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Title: Bentonite Evolution Under Experimental Repository Conditions

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Bentonite Evolution Under Experimental Repository Conditions

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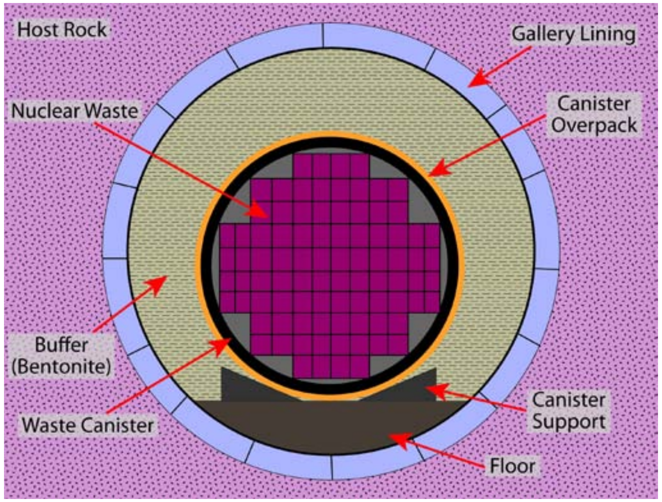
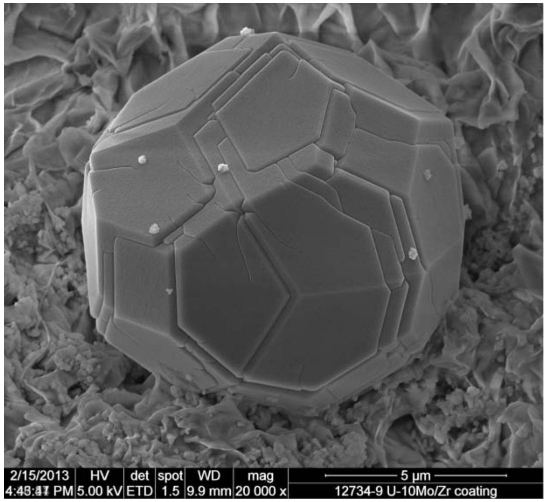


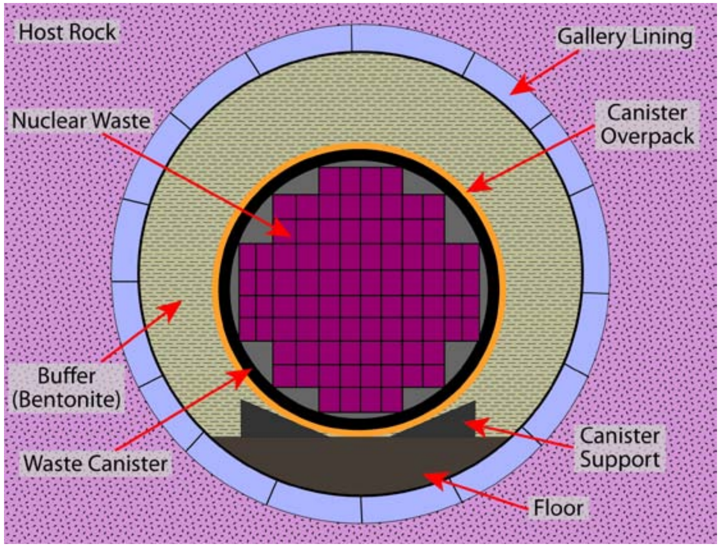


Outline

- **Background**
- **Experimental setup**
- **Aqueous Geochemistry**
- **Mineral Alterations**
  - Illitization (or lack thereof).
  - Zeolite alteration
  - Sulfide decomposition
- **Geochemical modeling**
- **Conclusions**

Background

- **Evaluate various generic geological repositories features for used nuclear fuel disposal.**
- **Waste canisters are surrounded with bentonite buffer acting as a barrier.**
- **Bentonite buffer performance confirmation is necessary.**



Investigation Focus

Characterize bentonite buffer stability at nuclear repository conditions.

Why bentonite?

- Very low permeability
- Swelling capacity to self heal upon crack formation.
- High affinity for radionuclide adsorption.

Table 5-2. Microstructural data and conductivities for MX-80 in Na form. Percolation with distilled water.

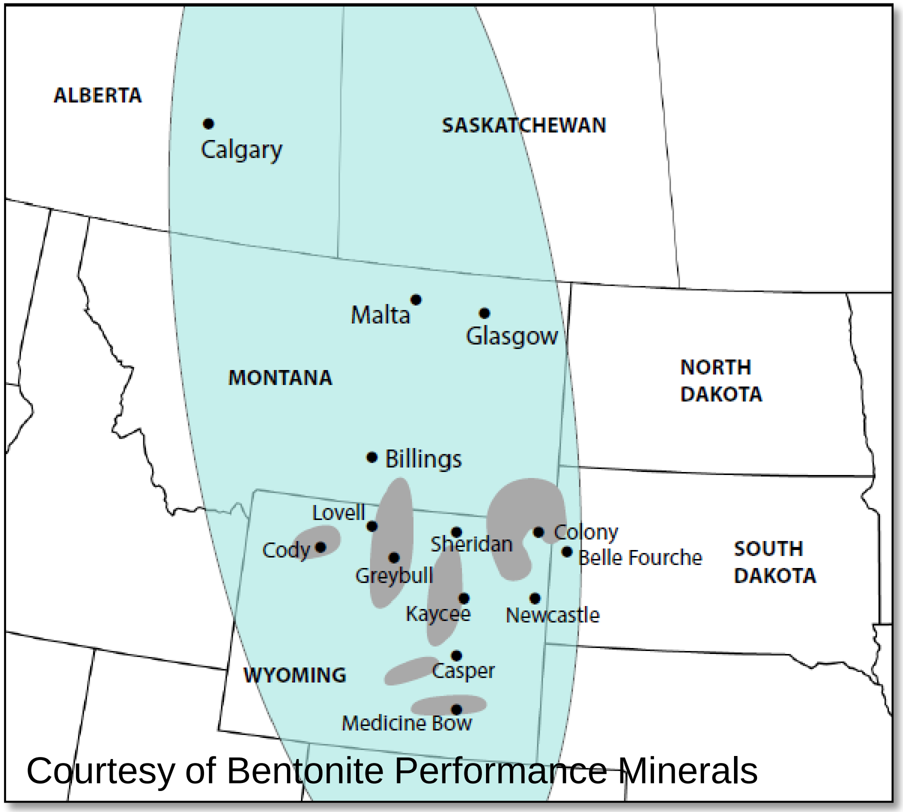
Bulk density kg/m^3	F_2	Gel density kg/m^3	Gel conductivity m/s	Calculated bulk cond. m/s	Experimental bulk cond. m/s
2130 Na	0.17	2000	7E-14	E-14	2E-14
1850 Na	0.24	1650	2E-12	4E-13	3E-13
1570 Na	0.80	1150	E-10	8E-11	8E-11

Table 5-7. Calculated and experimentally determined swelling pressures (p_s) of MX-80 saturated with distilled water [1].

