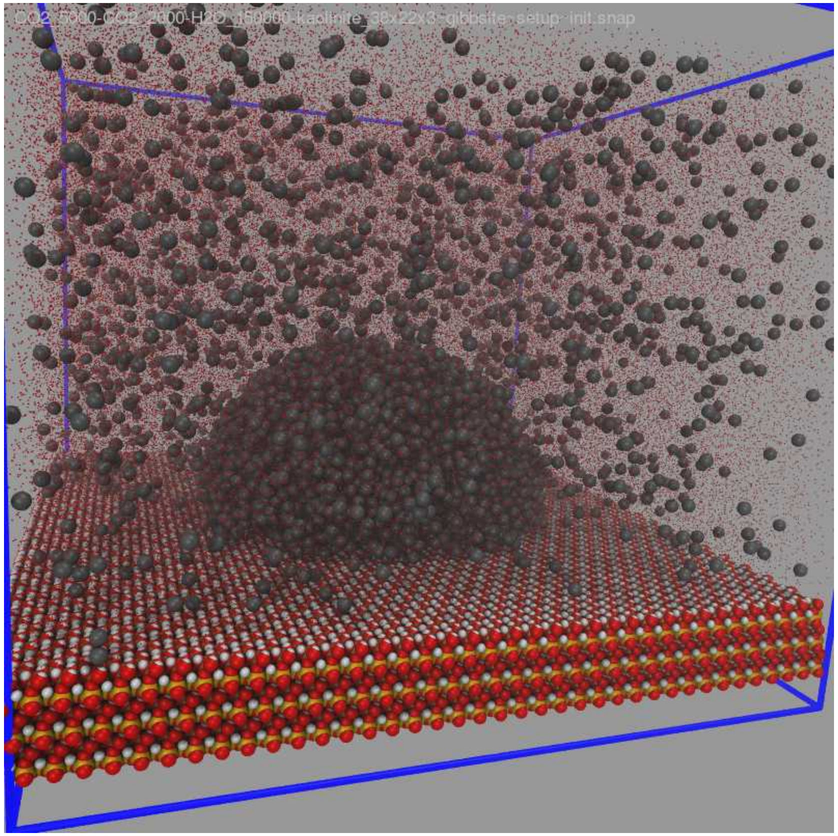
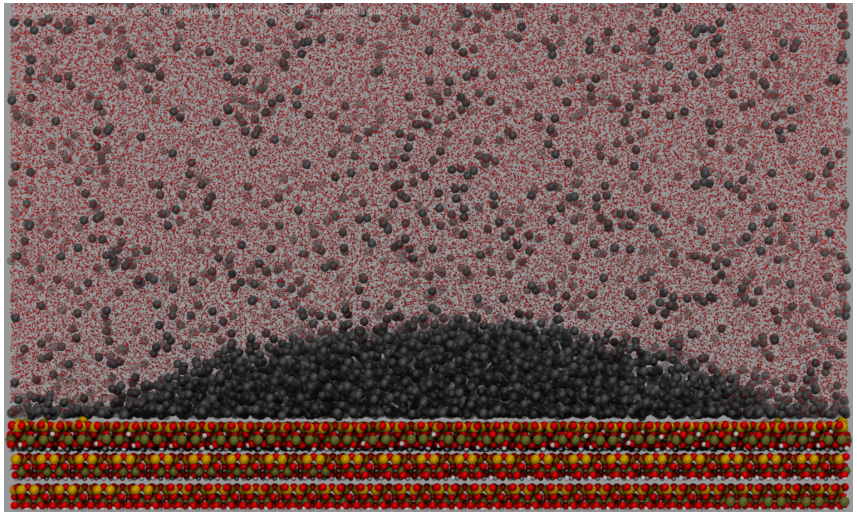
# supplementary slides

