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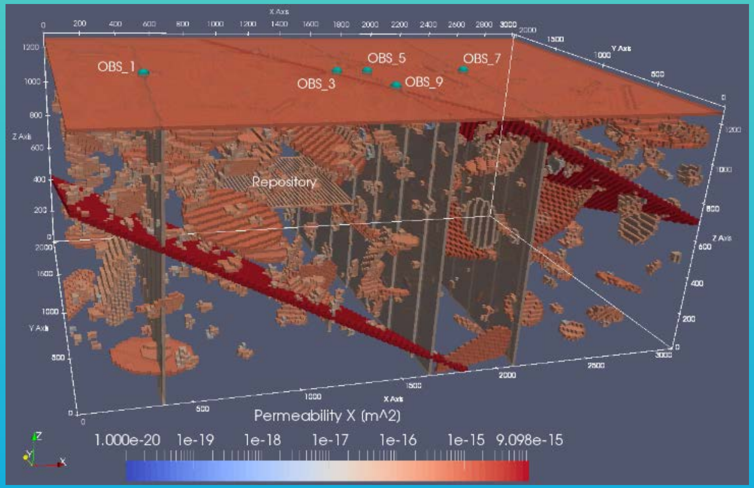

A Review of High Temperature Engineered Barrier Systems Experiments

Part 2 _Summary of High Temperature Engineered Barrier System Experiments (Los Alamos National Laboratory)

U.S. Nuclear Waste Technical Review Board
Public Meeting
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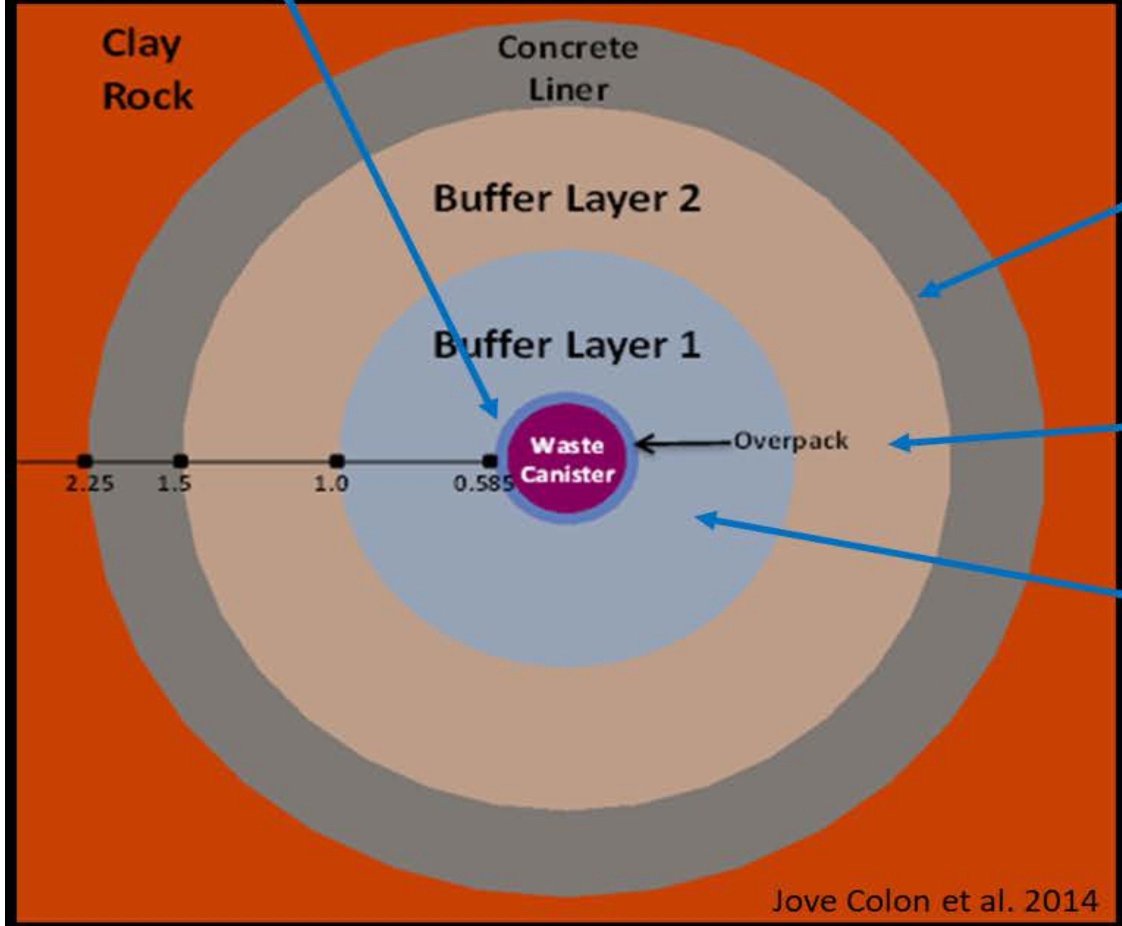
Schematic of clay barrier configuration - the Engineered Barrier System

