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Thermal Implications on Transport in Bentonite: Using Full-Scale Engineered Barrier Experiment-Dismantling Project (FEBEX-DP) Samples for Laboratory Studies and Model Testing

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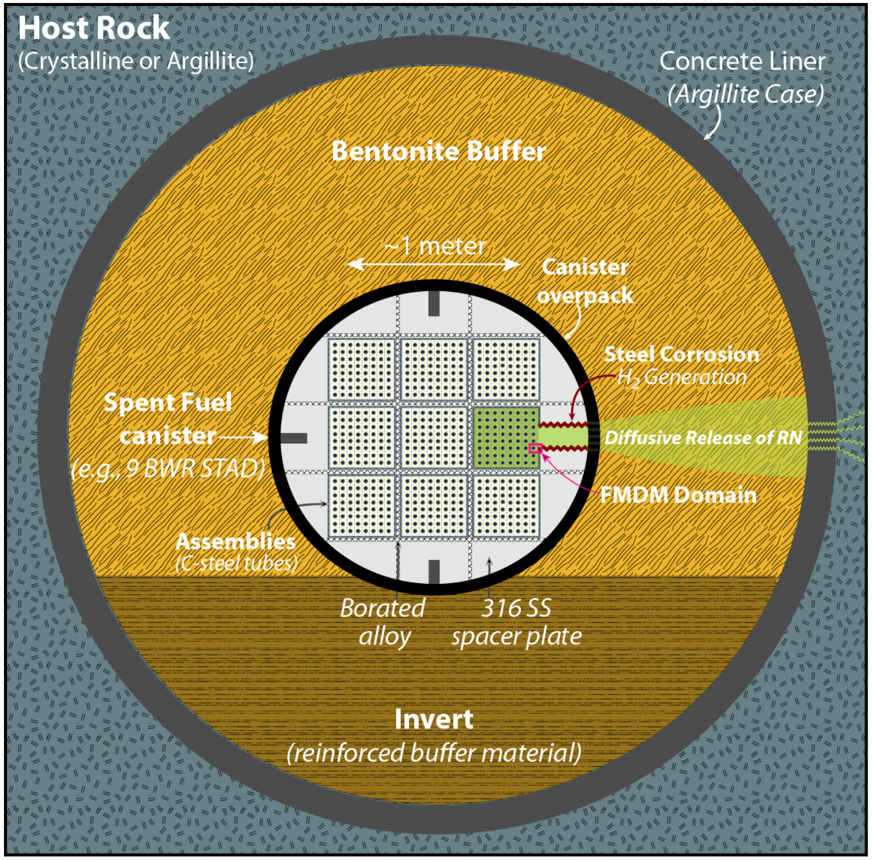
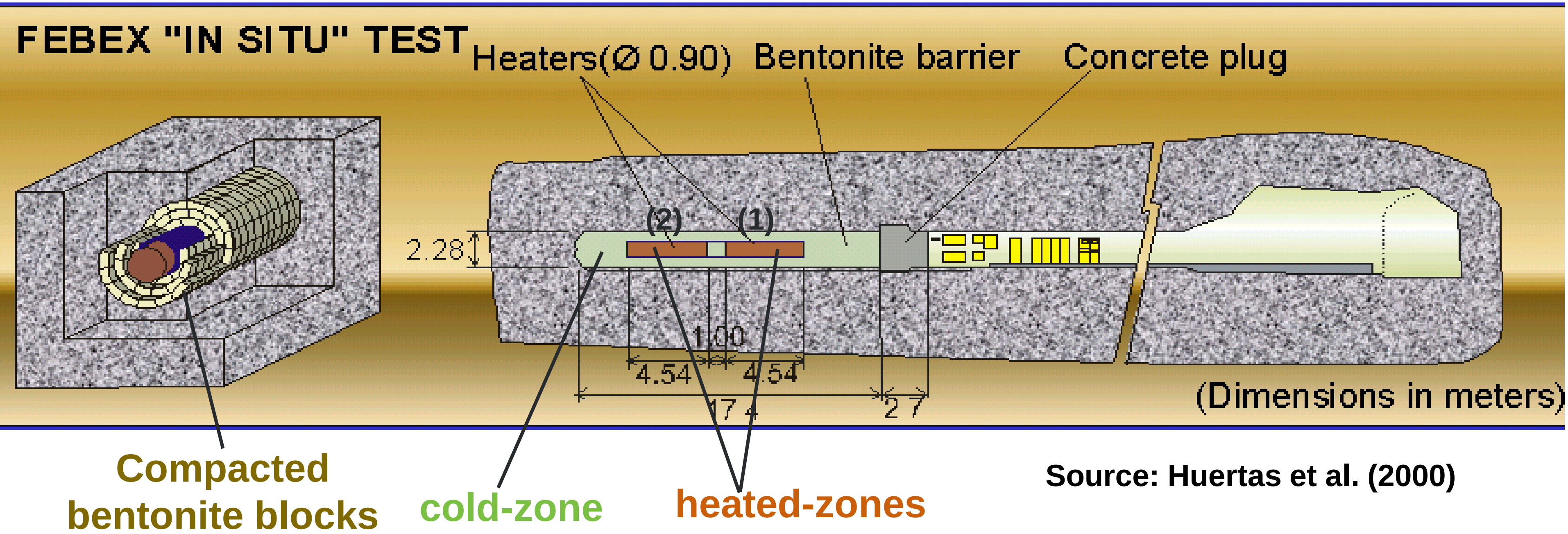
What is the Engineered Barrier System (EBS)?

- **EBS definition from the US Nuclear Regulatory Commission (10 CFR 60.2)**
  - "Engineered barrier system means the waste packages and the underground facility"
- **EBS definition from to the NEA/OECD EBS State-Of-The-Art Report (2003):**
  - "The "engineered barrier system" represents the man-made, engineered materials placed within a repository, including the waste form, waste canisters, buffer materials, backfill and seals."



Generic EBS concept with bentonite barrier showing a canister breaching scenario (Jerden et al. 2019)
FMDM = Fuel Matrix Degradation Model

FEBEX Full Scale Heater Test Experiment



Source: Huertas et al. (2000)

- Conducted by ENRESA under auspices of the EU at the Grimsel Test Site (GTS) in Switzerland
- Bentonite was compacted into blocks at 1650 kg/m^3 dry density and placed in a radial arrangement surrounding 2 heaters
- Heaters operated at a maximum of 100 °C – Heater 1 operated for 5 years; heater 2 operated for 18 years
- FEBEX-DP samples were obtained from heater 2 dismantling in 2015 after 18 years of heating
- Unique opportunity for long-term full-scale heater test and sample / data availability