# siloxane (hydrophobic) surface
# $CO_2$ in $H_2O$

**initial**

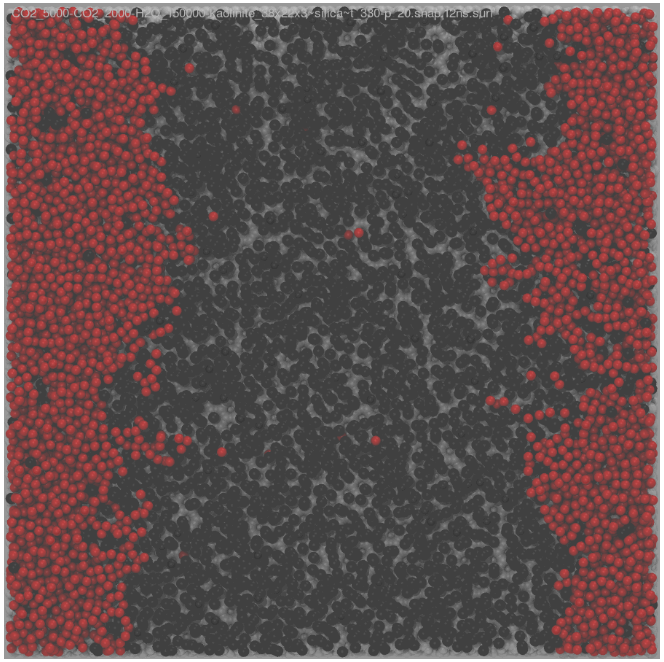


**final**

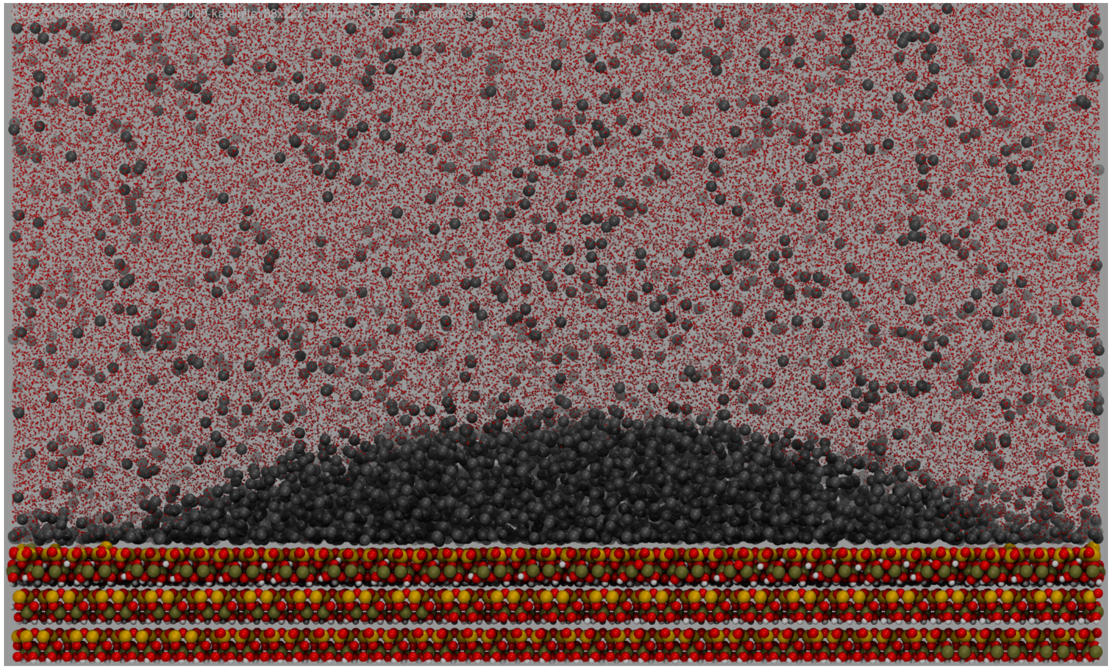


