Experimental Evaluation of Water Films on Mineral Surfaces in Hydrous Supercritical CO_2

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The Behavior of Water in Supercritical CO_2:

Water Adsorption and Capillary Condensation

At CO_2 storage sites, CO_2 is injected dry, but the water content increases over time as water is absorbed from formation brines. As the activity of water in the scCO_2 increases, water films will form and thicken on mineral surfaces in the dryout zone around the injection point. Changes in the water activity and the development of water films will affect:

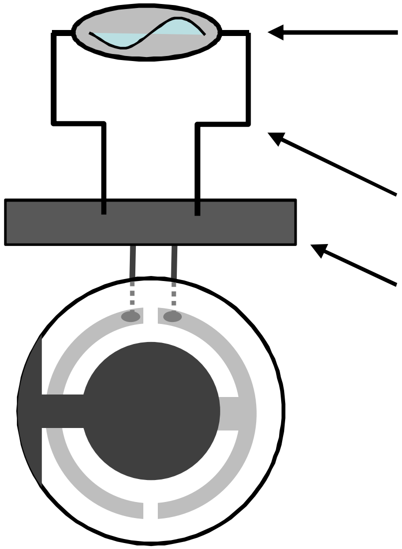
- Mineral surface reactivity
- CO_2 injectivity
- The relative permeabilities of CO_2 and water in the host and caprock
- Clay shrink/swell properties

Here, we assess the development and evolution of water films on silica in supercritical CO_2, and the shrink-swell behavior of clays, which are important components of the caprock seal systems in proposed storage reservoirs. Ambient-pressure data are also collected, to provide a baseline for understanding the high-pressure results.

Direct measurement of water uptake in $scCO_2$

Quartz Crystal Microbalance (QCM)

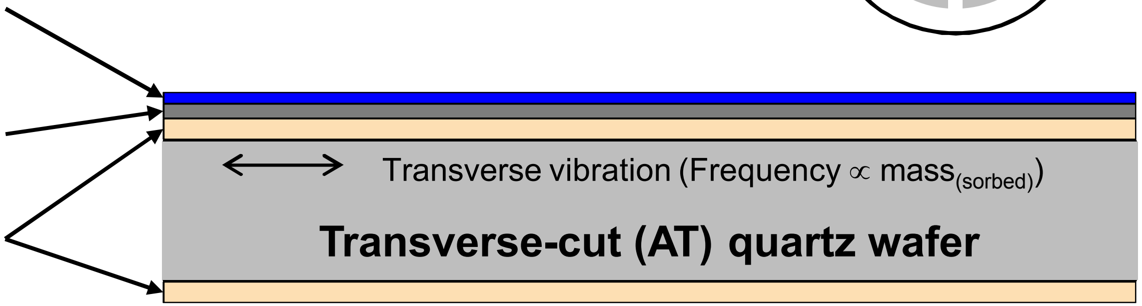
Tiny mass changes are measured by a change in the vibrational frequency of the piezoelectrically stimulated quartz wafer. The active area is the area of overlap between the two electrodes (38 mm^2)



Oscillator circuit, frequency monitor, and power supply

Electrical leads

High pressure pass-through



Deposited/sorbed mass

Amorphous silica layer

Gold electrodes

Transverse vibration (Frequency $\propto$ $mass_{(sorbed)}$)

Transverse-cut (AT) quartz wafer

Models for frequency response to mass loading:

Ambient systems

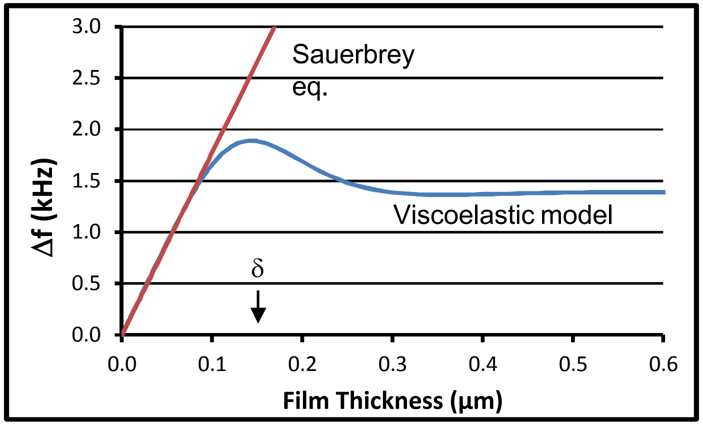
- Sauerbrey equation:
  - Assumes sorbed material behaves elastically (mechanical properties equivalent to quartz)

$$\Delta f = -C_f \Delta m$$

- For a viscoelastic film (Rodahl and Kasemo, 1996):
  - Loss of film-crystal coupling by two mechanisms
    - Layer slip (captured by *X*, the coefficient of friction)
    - Viscous losses (captured by β, which includes film viscosity, η_f)
    - However, if film thickness is significantly smaller than the decay length of the fluid shear wave (δ = 0.15 µm for water), viscous losses are negligible.

