The Role of Zeolite Phase Transformations in Deep Borehole Seals

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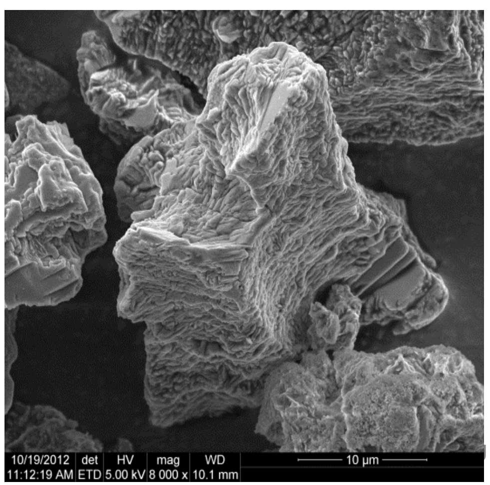
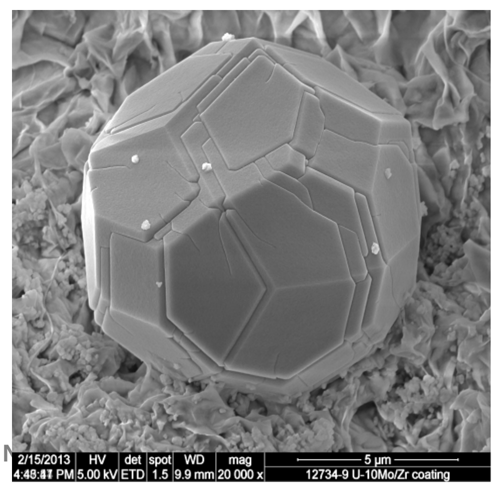




Repository Program Objectives

U.S. Used Fuel Disposition Campaign Deep boreholes Program

- Use mine-run, unpurified bentonite and highly saline brines
- Investigate chemical evolution in a bentonite buffer at deep borehole temperature and pressure.
  - Silica generation and cation exchange

Zeolites – recognize significance of their growth

Previous EBS work identified clinoptilolite, analcime, wairakite

Scenarios – Base of Seals, Bottom of Hole

Base of Seals : 150 – 175 C, 300 bar, 8 week (hydrostatic) - ongoing

Bottom of Borehole: 400 C, 1 Kbar, 2 week (lithostatic) - results

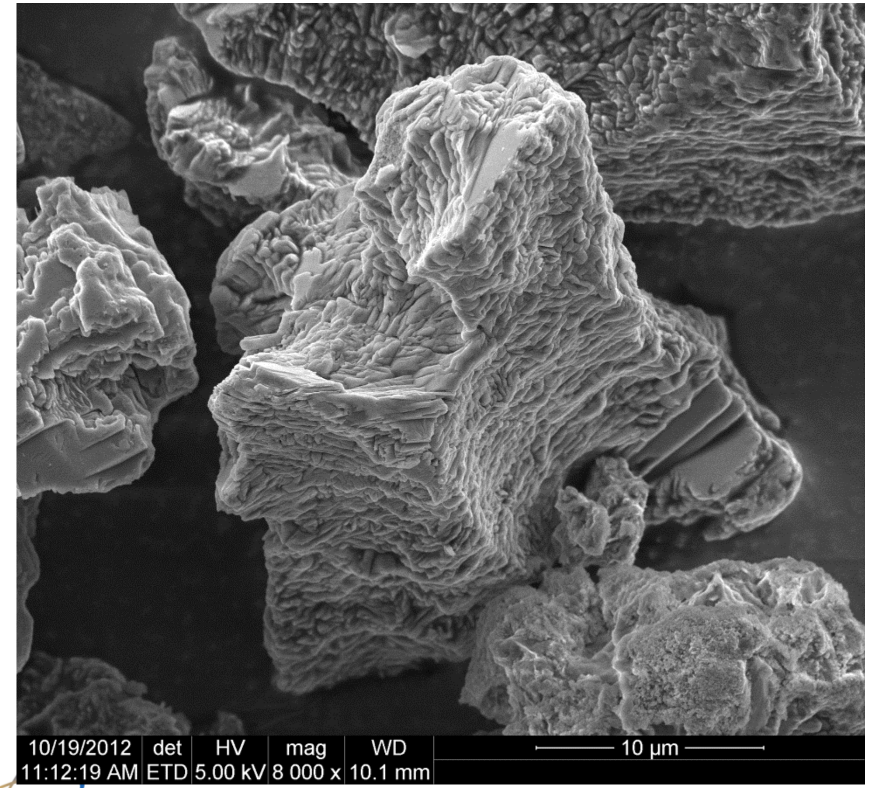
Experimental conditions for bottom of borehole