# siloxane (hydrophobic) surface
# $CO_2$ in $H_2O$ – final configuration

**top view**



**front view**



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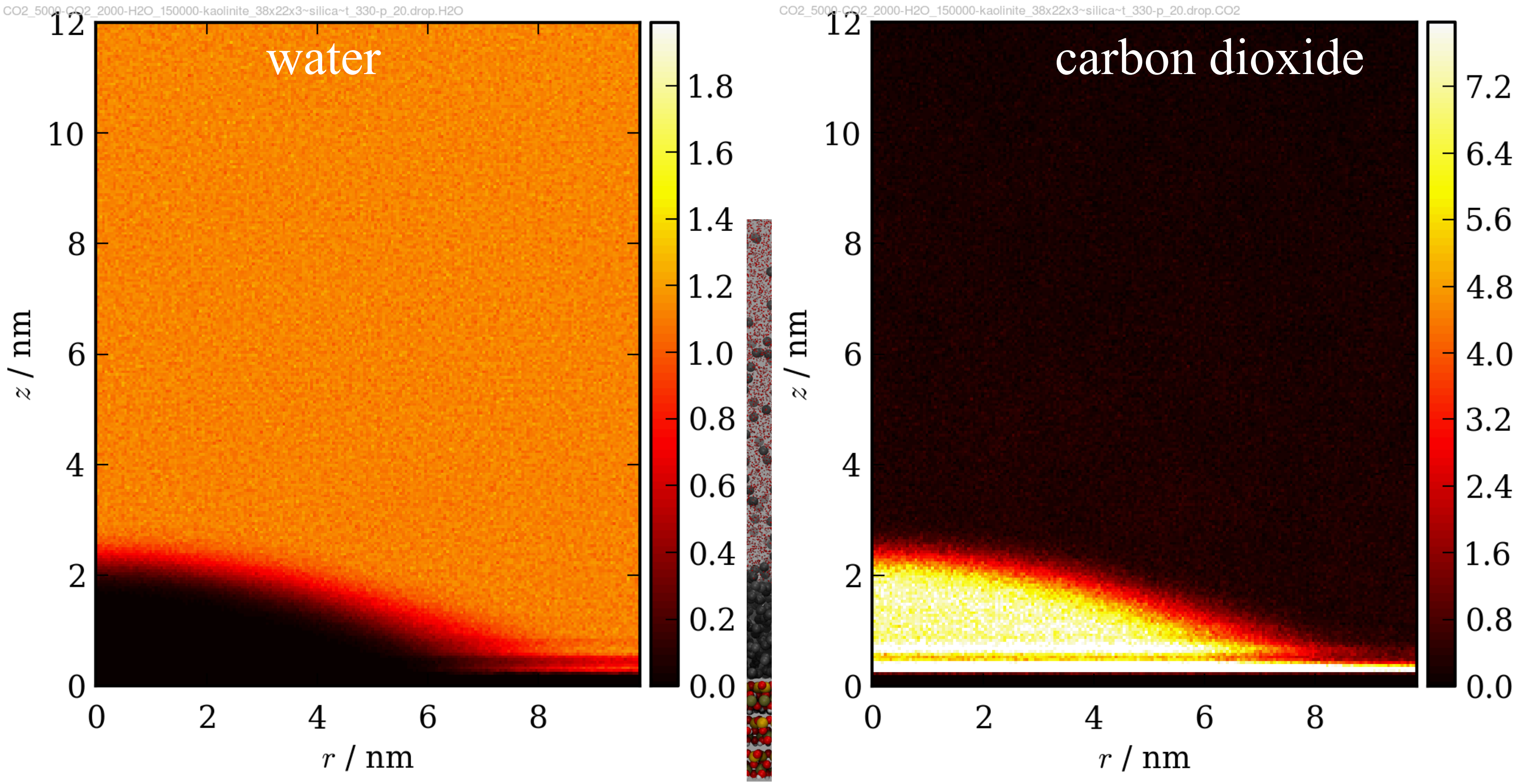
