EGU 2019 - Vienna

Engineered Barrier System (EBS) hydrothermal experiments for a Grimsel granodiorite host rock: Mineralogical evolution at repository pressures and temperatures

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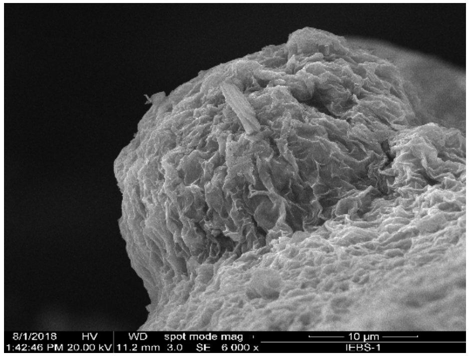
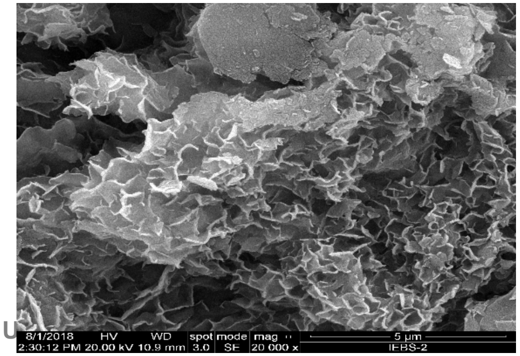
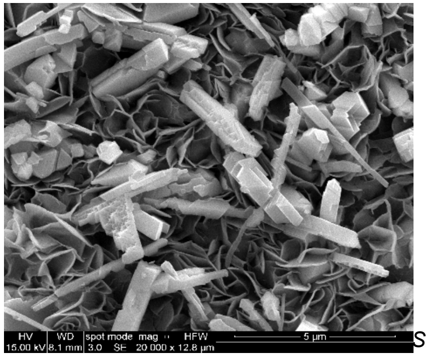






Grimsel hydrothermal experiment mineral changes - outline

- Experiment parameters (Use mine-run, unpurified bentonite, steel, and K-Ca-Na-Cl brines)
- Investigate chemical evolution of clay mineralogy at repository temperature and pressure (**250 °C, 150 bar)**.
- **Comparison to Argillite host rock experiments**
- Summary

Experimental Conditions

Experimental Reactants

- Unprocessed Wyoming bentonite (80wt%)
- Grimsel granodiorite (20 wt%)
- $f(O_2)$ buffered at ≈ IM (iron-magnetite)
- 304, 316 and low carbon steel
- Ns-Ca-K-Cl-CO_3 brines, 1900 ppm

(9/1 water /rock ratio)

- 250°C, 150 bar, 6 weeks

Synthetic groundwater chemistry used in the IEBS experiments.

Components	Concentration (M)
Na_2SO4	9.08×10^{-4}
KCl	6.44×10^{-5}
$MgCO_3$	5.06×10^{-4}
$NaHCO_3$	3.25×10^{-3}
$CaCl_2$	1.72×10^{-4}
H_4SiO_4	5.73×10^{-4}

Initial brine chemistry

Grimsel granodiorite

Components	Concentration (M)
Na_2SO4	$9.08x10^{-4}$
KCl	$6.44x10^{-5}$
$MgCO_3$	$5.06x10^{-4}$
$NaHCO_3$	$3.25x10^{-3}$
CaCl	$1.72x10^{-4}$
H_4SiO_4	$5.73x10^{-4}$

- Modeled after porewater compositions at the Grimsel Test Site (Missana & Geckeis, 2006).
- pH = ~8.6

Precursor mineralogy

Quantitative X-Ray Diffraction (QXRD) analyses of the buffer clay (Wyoming Bentonite) the wall rock (Grimsel granodiorite). Mafic phases not identified in QXRD, however are present. Values are in weight percent

	Wyoming Bentonite	Grimsel Granodiorite
Analcime / Wairakite	b.d.l.	
Clinoptilolite	12.0	
Smectite	66.4	
Kaolinite	b.d.l.	
Albite		25.14
Plagioclase	8.3	
Orthoclase		30.84
Anorthite		
K-Feldspar	b.d.l.	
Biotite	2.8	??
Muscovite		
Chlorite	b.d.l.	
Calcite	5.5	
Dolomite	+	
Quartz	0.9	44.02
Cristobalite/ Opal-C	1.8	
Pyrite	0.4	
Siderite	1.8	
Total:	100.0*	100.00

* recalculated

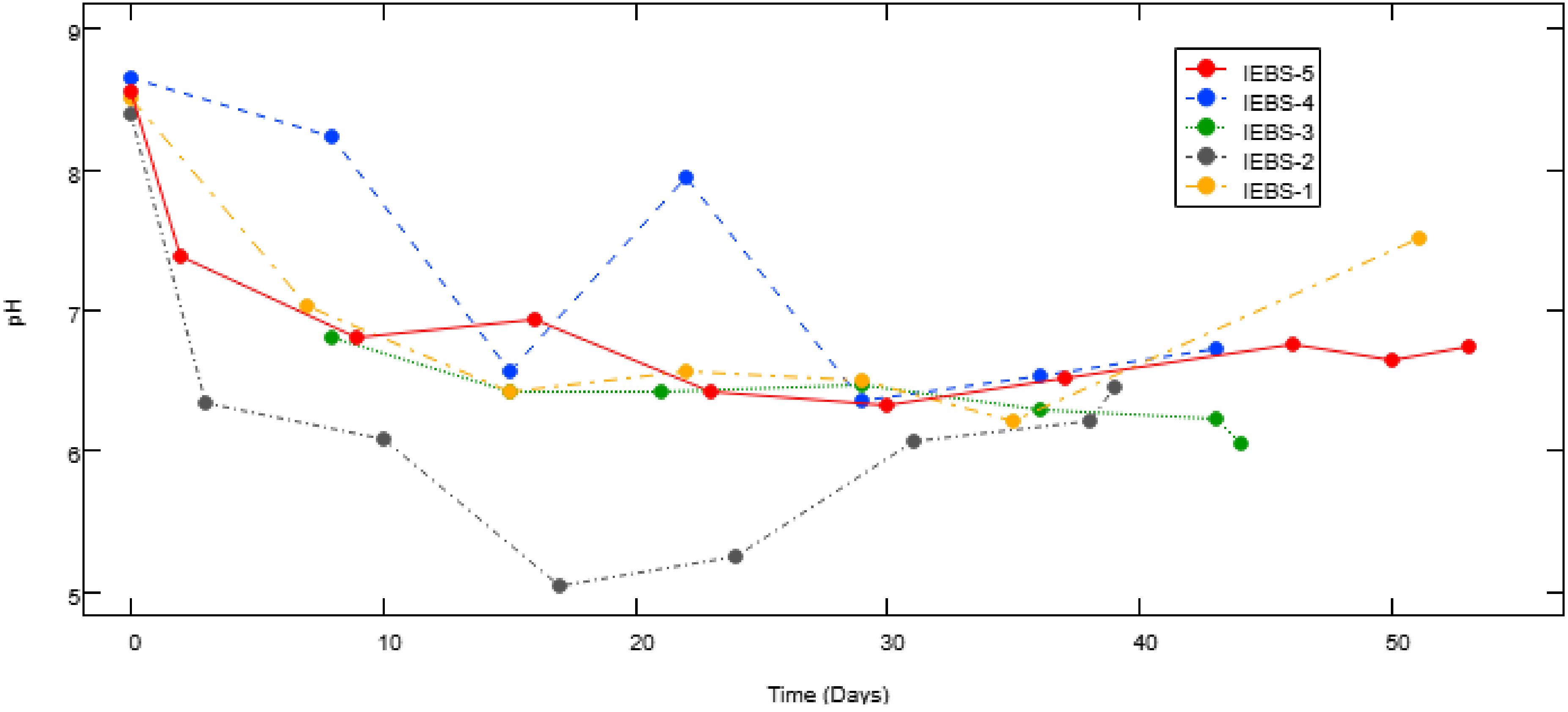
Post experiment QXRD mineralogy

	Wyoming Bentonite	BG-C-49-1 Granite	IEBS-1 Bentonite only	IEBS-2 316 SS
			6 weeks 250°C	6 weeks 250°C
Analcime / Wairakite	b.d.l.			
Clinoptilolite	12.0		?	?
Smectite	66.4		11.73	
Kaolinite	b.d.l.			
Albite		25.14	14.81	4.87
Plagioclase	8.3			
Orthoclase		30.84	19.51	9.47
Anorthite				43.55
K-Feldspar	b.d.l.			
Biotite	2.8			
Muscovite			28.02	23.68
Chlorite	b.d.l.			
Calcite	5.5			
Dolomite	+			
Quartz	0.9	44.02	26.17	18.68
Cristobalite/ Opal-C	1.8			
Pyrite	0.4			
Siderite	1.8			
Total:	100.0*	100.00	100.24	100.25

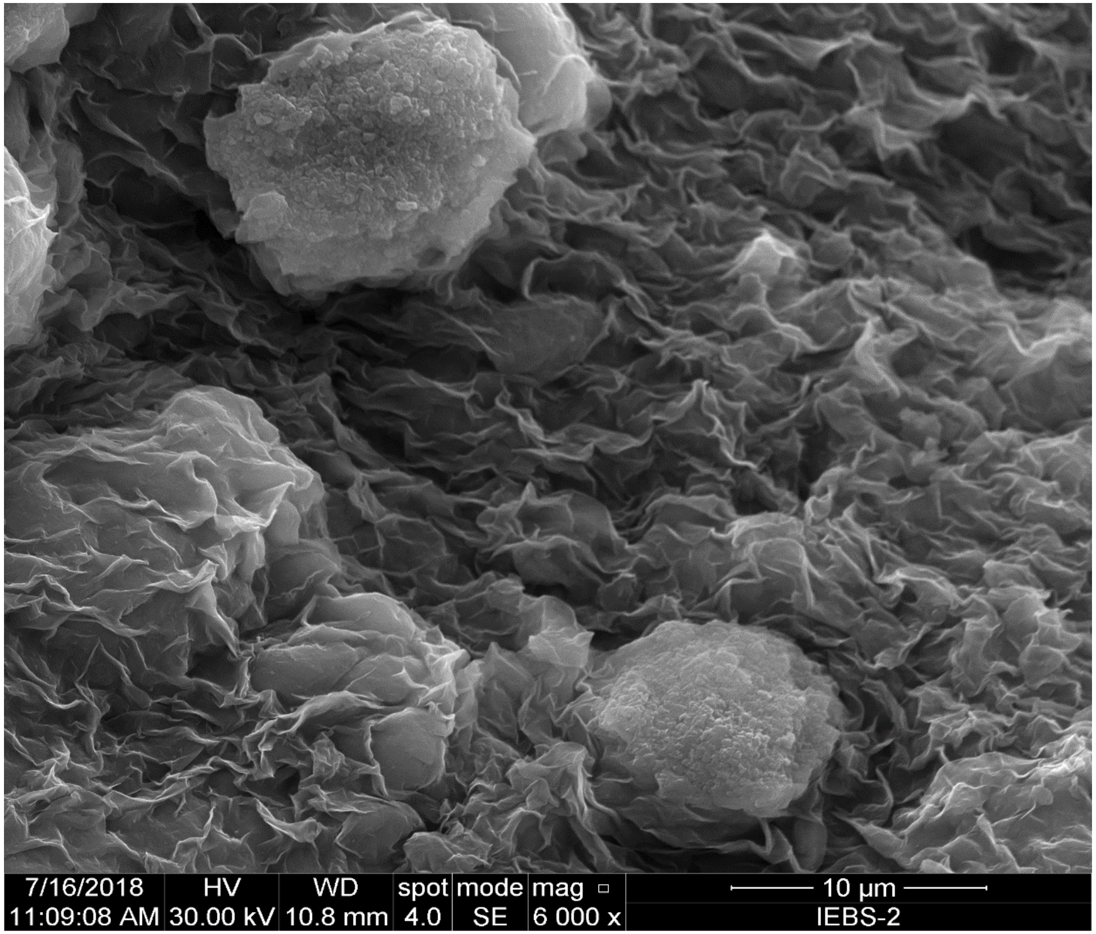
Salient mineralogy changes

- Smectite depleted
- Growth of muscovite
- Clinoptilolite stable, quartz increase but still SiO_2 saturated
- Generation of Al-Tobermorite
- Al-tobermorite ($Ca_{4.3}Si_{5.5}Al_{0.5}O_{16}(OH)_2 \cdot 4(H_2O)$).
- Al-tobermorite, have been observed in experiments involving bentonite and cement with highly alkaline bulk chemistries and pH > ~10 (Savage et al., 2007).