Mineralogical changes at the steel/bentonite interface

Waste package corrosion rate

- How does it evolve with time?
- What are the most important dependencies?



Reactions at the cement/bentonite interface

Major element chemistry controlling U speciation and surface complexation

Bentonite illitization

Radionuclide solubility and sorption

- Spatial heterogeneity?
- Temporal evolution?
- Most important dependencies?

Investigate chemical and mineralogical changes at repository temperature and pressure (300-250-200 °C, 150 bar)

Wyoming Bentonite

- 16 experiments, 300° C, 4 weeks to 6 months
- Ramped and isothermal temperature profiles
- Cu, LCS, 304 SS, 316 SS, graphite, or quartz sand added

Opalinus Clay only

- 1 experiment, 300° C, 6 weeks

Wyoming Bentonite + Opalinus Clay

Over 50 Experiments

- 5 experiments, 300° C, 6 weeks to 6 months
- 2 experiments, 200° C, 8 weeks
- Cu, LCS, 304SS, or 316 SS added

Wyoming Bentonite + Opalinus Clay + Ordinary Portland Cement (or low pH cement)

- 14 experiments, 200° C, 8 weeks (including 6 month experiment)
- LCS, 304SS, or 316 SS added

Wyoming Bentonite + Grimsel Granodiorite + low pH cement

- 10 experiments, 250° C, 6–8 weeks
- LCS, 304SS, or 316 SS added

Formation of Fe-rich clay at the steel interface

- Use mine-run, bentonite, steel, and K-Ca-Na-Cl brines

- Investigate chemical evolution of steel clay interface at repository temperature and pressure (**300 ° C, 150 bar)**.