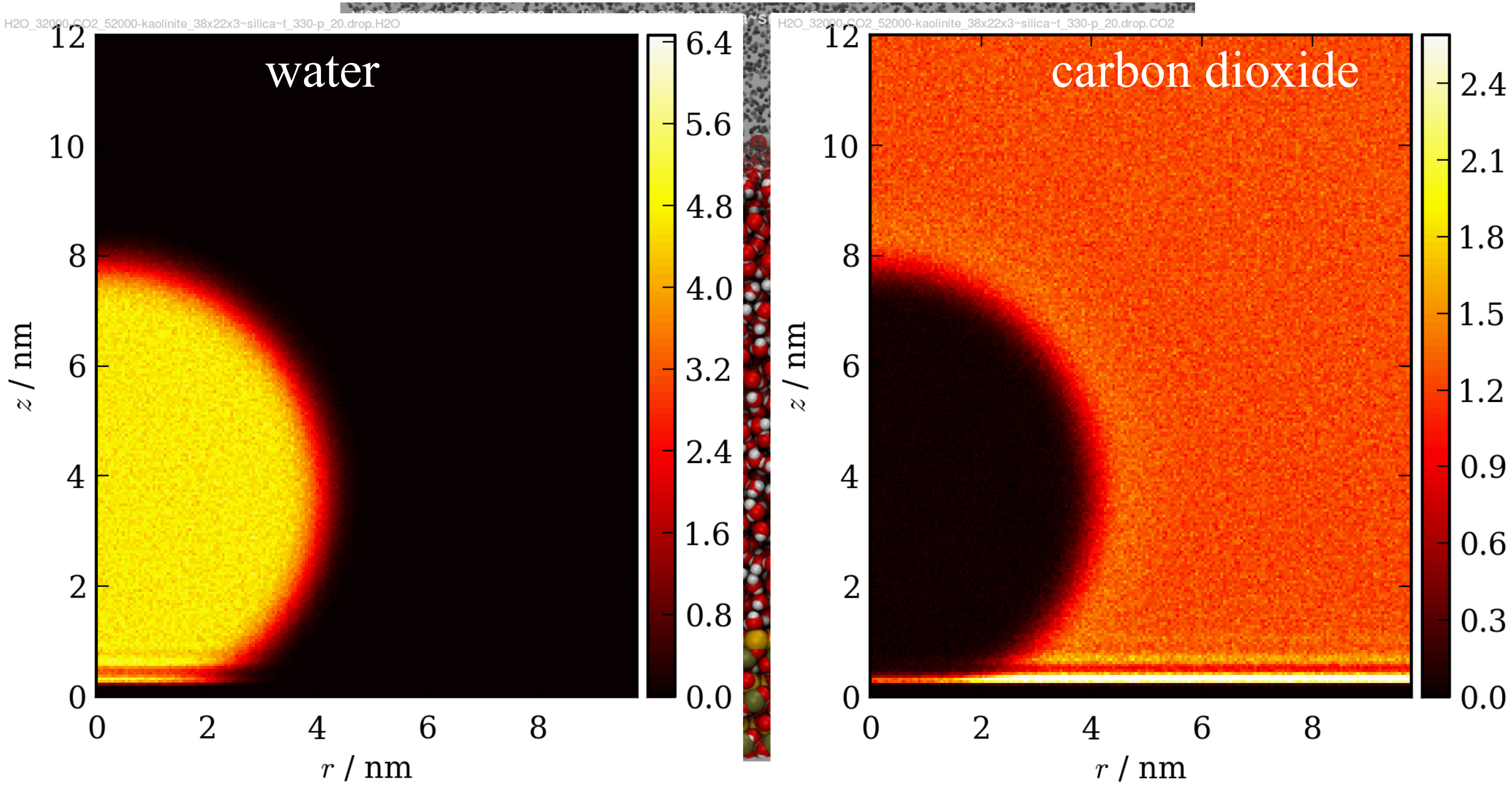
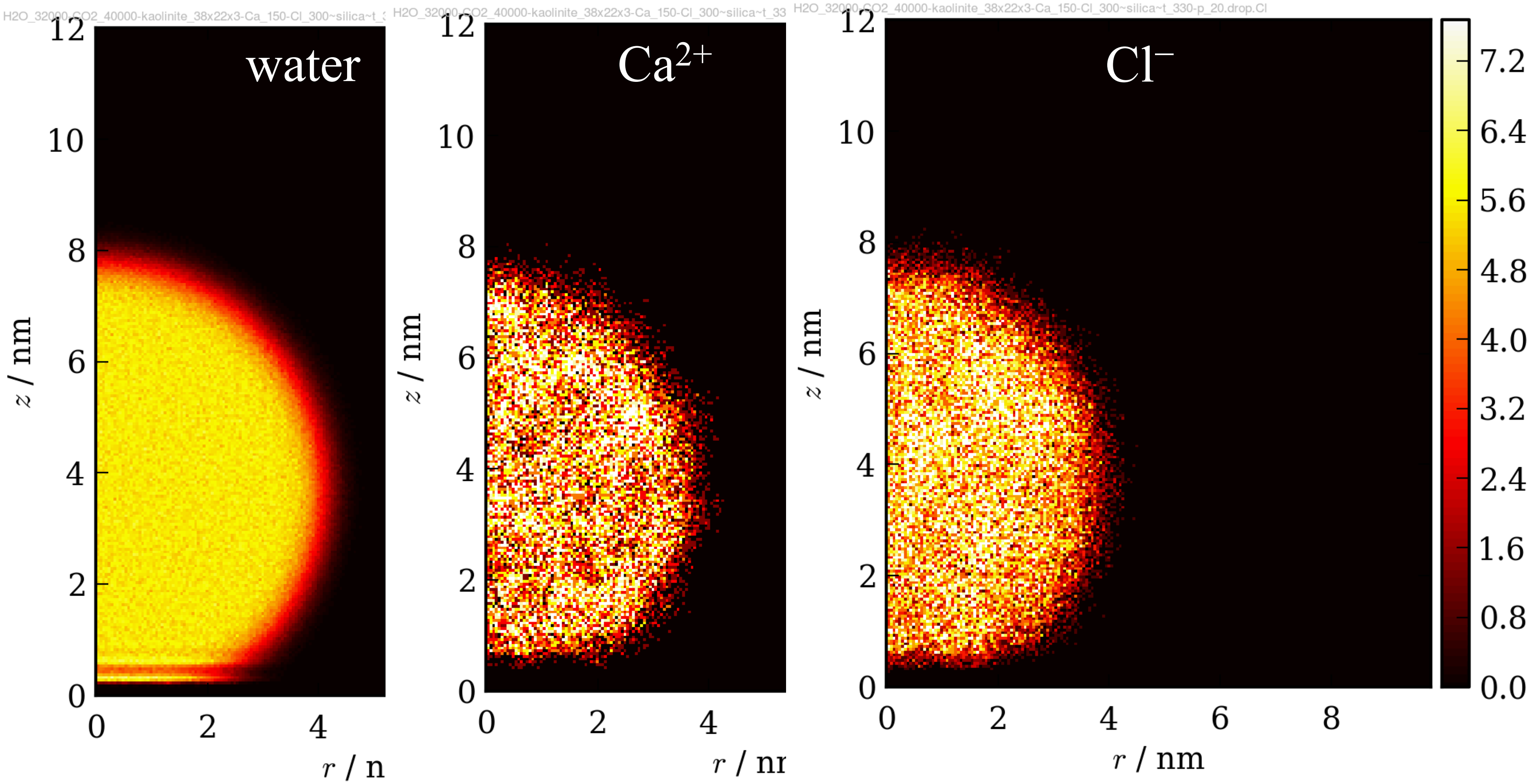
# siloxane (hydrophobic) surface
# $CO_2$ in $H_2O$ – final configuration