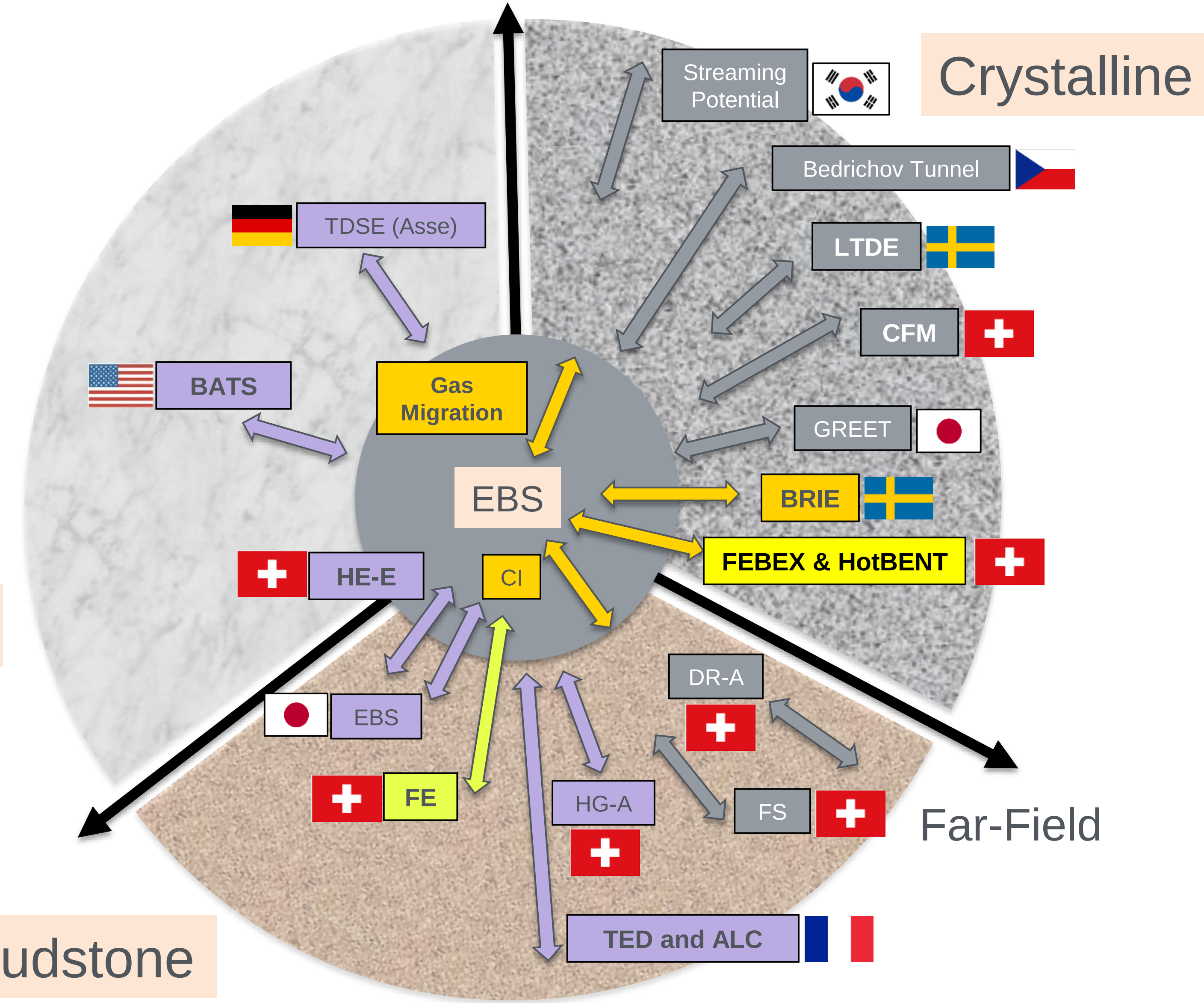
Goals

- **Investigate the effects of temperature on bentonite clay barrier interactions:** clay phase change / degradation, smectite swelling, and structure / composition
- **Investigate the effects of changing chemical conditions and temperatures** on uranium(VI) sorption and diffusion.
- **Reduce the uncertainty** in actinide sorption / diffusion sub-models that are part of performance assessment (PA) models for waste repositories.

International URL Portfolio in a Nutshell

Key R&D Issues

- Near-Field Perturbation
- Engineered Barrier Integrity
- Flow and Radionuclide Transport
- Demonstration of Integrated System Behavior



Repository Phases and Relevant Processes

Key R&D Issues

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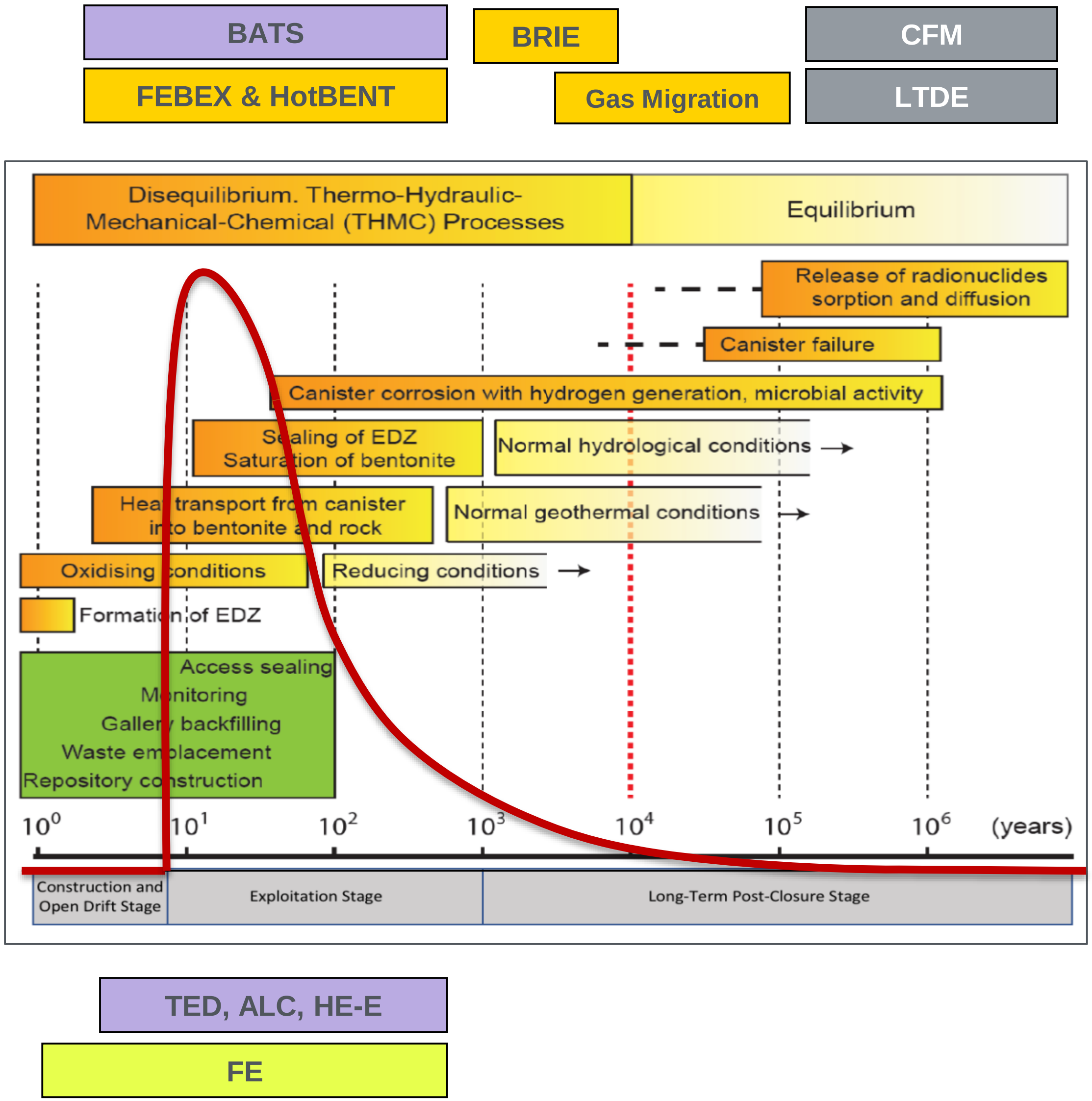
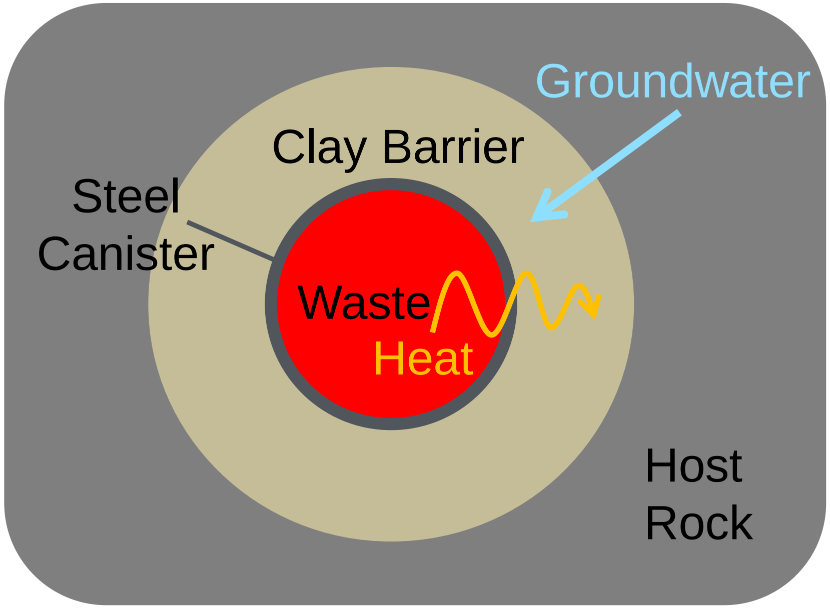


Understanding radionuclide adsorption to clay under realistic waste-disposal scenarios