Bulk density kg/m^3	$1-F_3$	Density of massive part, kg/m^3	p_s of massive part, MPa	Calculated bulk p_s MPa	Experimental bulk p_s MPa
2130 Na	0.93	2150	15.0	14.0	14.0
1850 Na	0.80	1900	1.5	1.2	1.0
1570 Na	0.75	1750	0.5	0.4	0.3

Pusch, R. (2001) SKB TR-01-08

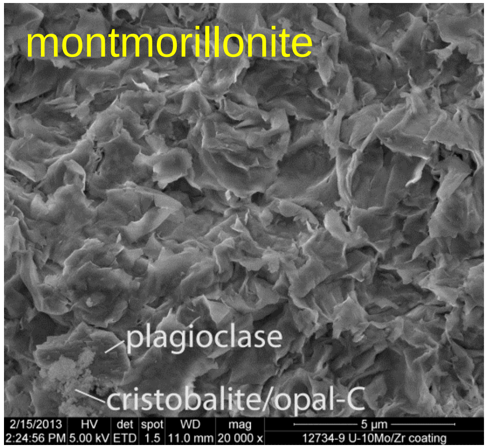
Bentonite and origins

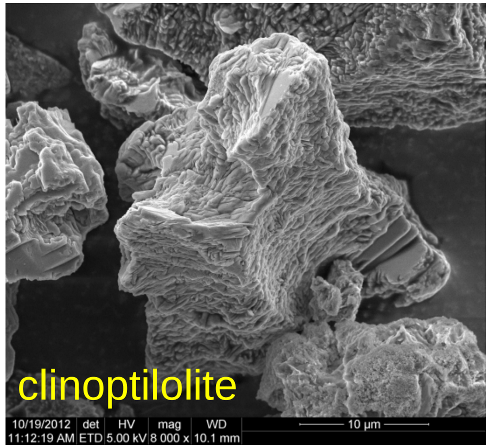


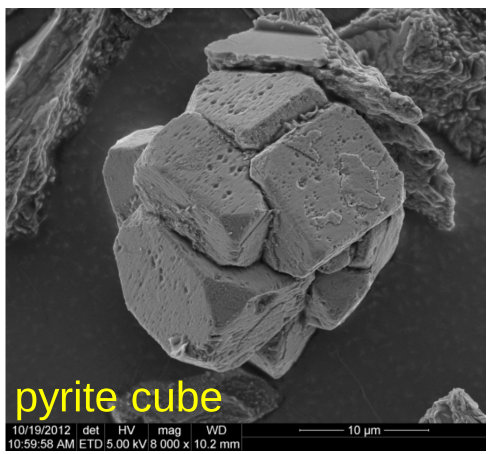
- Active Bentonite Mining Area
- Area of Noncommercial Bentonite Occurrence

- Late Cretaceous volcanism
- Ash deposited in Mowry Seaway
- Alkaline groundwater devitrified volcanic ash.
- Na-montmorillonite (70-90 wt.%)

Bentonite characteristics







- Reducing horizon
  - Pyrite
  - Ferrous-Fe dominant (higher layer charge)
- Bentonite Mineralogy, wt. %

Montmorillonite	72
Clinoptilolite	13
Feldspar	9
Biotite	3
Cristobalite/Opal-C	2
Quartz	1
Pyrite	0.4

- Montmorillonite

  $(Na_{.31},Ca_{.04},K_{.01})(Al_{1.53},Fe_{.21},Mg_{.18},Ti_{.01})(Si_{3.98},Al_{.02})O_{10}(OH)_2$

- Clinoptilolite

  $(Na_{4.30},Ca_{0.39},K_{0.14,}Mg_{0.20})(Si_{29.82,}Al_{6.28},Fe_{0.03})O_{72}\cdot nH_2O$

Experimental conditions

Experimental Reactants

- Unprocessed, Wyoming bentonite
- K-Na-Ca-Cl-based solution
  - Synthetic Stripa V2 (69-4) groundwater
  - ~1,900 ppm total dissolved solids
- Brine/bentonite ratio of ~9:1
- Reducing redox
- Inclusion of metal plates
  - 304 SS, 316 SS, Low-C Steel, Copper

Heating Conditions

- ~160 bar; 120 to 300 ºC; 5 weeks
- ~160 bar; isothermal 300 ºC; 6 weeks

Analytical Techniques

- Mineralogical (XRD, XRF, SEM)
- Aqueous (ICP, Alkalinity)
- GWB Geochemical Modeling