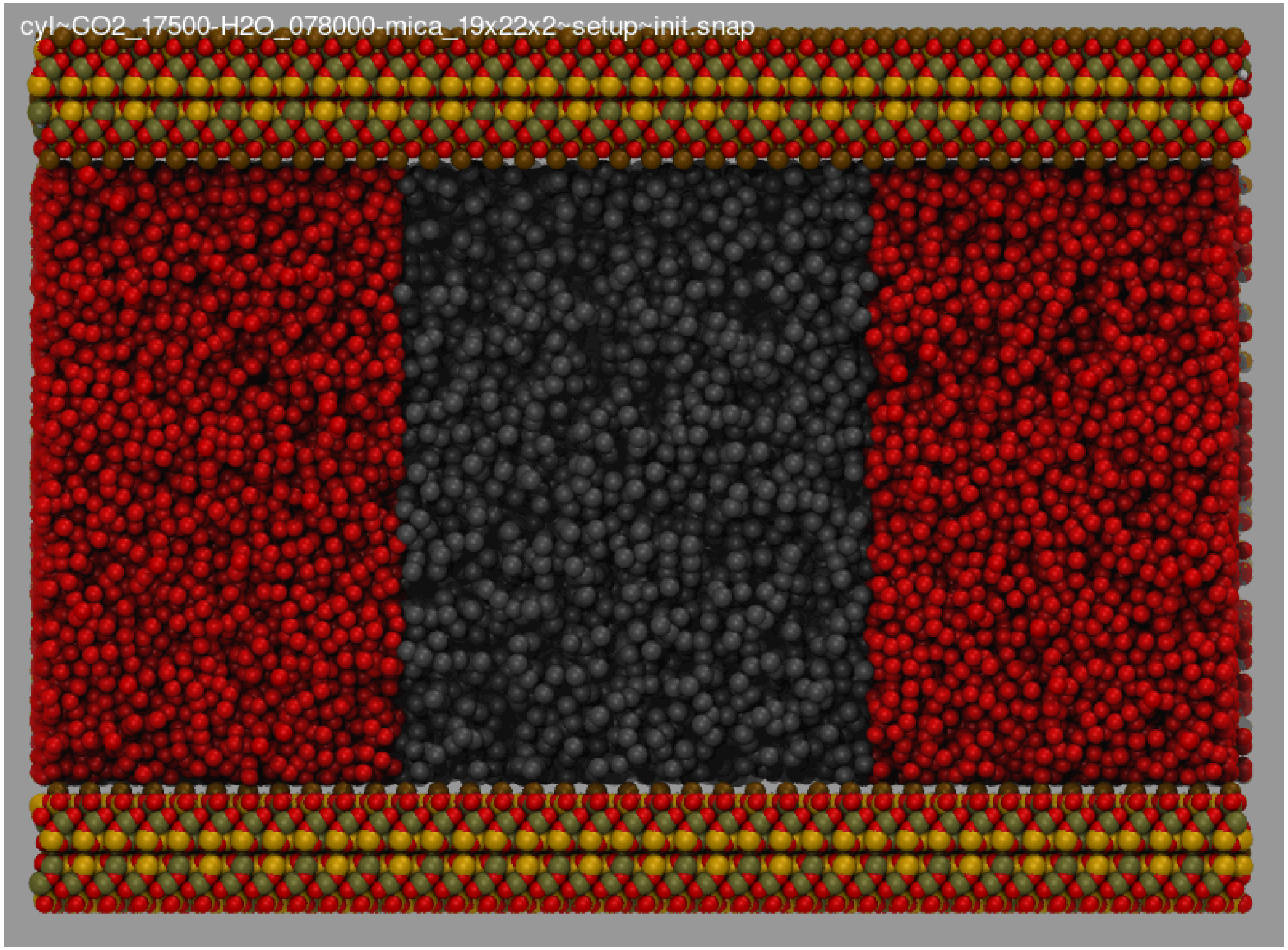
# siloxane surface – $H_2O$ in $CO_2$



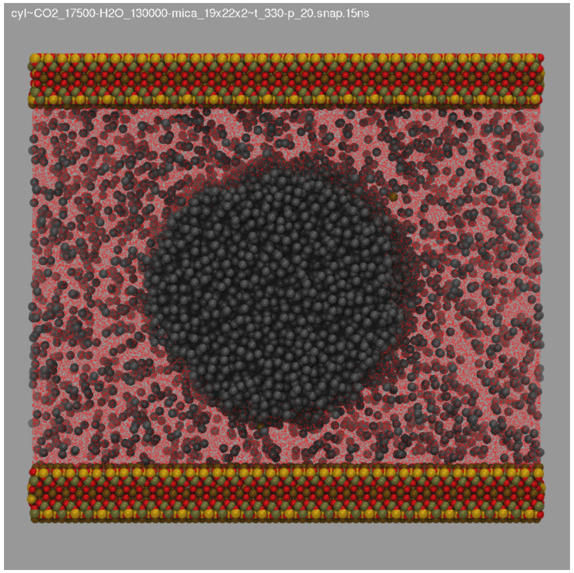
# siloxane surface – 0.2M $CaCl_2$ in $CO_2$

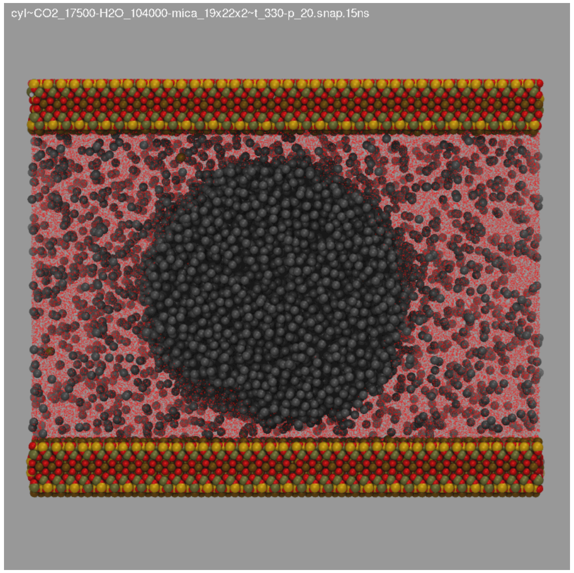


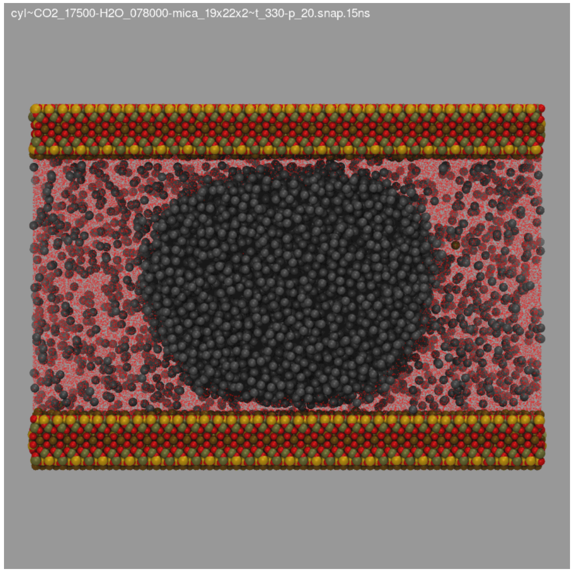
# $CO_2$ and $H_2O$ in mica slit pores initial configuration