Experimental fluid pH trends

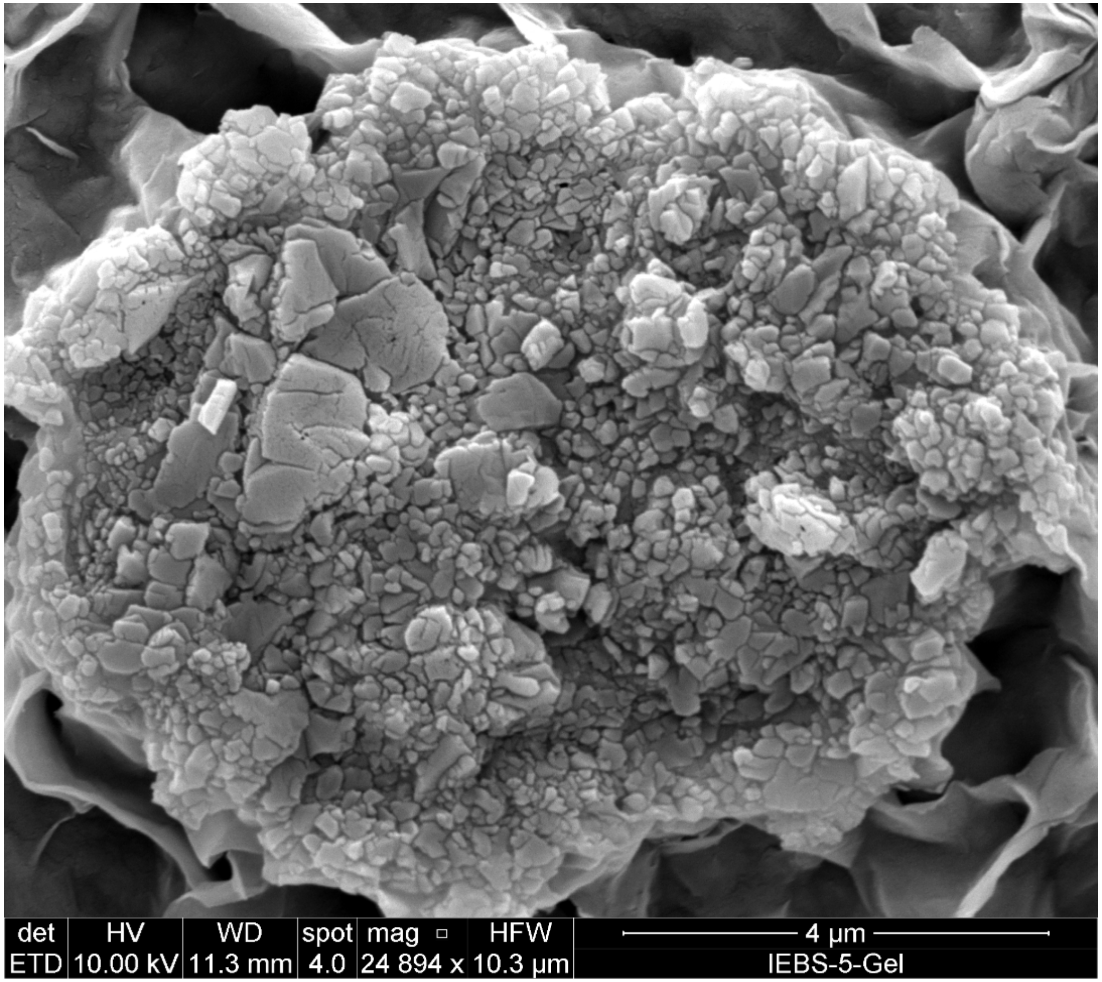


Al-Tobermorite in Smectite groundmass

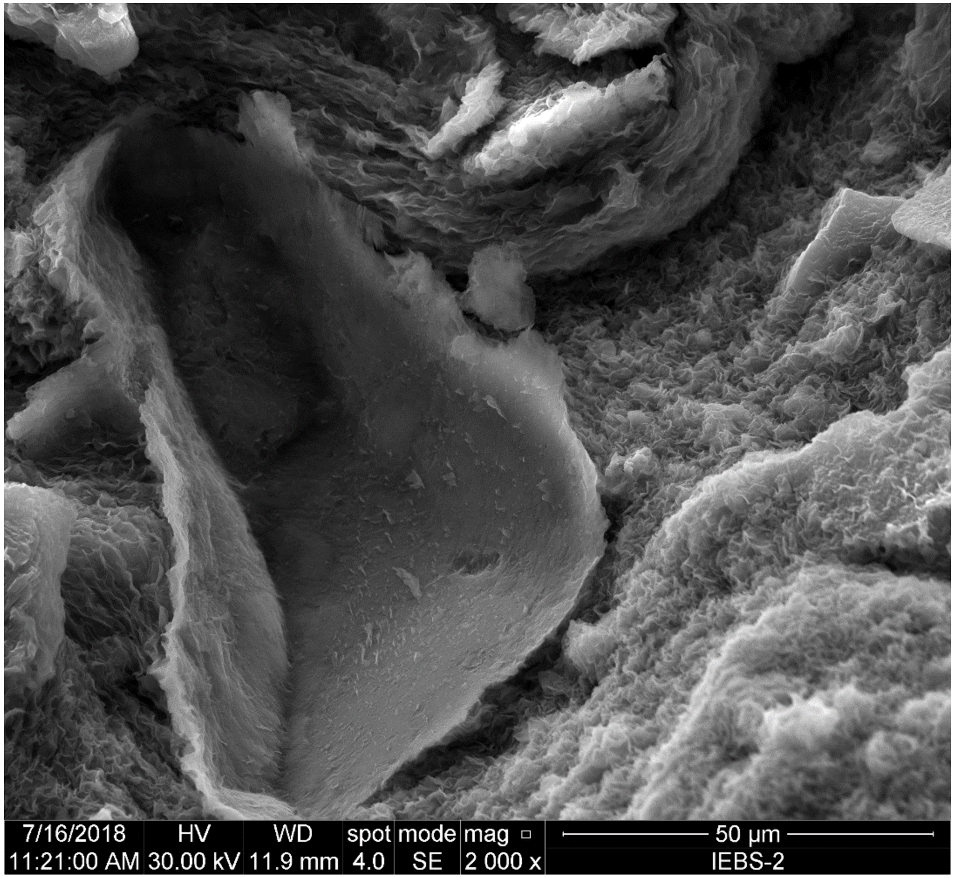


Calcium-aluminium-silica-hydrate(CASH) mineral not fully developed

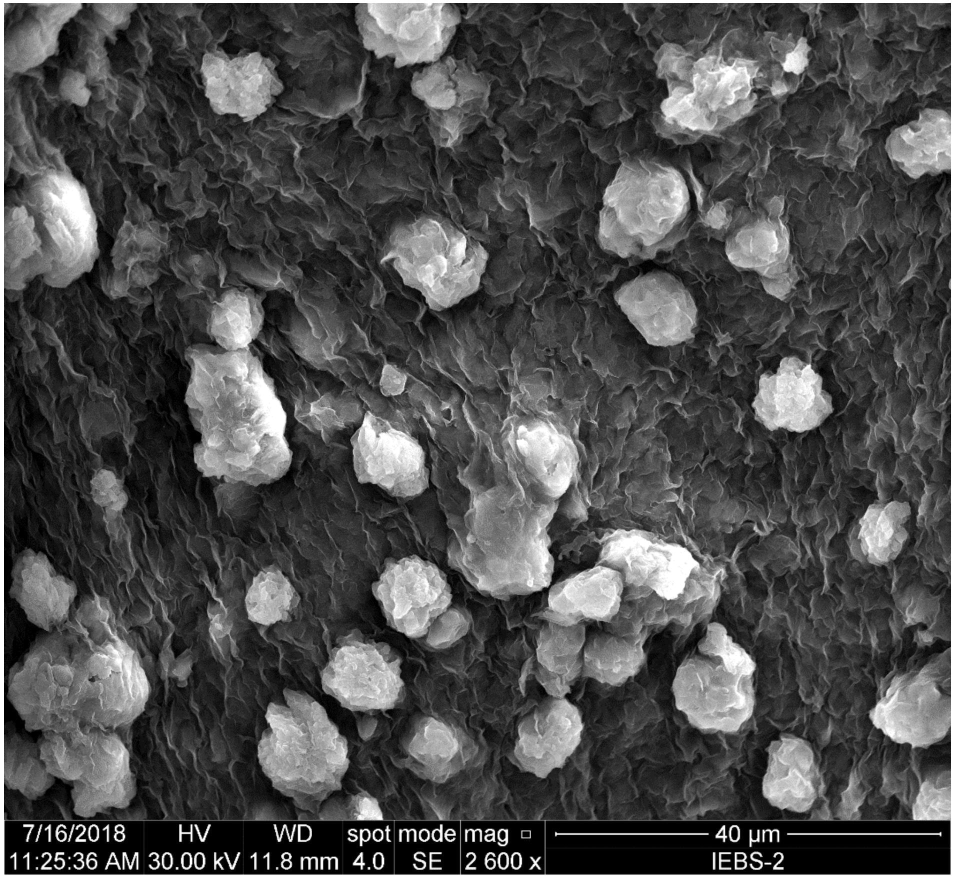
Al-Tobermorite + carbonate



Chlorite in matrix



Granular gypsum in smectite



Comparison to argillite host rock experiments

Grimsel Granodiorite

- Temperature = 250°C
- Carbonate rich brine
- Smectite recrystallized to → muscovite
- Al-tobermorite
- Accessory chlorite and gypsum

Opalinus Clay

- Temperature = 300°C
- NaCl rich brine
- Little structural changes to smectite observed (i.e., no I/S)
- Analcime - wairakite$_{ss}$

Conclusions

- Engineered Barrier Systems using bentonite backfill / buffer in a high temperature, pressure repository must consider system bulk chemistry.
- Characterization ongoing
- Al-tobermorite generated at lower than expected pH
- Favored over analcime, but may be metastable precursor at lower temperatures.
- Future investigations will focus on why CASH minerals formed instead of analcime–wairakite$_{ss}$ in the experiments with Grimsel granodiorite and Wyoming bentonite.

Acknowledgements

This project was funded by U.S. Department of Energy, Office of Nuclear Energy, Spent Fuel & Waste Science and Technology Campaign

SF-19LA01030102

Steve Chipera, Lindsey Hunt, George Perkins, Emily Kluk and Oana Marina provided assistance in the laboratories.

LA-UR-19-20137

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Grimsel hydrothermal experiment

QUESTIONS?

Mineralogical and geochemical evolution of engineered barrier materials in an argillite-hosted nuclear waste repository: Wyoming Bentonite and Opalinus Clay hydrothermal experiments

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Funded by the US Department of Energy Used Fuel Disposition Campaign

ABSTRACT

High temperature (200–300°C) and pressure (~150 bar) hydrothermal experiments were conducted to evaluate the stability of engineered barrier system (EBS) materials within an argillite-hosted nuclear waste repository. Eight experiments involving Opalinus Clay (shale) from Mont Terri, Switzerland and Wyoming Bentonite from Colony, WY were designed to mimic hydrothermal reactions within Opalinus Clay wall rock and at the interface between wall rock and Wyoming Bentonite, both in the presence of synthetic Opalinus Clay groundwater. Experiments were reacted at high temperature repository conditions for between 6 weeks and 6 months.

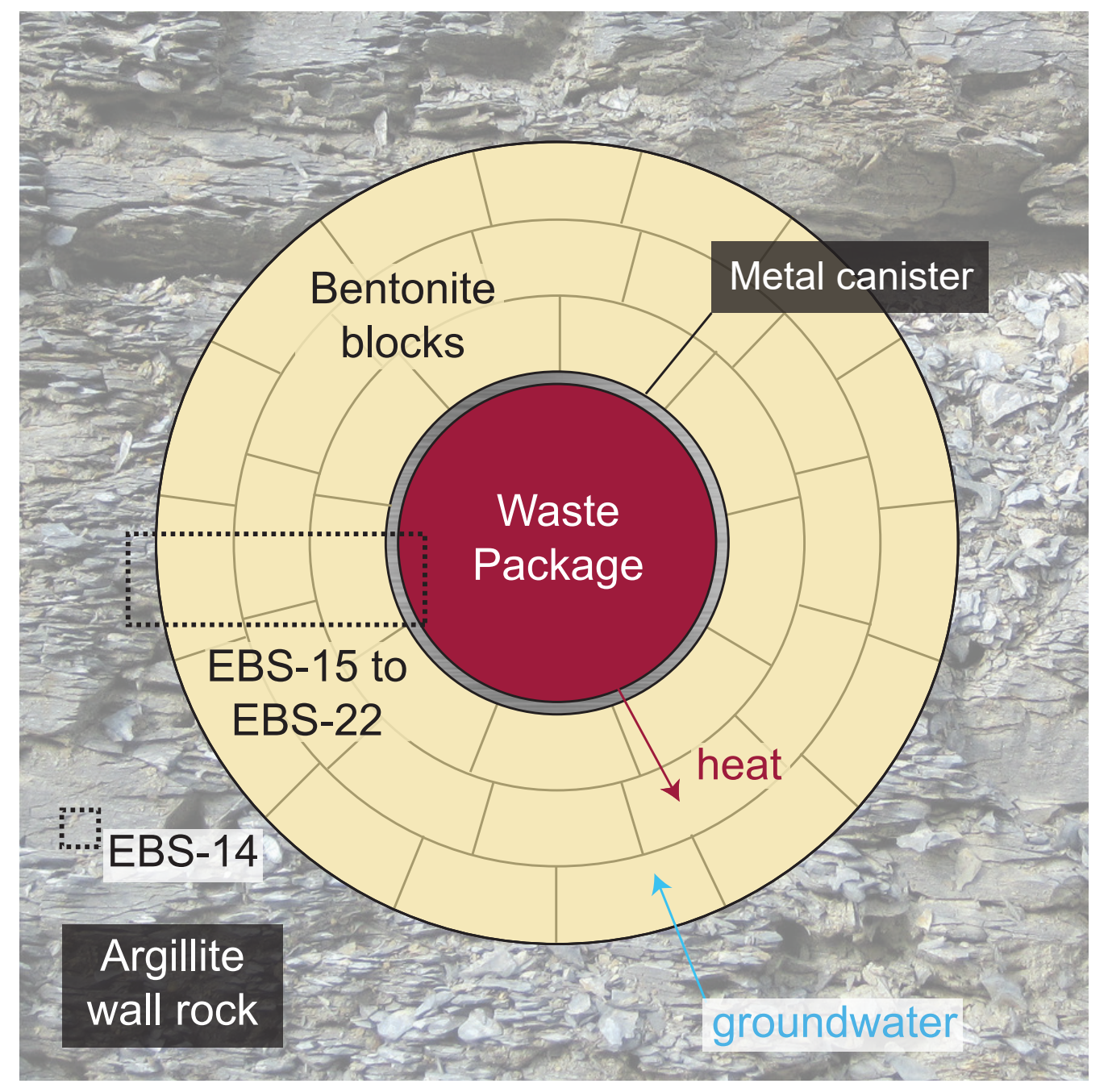
Fluid samples were collected periodically throughout the experiment duration and analyzed for major cations and anions. The pH (25°C) of the solution in each experiment started at ~7.5 and decreased to 5–6 by the end of the experiment. Aqueous SiO_2 remained under saturated with respect to quartz throughout the 200 and 300°C experiments. The solid-reaction products and were characterized post experiment via XRD, XRF, SEM, and EMPA. The major mineralogical products observed in the 6-week, Opalinus Clay-only 300°C experiment was the formation of abundant Ca-rich analcime (Na/Na+Ca = 0.21, Si/Al = 2.22) along fractures and edges of Opalinus Clay fragments. In comparison, analcime with an intermediate composition (Na/Na+Ca = 0.36–0.64, Si/Al = 2.67–2.97) formed in 6-week to 6-month 300 °C experiments that included Wyoming Bentonite and Opalinus Clay. The 6-month experiment produced analcime with the highest Si/Al ratio. Zeolite formation was not observed in 8-week, 200°C experiments. Preliminary XRD results from the clay-mineral fraction from the 6-month 300°C experiment do not exhibit significant smectite peak shifts or evidence of illite-smectite interlayering. Further, the 100% expandability estimates from 002/003 glycol-saturated smectite peak positions indicate silica cementation did not occur. In comparison, XRD analyses of Opalinus Clay fragments indicated some authigenic illite growth.