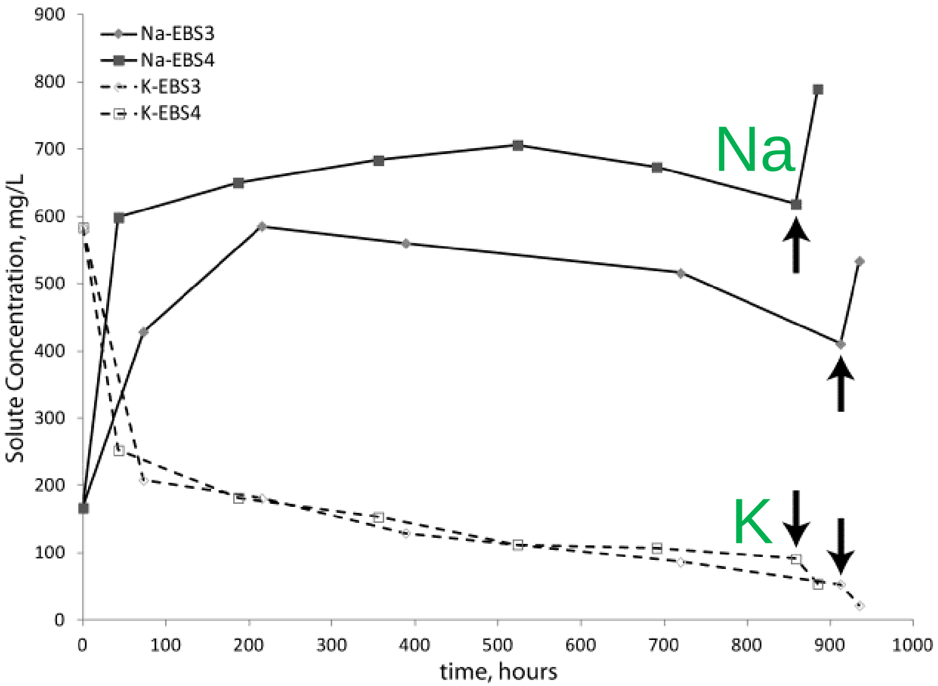
Aqueous Geochemistry

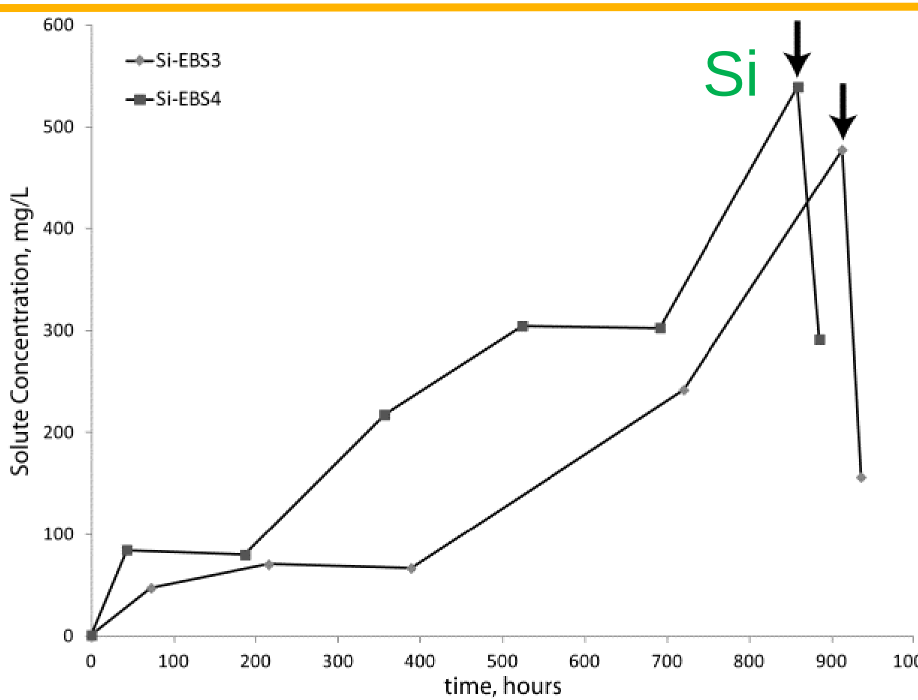
Na-K exchange

SiO_2 evolution

Al availability

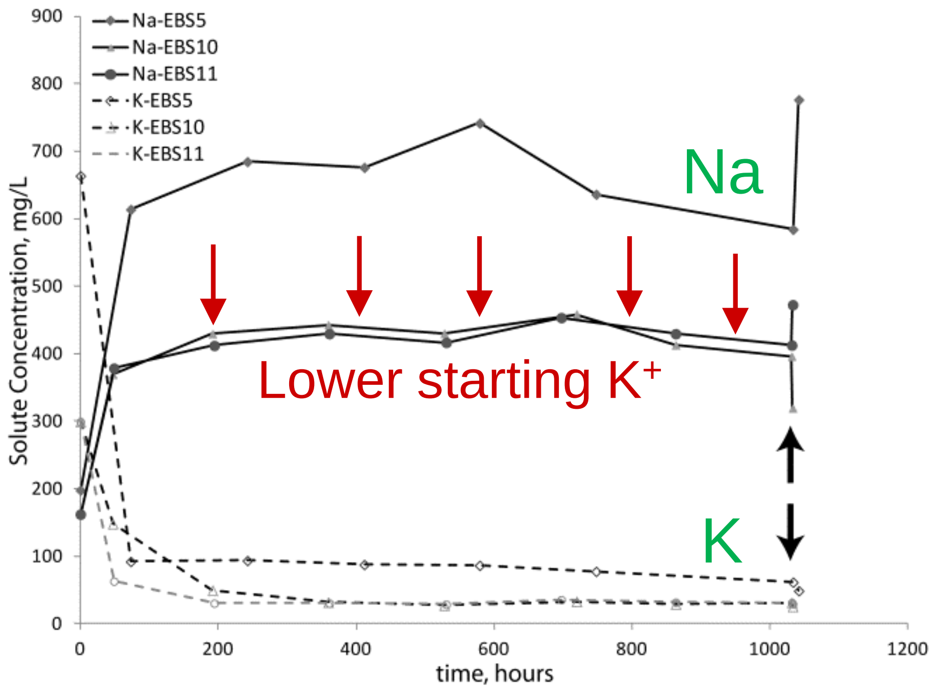
Ramped: solution evolution

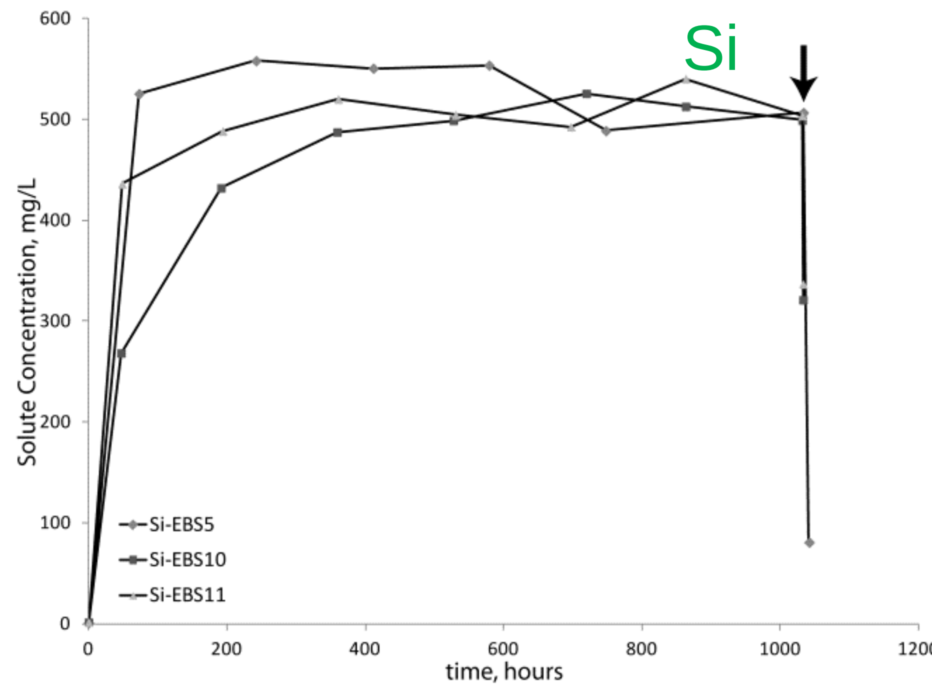




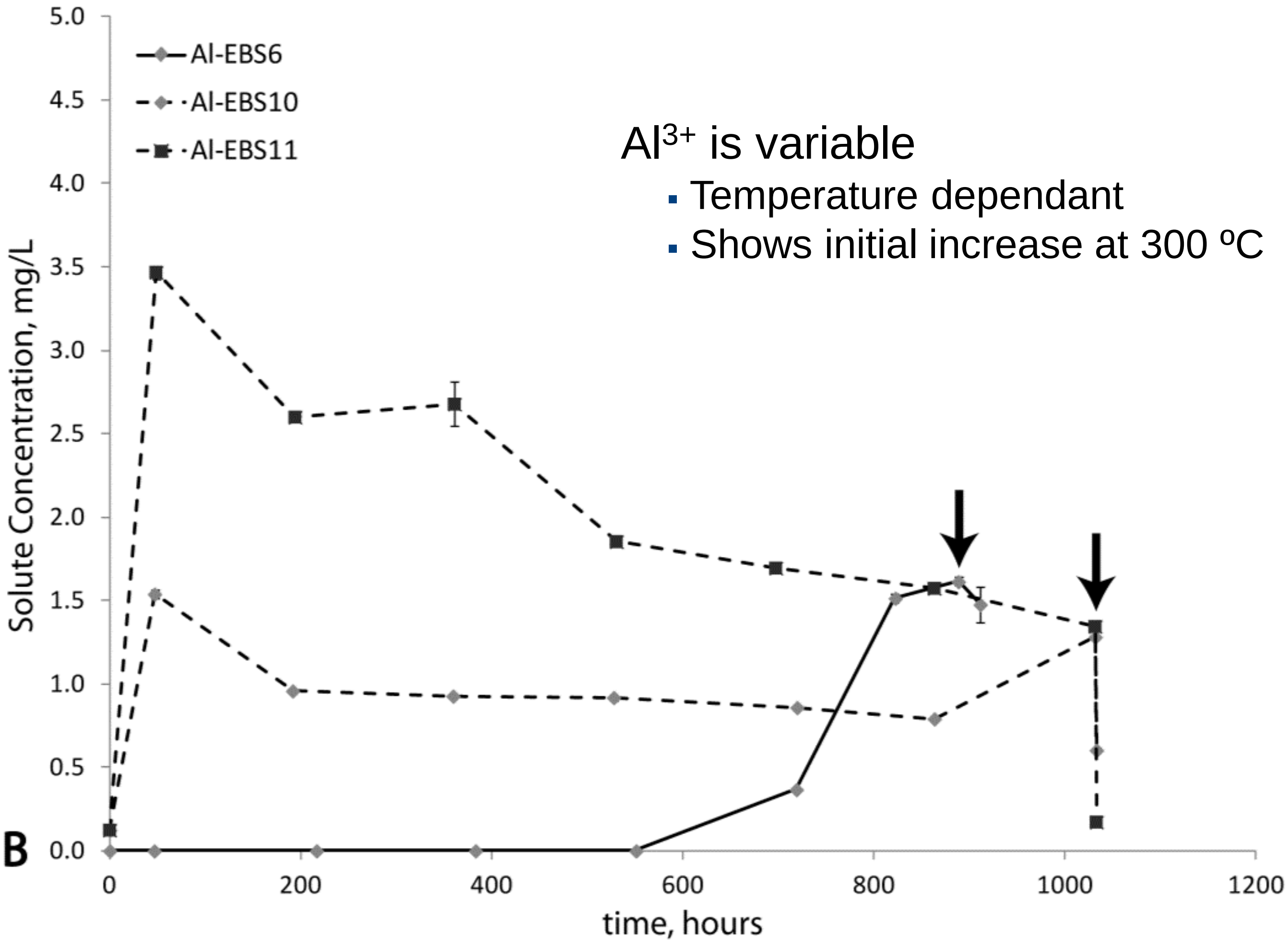
- K^+ is exchanged for Na^+
  - Na^+ release dependant on K^+
  - Na^+ conc. sustained by exchange
- SiO_2 saturation
  - Temperature dependant
  - Cristobalite saturation

