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Fuel Cycle Technologies

Brine migration in salt

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Uncertainties in U.S. salt repositories

- **Liquid / vapor migration in salt unresolved**
  - Toward or away from heat source (Roedder, 1984)?
  - What happens at Intersect grain boundaries? Follow boundaries or straight through?
  - Decrepitation at surface boundaries?
- **Phyllosilicate or sulfate dehydration / phase transformation**
  - Clays can dehydrate/rehydrate under certain conditions (Vidal and Dubacq, 2009)
  - These changes can influence their capacity to retain water and their sorption/desorption capacity (Altaner and Ylagan, 1997)
  - Above certain temperatures(300 – 400 ºC), clays irreversibly transform to mica (lose water & volume) (Meunier et al., 1998)
  - Gypsum to anhydrite transformation (Shcherban and Shirokikh, 1971) produces a large water release (21% wt. loss) and volume reduction (~40%). Water loss from structure and volume contraction may induce fractures
  - WIPP corrensite, Naica Mexico gypsum, and WIPP bassanite, anhydrite

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Presentation Outline

- **Free fluid migration in single salt grains**
  - Single (liquid)
  - two phase (liquid and gas)
  - Conclusions

- **Minerals (clay/sulfate) taken to higher temperatures**
  - dehydration
  - phase change possibilities
  - Conclusions

- **Path Forward**

Sample Collection at WIPP

Large Halite samples – Panel 7
Boukhalfa, Dozier, Caporuscio

Contact - Orange Marker bed WIPP

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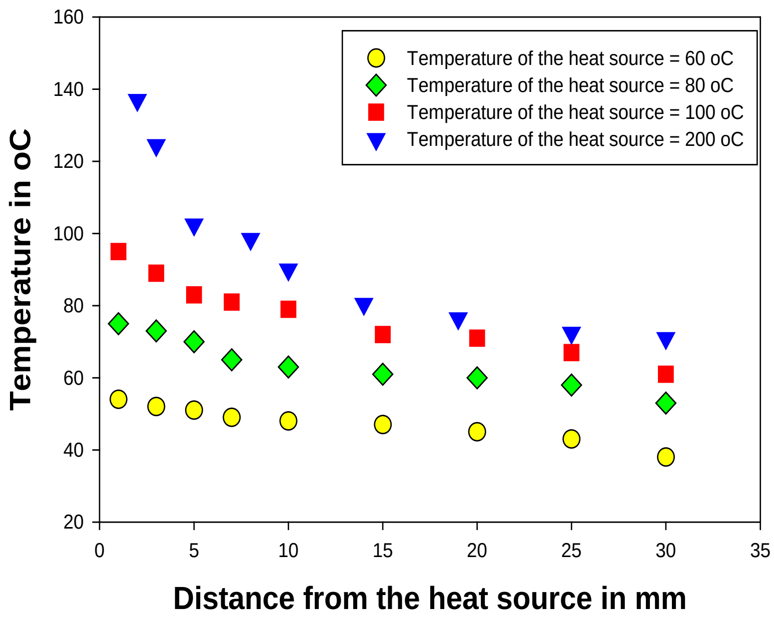
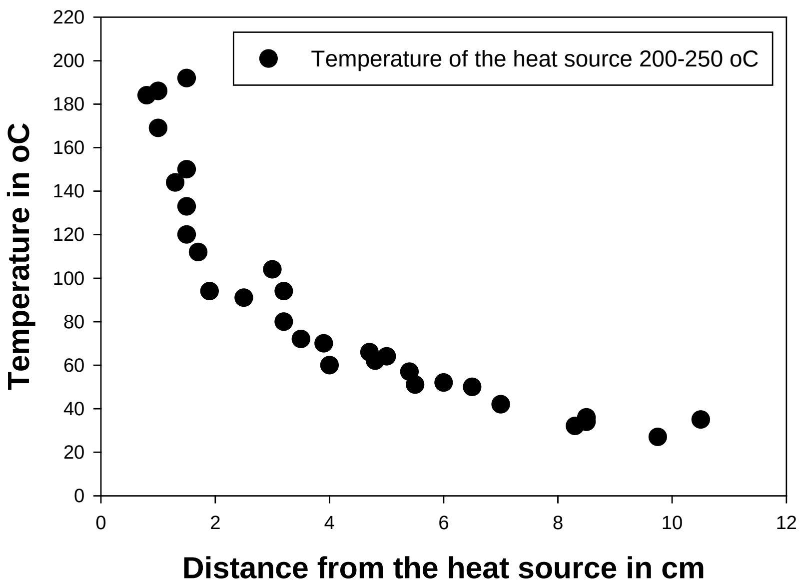
Temperature Profile in Heated Salt