<u>Experimental Reactants</u>

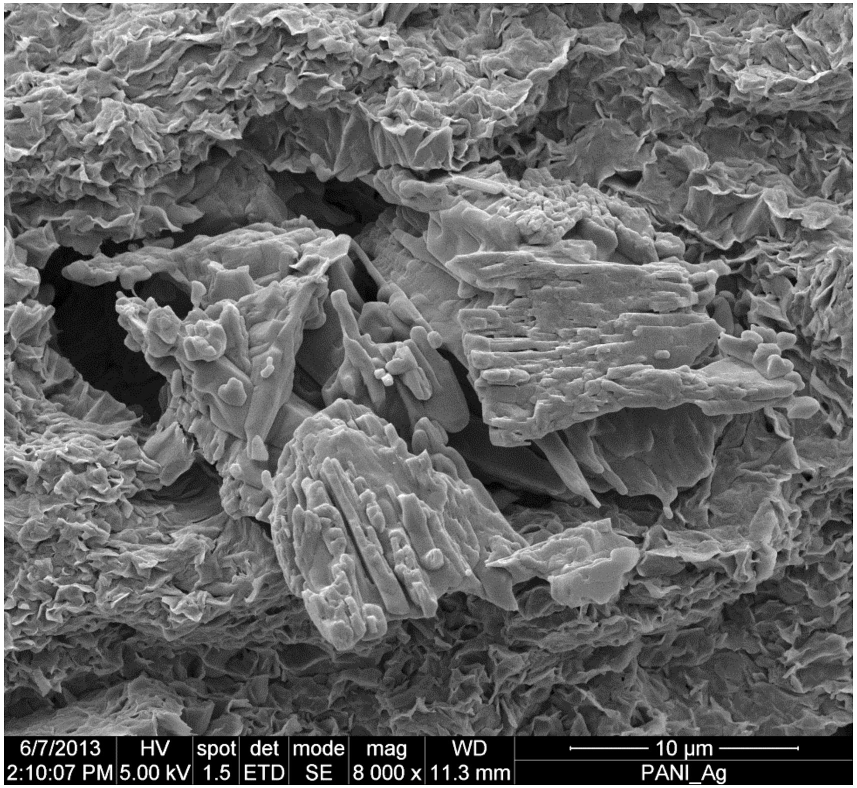
- Unprocessed Wyoming bentonite
- *f*(O_2) buffered at ≈ IM (iron-magnetite) univariant line
- Cs-Na-Ca-Cl-based solution: loaded at 2:1 W/R ratio
  - **NaCl, CaCl, Cs/Ca/NaCl brines, 2molal**
  - **400 C, 1 Kbar**