Isothermal, 300 °C: solution evolution





- K^+ is exchanged for Na^+
  - Na^+ release dependant on K^+
  - Na^+ conc. sustained by exchange
- SiO_2 saturation
  - Cristobalite saturation
  - Constant concentrations



Al^{3+} is variable

- Temperature dependant
- Shows initial increase at 300 ºC

Mineral Alterations

Illitization (or lack thereof)

Zeolite alteration

Sulfide decomposition

Major mineralogical alterations

Interface: Strong influence from "waste container"

Fe-rich phyllosilicates (saponite/chlorite) on steel

Chalcocite (Cu_2S) on copper

Bulk: 1) Zeolite alteration

Clinoptilolite 13 wt. % → 2 wt. %

Analcime 0 wt. % → 3 wt. %

2) $H_2S_{(aq,g)}$ formation

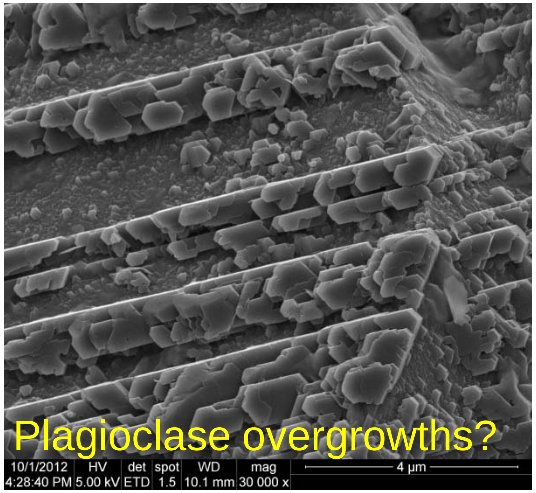
Pyrite decomposition 0.4 wt. % → N.D.

3) Silica formation

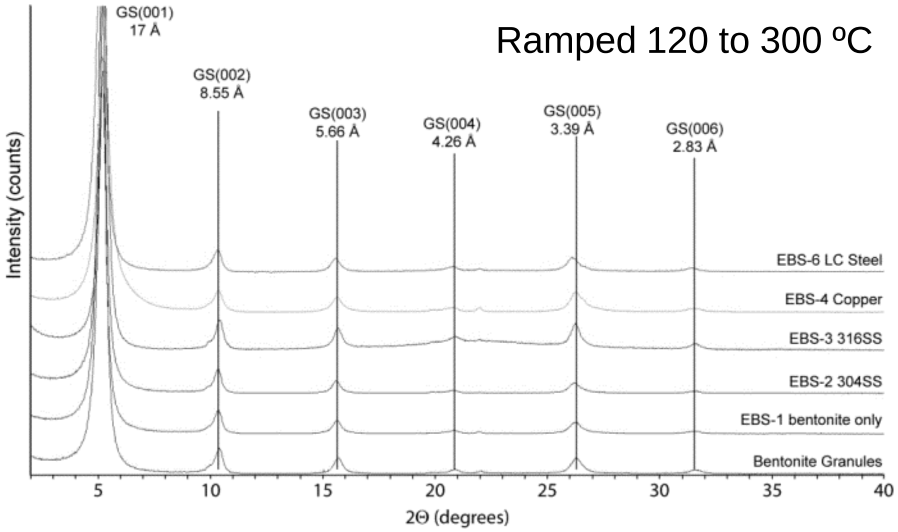
cristobalite/opal-C 2 wt. % → 4 wt. %

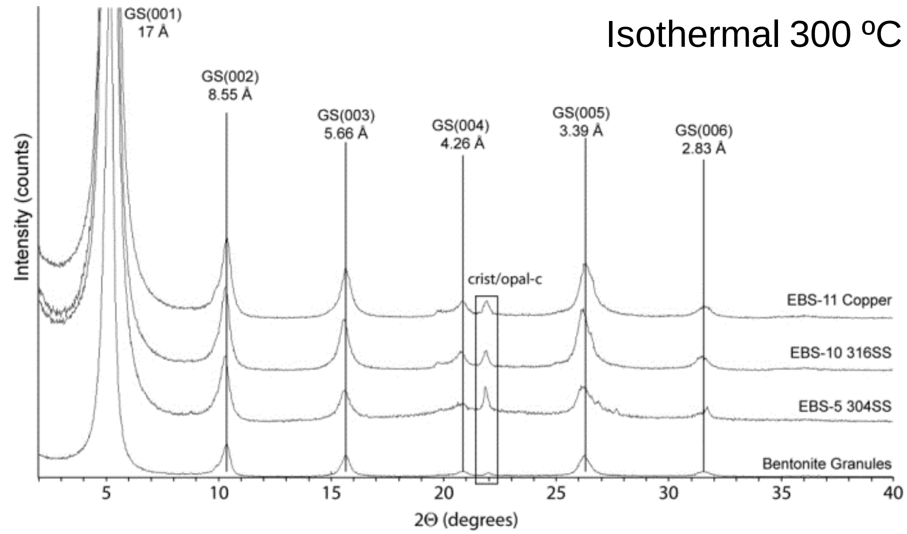
4) Authigenic illite formation ???

5) Feldspar overgrowths ???



Montmorillonite ‘stability’





$(Na_{.28},Ca_{.05},K_{.06})(Al_{1.49},Fe_{.24},Mg_{.18},Ti_{.01})(Si_{3.98},Al_{.02})O_{10}(OH)_2$

$(Na_{.31},Ca_{.05},K_{.02})(Al_{1.46},Fe_{.26},Mg_{.19},Ti_{.01})(Si_{3.83},Al_{.17})O_{10}(OH)_2$

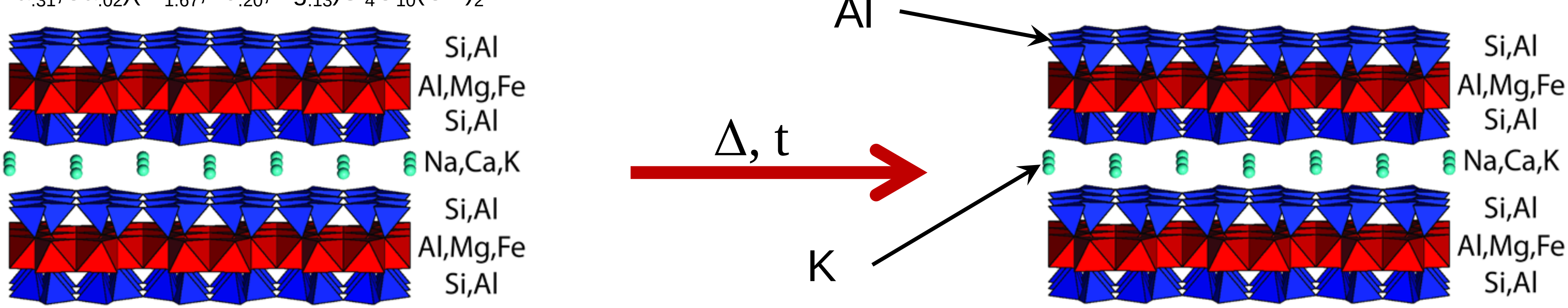
- No illitization via I/S intermediate
- K-enrichment of montmorillonite
  - Na ↔ K exchange buffering the solution chemistry
- 300 ºC experiments yielded cristobalite/opal-C in clay fraction