- **Mineral phase changes**

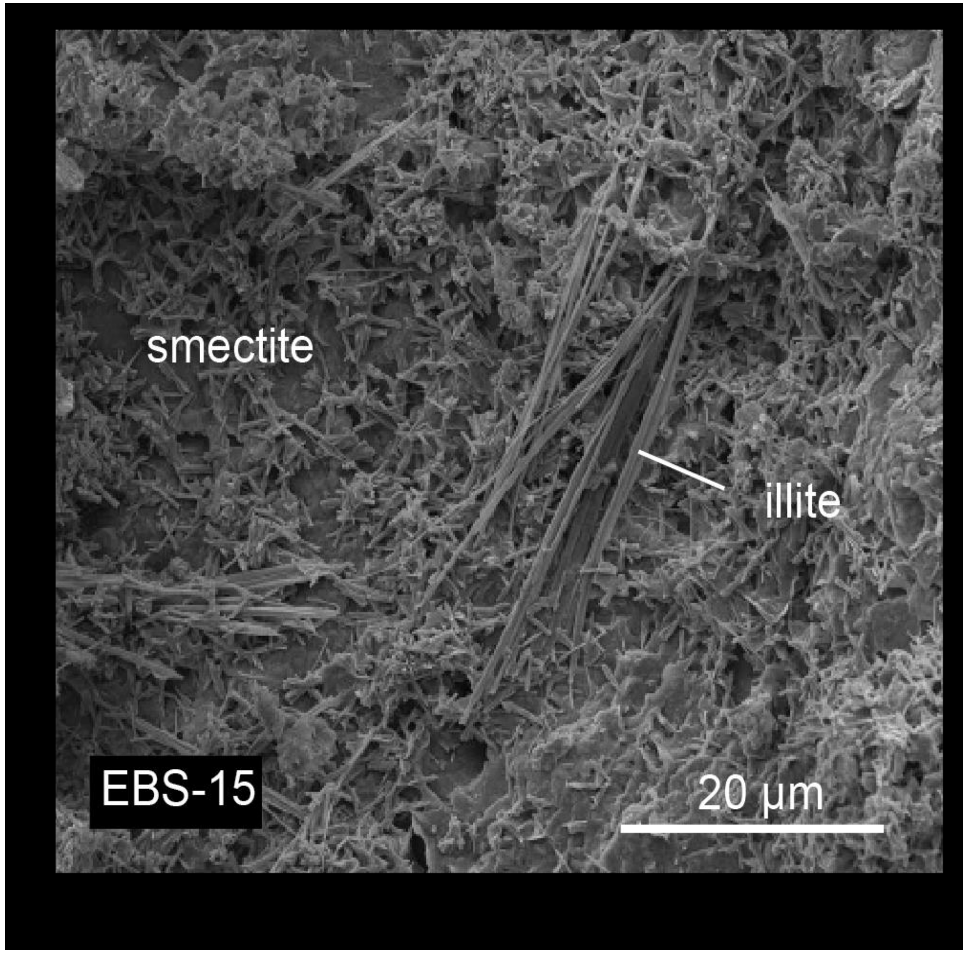
- **Fe1.22Cr0.37Ni0.22+ 1.32/2 H2O + Na0.33(Al1.67,Fe3+0.20,Mg0.13)Si4O10(OH)2→**
- **Stainless-steel + water + Montmorillonite**

- **Na0.33Fe3(Si3.67,Al0.33)O10(OH)2+ 0.13Mg+++ 1.34Al++++ 0.33SiO2**
- **Fe-saponite Opal**

Clay Mineral & Argillite rock Summary

- **Opalinus Clay + Wyoming Bentonite**
- Smectite structure most affected in:
- —6 month/300° C experiment
- —8 week/200° C saline experiment
- Minor interlayered illite-smectite
- Illite nucleation on pre-existing illite in Opalinus Clay
- QXRD: increase in wt.% of clay fraction

- **Portland Cement**
- Swelling decrease
- Clay degradation
- Montmorillonite →tobermorite