$$\Delta \square = \mathrm{Im}\left[-\frac{\square\square\square_{\square\square\square}\square}{2\pi\square_{\square}\square_{\square}(\square\square\square_{\square\square\square}+\square)}\right]$$

Assuming no-slip condition



Modified from Rodahl and Kasemo (1996)

Models for frequency response to a fluid film in liquids:

$scCO_2$ systems

- Frequency change due to contributions from:
  - mass change
  - pressure
  - density and viscosity
  - surface roughness

$$\Delta f = \Delta f_m + \cancel{\Delta f_p} + \cancel{\Delta f_\eta} + \Delta f_r$$

Negligible at constant P, T

- The response to mass is given by:

$$\frac{\Delta \text{[illegible]}}{\text{[illegible]}_{\text{[illegible]}}} = \frac{-\text{[illegible]}_{\text{[illegible]}}}{\text{[illegible]}_{\text{[illegible]}}}\left(1 - \text{[illegible]}_{\text{[illegible]}}\frac{\text{[illegible]}^2_{\text{[illegible]}}}{\text{[illegible]}_{\text{[illegible]}}}\right)$$

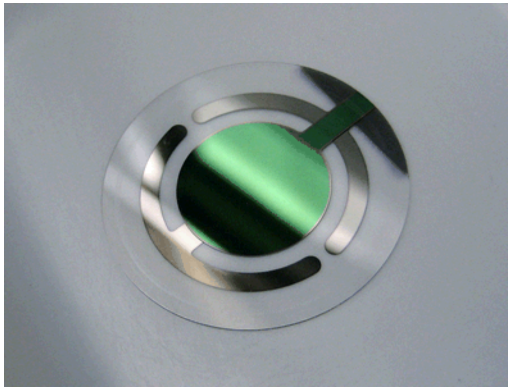
Where:

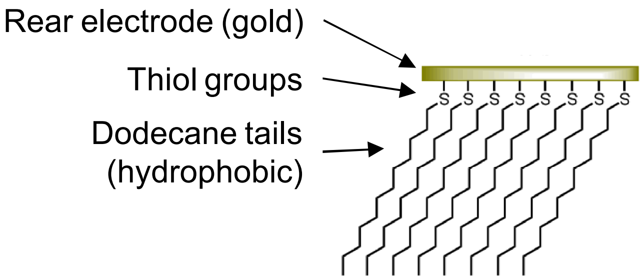
  - Z_x is the acoustic impedance of material *x*
  - f_f is the fundamental frequency (unloaded)
  - J_F is the viscoelastic compliance of the film

Water film development on silica

- **Samples Evaluated:**
  - **Amorphous silica**
    - **Inficon© stock 9 MHz crystals, with silica coatings on the front side**
    - **Back side treated with dodecanethiol to minimize sorption to the gold**
- **Conditions:**
  - **Ambient pressure**
    - **N_2 and CO_2, 60ºC**
  - **High pressure**
    - **60ºC, 8.3 MPa**
    - **35ºC, 10 MPA, 45ºC 14.5 MPa**

Silica-coated crystal





Rear electrode (gold)

Thiol groups

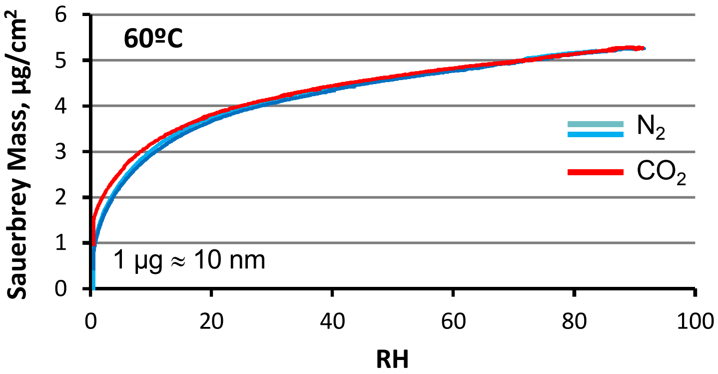
Dodecane tails (hydrophobic)