The transformation of Na-montmorillonite to illite within the Wyoming Bentonite EBS material was likely limited by the bulk chemistry of the system (i.e., low potassium and aluminum, silica saturation). Authigenic illite within Opalinus Clay fragments likely nucleated on pre-existing illite in the shale. Previous experiments with only Wyoming Bentonite documented the transformation of precursor clinoptilolite into analcime with a sodium- and silica-rich composition (Na/Na+Ca = 0.80–0.90, Si/Al = 3.05–3.38). Results from Opalinus Clay-only 300°C experiments indicate that the dissolution and re-precipitation of other phases, such as kaolinite, calcite, and smectite, may also contribute to zeolite formation, as Opalinus Clay does not contain the clinoptilolite precursor. Further, the low permeability of the Opalinus Clay rock limited authigenic analcime formation to fractures. These results are significant for understanding zeolite formation, clay mineral stability, and silica precipitation within EBS materials of a high-temperature repository.

ENGINEERED BARRIER SYSTEMS

The Spent Fuel and Waste Science and Technology program of the U.S. Department of Energy (DOE) aims to investigate the design and safety function of generic nuclear geologic repositories in a variety of geologic settings. The proposed design of the repository varies, but typically includes a metal canister, surrounded by bentonite-clay backfill, and emplaced within a host rock. Potential candidate geologic settings for the repository include crystalline, argillite, and salt formations. This experimental study is focused on an argillite-hosted repository, and the interaction of Opalinus Clay (argillite wall rock) and Wyoming Bentonite (clay backfill).

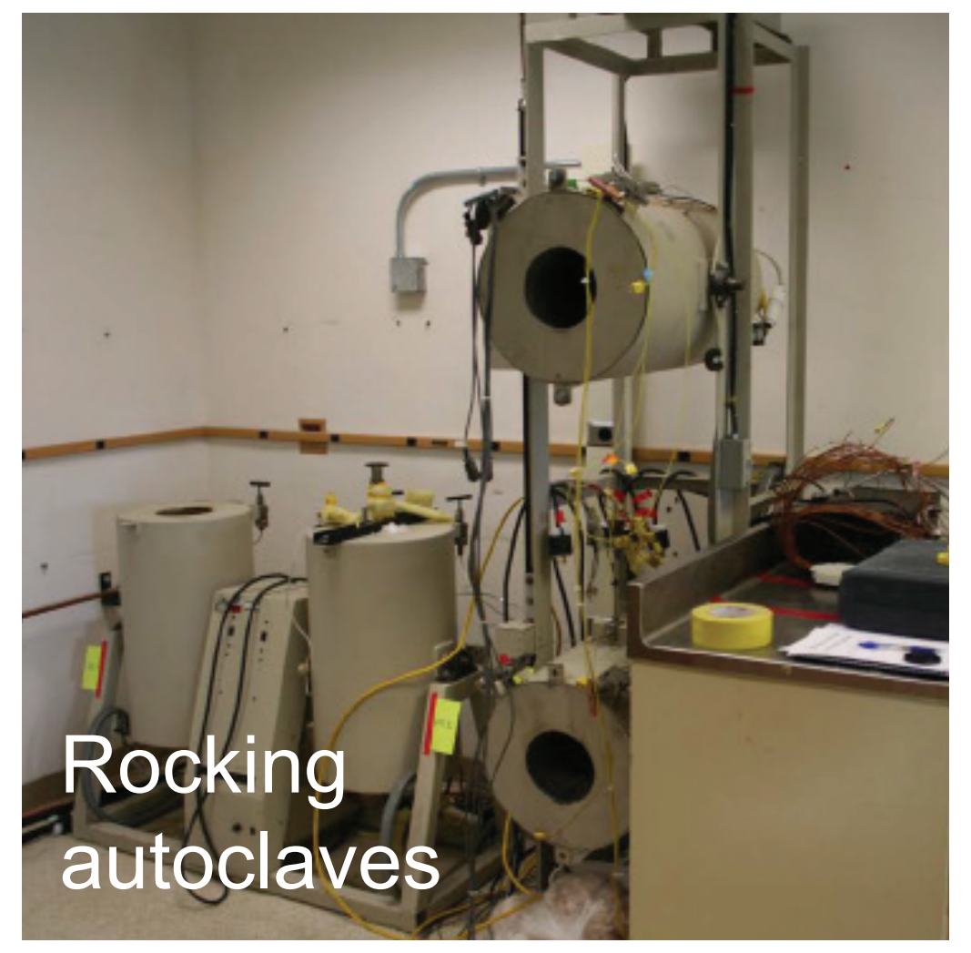
The proposed components of the repository all have favorable properties for isolating radioactive material at ambient temperatures and pressures and under dry conditions. However, the U.S. has considered storing spent nuclear fuel, such as pressurized water reactors (PWR), in dual-purpose canisters, which can be used for storage and subsequent disposal, but may increase the temperature of the repository. Modeling of the thermal evolution of 32-PWR waste package emplaced within shale host rock with 60 gigawatt-days per metric ton burnup shows that the bentonite–waste package interface has the potential to reach 299°C after 85 yr (25 year ventilation; 15 m package spacing; Greenburg et al., 2013). At these temperatures and with the presence of water, irreversible mineralogical changes will occur within the bentonite buffer and at the wall rock-bentonite interface.



Schematic of an argillite-hosted repository

HYDROTHERMAL EXPERIMENTAL APPROACH

Experimental hydrothermal petrology laboratory at LANL



Reactants (Table 1) were loaded into a flexible gold reaction cell and fixed into a 500 mL gasket confined closure reactor (Seyfried et al. 1987). Experiments were pressurized to ~150 bar (mimicking hydrostatic pressures for a shallow repository) and were heated to either 200 °C or 300 °C. Six experiments (EBS-14, EBS-15, EBS-17, EBS-19, EBS-21, and EBS-22) were run for a total of six to eight weeks. One experiment (EBS-20) was run for 6 months.

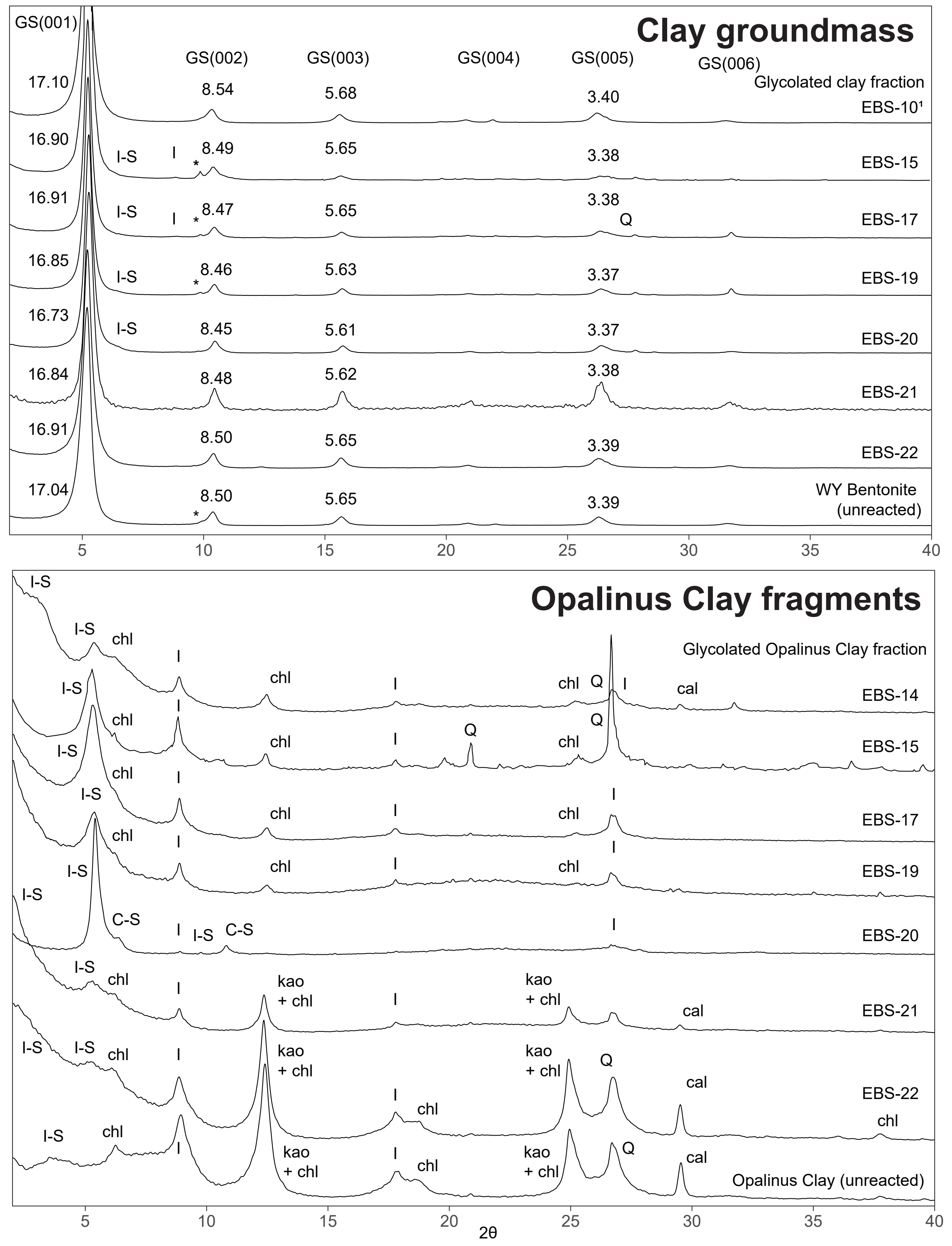
Table 1. Experiment components

Experiment	Synthethic groundwater (mL)	Opalinus Clay (g)	Wyoming Bentonite (g)	EBS metal type	EBS metal (g)	Fe° (g)	Fe_3O_4 (g)	Deviations	Run T (°C)	Run time
EBS-14	128	14.86	-	-	-	0.48	0.48	OC only	300	6 weeks
EBS-15	159	3.68	14.72	316 SS	12.63	0.59	0.59	-	300	6 weeks
EBS-17	155	3.61	14.44	Copper	12.21	0.58	0.58	-	300	6 weeks
EBS-19	120	3.70	14.82	304 SS	6.55	0.60	0.59	-	300	6 weeks
EBS-20	261	5.80	29.08	316 SS	6.60	0.95	0.95	-	300	6 month
EBS-21	126	2.63	10.47	316 SS	9.14	0.33	0.33	+ 1 M NaCl	200	8 weeks
EBS-22	132	7.29	7.30	316 SS	9.98	0.51	0.50	50:50 OC:WB	200	8 weeks

XRD analysis of oriented clay fractions

The clay groundmass of the reaction products has a similar clay mineral signature to that of unreacted Wyoming Bentonite.
Smectite from the 6-month (EBS-20) and the high saline brine (EBS-21) experiments have the great change in montmorillonite structure.