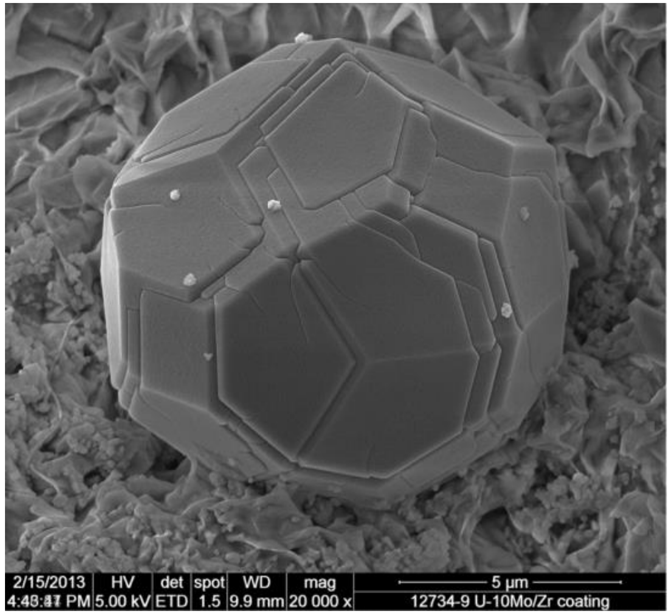


Zeolite and silicate mineral reaction products

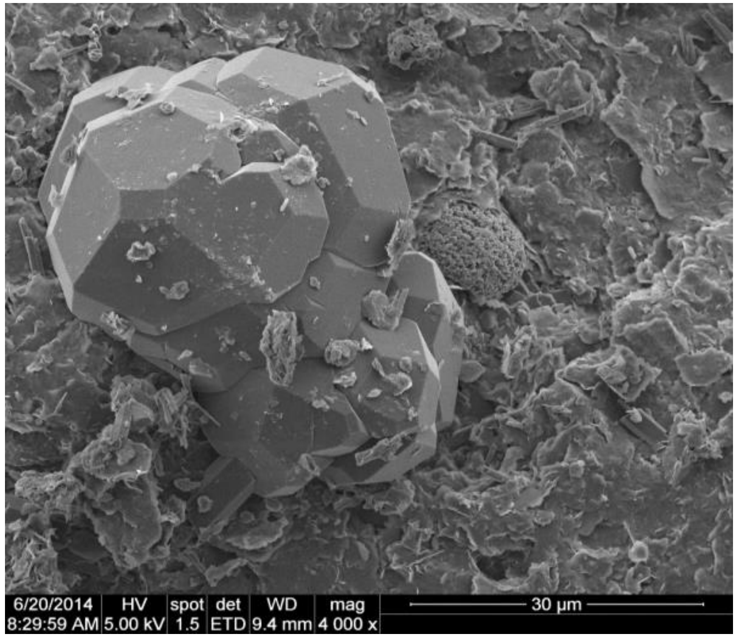
- WY bentonite + Stripa GW → clinoptilolite (cpt) + analcime
- WY bentonite + Opalinus Clay + Opalinus Clay GW → cpt+ analcime-wairakite
- WY bentonite + Opalinus Clay + Cement+ Opalinus Clay GW → cpt+ tobermorite+ garronite + analcime
- WY bentonite + **Grimsel Granodiorite + Grimsel GW→ Al-tobermorite (no zeolite minerals observed)**

Analcime –wairakite solid solution formation

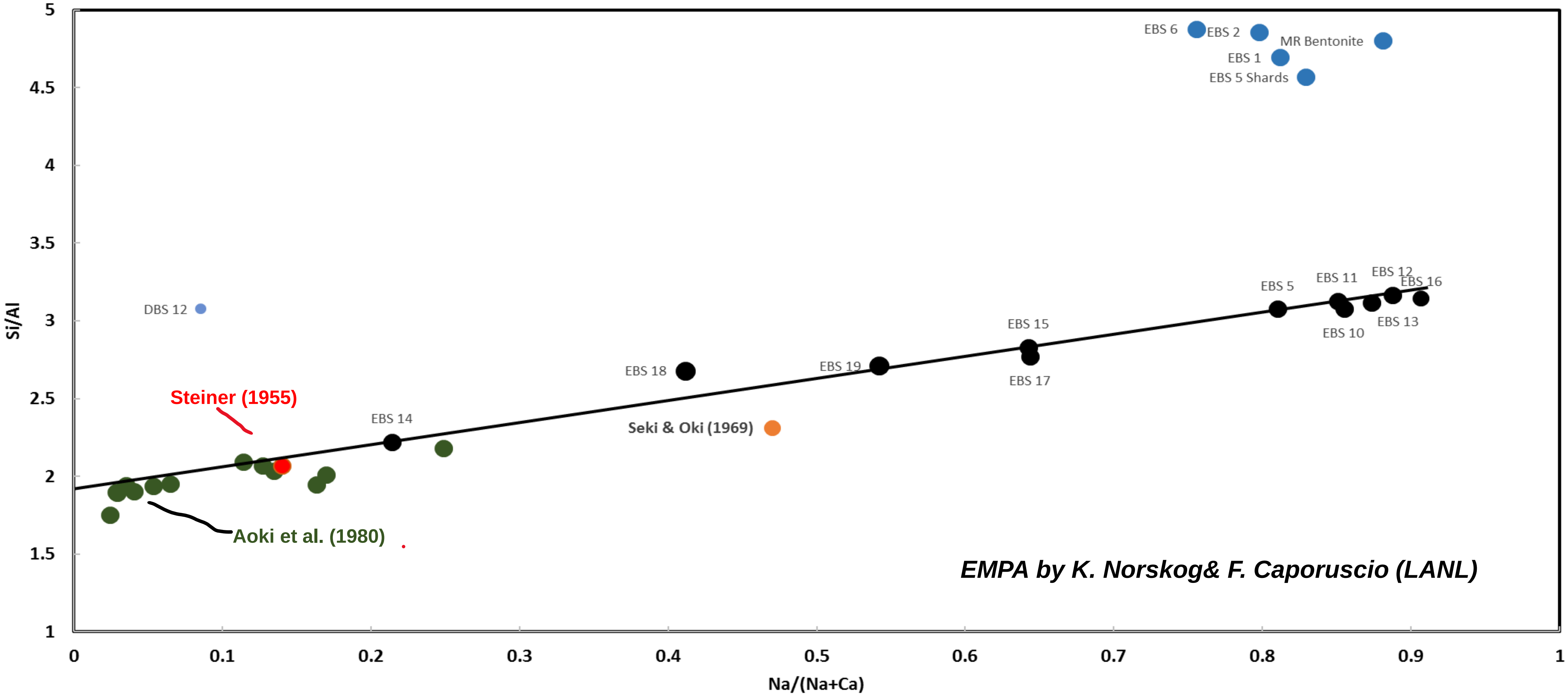
- Formation of analcime from dissolution of clinoptilolite in bentonite buffer