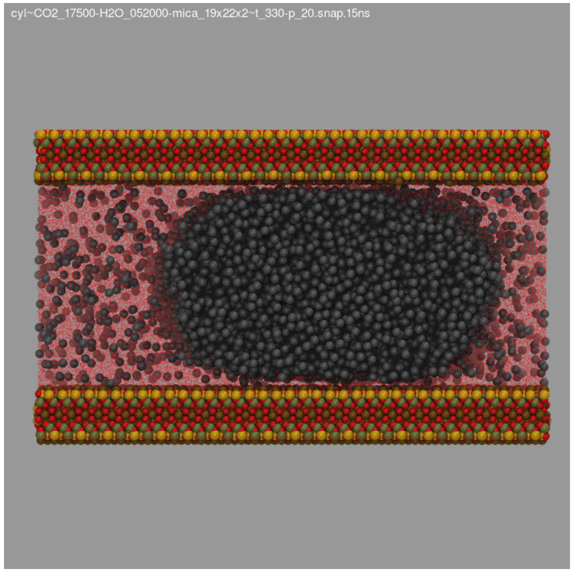


# $CO_2$ and $H_2O$ in mica slit pores final configurations

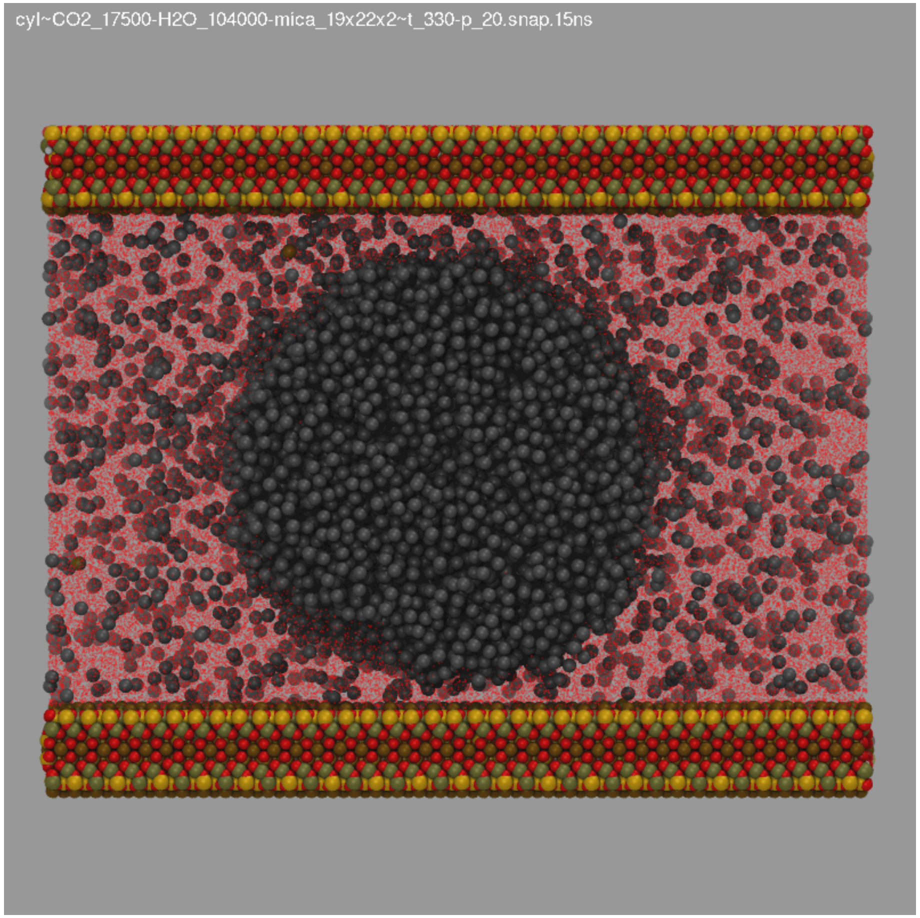