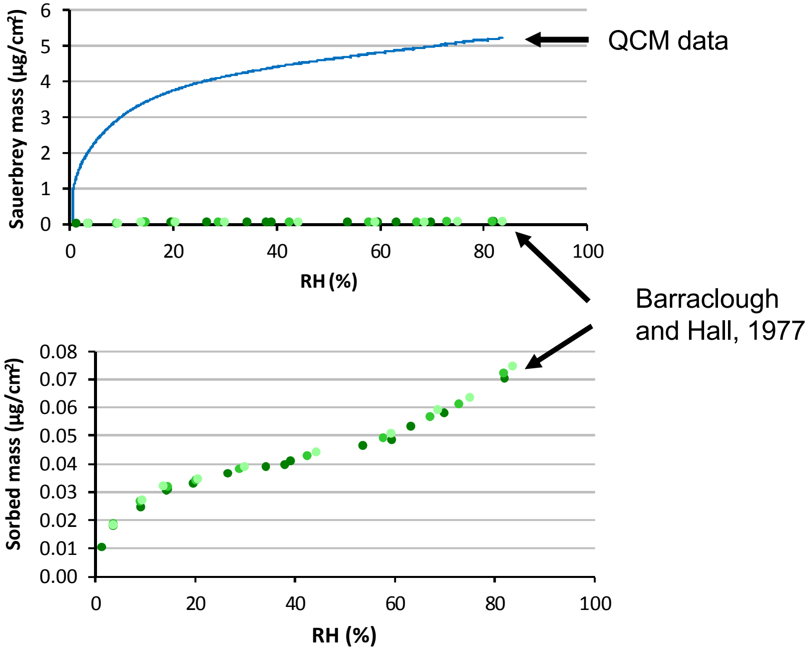
Ambient pressure systems:

Measured water adsorption isotherms on silica

Adsorption isotherms

- Reproducible from run to run, crystal to crystal
- Water isotherms in 1 bar CO_2 and N_2 are essentially identical (no surface charge effect?)
- Large frequency shift suggests thicker films than anticipated (tens of nm)
- Not consistent with water sorption isotherms measured with BET-type methods (e.g., Barraclough and Hall, 1977). Isotherms are about 2 orders of magnitude too high

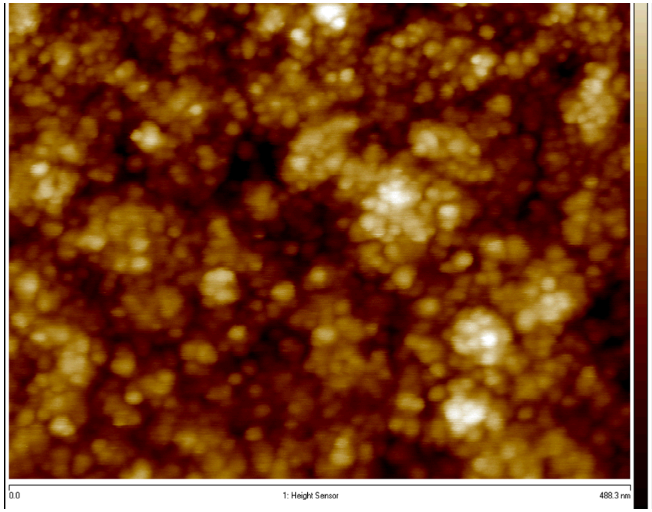


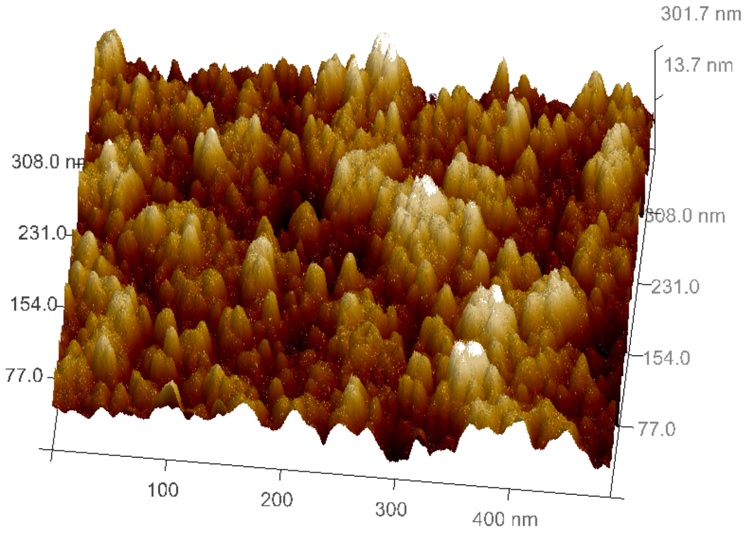


Why such a large frequency shift?