Smectite ~ -0.33

$(Na_{.31},Ca_{.02})(Al_{1.67},Fe_{.20},Mg_{.13})Si_4O_{10}(OH)_2$

Illite ~ -0.90

$K_{.90}(Al_{1.67},Fe_{.20},Mg_{.13})(Si_{3.43},Al_{0.57})O_{10}(OH)_2$

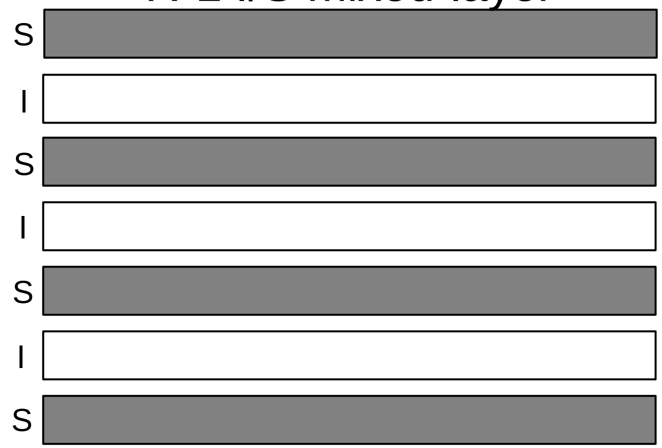


Consume

$+ K^+_{(aq)}$

$+ Al^{3+}_{(aq)}$

R-1 I/S mixed-layer

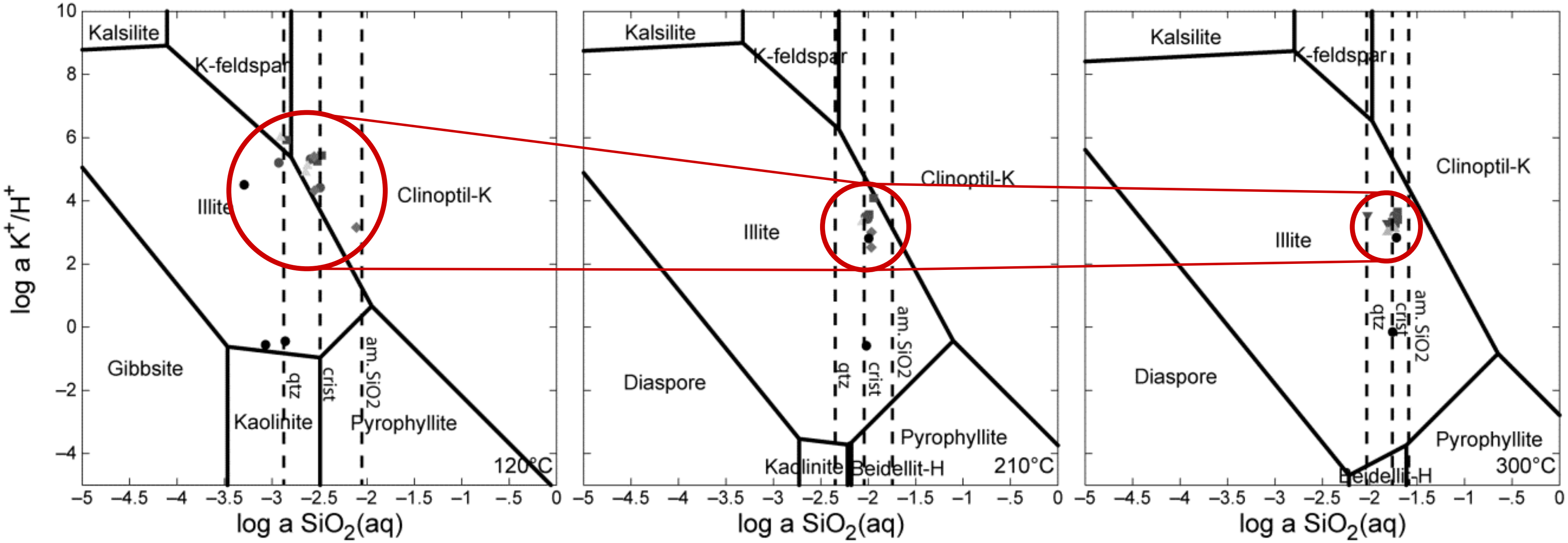


Release

$+ Na^+_{(aq)}$

$+ H_2O$

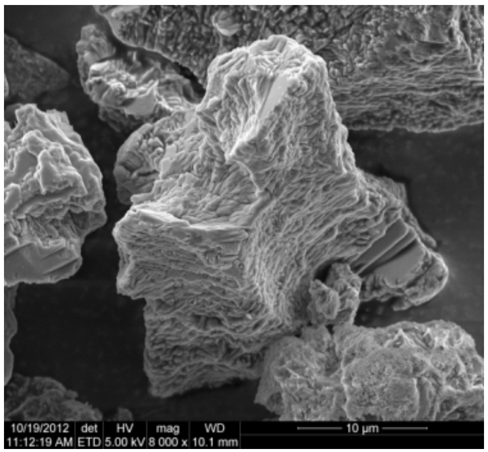
$+ SiO_{2(aq)}$



- Solution chemistry falls within illite field, but illitization does not occur.
- Saturated with respect to cristobalite, but only 2% cristobalite.
    - Smectite and zeolite probably controlling Si concentrations.
- Controls on illitization not well established.

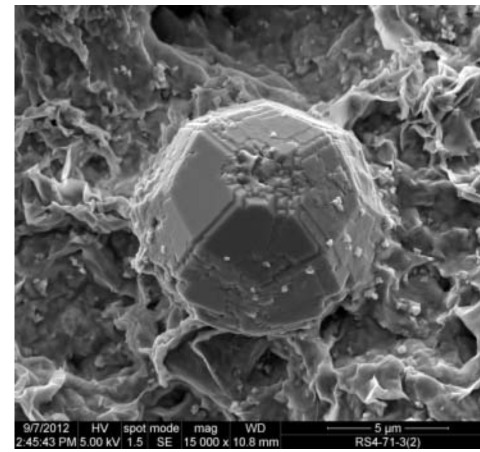
Zeolite dissolution-recrystallization

Clinoptilolite



$\xrightarrow{\Delta,\ t}$

Analcime



$(Na_{4.30},Ca_{0.39},Mg_{0.20},K_{0.14})(Si_{29.82,}Al_{6.28},Fe_{0.03})O_{72}\cdot 21H_2O$