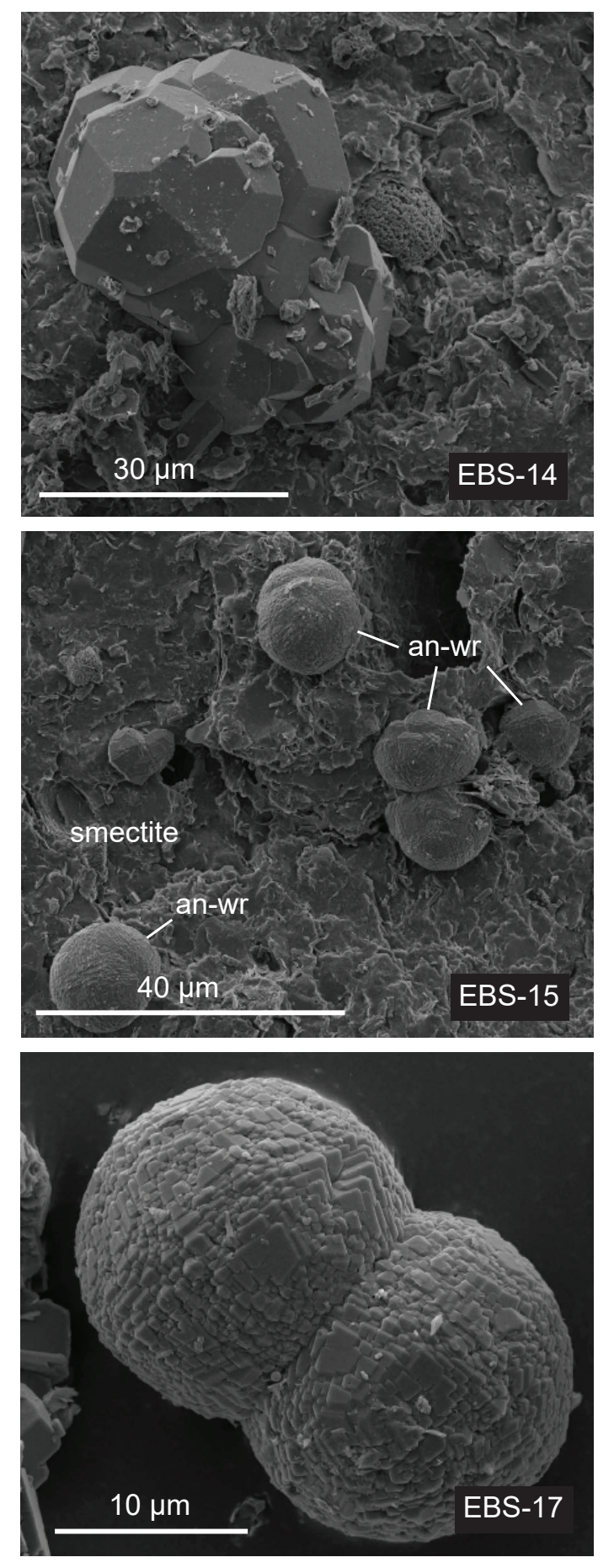
The clay mineralogy of the Opalinus Clay fragments changes drastically to include illite-smectite, chlorite-smectite, chlorite, and illite. Kaolinite is reactive at 300°C and in EBS-21, but largely stable in EBS-22.

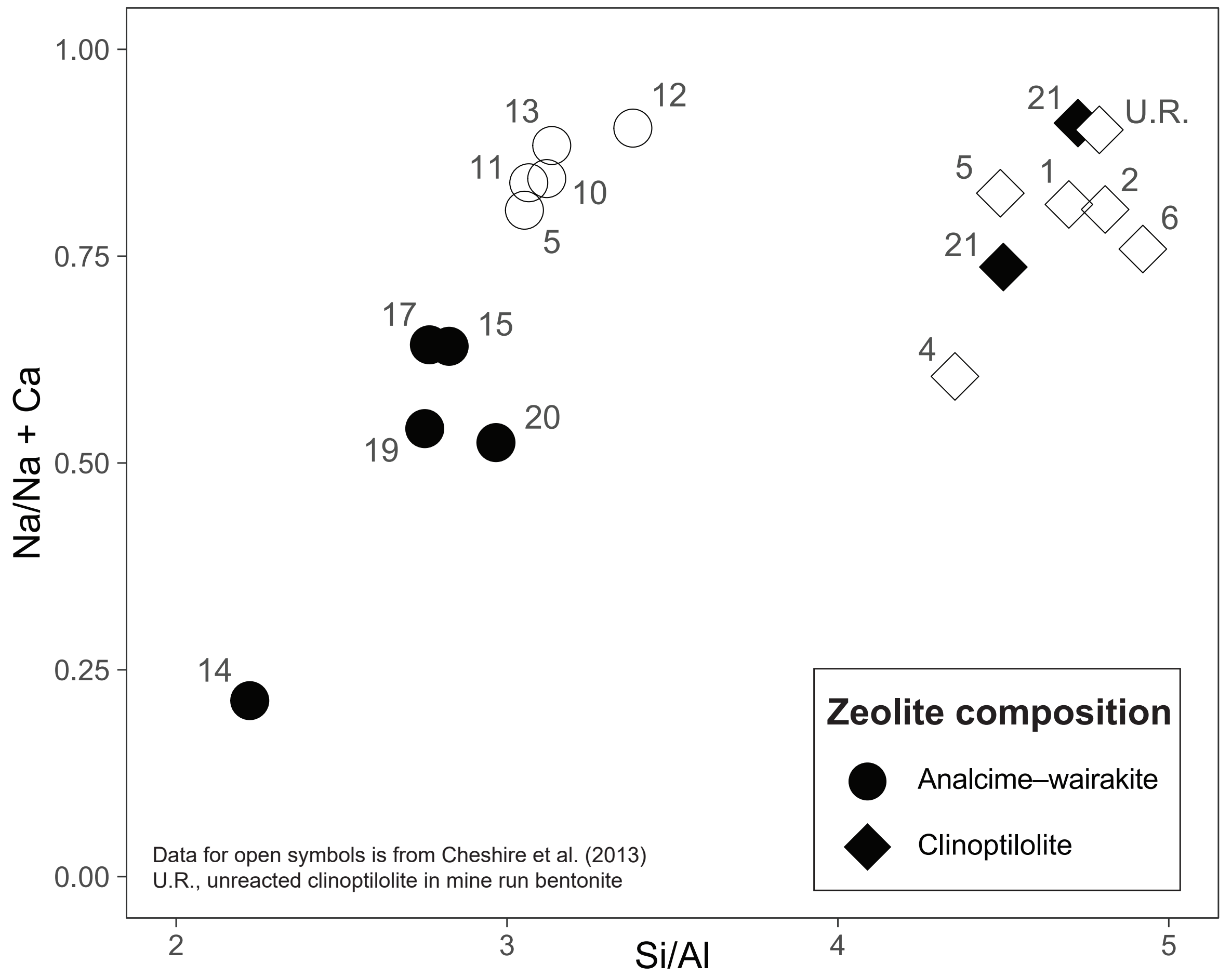


Mineral abbreviations: cal, calcite; chl, chlorite; C-S, chlorite-smectite; GS, glyocated smectite; I, illite; I-S, illite-smectite; Q, quartz; *, clinoptilolite. [1]Data for comparison from clay from a 6 week, 300 ºC experiments with Wyoming Bentonite only from from Cheshire et al. (2014).

ZEOLITE PARAGENESIS

- Analcime ($NaAlSi_2O_6 \cdot H_2O$) with variable Ca content formed in the 300 ºC experiments.
- EBS-14 (Opalinus Clay ony): analcime likely formed from kaolinite, calcite, and quartz present in the precursor Opalinus Clay.
- Wyoming Bentonite + Opalinus Clay: analcime compositions are between analcime formed in Opalinus Clay only experiments (EBS-14) and Wyoming Bentonite only experiments (EBS-5 through EBS-13)
- EBS-15 to EBS-20: analcime likely formed from kaolinite, quartz, and calcite in the Opalinus Clay fragments and from precursor zeolite and clay minerals in the clay groundmass.

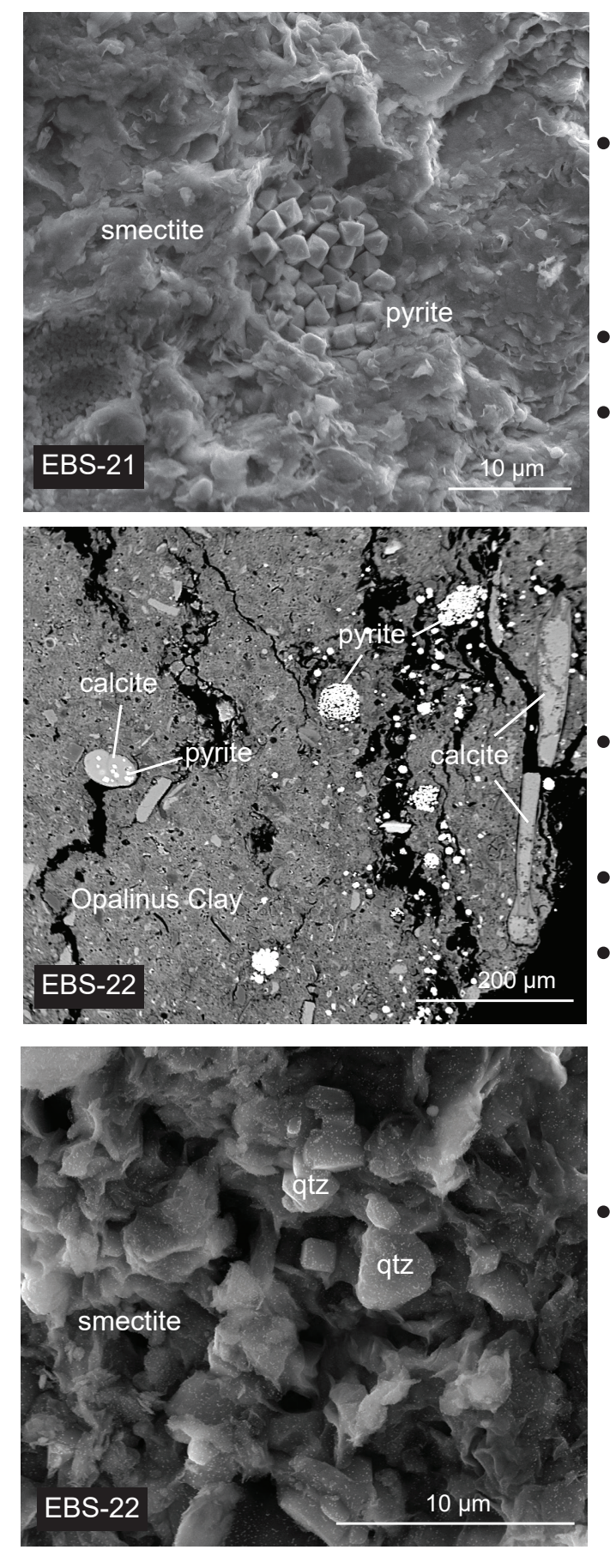




Data for open symbols is from Cheshire et al. (2013)
U.R., unreacted clinoptilolite in mine run bentonite

REACTION PRODUCT MINERALOGY

200 ºC Experiments (8 weeks)



EBS-21: NaCl brine

- Smectite reduced expandibility (I-S formation
- Kaolinite dissolution
- Halite precipitation

EBS-22: 50% OC, 50% WB

- No smectite structural changes
- Quartz precipitation
- Slight mineralogy changes to the Opalinus Clay fragments
- No zeolite formation observed.

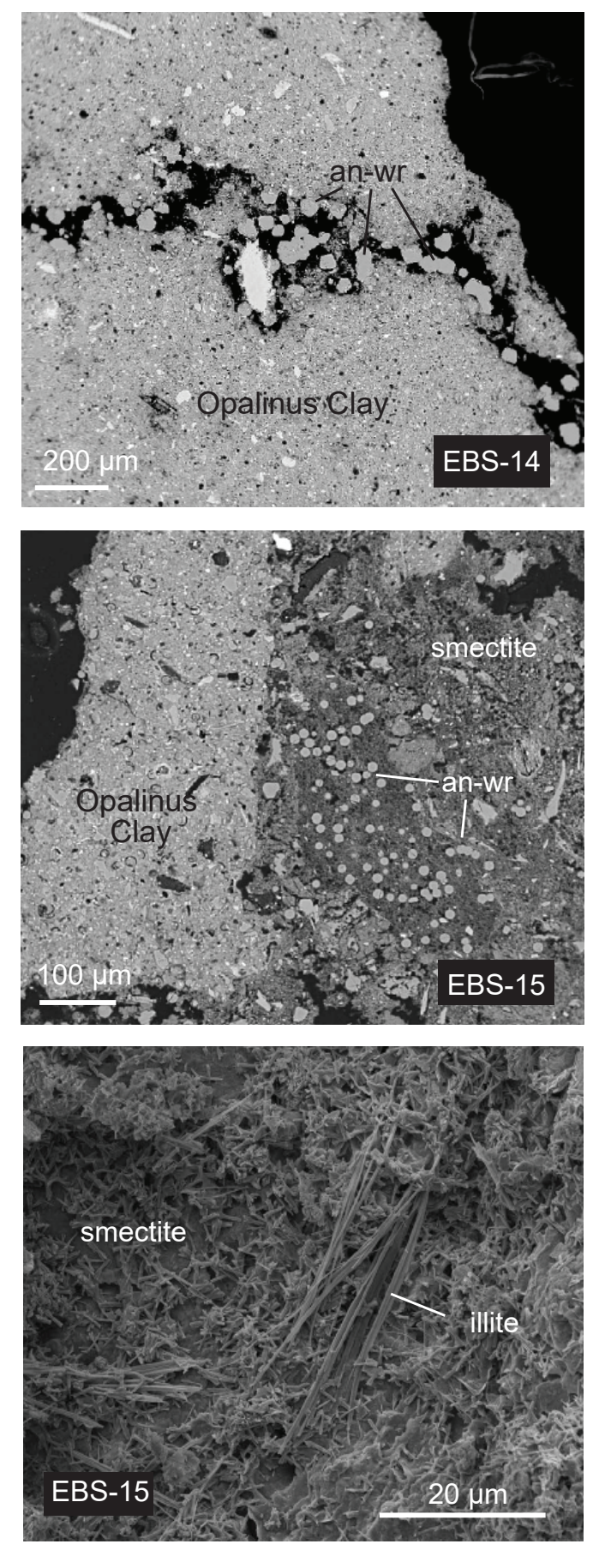
300 ºC Experiments (6 weeks to 6 months)