Surface roughness?

- The silica layer on QCM crystals surface topography about 14 nm—surface area only about 8% higher than the nominal area. Insufficient to account for the observed high adsorption of water
- The 500 nm thick silica layer is porous—capillary condensation into nanopores may account for additional mass gain.

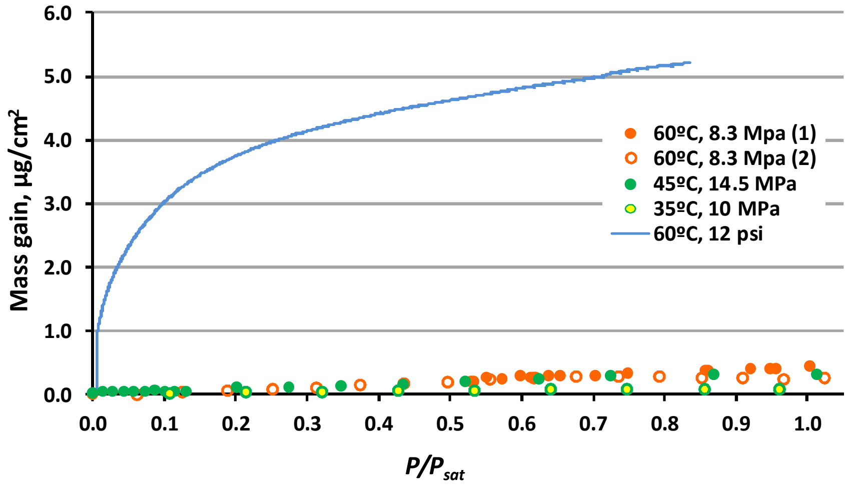


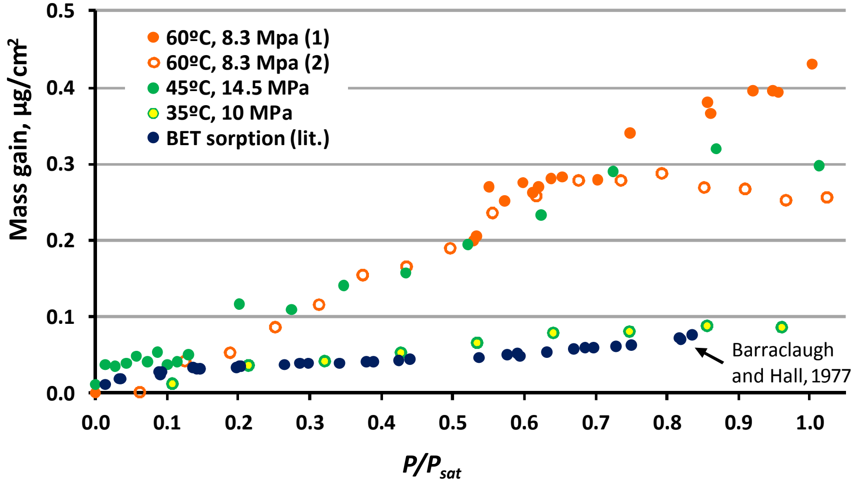


Water Adsorption in Supercritical CO_2

Adsorption isotherms

- Water adsorption is about 1/20 that observed at ambient conditions
- Sorption still greater than the nominal surface area (except 35ºC data)
- Possible interpretation: under ambient conditions, nanopores in the silica layer are filling via snapoff. Mass gain is proportional to pore volume. In $scCO_2$, pores are not filling—mass gain is proportional to pore surface area.