Clinoptilolite SEM Images

Clinoptilolite after glass shard – WY bentonite



Clinoptilolite dissolution- EBS12- low water content



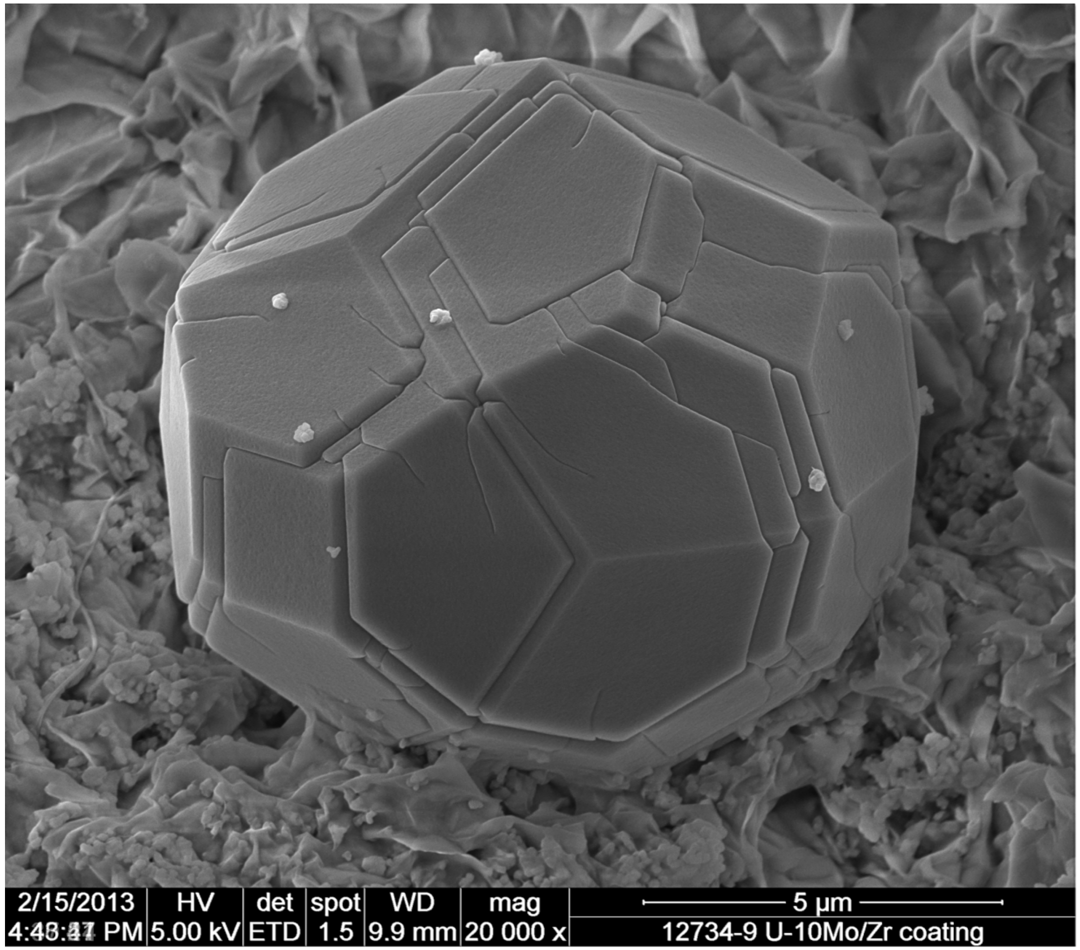
Zeolite transformation at high temperature

- **clinoptilolite → analcime + SiO_2 + H_2O**

- **$(Na,K,Ca)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_{36} \cdot 2H_2O \rightarrow Na_6Al_6Si_{12}O_{36} + SiO_2 + 2H_2O$**

- **Phase change as low as 100 ºC (Smyth, 1982, Masuda, et al., 1996)) however most occurred between 200-300 ºC in our experiments**

EBS5 - Analcime reaction product



Opalinus Clay Experiments

Three experiments

EBS-14 Opalinus Clay (O.C.) only – 300 ºC isothermal, 6 week, O.C. groundwater

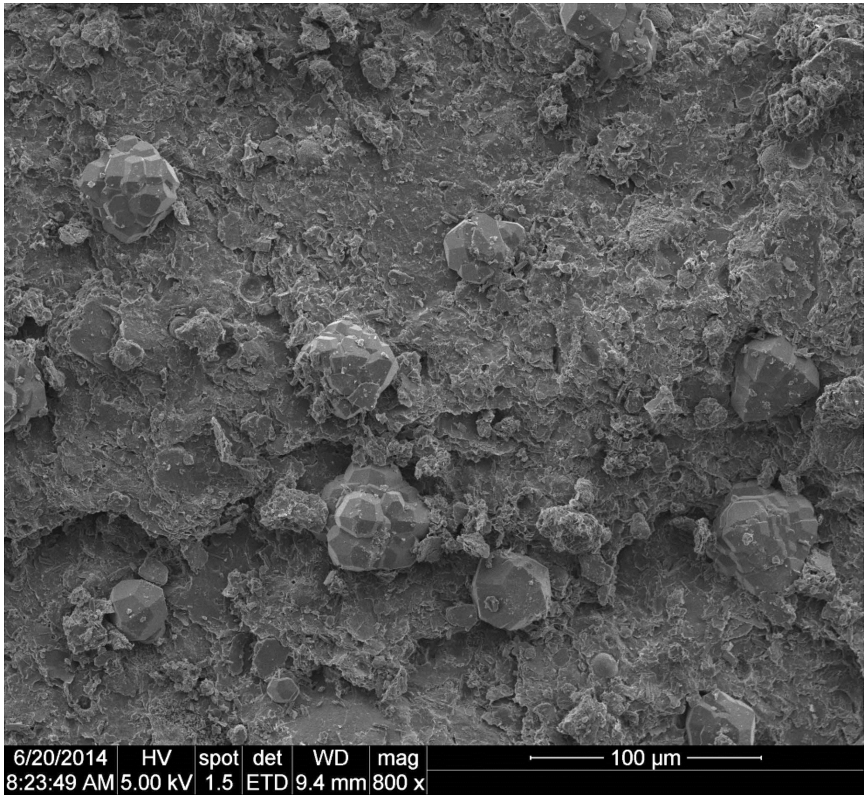
EBS-15 – As above + WY bentonite + 316 S.S.