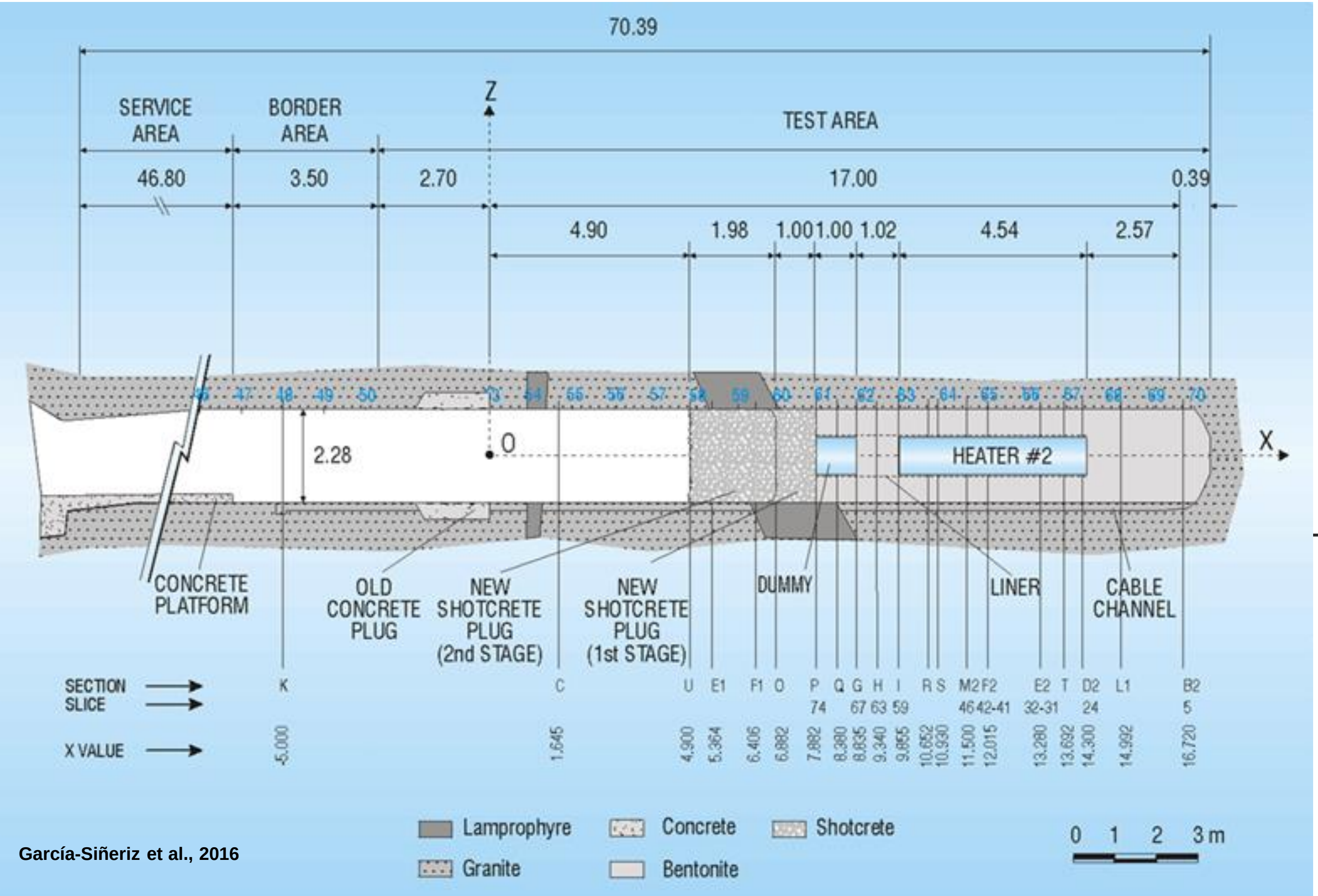
- Heat-generating waste canisters increase temperatures of surrounding engineered barriers
- Groundwater Intrusion from surrounding host rock

- Variable saturation across clay barrier
- Changes in pore water chemistry
- Changes in accessory mineral assemblage (e.g., calcite, pyrite)
- Changes in clay structure/composition (e.g., illitization, ion exchange)



- Changes in aqueous radionuclide (RN) speciation
- Changes in mineral sorption capacity
- Changes in swelling behavior

FEBEX-DP Experiment: Sampled Sections

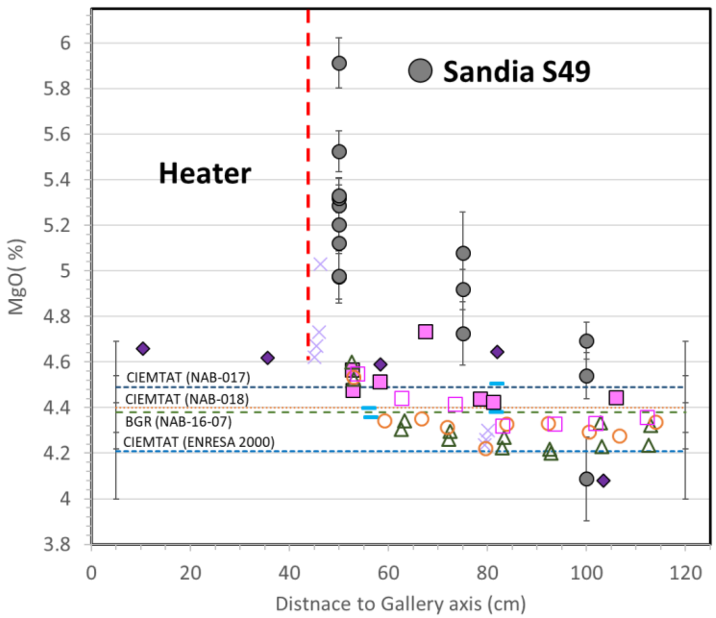


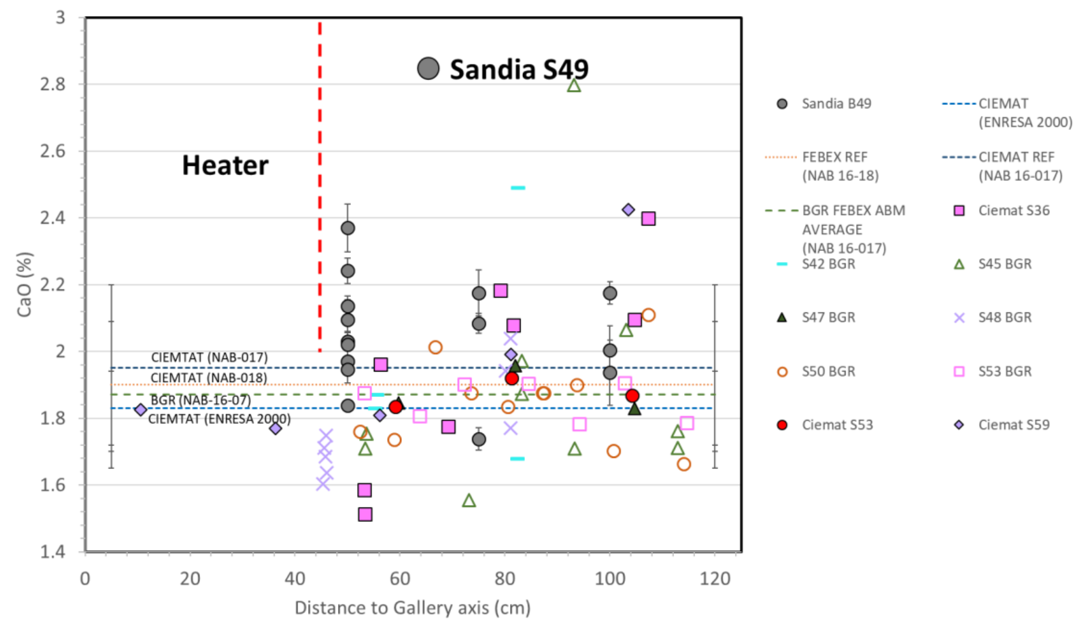
García-Siñeriz et al., 2016

FEBEX-DP

- **Section 49 samples (near longitudinal central area of heater)**
- **Bentonite samples from close to the heater towards the outer parts of the barrier**
- **X-Ray Fluorescence (XRF) bulk composition, X-ray CT-scan, µ-XRF, SEM-EDS, X-Ray Diffraction (XRD), Thermogravimetric analysis (TGA)**

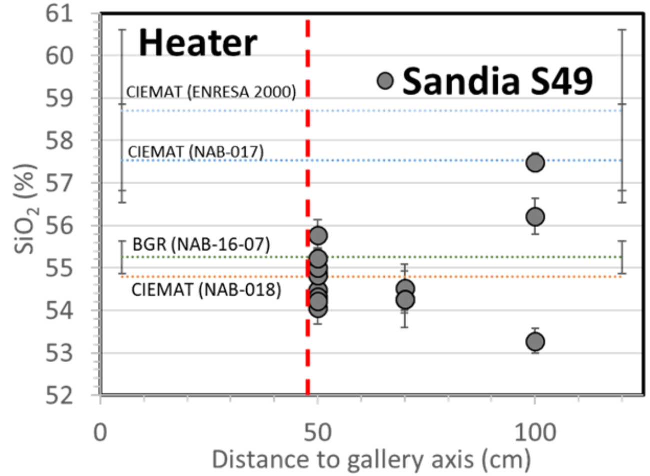
FEBEX-DP Bulk Bentonite Samples: X-ray Fluorescence (XRF)