$(Na_{0.64},Ca_{0.05})(Si_{2.23},Al_{0.77})O_6\cdot 1H_2O$

<u>Consume</u>

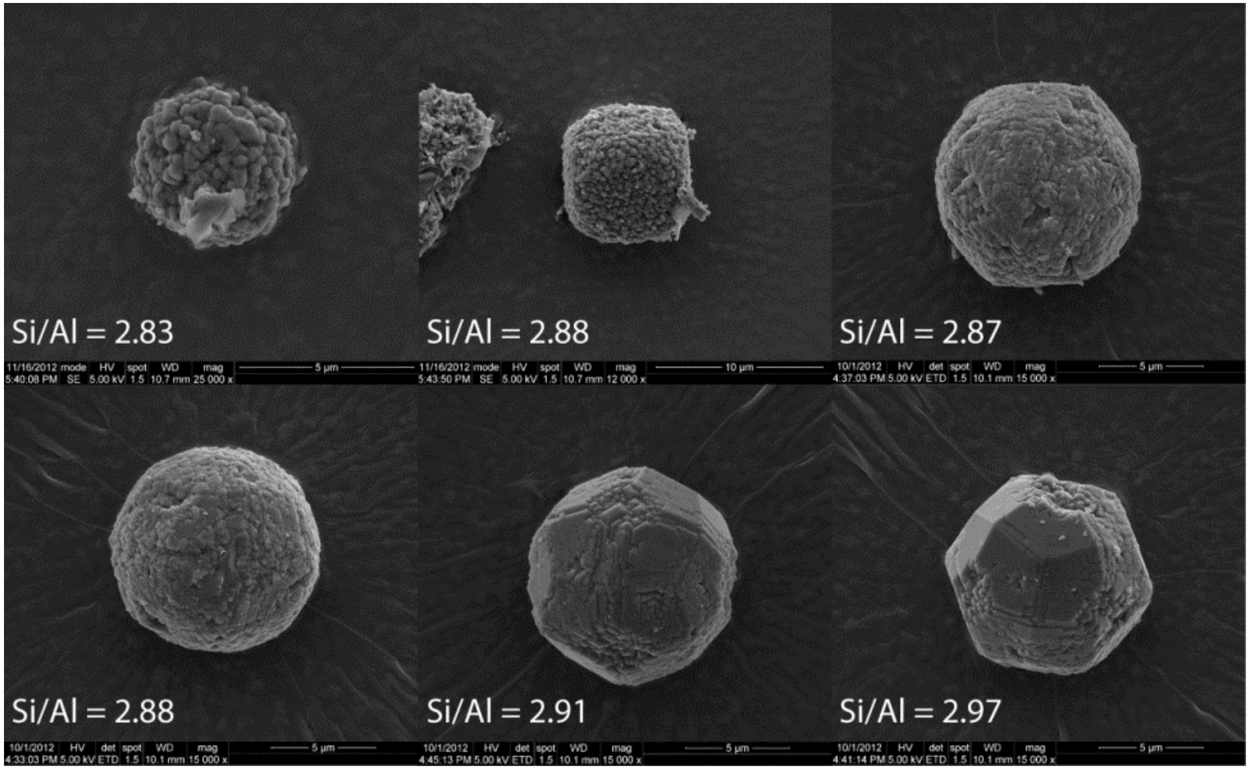
$+\ Na^+_{(aq)}$

<u>Release</u>

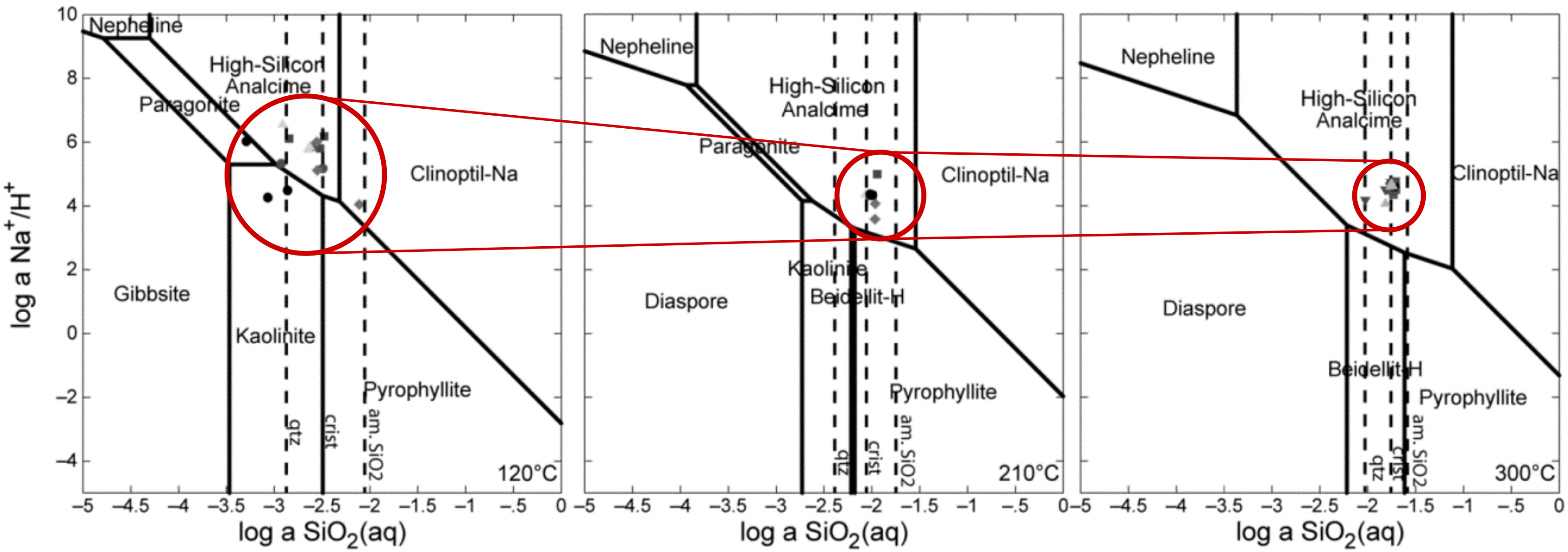
$+\ K^+_{(aq)}$

$+\ H_2O$

$+\ SiO_{2(aq)}$

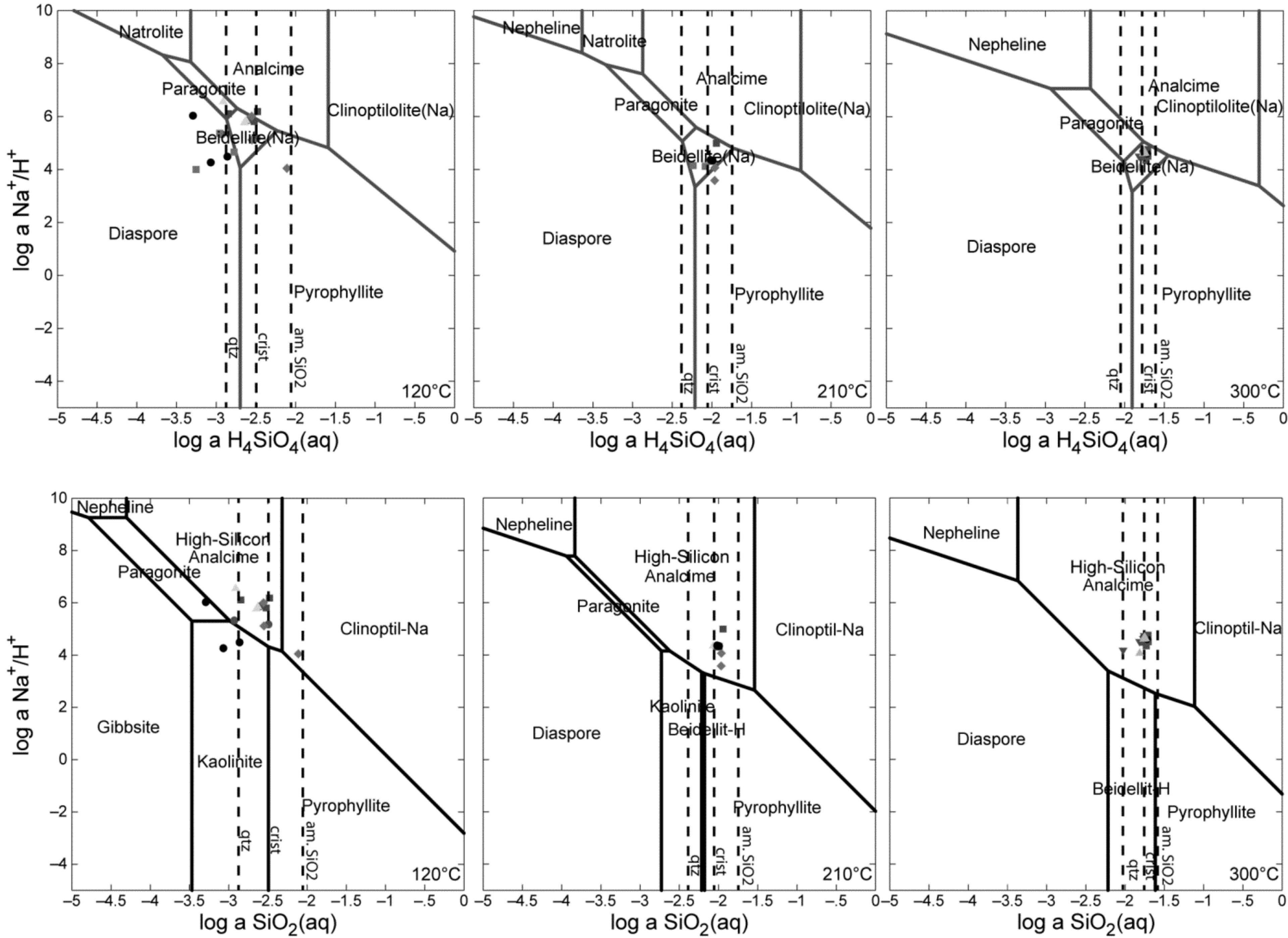


- Initial formation occurs as clusters of “nm” crystallites
- Ripens into 5-10 μm, subhedral trapezohedra
- Si/Al 2.83 to 2.97 during ripening process

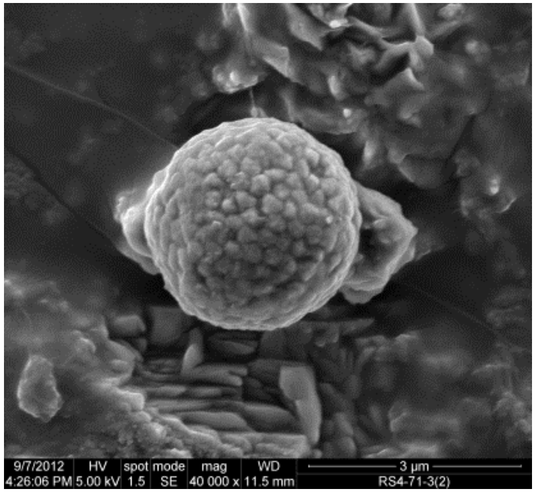


- Solution chemistry converges to a uniform composition within high-silicon analcime stability field early during reaction
- Saturated with respect to cristobalite
- Do not see analcime until long-term, 300 ºC reaction →

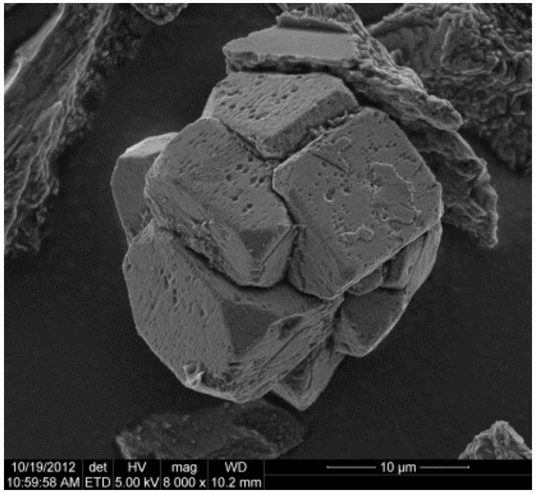
suggesting kinetics is determining the occurrence


Natrolite
Analcime
Paragonite
Clinoptilolite(Na)
Beidellite(Na)
Diaspore
Pyrophyllite
qtz
crist
am. SiO2
120°C
log a Na+/H+
log a H4SiO4(aq)
Nepheline
210°C
300°C
High-Silicon Analcime
Gibbsite
Kaolinite
Clinoptil-Na
Beidellit-H
log a SiO2(aq)

Pyrite decomposition



- Sulfide formation
- Odor evolved with steel.
- No odor with copper.
- Minor abundances, but serious implications for repository system.



$$FeS_{2(pyrite)} + 2H^{+} + nCl^{-} + H_2O_{(aq)} \rightarrow FeCl_n^{2-n} + 2H_2S_{(aq,g)} + ½O_2$$