EBS-14: OC only

- Kaolinite, calcite, K-feldspar, and quartz reduced
- Analcime formation on cracks, edges, and voids of shale fragments

EBS-15 to -20: 20% OC, 80% WB

- Minor I-S formation
- Analcime formation in clay groundmass and along cracks and edges on the Opalinus Clay fragments
- Discrete illite nucleated on precursor illite present in Opalinus fragments



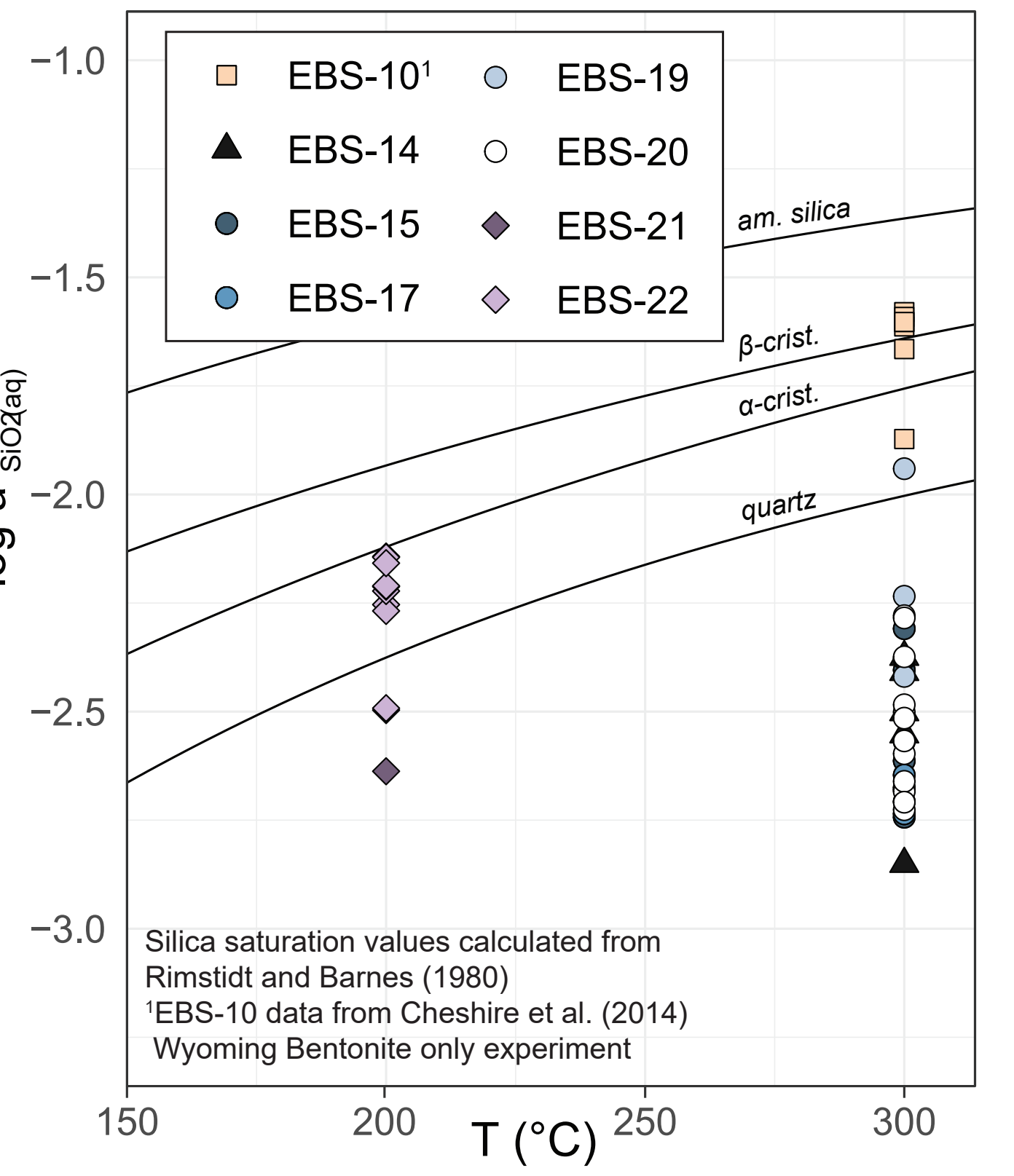
Quantitative XRD results

SAMPLE ID	WB	OC	EBS-10[1]	EBS-14	EBS-15	EBS-17	EBS-19	EBS-20	EBS-21	EBS-22
NON-CLAY FRACTION			WB	OC	WB + OC (300ºC)				WB + OC (200ºC)	
Quartz	1	14	3	7	4	3	4	4	3	6
K-Feldspar	1	6	0	1	1	1	1	1	1	1
Plagioclase	6	3	8	2	8	10	12	10	5	6
Apatite	0	0	0	1	0	1	1	0	0	1
Calcite	0	16	0	8	0	0	0	0	1	4
Dolomite	0	1	0	1	0	0	0	0	0	0
Gypsum	0	0	0	0	0	0	0	0	0	0
Halite	0	0	0	0	0	1	1	0	4	1
Anatase	0	0	0	1	0	0	0	0	0	0
Sphalerite	0	0	0	0	0	0	0	0	0	0
Clinoptilolite	13	0	6	0	11	8	12	4	6	3
Analcime	0	0	1	3	1	3	0	1	0	0
Wairakite	0	0	0	0	0	0	0	0	0	0
Cristobalite	2	0	2	0	0	0	0	0	0	0
Magnetite	0	0	0	0	0	0	0	0	0	0
Tobermorite	0	0	0	0	0	0	0	0	0	0
Amorphous-Missing	0	0	0	0	0	0	0	0	0	0
TOTAL	23	40	20	23	25	26	31	21	22	23
CLAY FRACTION										
Smectite + Illite + I/S	71	24	79	57	69	70	64	75	76	63
Mica	4	7	1	11	5	3	3	3	1	4
Chlorite	2	9	0	8	1	1	1	1	1	3
Kaolinite	0	17	0	1	0	0	0	0	0	6
TOTAL	77	58	80	77	75	74	69	79	78	77

[1]Data for comparison from clay from a 6 week, 300 ºC experiments with Wyoming Bentonite only from from Cheshire et al. (2014).

IMPLICATIONS FOR AN ARGILLITE-HOSTED NUCLEAR WASTE REPOSITORY

- All 300 °C systems have aqueous silica values that indicate undersaturation with respect to quartz.
- Analcime is a significant mineralogical product both within the bentonite EBS material and along cracks and edges of the argillite wall rock.
- At high temperatures (i.e., ~300 °C) zeolites may form at low pH (5–7), but not observed in 200°C experiments.
- Increased salinity observed to accelerate clay mineral reactions.
- Transformation of Na-montmorillonite to illite is limited by the bulk composition of the system (low K, Al).



Silica saturation values calculated from Rimstidt and Barnes (1980)
[1]EBS-10 data from Cheshire et al. (2014) Wyoming Bentonite only experiment

ACKNOWLEDGEMENTS

We thank Emily Kluk at Los Alamos National Laboratory and Steve Chipera at Chesapeake Resouces for XRD assistance. Scanning electron microscopy facilities were provided by the Materials Science and Technology group at Los Alamos National Laboratory. George Mason and Lindsay Hunt at the University of Oklahoma assisted with the EMP analyses. Bentonite Performance Minerals, L.L.C. provided the bentonite used in this study. Opalinus Clay was sourced from Florian Kober (NAGRA). Funding was through the Department of Energy's Used Fuel Disposition campaign. Los Alamos National Laboratory has assigned free release number LA-UR-19-22814 to this document.

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LA-UR-19-22814

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LA-UR-19-22825

Cesium Entrapment in Zeolites within Engineered Barrier Systems

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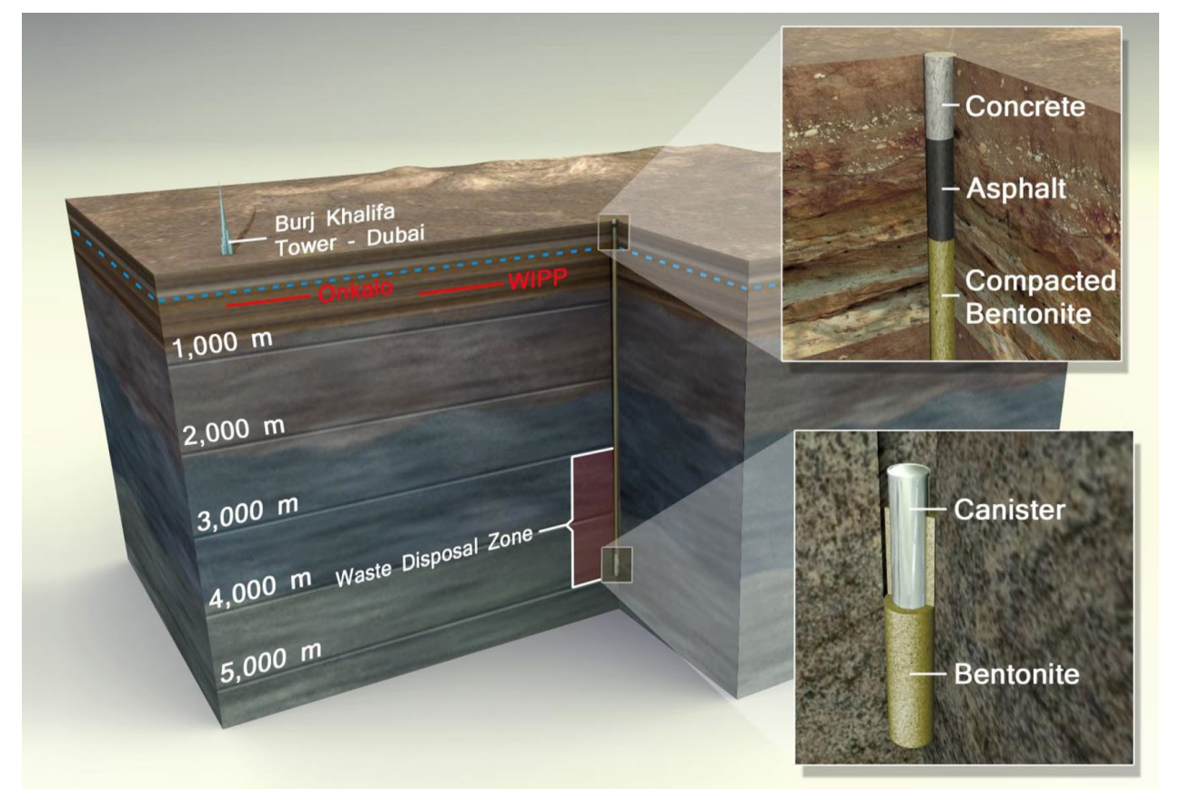
Introduction

Radionuclide migration in reference deep borehole (DBH) and engineered barrier systems (EBS) is a concern regarding bentonite seal stability and nuclear waste isolation after emplacement. In both designs, bentonite may be present as a barrier between the canister and host rock to provide a physical barrier and a chemical barrier by attenuating radionuclide migration, such as Cs, if a release occurs. Zeolites are common hydrothermal products from degradation of bentonite clay materials: clinoptilolite /glass (Caporuscio et al., 2015). At elevated repository temperatures and in the presence of a Cs-rich hydrothermal fluid, Cs-rich zeolites may crystalize from the bentonite and entrain radionuclides.

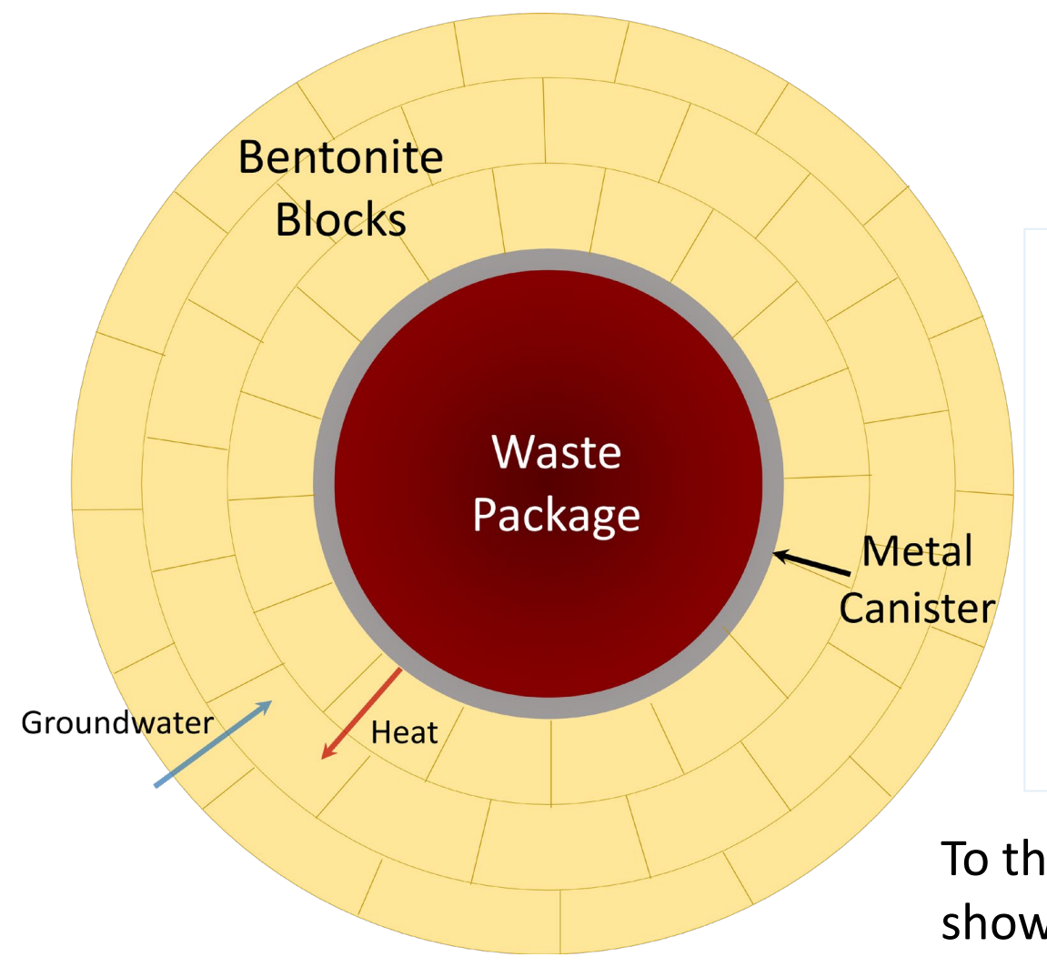
Determining the interaction between bentonite and potential Cs-rich hydrothermal fluid is important for evaluating Cs isolation during mineral alteration in a high temperature nuclear waste repository.