EBS-17 - As above + WY bentonite + Cu

Opalinus Clay Brine

	Type Solution	Actual Solution
Species	mg/L	mg/L
Ca^{2+}	421	426
Cl^{-}	5672	6470
CO_3^{2-}	162	n.m.
K^{+}	221	225
Na^{+}	3885	3846
Si	5	1
SO_4^{2-}	2305	998
Sr^{2+}	27	0.16
TDS	11502	12153
pH	7.24	7.50
Experiment Used		EBS 14, 15, 17

EBS-14 – Wairakite produced as reaction product



Mixed clay experiments – Opalinus + WY Bentonite

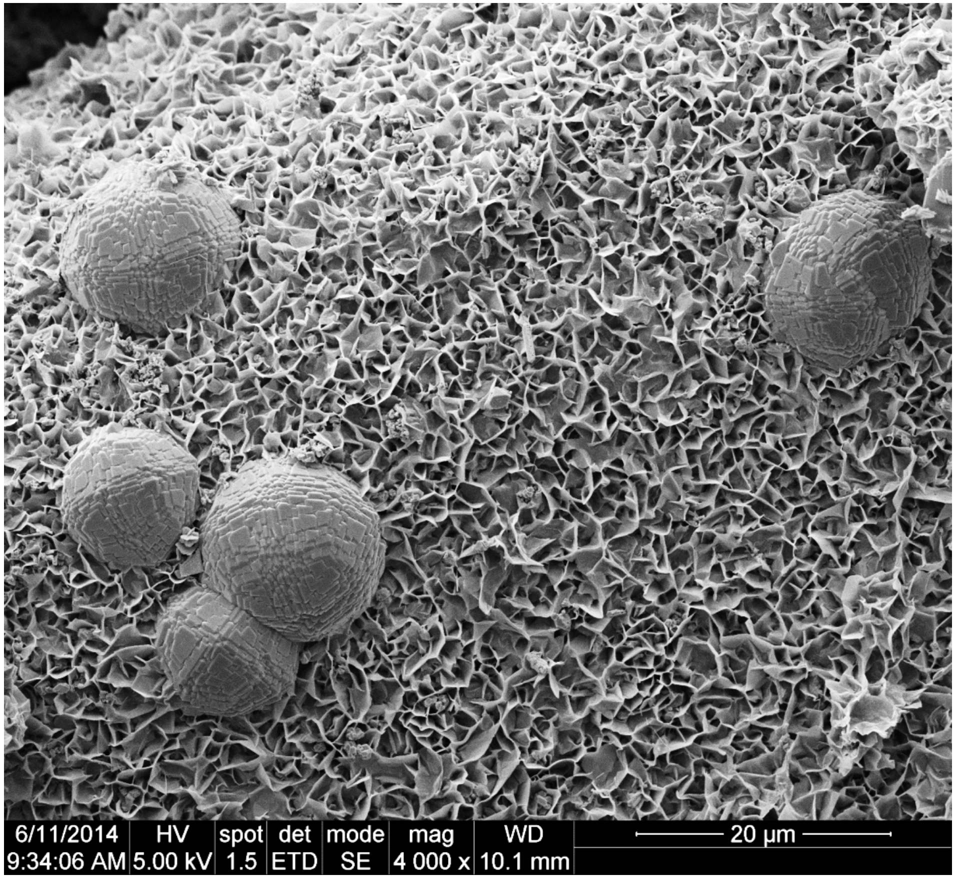
- **Experiments EBS-15 (316 SS) and EBS-17 (Cu)**
- **Brine : Opalinus Clay groundwater**