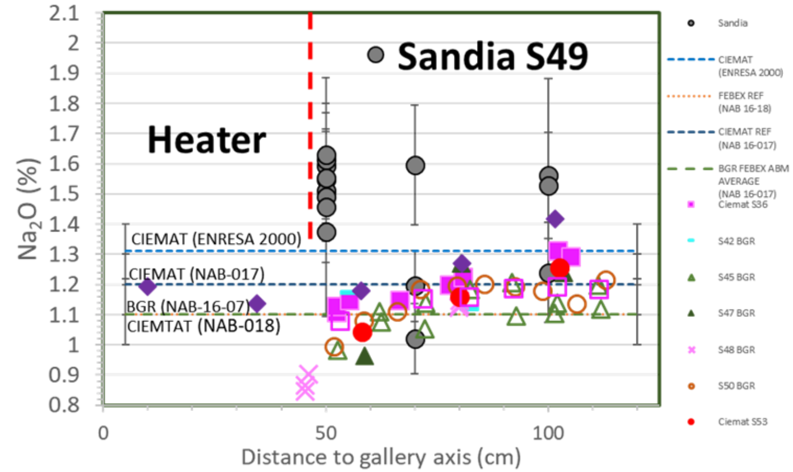


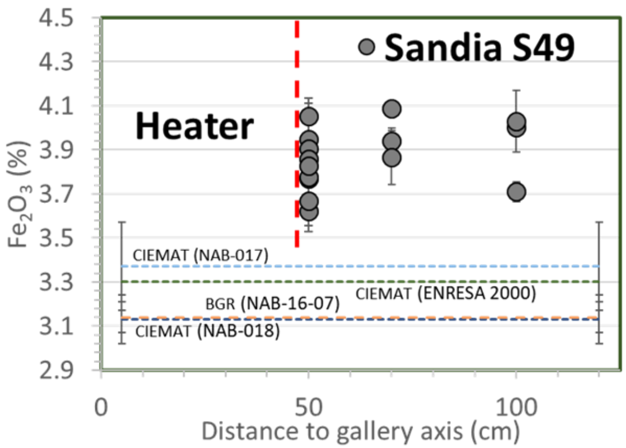


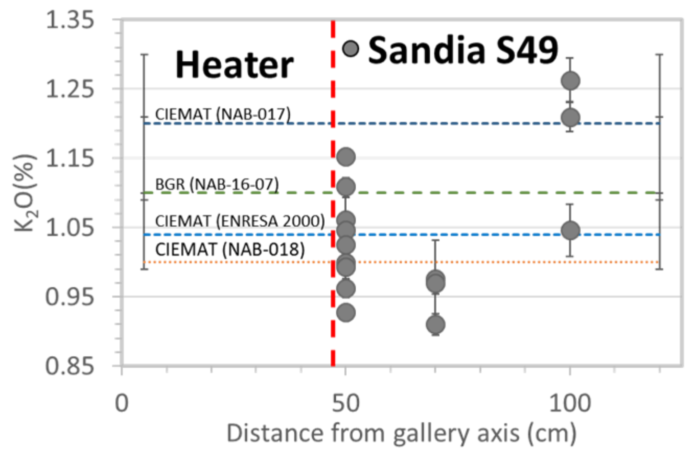
- Mg enrichment towards the heater surface – zones of increasing dry out conditions
- Bulk MgO content far from heater nominally within the bounds of other lab analyses
- Overall, CaO content is relatively variable close to the heater surface
- Mg enrichment(?):
  - Enhanced Mg content due to elevated temperatures?
  - SEM-EDS didn't show newly-formed Mg-bearing phases within the clay matrix

FEBEX-DP Bulk Bentonite Samples: X-ray Fluorescence (XRF)



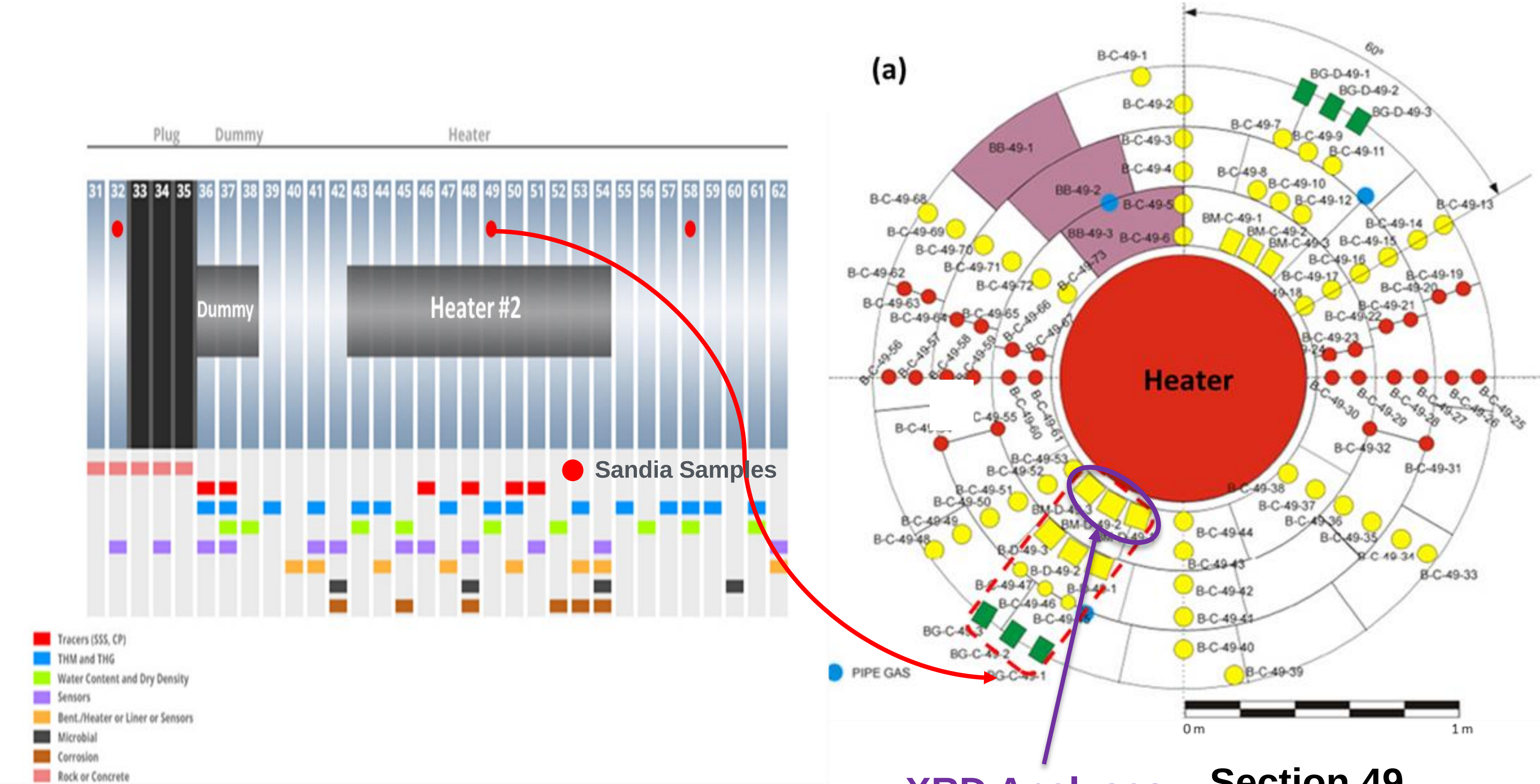






- Large uncertainties on Na_2O content – Issues with detection limits
- Slightly enriched in Fe_2O_3 relative to reference bentonite compositions
- Fe_2O_3, SiO_2, & K_2O fall within the range of reference bentonite compositions

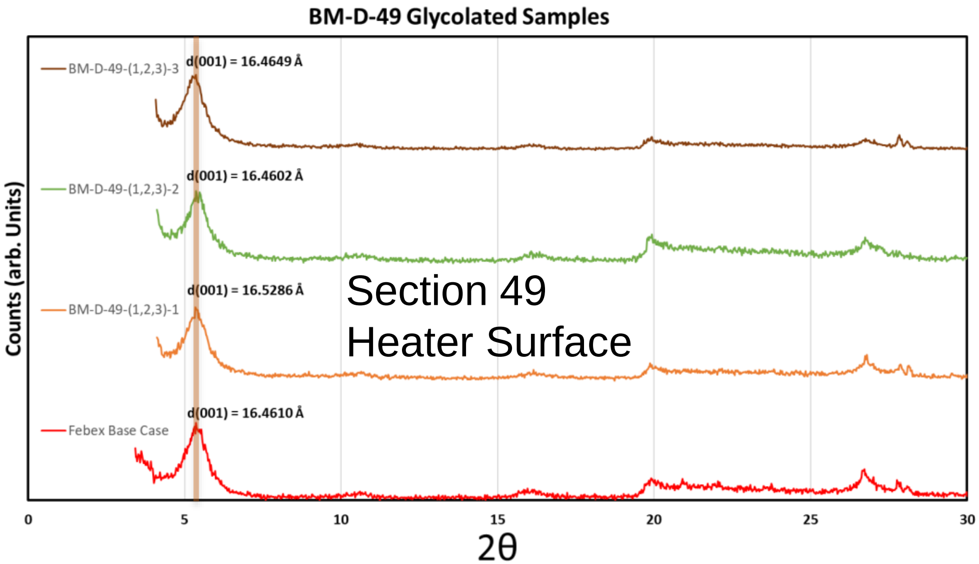
FEBEX-DP Experiment: Sampled Sections cont.