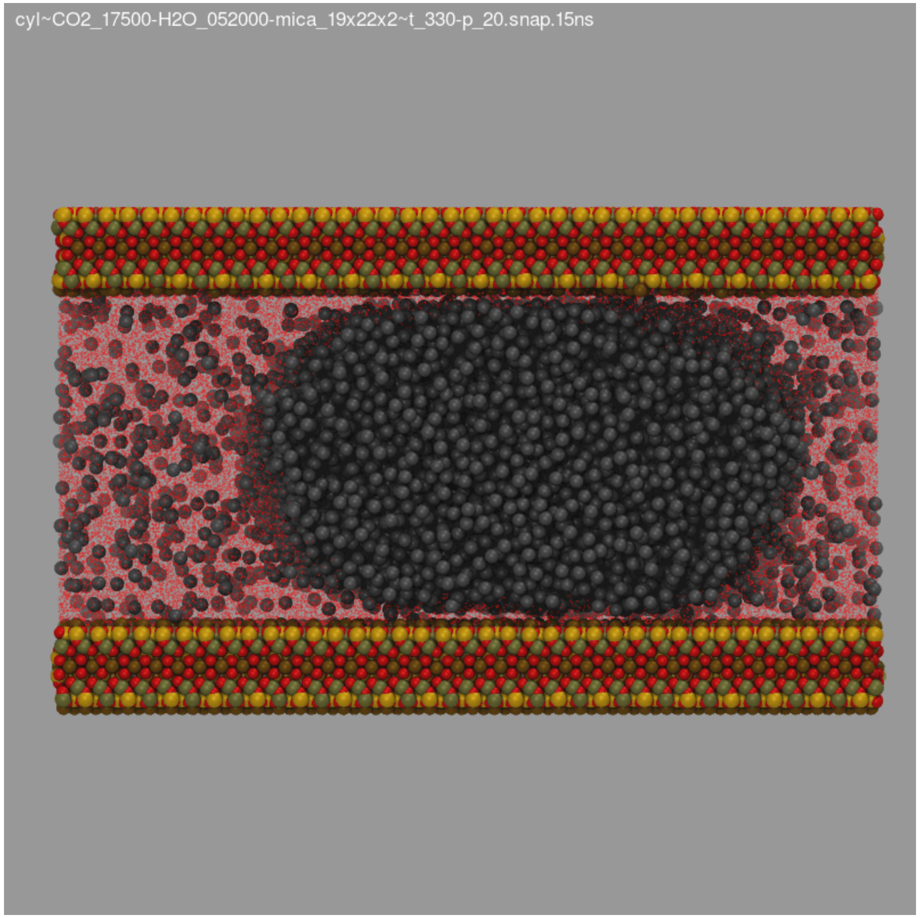




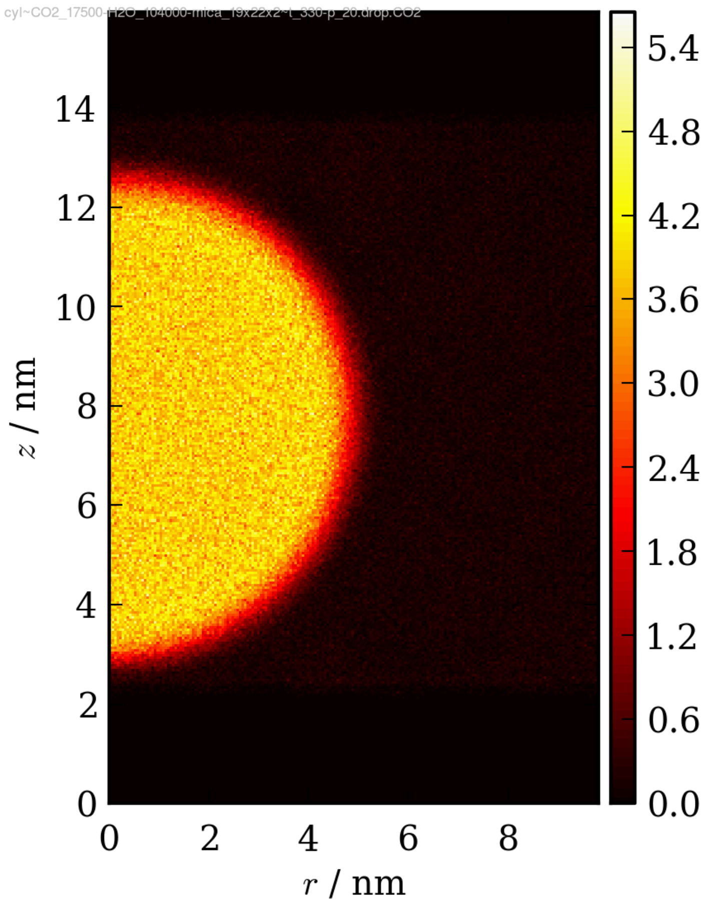


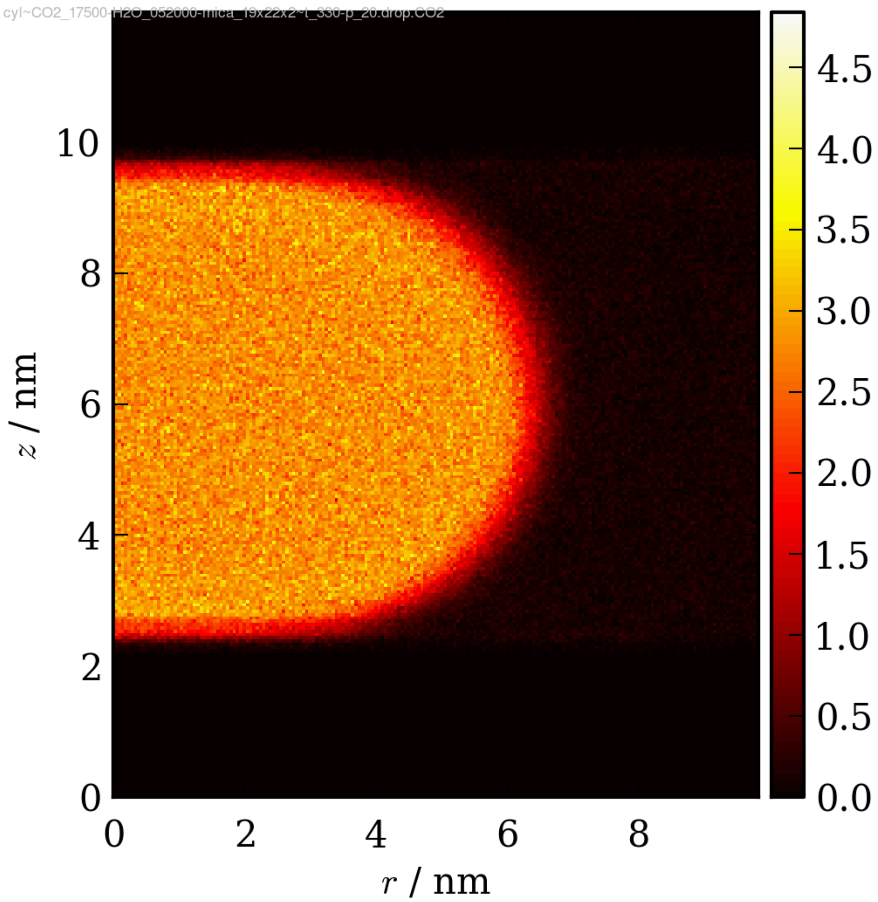
# $CO_2$ and $H_2O$ in mica slit pores final configurations