- *Temperature profile in salt crystals*



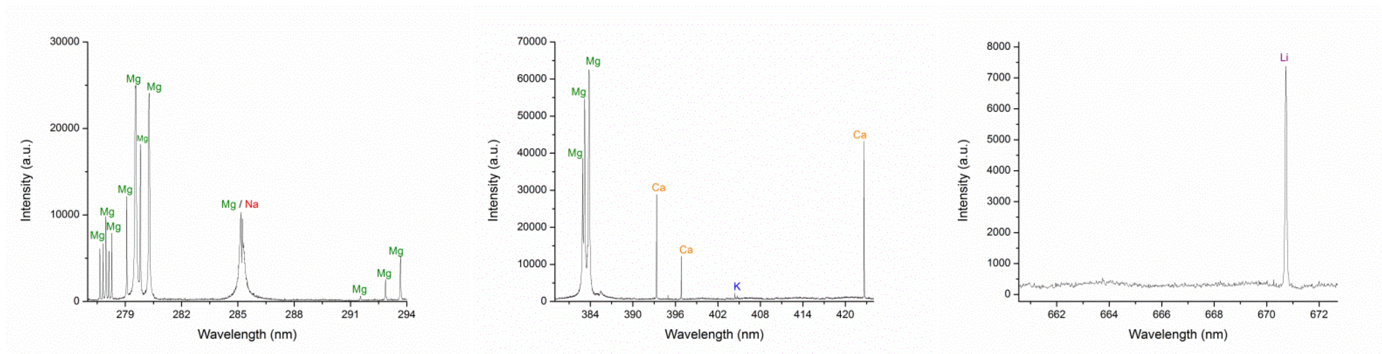
- *Temperature profile in crushed salt*



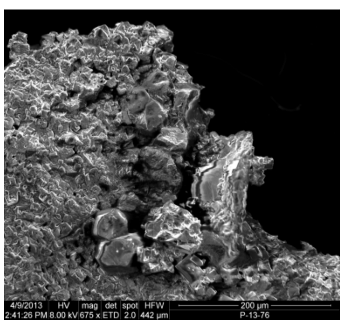
- ***Low coupling between the heat source and salt***
- ***Temperature drops exponentially away from the heat source***

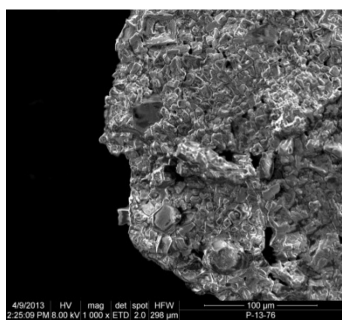
Brine Inclusion Analysis by SEM/EDS and LIBS

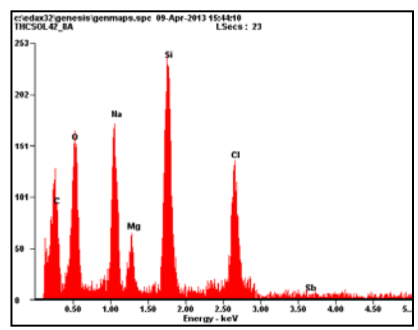
Laser-induced breakdown spectroscopy analysis of brine inclusions in salt crystals