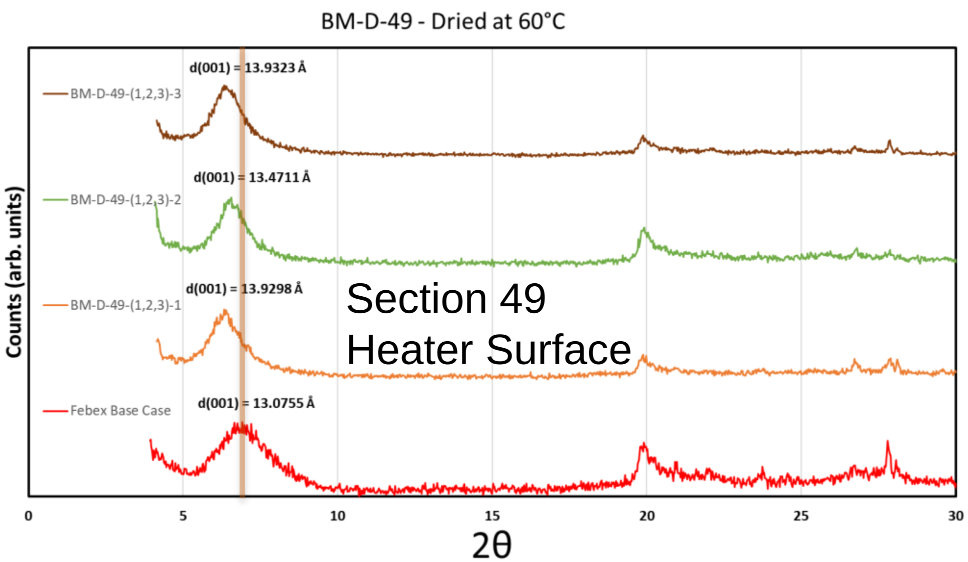


Section 49

XRD Analyses samples close to heater surface

FEBEX-DP: Bentonite X-ray Diffraction (XRD)

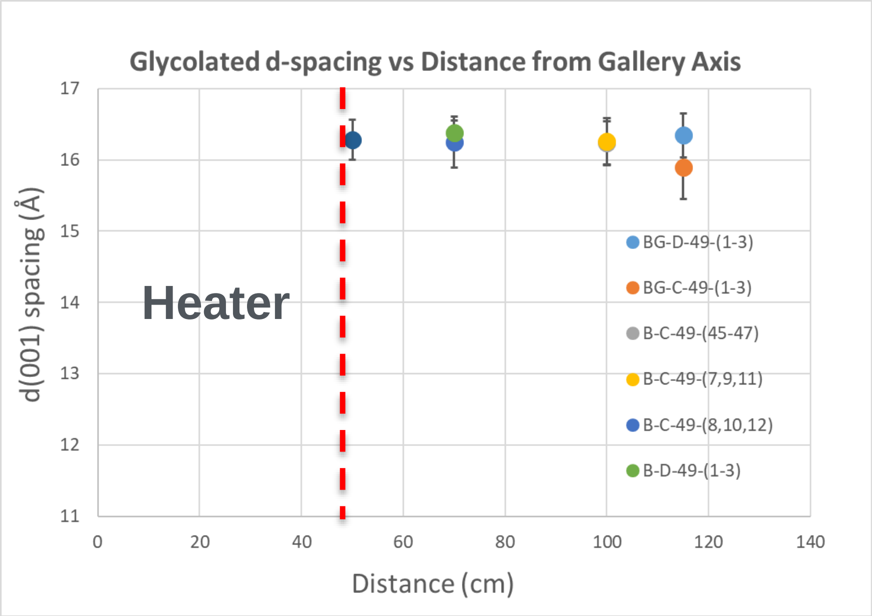


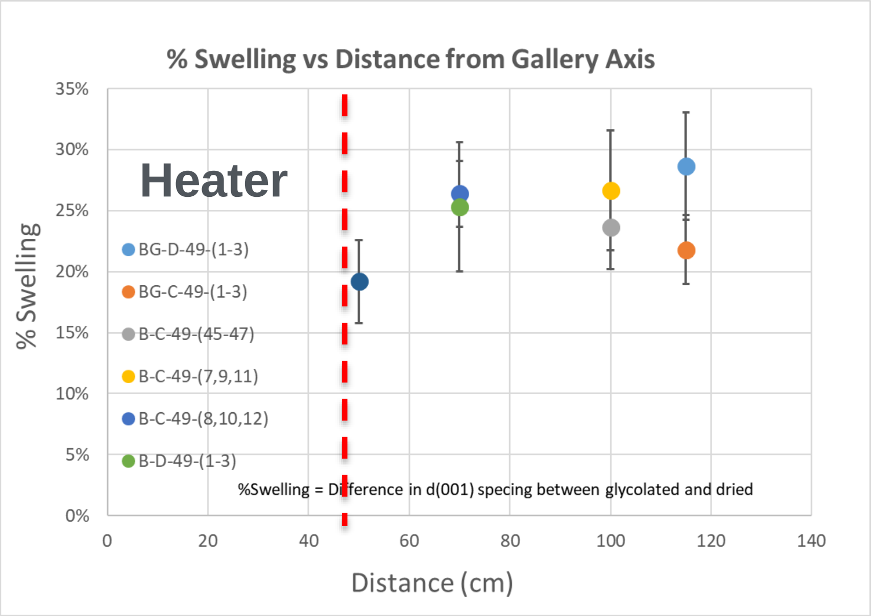


Smectite Clay Structural Characterization:

- Comparison of XRD spectra across sampled domains
- Evaluate d(001) spacings as a function of distance from heater surface
- Smectite d(001) spacings close to the heater surface showed most differences relative to base case FEBEX bentonite
- d(001) spacings from glycolated samples (max. clay expansion) are similar for samples close and far from heater surface
- However, consistent d(001) spacing deviations are observed for dried samples
- Overall, XRD profiles are similar to those reported by others in the FEBEX-DP project

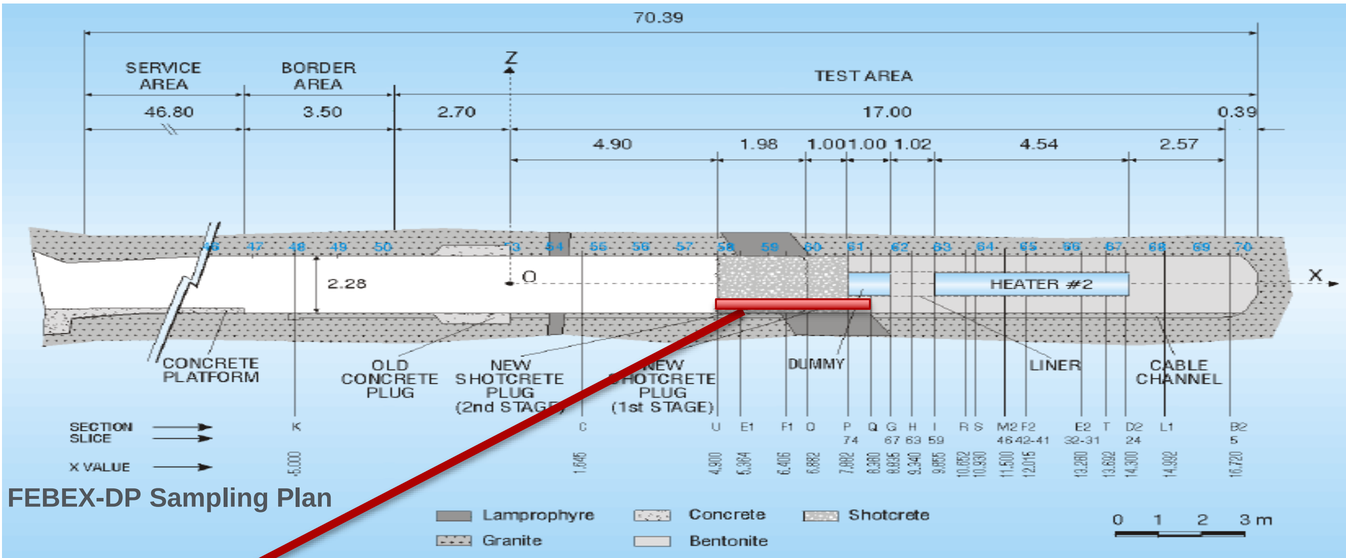
FEBEX-DP: Bentonite X-ray Diffraction (XRD)