- Formation of analcime–wairakite from precursor kaolinite in Opalinus Clay



Zeolite formation mechanisms
Glass in Bent →Clinoptilolite →Analcime
Kaolinite in OPA →Wairakite



Jové Colón et al. (2017)

Stability of CASH minerals -summary

- With the addition of Ordinary Portland Cement at 200° C:
- Montmorillonite in Wyoming Bentonite breaks down to form tobermorite
- CASH phases (such as tobermorite) are precursor phase to analcime/garronite, which are spatially associated/intergrown.
- Tobermorite is interlayered with montmorillonite → tobermorite peaks are significant in the XRD patterns of the clay fraction).

- The change in smectite abundance is significant.
- For example, EBS-26, smectite is reduced by ~19 wt% and zeolites (analcime + garronite) increase by ~14 wt%.

- Estimation of the before and after experiment wt% clinoptilolite is unchanged or slightly reduced (~8 wt% to 4–8 wt%, respectively) in all the experiments with cement → interaction of other phases (i.e., calcite, clay) form zeolites

Comparison of Wyoming Bentonite to Opalinus Clay ±Wyoming Bentonite ±Portland Cement

Wyoming Bentonite only:

- Smectite stable (no illite)
- Clinoptilolite/glass → analcime at 300° C

Bentonite + Opalinus Clay:

- Smectite →illite/smectite, some discrete illite formation
- Analcime/wairakite formation at 300° C

Bentonite + Opalinus Clay + Portland Cement:

- Significant smectite loss, illite-smectite and discrete illite formation
- CASH mineral generation
- Montmorillonite → tobermorite, garronite + analcime observed at 200° C

Comparison of crystalline to argillite host rock experiments

Grimsel Granodiorite

- Temperature = 250° C
- Carbonate rich brine
- Al-tobermorite
- Accessory chlorite and gypsum
- No illite or illite-smectite observed
- Bentonite colloids (not stable in experiment, formed during quench, Garcia-Garcia et.al. 2009)

Opalinus Clay

- Temperature = 300° C
- NaCl-rich brine
- Analcime –wairakitess
- Minor illite-smectite, discrete illite

Summary – Bentonite only / Corrosion

Engineered Barrier Systems using bentonite backfill / buffer in a high temperature, pressure repository must consider system bulk chemistry.