$$FeS_{2(pyrite)} + H_2O = Fe^{2+} + 1/4\ H^{+} + 1/4\ SO_4^{2-} + 7/4\ HS^{-}$$

$$H_2S_{(aq)} = H^{+} + HS^{-}$$

$$H_2S_{(g)} = H^{+} + HS^{-}$$

Sulfide < 0.5 wt.%
Total sulfur < 1 wt.%

SKB Restrictions (Börjesson et al., 2010)

Key Observations

- Na-bentonite buffers the Na/Ca/K groundwater concentrations.
- High Na^+ activity and restricted K^+ supply inhibit/retarding illitization.

- Clinoptilolite to analcime occurs in a High-Si environment.
- Produces a -17% volume change (~2 % bulk bentonite volume).

- Sequester Al (zeolites, feldspars) appears to inhibit illitization.
- Mineral dissolution/alteration appears to control the silica activity.

- Waste canister material seem to have no effect on bentonite.

Conclusions

- **Montmorillonite did not undergo illitization (T > 300 °C) under the experimental conditions.**
- **The environment surrounding the bentonite is key in controlling the mineral reactions, subsequently the bentonite stability.**
  - K^+, Na^+, silica activities are key to maintaining a viable montmorillonite
- **Silica controlled by the entire system, not just illitization.**
- **Have to evaluate the entire system, before determining the long-term stability of bentonite.**
- **Need good and representative thermodynamic data and mineral compositions for accurate long-term modeling.**