Above is a schematic of a Deep Borehole (DBH) emplaced in bedrock with a bentonite and concrete fill on top (Arnold et al., 2013)

Representative Deep Borehole

- 5.0 km deep borehole
- Waste canisters emplaced in the lowest part of the borehole above bentonite
- The lower plugging zone is sealed with concrete and bentonite
- P,T condition range from 300 to 1500 bar and 200 to 700 °C (Arnold et al., 2013)

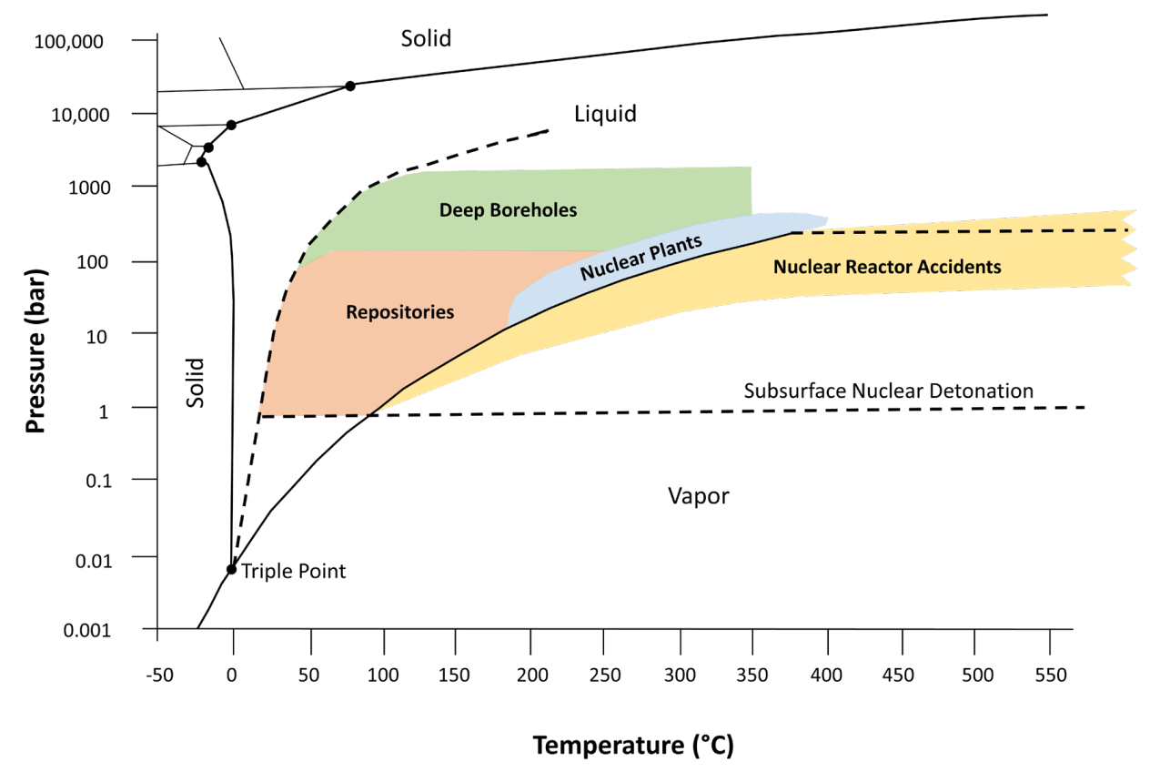


Engineered Barrier Systems

- Emplace the steel waste canister in a geological repository with a bentonite barrier between the canister and host rock
- Has the potential to reach 299 °C after 85 years at the waste package-bentonite interface (Greenburg and Wen, 2013)

To the right is a generalized cross section of a Engineered Barrier System (EBS) showing the waste package packed in Wyoming Bentonite.

Background



Pressure and temperatures typical of different nuclear storages, plants and accidents. Addition lines represent phases present at these conditions.

- U.S. DOE initiated Spent Fuel and Waste Science and Technology program to investigate the safety function of materials within an bentonite-hosted nuclear waste repository
- Bentonite is used due to its availability and high clay mineral content
  - A chemical barrier: Clay minerals can attenuate radionuclide migration
  - A physical barrier: Clay has the ability to swell, seal cracks, and prevent infiltration of groundwater from interacting in waste package
- ^{137}Cs (or radiocaesium) is formed as one of the more common fission products by the nuclear fission of U-235 and other fissionable isotopes in nuclear reactors and nuclear weapons
- Cs is problematic due to its high water solubility, allowing Cs to easily move and spread in groundwater

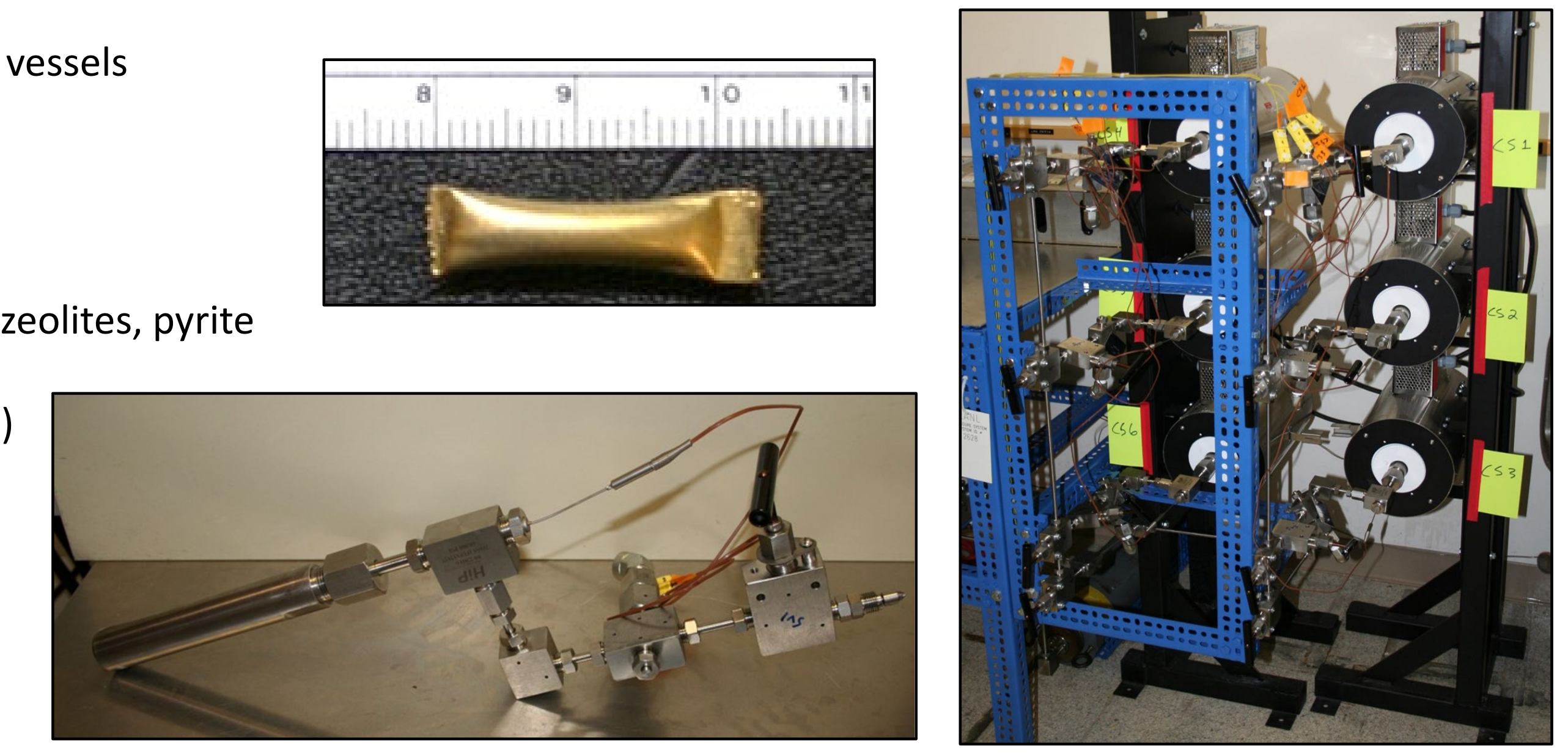
	Wyoming Bentonite
Analcime / Wairakite	b.d.l.
Clinoptilolite	12.0
Smectite	66.4
Kaolinite	b.d.l.
Plagioclase	8.3
K-Feldspar	b.d.l.
Biotite	2.8
Chlorite	b.d.l.
Calcite	5.5
Dolomite	+
Quartz	0.9
Cristobalite/ Opal-C	1.8
Pyrite	0.4
Siderite	1.8
Total:	100.0*

Table: Quantitative X-ray Diffraction (QXRD) analyses of the buffer clay (WY Bentonite) the wall rock (Opalinus Clay

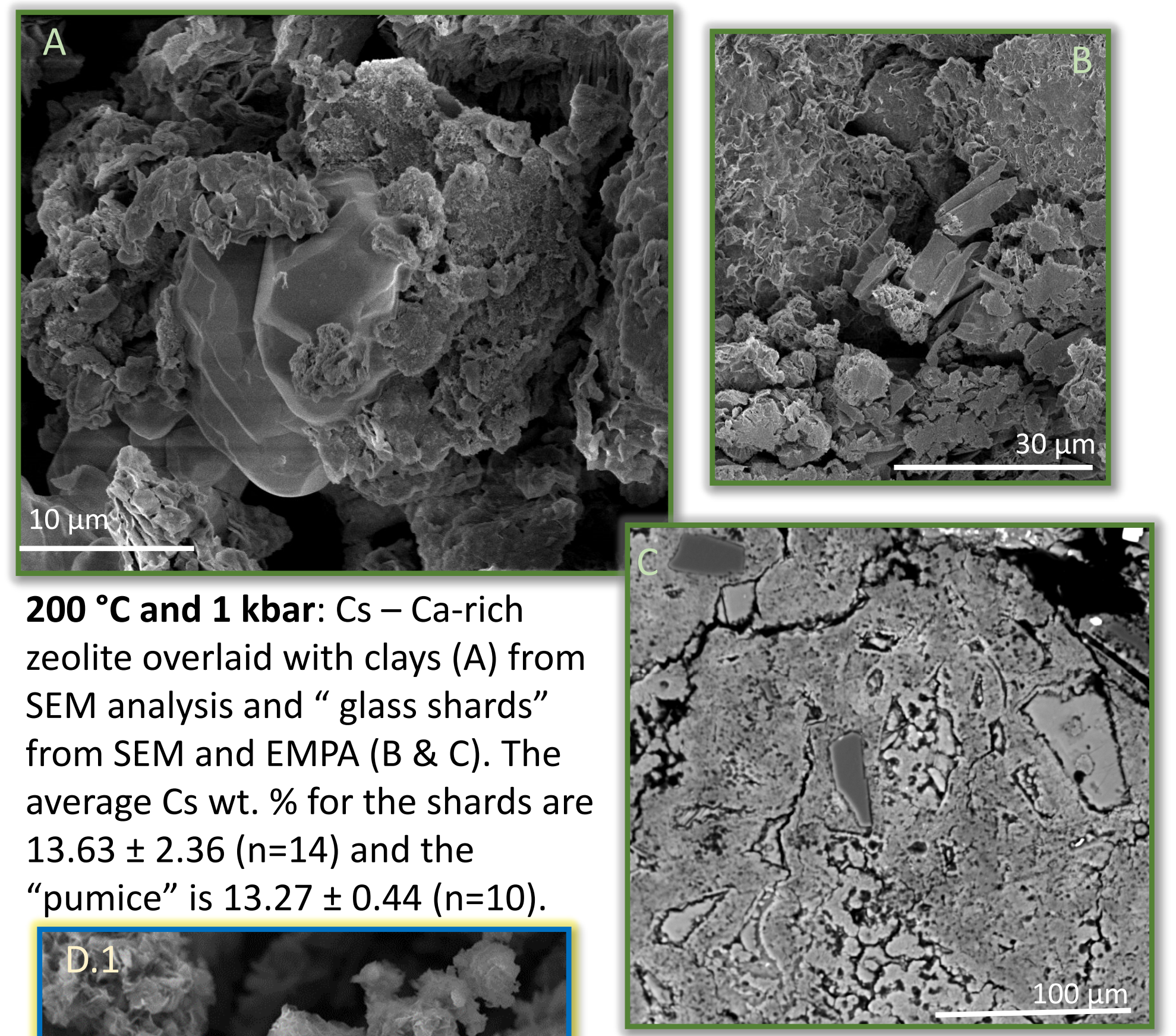
*Represents data set was normalized to 100.0, b.d.l is below detect limits and (+) represents material detectable but below 0.5 wt. %.