- **Analcime in early experiments**
- **Wairakite in Opalinus Clay experiment**

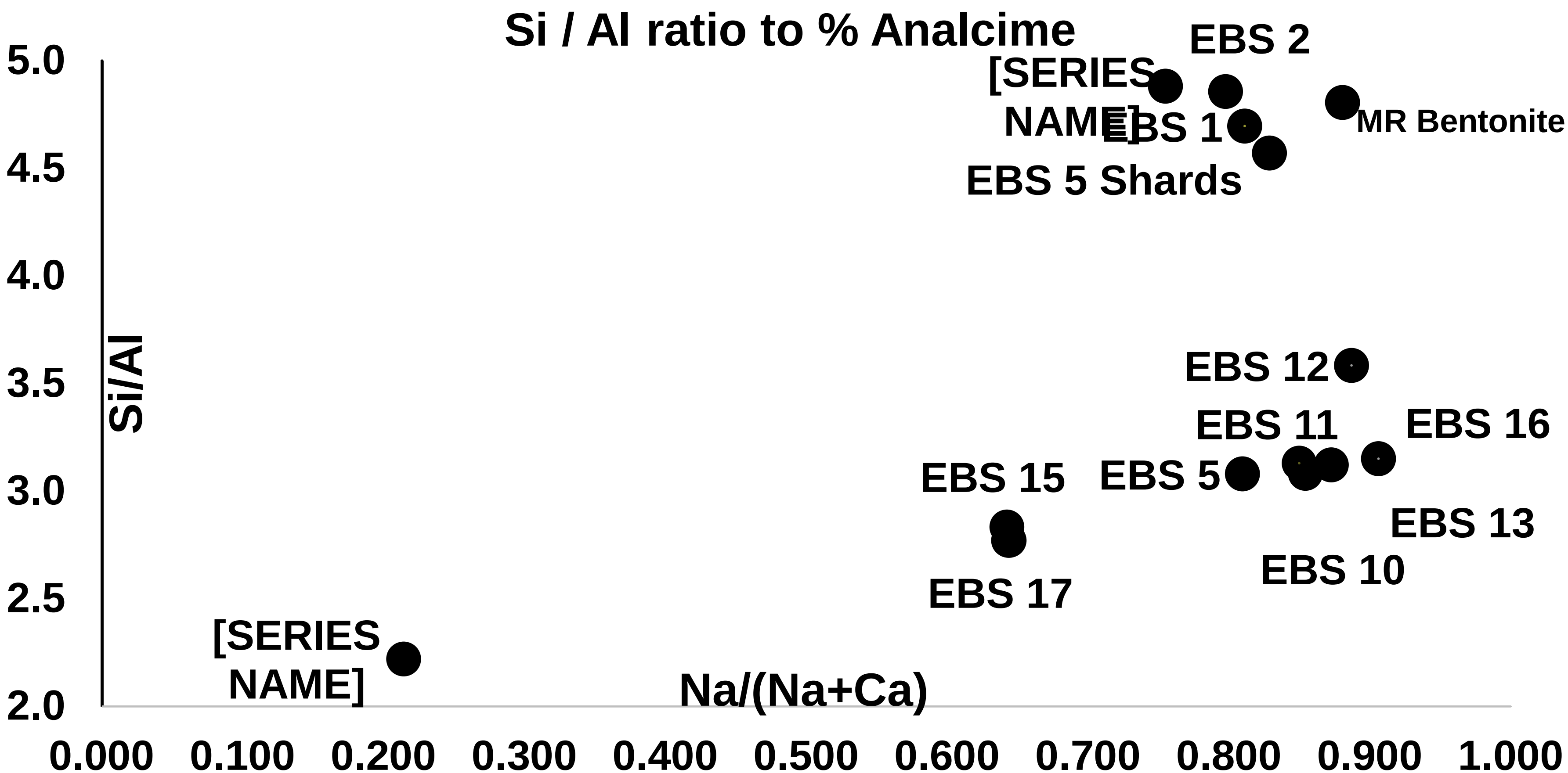
- **One would expect a high temperature zeolite somewhere in the Analcime – Wairakite solid solution join**