Bentonite alteration

- **High Na+ activity and restricted K+ supply inhibit/retarding illitization.**
- **Clinoptilolite to analcime highly sensitive to reaction conditions**
- **Very slow kinetics, with sequestered Al3+inhibiting illitization.**

Steel Corrosion

- **Metal acts as a mineral growth substrate: Fe-saponite created at steel /clay interface, minor chlorite.**
- **Growth of Fe-rich clays increase waste canister's active surface area, providing increased actinide retention**.

Summary –Opalinus wall rock

Opalinus Clay + Wyoming Bentonite

- Smectite structure most affected in:
  - 6 month/300° C experiment
  - 8 week/200° C saline experiment
- Minor interlayered illite-smectite
- Illite nucleation on pre-existing illite in Opalinus Clay
- QXRD: increase in wt.% of clay fraction

+ Portland Cement

- Swelling decrease
- Clay degradation
- Montmorillonite → tobermorite
- Significant authigenic silicate phases (analcime, garronite)

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REFERENCES

- Cheshire, M., F.A. Caporuscio, M.S. Rearick, C.F. Jové-Colón, and M.K. McCarney, Bentonite evolution at elevated pressures and temperatures: An experimental study for generic nuclear repository designs. American Mineralogist, 2014. 99: p. 1662-1675.
- Cheshire, M.C., F.A. Caporuscio, C.F. Jové-Colón, and K.E. Norskog, Fe-saponite growth on low-carbon and stainless steel in hydrothermal-bentonite experiments. Journal of Nuclear Materials, 2018. 511: p. 353-366.
- Eberl, D.D., Velde, B., and McCormick, T. (1993). Synthesis of illite-smectite from smectite at Earth surface temperatures and high pH. *Clay Minerals*, 28, 49-60.
- Garcia-Garcia, S., Wold, S., and Jonsson, M. (2009). Effects of temperature on the stability of colloidal montmorillonite particles at different pH and ionic strength. *Applied Clay Science,* 43(1), 21-26.
- Moore, D. M. and Reynolds, R.C. (1997). X-ray Diffraction and the identification and analysis of clay minerals. *Oxford University Press*, New York, New York, 377.
- King, F., Lilja, C., Pedersen, K., Pitkänen, P., Vähänen, M., 2010. An update of the state-of-the-art report on the corrosion of copper under expected conditions in a deep geologic repository. Swedish Nuclear Fuel and Waste Management Co. (SKB), Technical Report TR-10-67, 180.
- Jové-Colón, C.F., Y. Wang, T. Hadgu, L. Zheng, J. Rutqvist, H. Xu, K. Kim, M. Voltolini, X. Cao, P.M. Fox, P.S. Nico, F.A. Caporuscio, K.E. Norskog, M. Zavarin, T.J. Wolery, C. Atkins-Duffin, J.L. Jerden, V.K. Gattu, and W.L. Ebert, Evaluation of Used Fuel Disposition in Clay-Bearing Rock (SFWD-SFWST-2017-000006), 2017, Sandia National Laboratories: Albuquerque, NM. SAND2017-10533 R. 442 pp.
- Sauer, K.B., Caporuscio, F.A., Rock, Marlena J., Cheshire, M.C., Jove Colon, Carlos F. 2020, Hydrothermal interaction of Wyoming Bentonite and Opalinus Clay: Clays and Clay Min., 68, 144-160
- Seki, Y. and Y. Oki, Wairakite-analcime solid solutions from low-grade metamorphic rocks of the Tanzawa Mountains, Central Japan. Mineralogical Journal, 1969. 6(1-2): p. 36-45.
- Steiner, A., Wairakite, the calcium analogue of analcime a new zeolite mineral. Mineralogical Magazine, 1955. 30(230): p. 691-698.
- Taniguchi, N., Kawasaki, M., 2008. Influence of sulfide concentration on the corrosion behavior of pure copper in synthetic seawater. J Nucl. Mater. 379, 154-161.