Methods

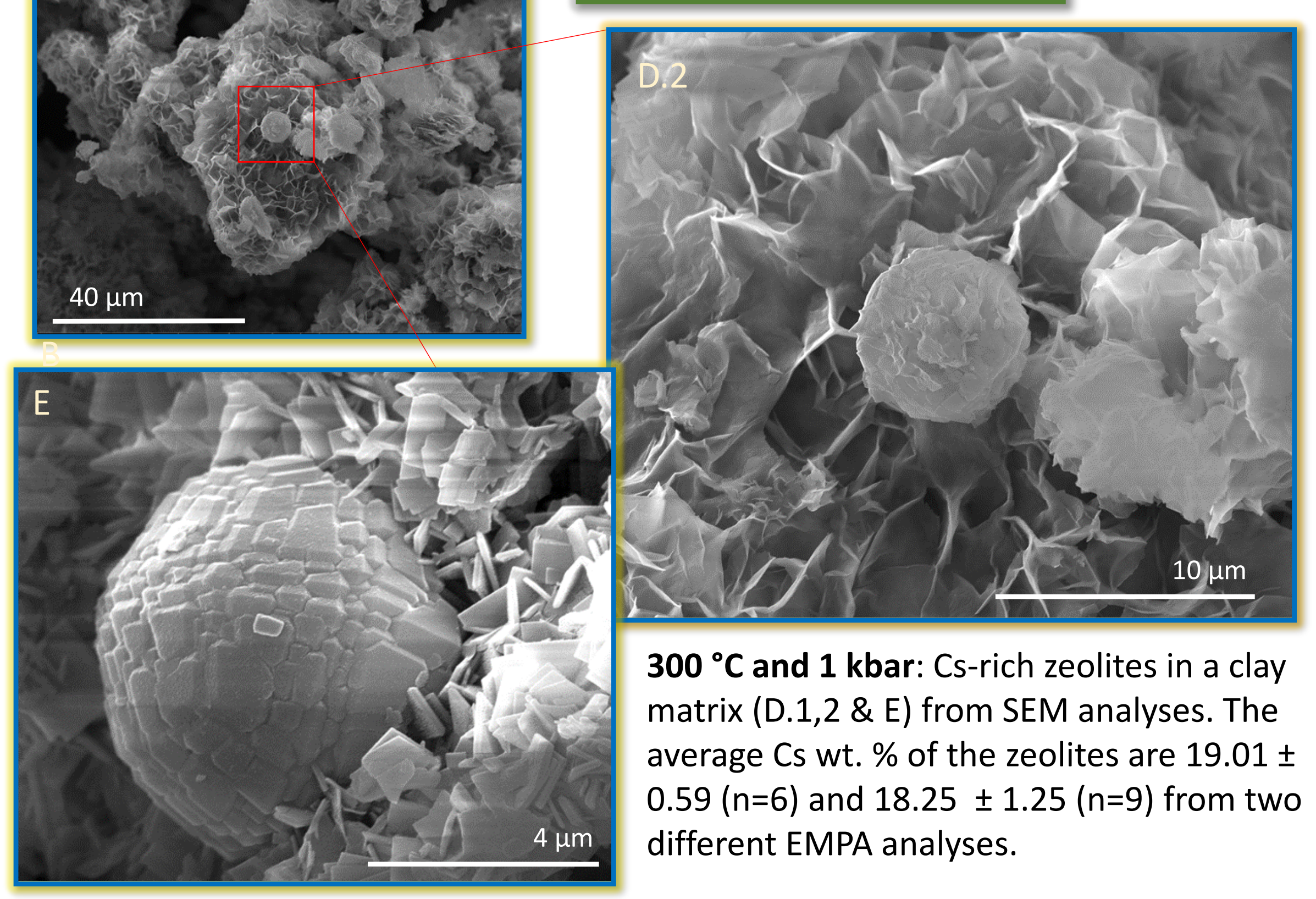
- Experiments conducted in Udiment 870 cold-seal pressure vessels
- Temperature: 200, 300 and 400 °C
- Pressure: 1000 bars
- Au capsules were loaded with:
  - Unprocessed bentonite from Colony, Wyoming, USA
    - Contains smectite with impurities- feldspars, silica, zeolites, pyrite (see Table)
  - 2 equilimolar $CaCl_2$-NaCl-CsCl-H_2O fluid (2:1 water:rock)
    - Starting pH of 5.76
- Buffered at Fe_3O_4 - Fe°
- Durations of 14 days
- Experiments characterized by SEM-EDS (imaging) and EMPA (mineralogy)



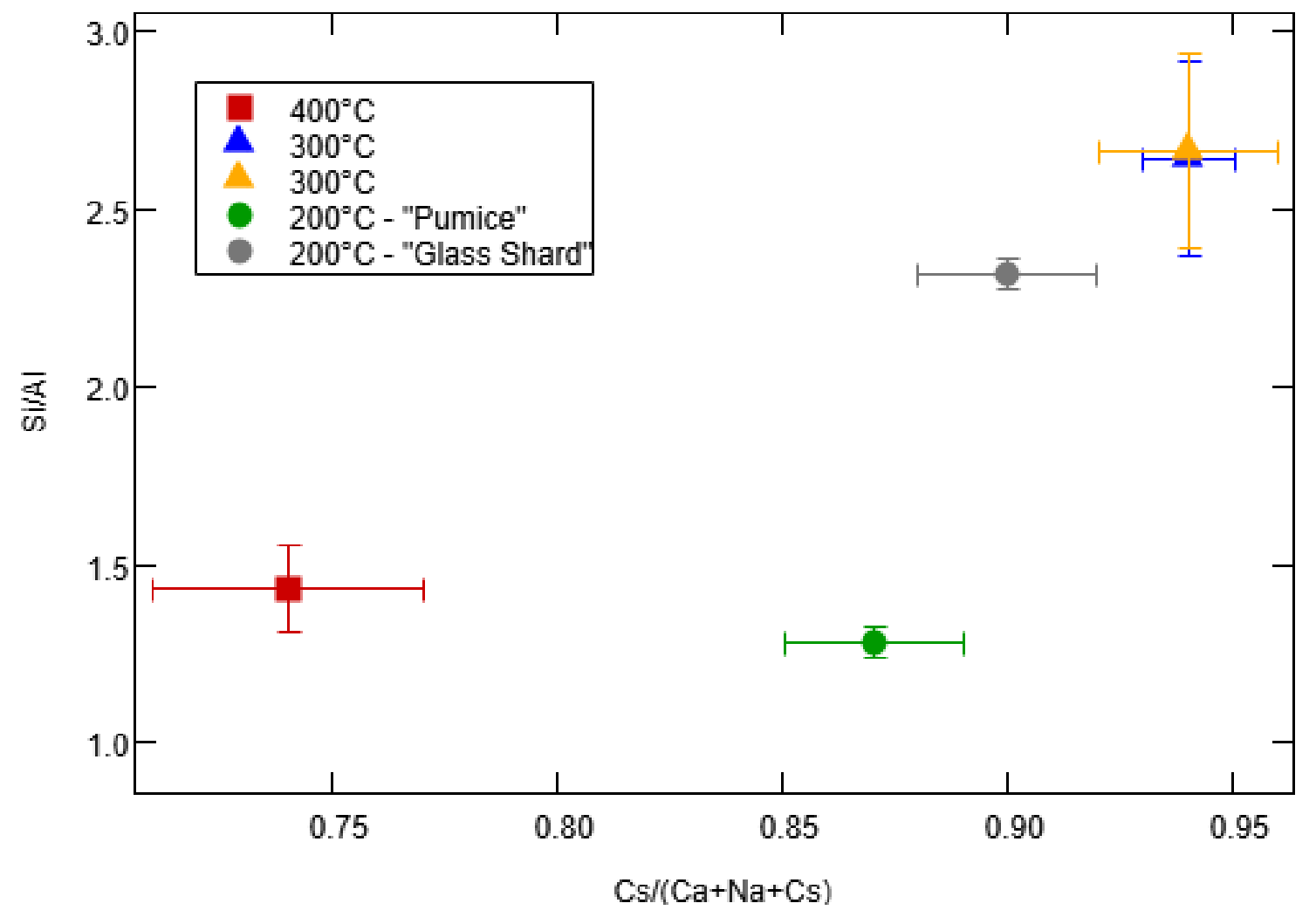
Results



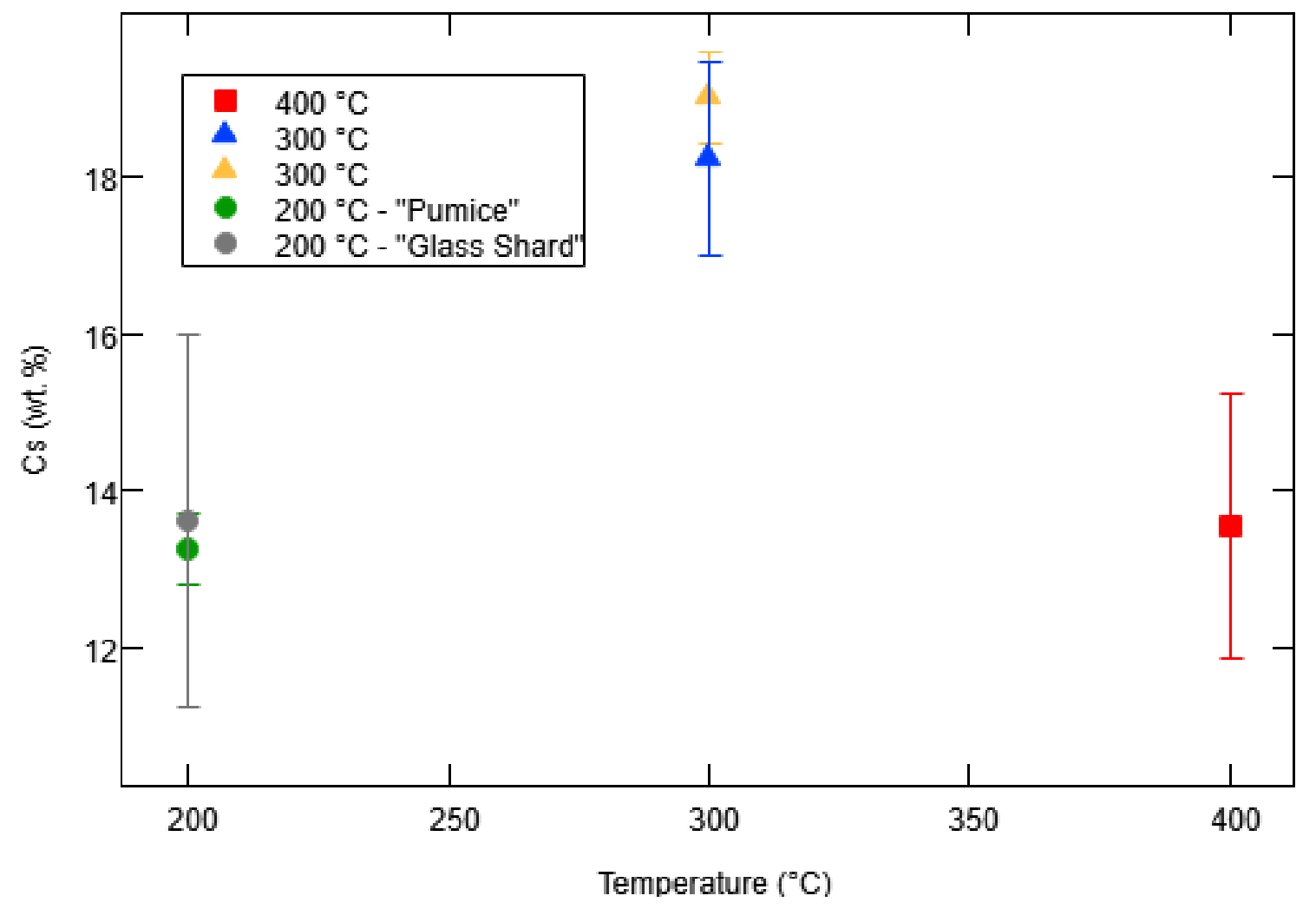
200 °C and 1 kbar: Cs – Ca-rich zeolite overlaid with clays (A) from SEM analysis and " glass shards" from SEM and EMPA (B & C). The average Cs wt. % for the shards are 13.63 ± 2.36 (n=14) and the "pumice" is 13.27 ± 0.44 (n=10).