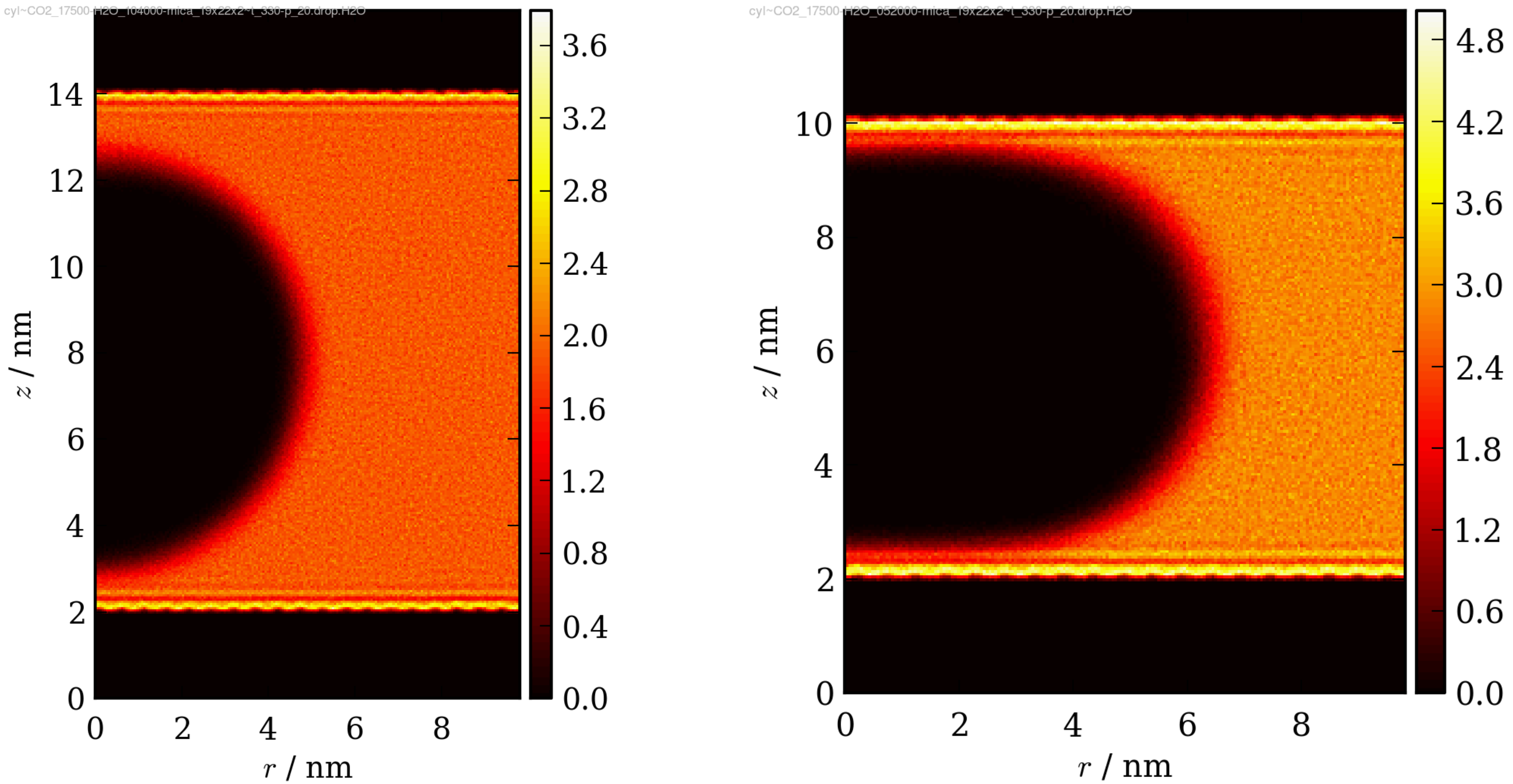


# $CO_2$ and $H_2O$ in mica slit pores
# $CO_2$ density





# $CO_2$ and $H_2O$ in mica slit pores
# $H_2O$ density



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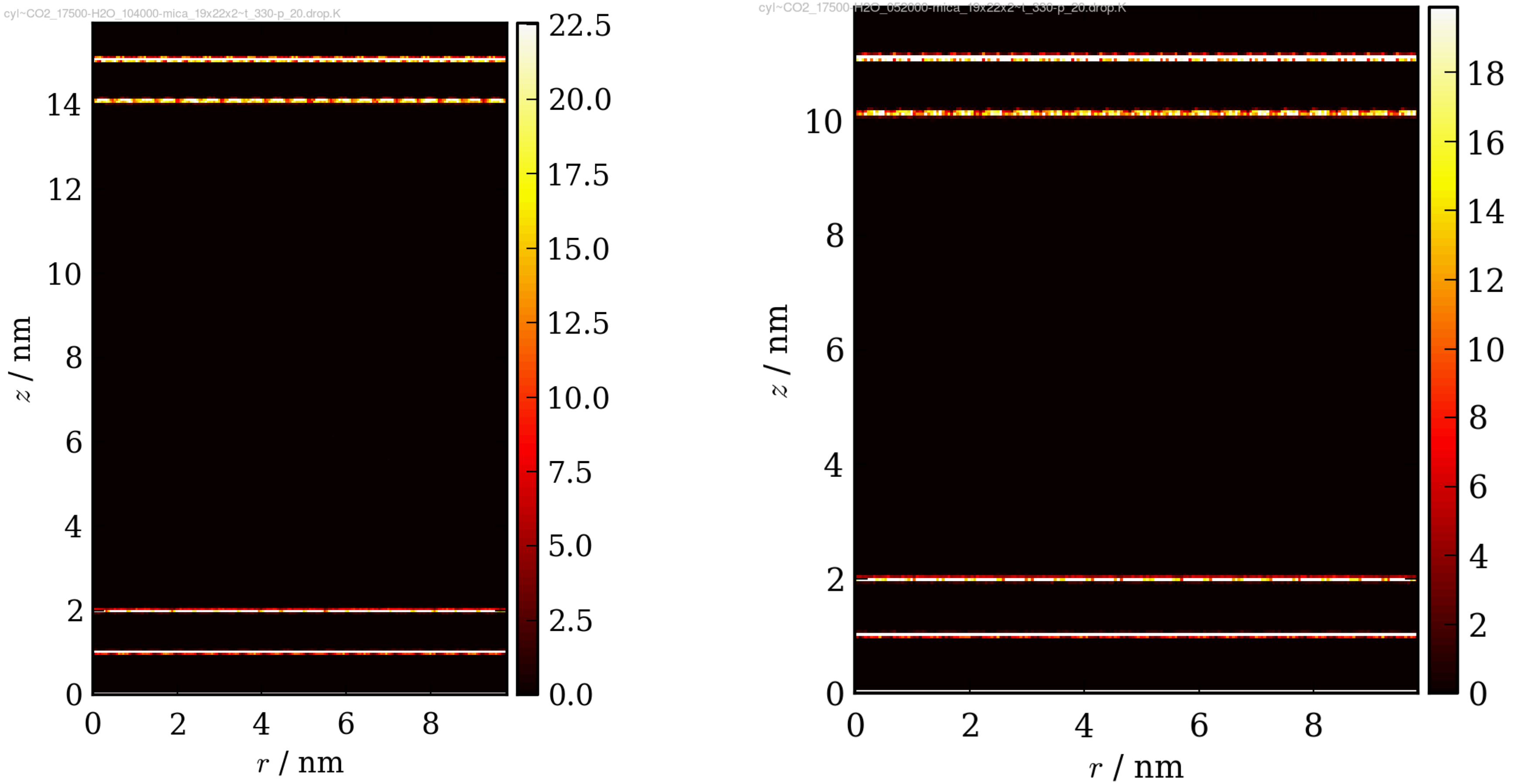
# $CO_2$ and $H_2O$ in mica slit pores
# $K^+$ density



# Summary

- kaolinite hydrophilic surface
  - layers of water (and ions) completely displace $CO_2$
- kaolinite hydrophobic surface
  - strong $CO_2$ wetting in presence of water and brine
  - weak water and brine wetting in presence of $CO_2$
- mica slit pores
  - unconfined $CO_2$ is completely displaced by well-developed water layers
  - strongly confined $CO_2$ displaces diffuse water layers, slightly altering contact angle