Results consistent with water film models

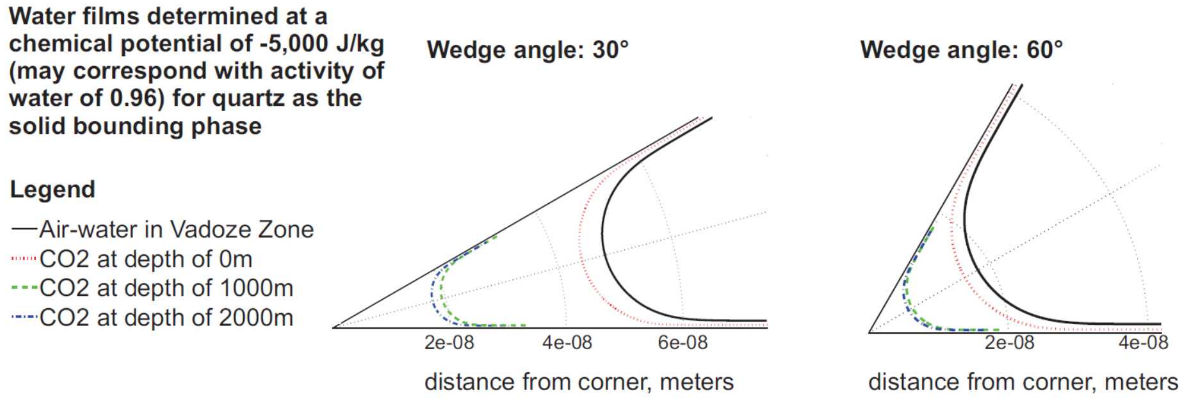
Water film models for adsorption and capillary condensation have been developed by Tokunaga (2011, 2012), Heath et al. (in prep). Disjoining pressure is a function of water film thickness:

$$\Pi(h) = \Pi_{VDW}(h) + \Pi_E(h) + \Pi_S(h)$$

But will be equivalent to the chemical potential of water in the supercritical phase. Therefore, film thickness is a function of the a_w in the $scCO_2$. Capillary condensation is modeled using the Kelvin equation.

Model predictions

- Water films in $scCO_2$ will be thinner than in air.
- Capillary condensation and pore filling via snapoff will be more limited in $scCO_2$.



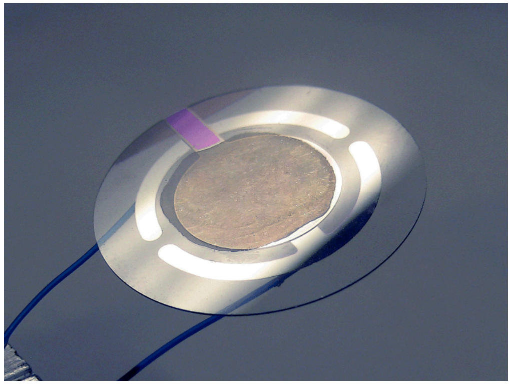
Water films determined at a chemical potential of -5,000 J/kg (may correspond with activity of water of 0.96) for quartz as the solid bounding phase

Heath et al. poster this afternoon (session H23D)

Water uptake by montmorillonite clays

- **Samples Evaluated:**
  - **SWY-2 montmorillonite (Clay Mineral Society)**
  - **Fine size fraction washed with Na, K, Ca, Mg chloride to make homionic**
  - **Mounted using the Millipore filter transfer method (peeling was common, especially in $scCO_2$)**
- **Conditions:**
  - **Ambient pressure**
    - **60ºC, N_2 and CO_2**
  - **$scCO_2$**
    - **60ºC, 8.3 MPa**
- **Issues**
  - **Clay films peeled, especially in $scCO_2$**
  - **Under heavy loading (clay films) gold electrodes tended to delaminate from the QCM crystal.**

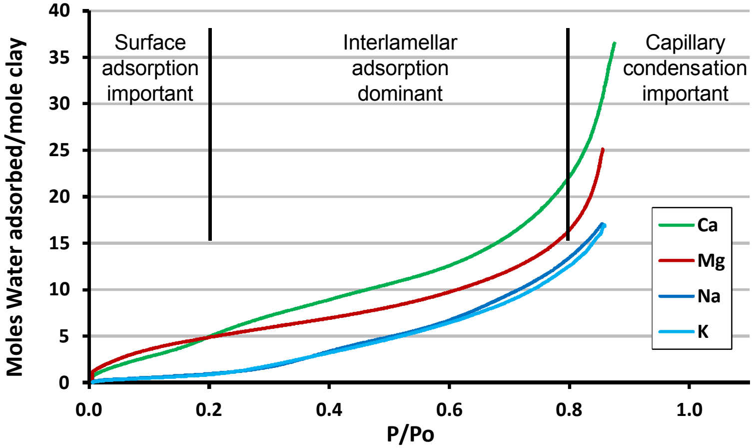
Clay mount



Water uptake by homionic clays

Water adsorption occurs by several mechanisms (Behrend et al., 1995, Cases et al., 1997)