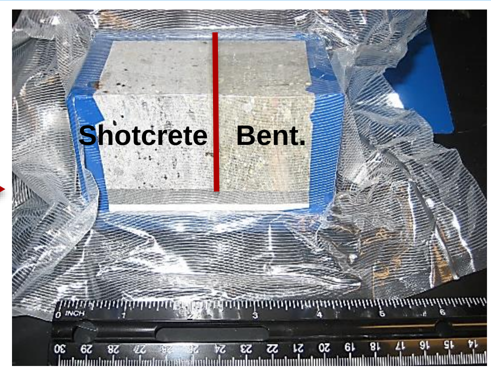


- No apparent effect of elevated temperatures on d(001) spacing for glycolated clay samples
- Slight decrease in swelling extent for samples in contact or close to the heater surface
- Prolonged exposure of bentonite to T = 95 – 100 ºC causes some changes in swelling
  - **Correlate with compositional changes in clay close to heater surface**

FEBEX-DP: Shotcrete – Bentonite Interface Core Extraction



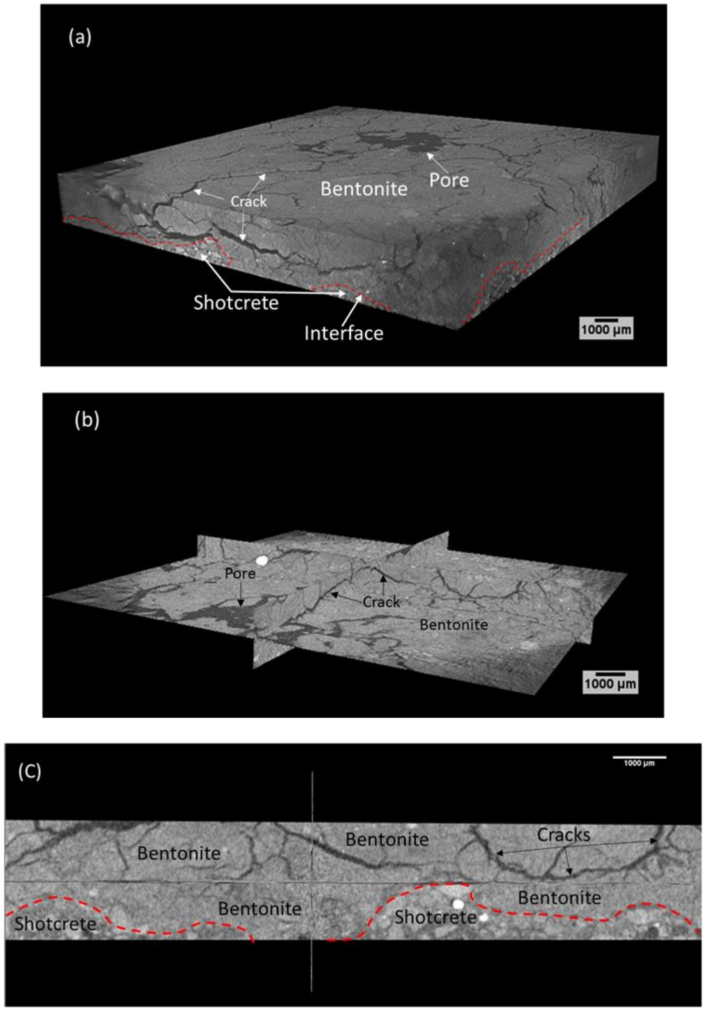
Mäder et al. (2016)



C. F. Jove Colon (SNL)

- **Shotcrete/bentonite interface sampling**
- **Characterization studies cement/bentonite interactions**
  - **Phase identification (SEM-EDS, XRD, µ-XRF)**
  - **X-ray CT Scan: micron-scale structures**

Bentonite – Concrete Interface Characterization (X-ray CT Scan)



- **Main Features:**
  - **Occurrence of microcracks and pore spaces – connected in many cases**
  - **“Craquelure” or “chickenwire” microcrack pattern (desiccation)**
  - **Some embedded granular material in bentonite matrix with radiating cracks**
  - **Heterogeneous microcrack spatial distribution → localized regions with no cracks**
- **Crack – Pore pathways:**

<u>Bentonite:</u>

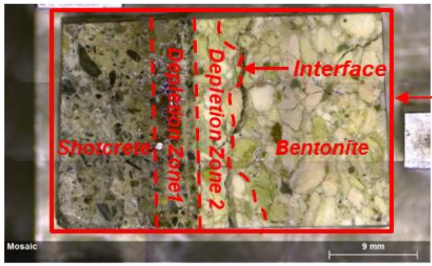
- **Continuous and discontinuous pore-microcrack networks (2D & 3D)**
- **Large pores tend to be connected to microcracks**

<u>Shotcrete:</u>

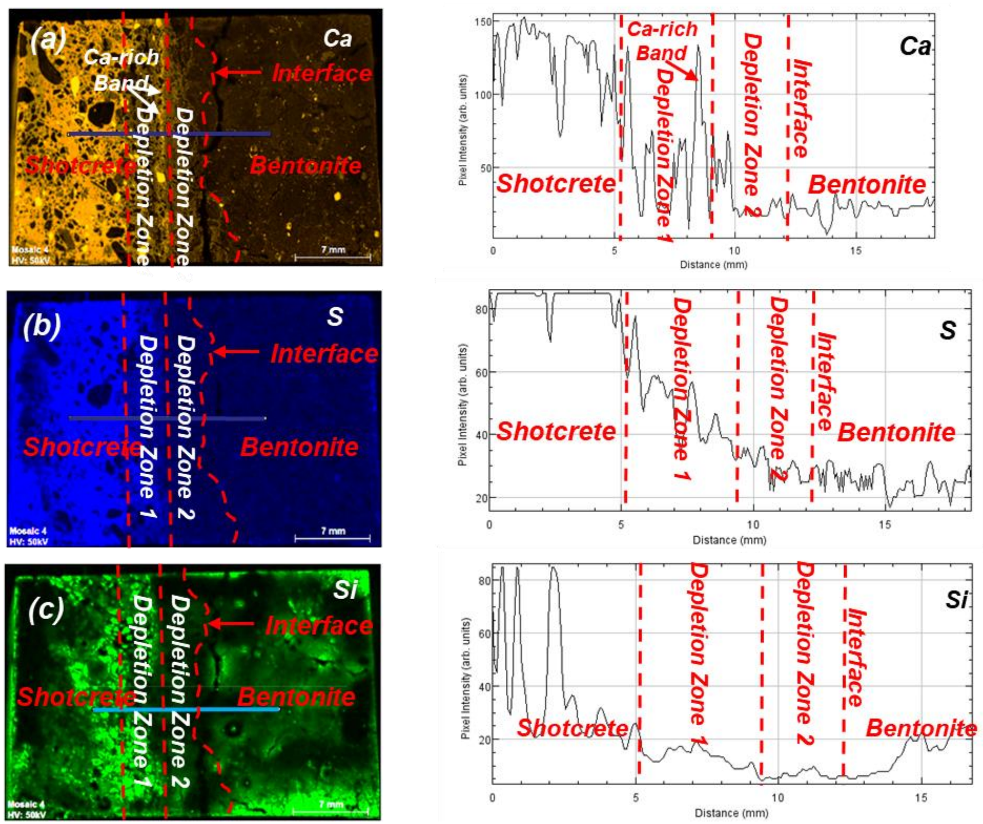
- **Bentonite: Large pores tend to be connected to microcracks**
- **No or little microcracks**
- **Isolated pores except at the interface**

Shotcrete - Bentonite Interface Characterization (μ-XRF)

Thin Section



- 34.744 mm x 23.88 mm Scan Area,
- 30μm Spot to Spot Distance,
- 25μm Spot Size,
- X-ray Energy 50kV/200μA
- ~90 min to complete sample

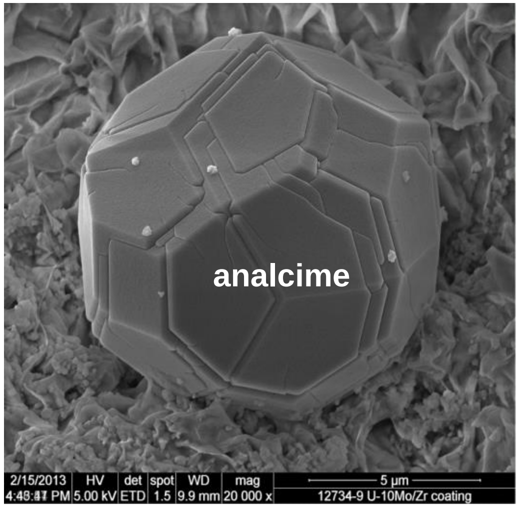


- **Main Features**
  - **Compositional map at thin section (mm) scale – Scanning at the μm scale**
  - **Sharp compositional changes at the bentonite-shotcrete interface**
  - **Consistent spatial correlation among various elements across interface**
- **Compositional Gradients**
  - **Depletion on shotcrete side of the interface → Leaching?**
  - **Bentonite seems compositional homogeneous at the interface**
  - **Limited reaction front?**