Acknowledgements

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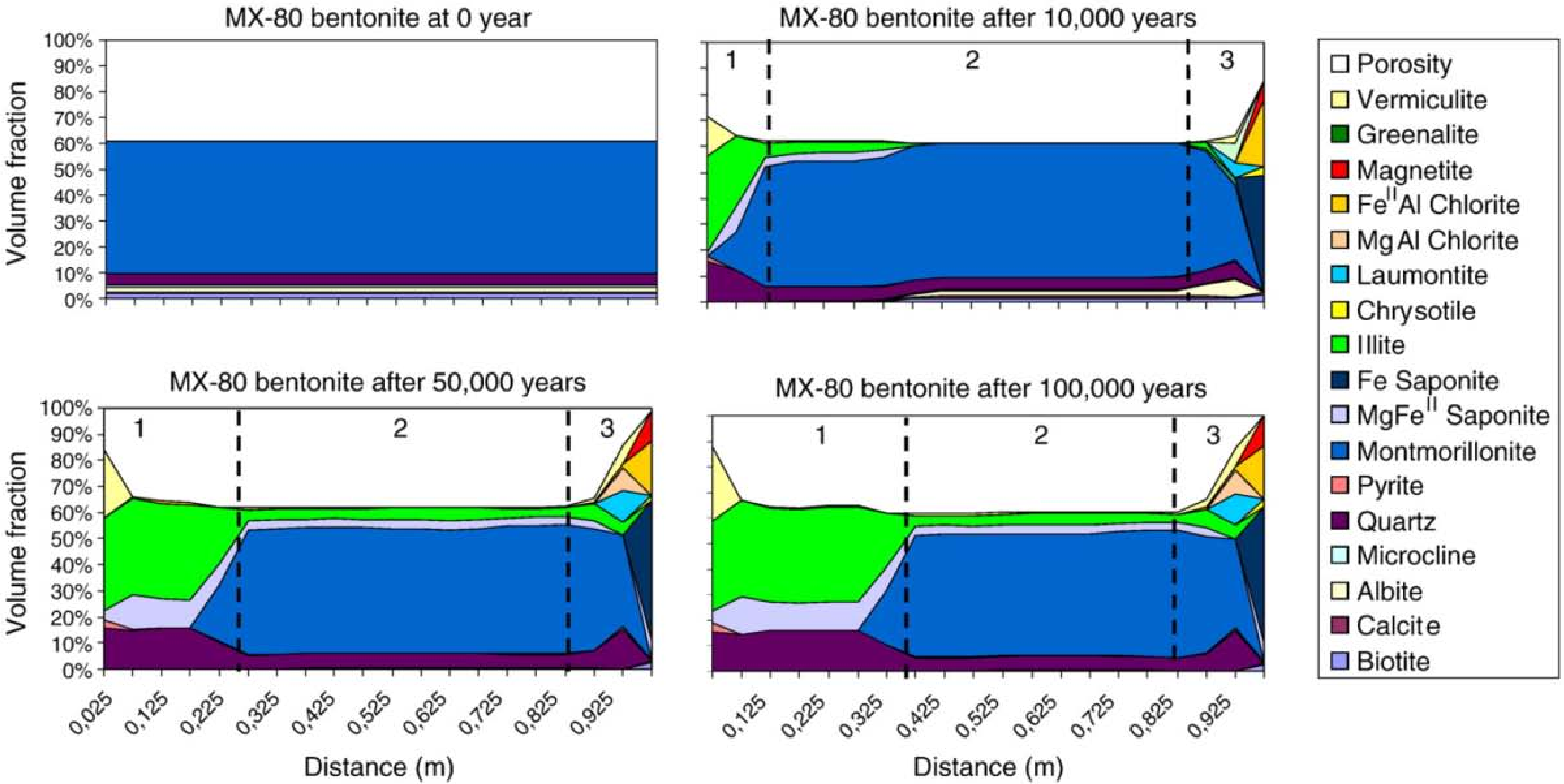
U.S. DEPARTMENT OF ENERGY

Liz Miller and Emily Kluk provided assistance in the laboratories.

Thank You!

Questions?



from Marty et al., 2010

Implications to barrier properties

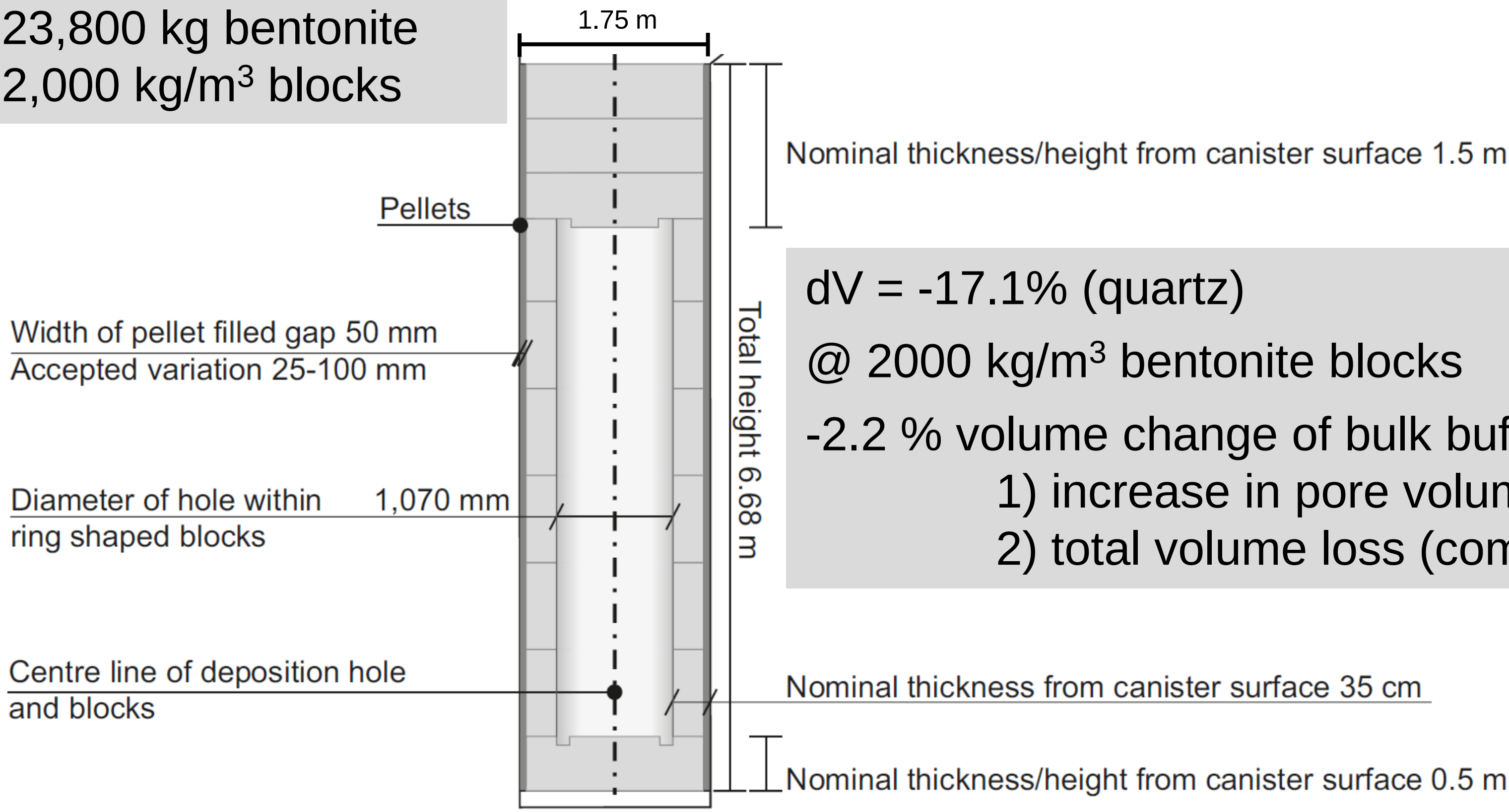
- **Mechanical/physical properties**
  - **Develop a 2% buffer volume loss or increased porosity**
  - **Release H_2O and SiO_2 (quartz, cristobalite, opal, amorphous)**

- **Radionuclide sorption properties**
  - **Clinoptilolite readily exchanges Ba, Cs, and Sr**
    - Minor surface sorption of actinide complexes
    - Negligible anion sorption/exchange
  - **Analcime affect exchange of the alkali and alkaline earths**
    - Minor effect on actinide sorption
    - Negligible anion sorption/exchange

Hypothetical situation

- 11.9 m³ bentonite
- 23,800 kg bentonite
- 2,000 kg/m³ blocks

Modeled from SKB TR-10-15



dV = -17.1% (quartz)

@ 2000 kg/m³ bentonite blocks

-2.2 % volume change of bulk buffer system

1) increase in pore volume
2) total volume loss (compaction)