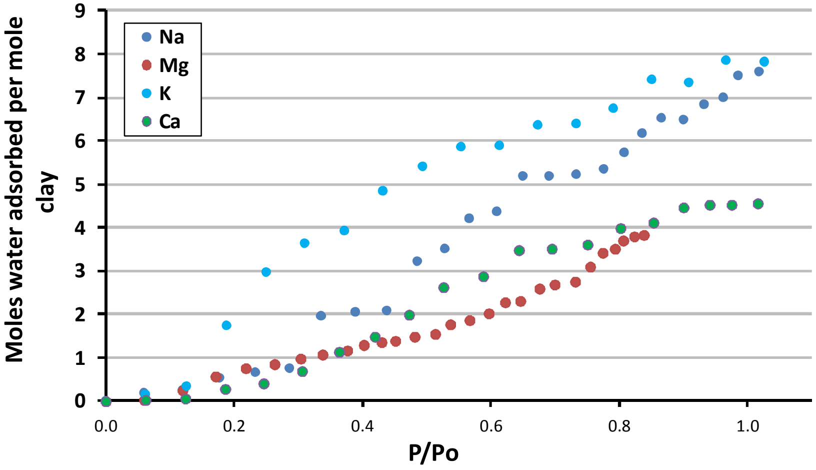
- Filling of interlamellar space (hydration of interlayer cations)
  - dominant mechanism over most of the range of a_w
  - accounts for a larger fraction of adsorbed water for divalent montmorillonites.
- Adsorption onto the crystallite surfaces—generally less than 20% of total water adsorbed. Most important at low a_w.
- Capillary condensation between clay crystallites—in ambient systems, accounts for the large increase in water adsorbed at high water activities.

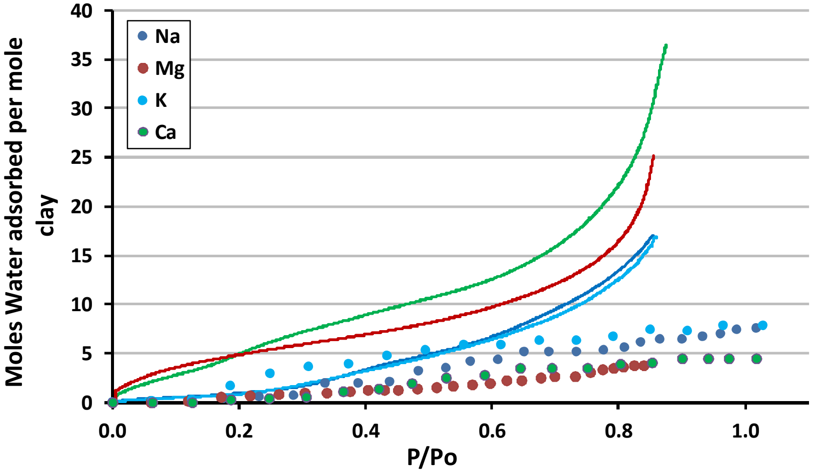


Measured water uptake by homionic clays in N_2, CO_2 and in $scCO_2$

Adsorption isotherms

- Ambient pressure, N_2 and CO_2
  - At a given a_w, divalent ions adsorb more water (typically observed)
  - A sharp increase in sorption is occurs at higher water activities (capillary condensation).
- $scCO_2$ (60±0.2ºC, 10.3 MPa)
  - In general, less water is absorbed than the ambient case
  - Monovalent clays absorb more water than divalent clays (about 2 times as much).
  - There is no large increase in adsorption at high P/P_o—capillary condensation not occurring?





Summary

- Water sorption isotherms for silica were measured by QCM
  - Sorption was apparently controlled by capillary condensation into the porous silica layer on the QCM crystal.
  - Mass increases in $scCO_2$ indicate that water films develop and grow on silica with increasing activity of water
  - However, sorption much lower in $scCO_2$ than in N_2 or CO_2 at ambient pressure, suggesting that water films are thinner
- Water adsorption by homionic montmorillonite clays
  - Under ambient conditions, clays displayed typical behavior, showing that QCMs can successfully be used to measure water uptake.
  - In $scCO_2$
    - Water sorption was less by divalent clays than monovalent clays (about half as much).
    - Water sorption did not increase rapidly at high a_w, suggesting limited capillary condensation between crystallites
- Both data sets are consistent with the water adsorption and condensation model (Heath et al., in prep.) that predict thinner water films and limited capillary condensation in $scCO_2$