Jové Colón et al. (2017)

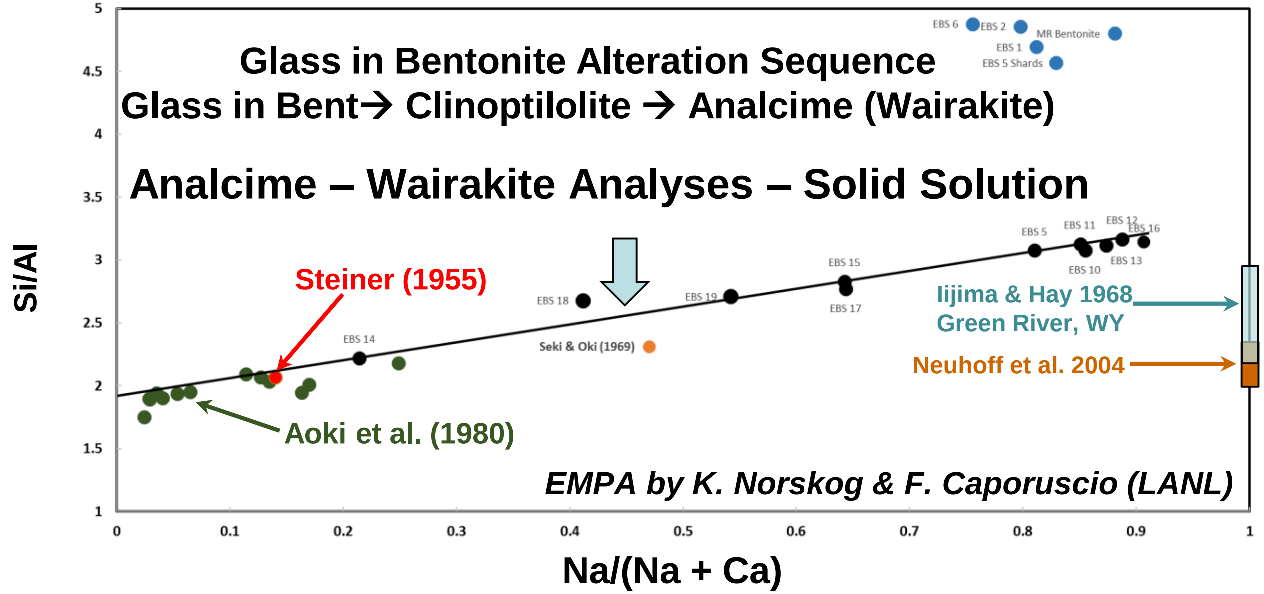
Authigenic zeolite produced from clinoptilolite / glass in bentonite interaction experiments

Analcime (Bentonite only)



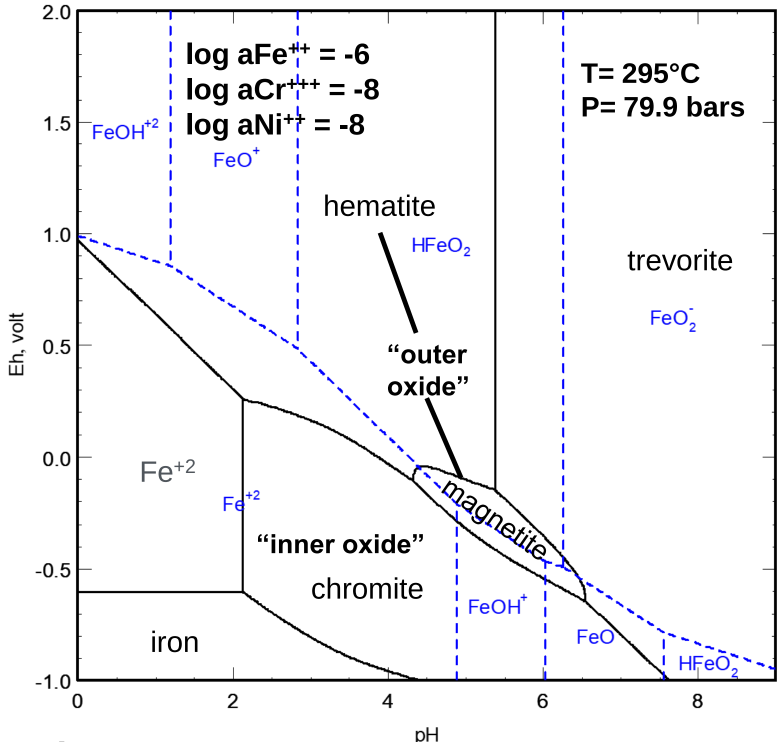
Wairakite-rich zeolite (Opalinus clay + Bentonite)

Jové Colón et al. (2017)

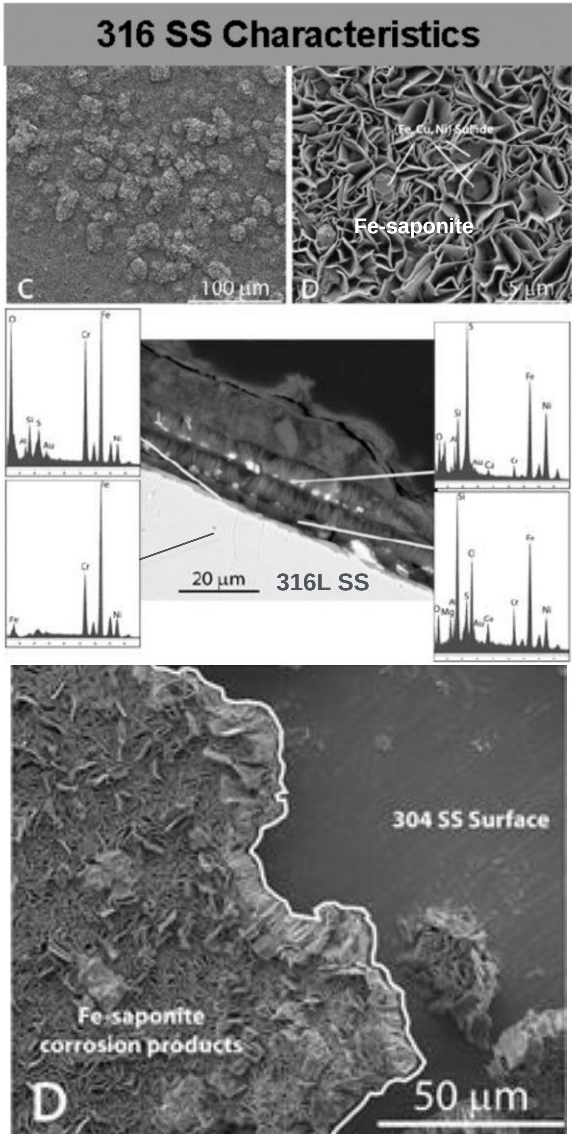


- **Bentonite Alteration and Zeolite Stability:**
  - **Glass alteration in bentonite → high Si**
  - **Formation of analcime – wairakite zeolites**
  - **Wairakite – analcime solid solution → expands zeolite stability**
  - **Little or no illite formation detected**
    - **High Si activities prevents illite stability?**

Bentonite – Steel Interaction Experiments

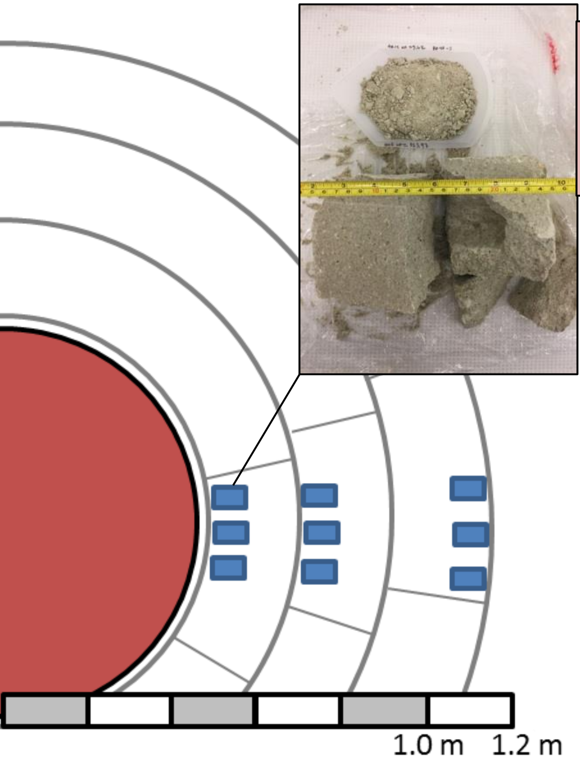


Cheshire et al. (2014)