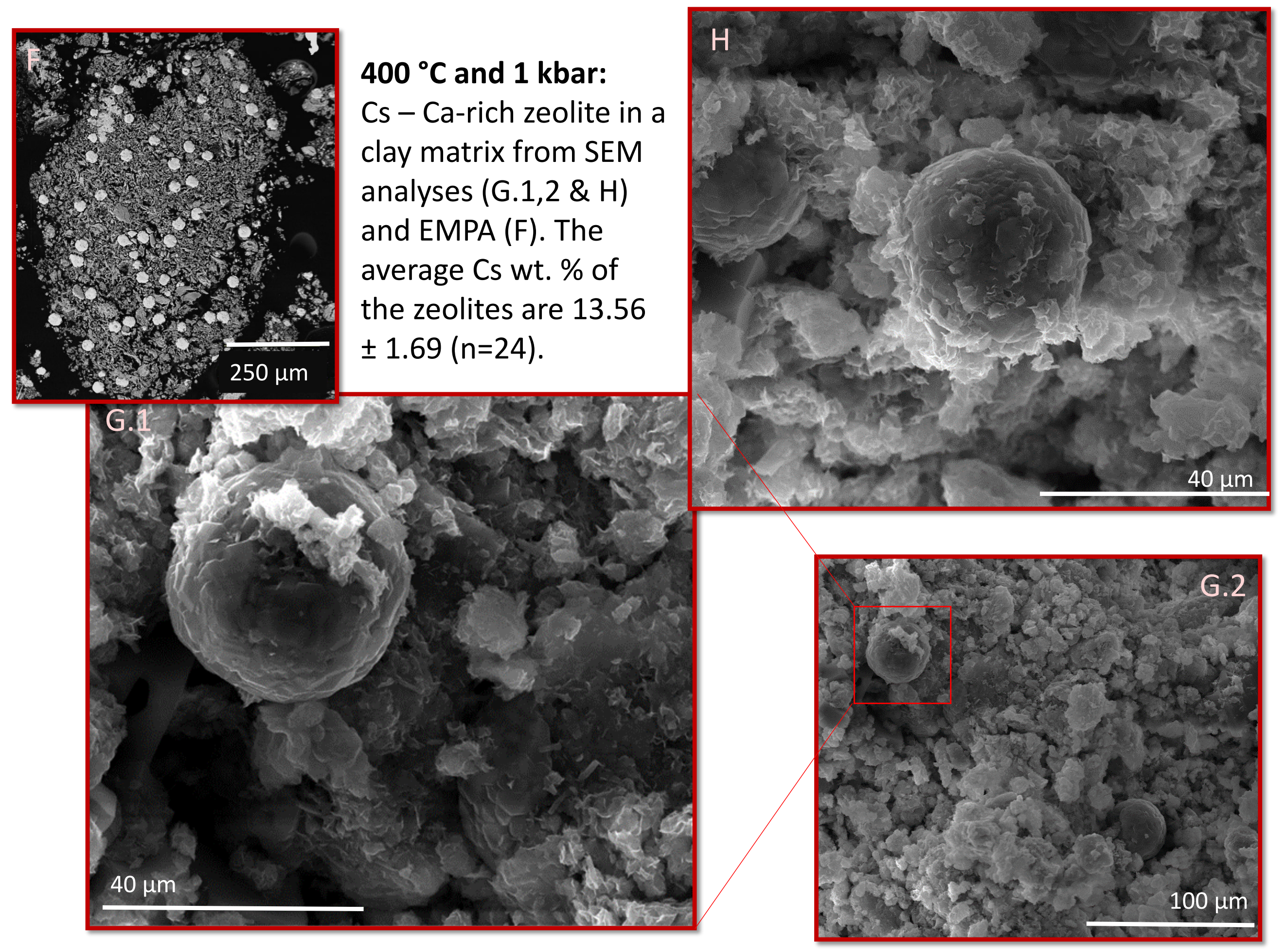
300 °C and 1 kbar: Cs-rich zeolites in a clay matrix (D.1,2 & E) from SEM analyses. The average Cs wt. % of the zeolites are 19.01 ± 0.59 (n=6) and 18.25 ± 1.25 (n=9) from two different EMPA analyses.



Normalized Cs concentrations to Ca and Na as a function of Si/Al ratio of the minerals. The Si/Al ratio is directly proportionally to the amount of Cs in the run product.

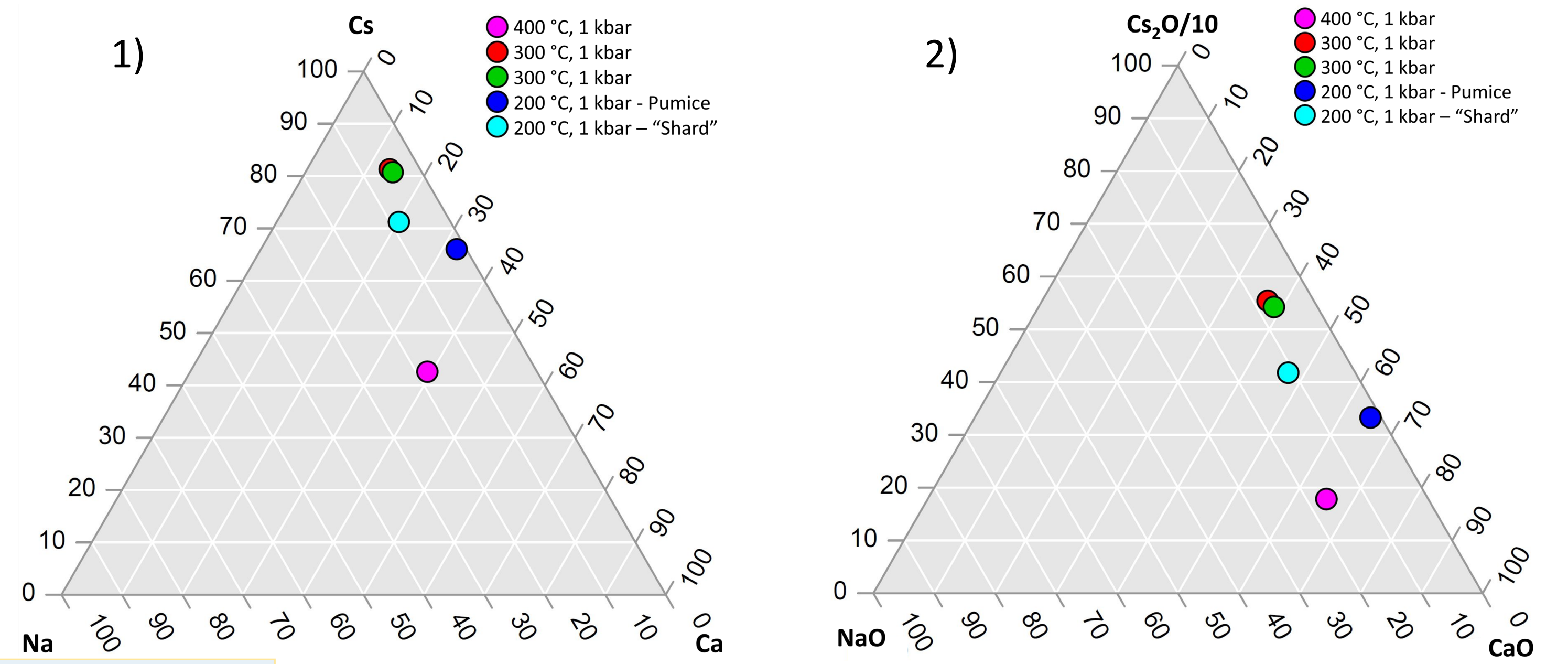


Cs concentrations as a function of temperature of the systems at 1 kbar. Cs concentration in the run product peaks at 300 °C.



400 °C and 1 kbar: Cs – Ca-rich zeolite in a clay matrix from SEM analyses (G.1,2 & H) and EMPA (F). The average Cs wt. % of the zeolites are 13.56 ± 1.69 (n=24).

Discussion



Ternary Diagrams. 1). The system Na-Cs-Ca for the experimental minerals at 1 kbar. 2). The system NaO-Cs_2O-CaO for the experimental mineral at 1 kbar. Cs_2O is divided by 10 to better show relationships.

- Clinoptilolite (and remnant glass/pumice) are present in the starting bentonite material and recrystallized to Cs-rich zeolites above 300 °C in the present of a Cs-rich brine
- Experiments document the incorporation of Cs into glass at 200 °C and zeolites at 300 and 400 °C
- Minerals tend to be Cs-rich, Na-poor with minor Ca
- Cs_2O is more abundant at lower temperature, whereas the 400 °C experiment contained higher CaO content
- Minerals containing high Si concentrations are more enriched in Cs

Conclusions

- Cs is incorporated into zeolites and glass in the presence of a Cs-rich brine
- The results demonstrate the temperature dependence of the formation of Cs-rich phases
  - Cs is better incorporated at moderate temperature typical of repositories
- When clinoptilolite alters from a high temperature thermal pulse of a repository, zeolites will form and exist as radionuclide sorbing phases

Future Work

- More experiments will be performed to include P,T conditions more similar to EBS.
- Other completed experiments were performed at variety temperature (250, 400, and 450 °C) and pressures of 500 and 1000 bars.
- Future work will re-explore 200 and 300 °C at 500 bars and longer run times.

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Acknowledgments

- This project was funded by DOE's Spent Fuel and Waste Science and Technology.
- Scanning electron microscopy facilities were provided by Materials Science and Technology group at LANL. Dr. George Morgan at the University of Oklahoma was instrumental in the obtaining of EMP analyses.

Stability of BORAL in dual purpose canisters – mineral and structural phase changes at elevated repository temperatures

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The U.S. Department of Energy is investigating the use of Dual Purpose canisters for spent nuclear fuel storage as a part of the Used Fuel Disposition Campaign. Such dry spent fuel canisters would be loaded with fuel bundles, and then transported and stored at a nuclear repository. Separating the fuel bundles is a composite thermal neutron absorber (trade name BORAL) consisting of sintered aluminium and boron carbide (B_4C) powders laminated within aluminium metal sheets.

This egg crate structure within the canisters is a vital component to prevent criticality issues.

Although various tests have been performed on BORAL, this material has not been subjected to hydrothermal conditions such as when a canister is breached after emplacement. A scoping experiment reacted BORAL coupons with DI water at 300 °C and 150 bar for 2 weeks.

The aluminium metal was converted primarily to boehmite as: $2Al_{(s)} + 2H_2O = 2AlO(OH)_{(s)} + H_{2(gas)}$. Over 1700 ml of H_2 gas were generated. The coupons doubled in volume and increased by ~63% in mass. The coupons remained structurally intact, but likely warped due to preferential crystal growth on the Al sheets. Reaction fluids were enriched in aluminium and boron. The reactivity of BORAL at hydrothermal conditions is significant for understanding material stability in a breached canister scenario.

Hydrothermal interaction of Opalinus Clay, Wyoming Bentonite, and Portland Cement

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The U.S. Department of Energy aims to characterize fluid-solid interactions at elevated temperatures of candidate engineered barrier system materials to isolate heat-generating spent nuclear fuel in a deep geological repository. Four hydrothermal experiments examining the interaction of Opalinus Clay (argillite wall rock), Wyoming Bentonite, and ordinary Portland Cement were conducted to understand the mineralogical and geochemical evolution of a high temperature repository with cement pore fluids. Experiments were conducted at ~9:1 synthetic Opalinus Clay groundwater:rock ratio, 200°C, and 150 bar for 8 weeks. Coupons of either 316 stainless steel (SS), 304 SS, or low carbon steel were added to simulate the presence of a waste cansiter. Results are compared to previous experiments with Wyoming Bentonite ± Opalinus Clay.

The aqueous geochemistry of the reaction fluid was monitored during each experiment. Quench pH (at 25 °C) dropped from initial values of ~10 to 8.5. Aqueous silica activities calculated at 200°C indicate undersaturation with respect to quartz. Characterization of the solid-phase run products show significant mineralogical changes in the Opalinus Clay fragments and bentonite clay. Quantitative X-ray diffraction (XRD) estimates show dissolution of montmorrilonite and XRD of the oriented clay fraction indicate the formation of illite-smectite and chlorite in the bentonite groundmass. Zeolite formation was abundant; large analcime crystals (up to ~0.5 mm diameter) are observed coating the Opalinus Clay fragments and within the clay matrix. Electron microprobe analyses of analcime crystals coating the Opalinus Clay fragments have higher Na/(Na+Ca) values but similar Si/Al ratios relative to the grains in the clay matrix.

In contrast, previous experiments with only Opalinus Clay and Wyoming Bentonite at 200 °C did not produce zeolites and no structural changes to montmorillonite were observed. These results highlight the potential for a highly reactive environment at the bentonite-cement interface within engineered barrier systems.

Attenuating Cesium Migration with Bentonite in Nuclear Repositories

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Radionuclide migration in deep borehole (DBH) and engineered barrier systems (EBS) is a concern regarding bentonite seal stability and nuclear waste isolation after emplacement. Zeolites are common products of bentonite in repository conditios and in the presence of a Cs-rich hydrothermal fluid, Cs-rich zeolites may crystalize as authegenic phases within the bentonite seal material. Determining the interaction between bentonite and a Cs-rich fluid is important for evaluating Cs isolation during mineral alteration of bentonite in nuclear waste repositories.

The experiments were conducted in cold-seal pressure vessels from 200 to 450 °C and 500 to 1000 bar, typically of P, T condition of both repositories. Gold capsules were loaded with a 2:1 water:rock ratio of unprocessed bentonite and an aqueous fluid containing 2 equilimolar $CaCl_2$-CsCl-NaCl. The run products were characterized via SEM (images) and EMPA (mineralogy).

EMPA at 200 °C and 1 kbars observed minor zeolites, but instead a Cs-rich glass and pumice (13.63 ± 2.36 wt.% Cs, n=14 and 13.27 ± 0.44 wt. % Cs, n=10, respectively) were observed. At temperatures of 300 °C and 1 kbar, Cs-rich zeolites was produced (19.01 ± 0.59 wt.% Cs, n=6 and 18.25 ± 1.25 wt.% Cs, n=9). Cs – Ca-rich zeolites formed during the 400 °C experiments (13.56 ± 1.69 wt. % Cs, n=24). Preliminary SEM-EDS analyses were performed on the other experiments. The 250 °C and 1 kbar show Cs wt.% of 21.61 ± 9.65 (n= 15). At 400 °C and 500 bars, Cs concentrations are 18.15 ± 6.72 wt.% (n=6). The experiment at 450 °C and 500 bars have Cs concentrations of 15.61 ± 5.27 wt.% (n=8).

The results demonstrate Cs entrapment in mineral alteration products varies with temperature and pressure. Cs was incorporated into zeolites and glass in the presence of a Cs-rich brine. The results demonstrate the temperature and pressure dependence of the formation of Cs-rich phases in which Cs is better incorporated at moderate temperature and presssures typical of respositories.