$$Na_3Al_6Si_{12}O_{36} \leftrightarrow Ca_3Al_6Si_{12}O_{36}$$

EBS15 Analcime$_{64}$--Wairakite$_{36}$



Analcime – Wairakite Solid Solution Determinations



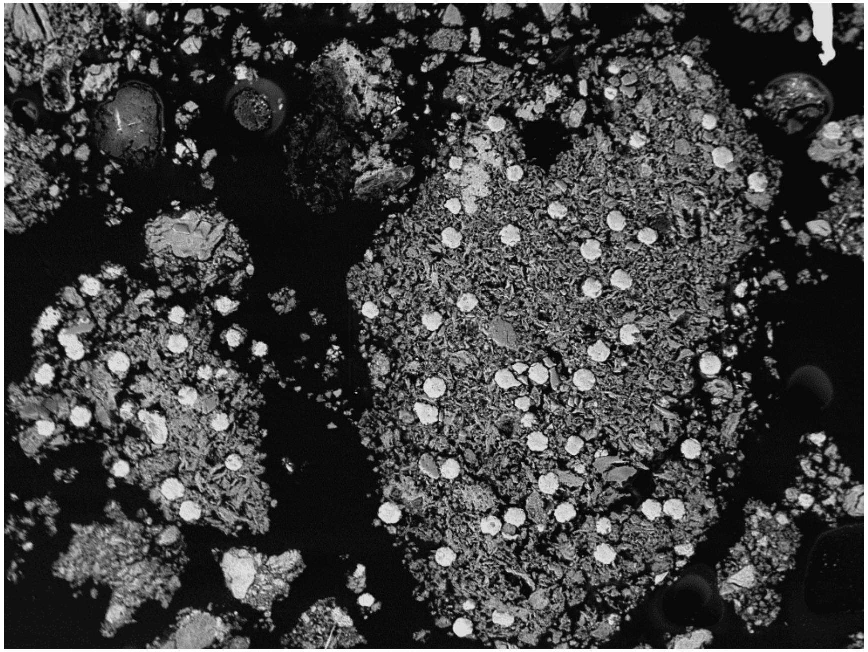
Pollucite Generation from Cs waste forms

- **Further experimental system – Explore the tertiary portion of this zeolite group.**
- **Cesium may be a waste stream disposed of in Deep Boreholes**
- **Would Cs be readily incorporated into analcime structure if canister failed post emplacement?**

Analcime ↔ Pollucite ↔ Wairakite

$Na_6Al_6Si_{12}O_{36} \leftrightarrow Cs_6Al_6Si_{12}O_{36} \leftrightarrow Ca_3Al_6Si_{12}O_{36}$

Pollucite created from bentonite clay at high P,T



SiO_2	56.64
Al_2O_3	18.63
FeO	0.68
MnO	0.01
MgO	0.05
CaO	4.95
Na_2O	1.27
K_2O	0.05
Cs_2O	13.56
Cl	0.2
F	0.01
O=Hal	-0.05
TOTAL	96.01

Average of 30 EMP analyses

$An_{18.3}\ Wrk_{39}\ Pol_{42.7}$

Conclusions

- Engineered Barrier Systems using bentonite backfill /buffer in a high temperature repository must be aware of system bulk chemistry.
- Na-rich / Ca-poor clays (WY bentonite) produces Analcime
- Ca-rich / Na-poor clay rock (Opalinus Clay) produces Wairakite
- Mixed system (Opalinus Clay + WY bentonite) generates Analcime – Wairakite SS
- Created Cs bearing zeolite (Pollucite) from bentonite and Cs/Ca/NaCl brine at high P,T
- This zeolite may be critical to isolating Cs contamination
- Need to now investigate stability field

Acknowledgements

This project was funded by U.S. Department of Energy, Office of Nuclear Energy, Fuel Cycle Technologies, Used Fuel Disposition Campaign.

FT-16LA08030802

Virgil Lueth, and George Mason provided assistance in the laboratories.

LA-UR-16-23849