- **Experiment**
  - **T = 300ºC; STRIPA brine**
  - **Wyoming Bentonite**
  - **316 Stainless Steel (SS), 304SS, low-C steel**
- **Results**
  - **Fe-Saponite growth perpendicular to metal substrate**
  - **S is generated from pyrite degradation in bentonite**
  - **Concurrent surface sulfide precipitation with Fe-saponite**

U(VI) adsorption experiments: FEBEX-DP clay samples that experienced different temperature and moisture regimes



Heated Zone:

- 50 cm from axis (Section 48)
- T= 95°C
- Moisture Content≅18%

Cold Zone:

- 50 cm from axis (Section 59)
- T= 20°C
- Moisture Content ≅ 25%

<u>Original FEBEX Bentonite Mineral Composition</u>*
92 % smectite (illite-smetite mixed layer, with ~11% illite layers)
2% plagioclase
2% quartz
2% cristobalite
<1% potassium feldspar, calcite, trydimite, Fe- and Al-oxides

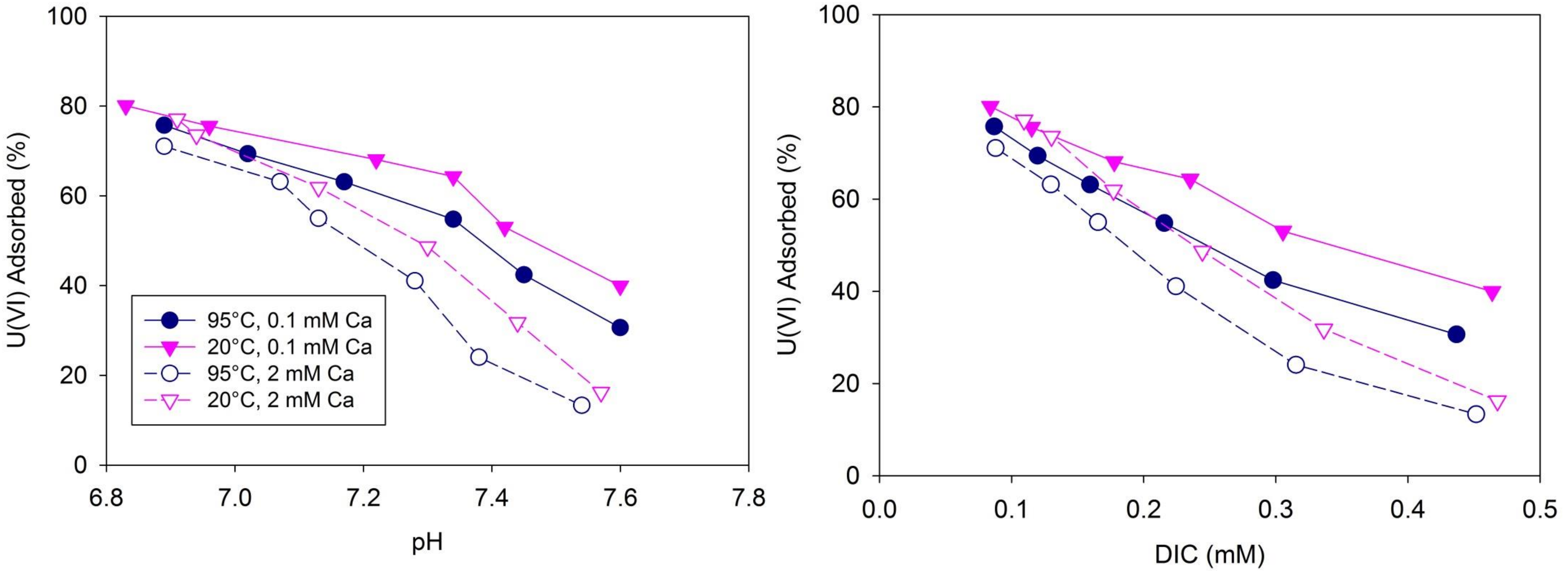
*Fernández et al. (2004)

Composite samples were created from 3 replicate blocks from each location, air-dried and sieved to < 63 μm.

Moisture content and temperature from Villar et al. (2018)

Lower U(VI) Sorption onto Heated Bentonite

< 63 μm fraction, bentonite composite samples, 0.5 g/L bentonite



Up to 10% lower U(VI) adsorption on heated bentonite.

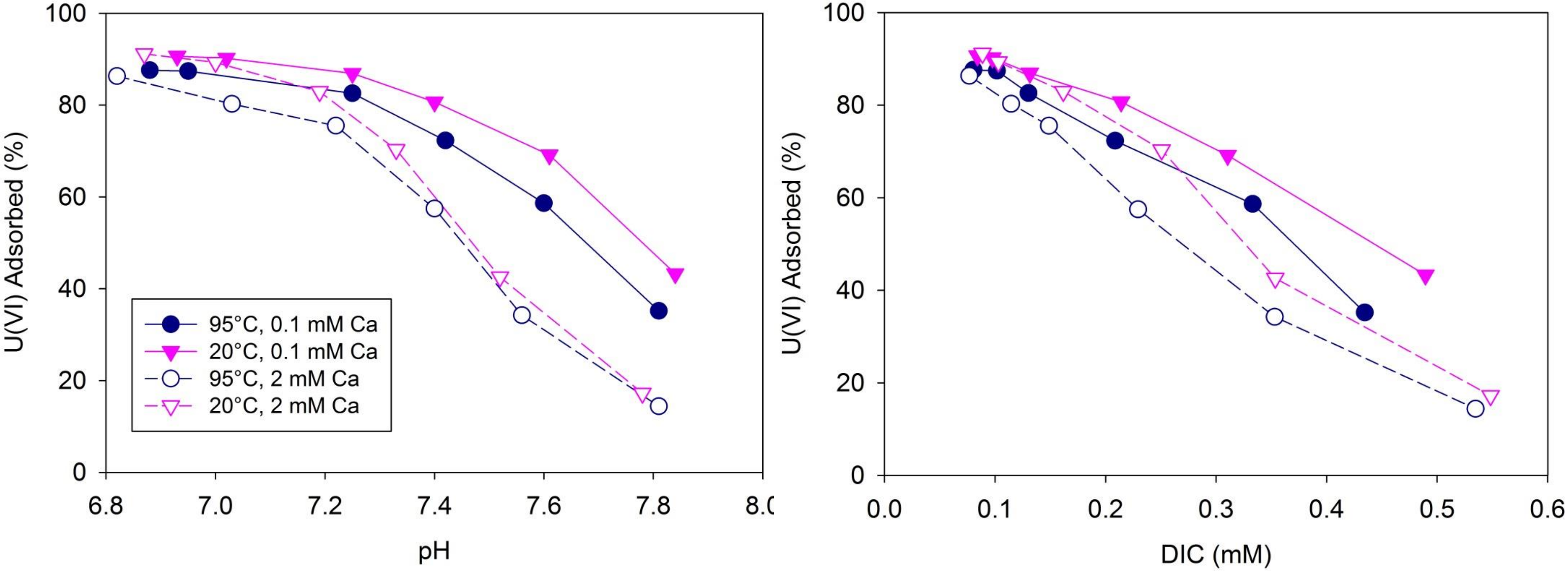
- Adsorption is lower in presence of 2 mM Ca compared to 0.1 mM Ca.
- Adsorption decreases as pH and DIC increase.

Possible reasons for lower U(VI) adsorption:

- aqueous U(VI) speciation
- relative fraction of clay (montmorillonite) mineral phase
- structure/composition of clay mineral fraction
- structure/composition of accessory mineral fraction (e.g., Fe-oxides)

U(VI) adsorption onto **purified** bentonite

< 2 μm fraction, carbonate minerals removed



Lower U(VI) adsorption on 95°C heated bentonite persists after purification.

- Consistently lower U(VI) adsorption onto 95°C heated sample in presence of 0.1 mM Ca
- Smaller difference in presence of 2 mM Ca
- As with bulk samples, U(VI) adsorption is lower at higher Ca concentration

Summary

- International collaborations on URL activities and partners provide unique opportunities for data and sample collection from heater tests
- Characterization and sorption studies of *post mortem* FEBEX-DP bentonite samples indicate:
  - Mg-enrichment in clay observed in bentonite close to the heated surface
  - Slight decrease in bentonite swelling also observed close to the heated surface
  - Lower U(VI) sorption for samples subjected to 95ºC relative to those exposed to ambient temperatures
  - Bentonite-cement interactions and cement leaching effects appear largely constrained to the interface
- Bentonite-metal interfacial interactions at elevated temperatures:
  - Produces zeolites (analcime) and sulfide phases
  - Fe-saponite growth perpendicular to the metal substrate
  - Little or no illite forms in the experiments and heater test

Acknowledgement

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Questions?

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