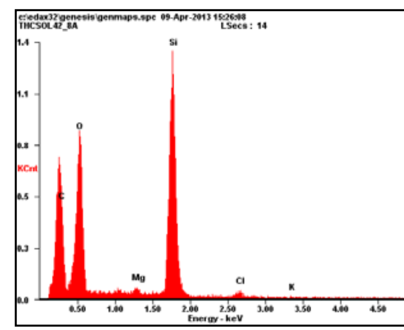


Brine composition analysis using SEM/EDS







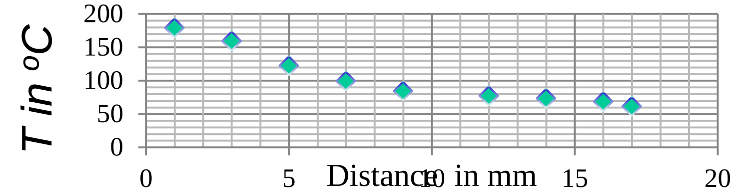


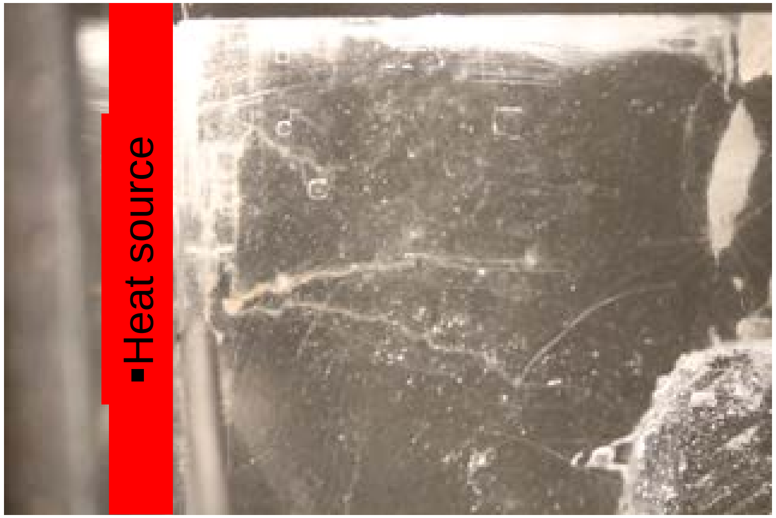
- *Brine inclusions composition varies significantly between inclusions, even within a single salt crystal*
- *Most inclusions are dominated by a Mg/Na Cl brine, however, minor elements such as Si, Li are common*

Liquid Inclusion Migration under Temperature Gradient

Conditions:

Temperature at the hot surface = 200 °C
Temperature at the cold side: ambient
Applied temperature gradient 30 hours
Temperature gradient: non linear

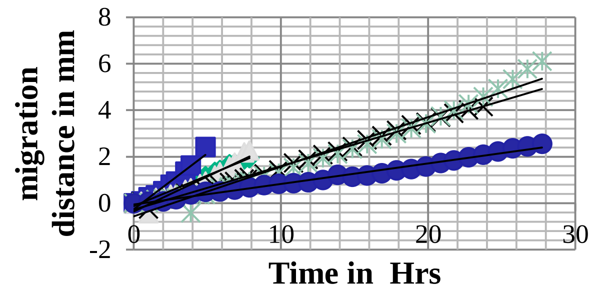




Two step migration mechanism

- *Transition state*: Inclusions change shape starting from the cold side
- *Steady State*: inclusions migrate at a constant rate

- ***Liquid inclusions migrate toward the heat source***
- ***The migration rate is mostly affected by the temperature of the salt and the size of the inclusion***

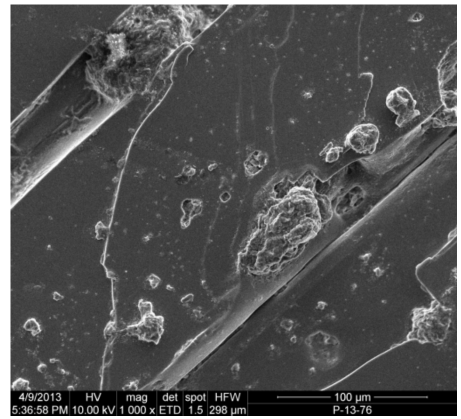


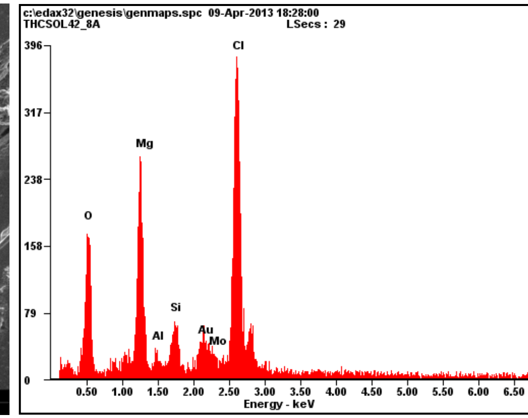
SEM/EDS analysis of brine migration channels and salt effloresces deposited along the migration pathway

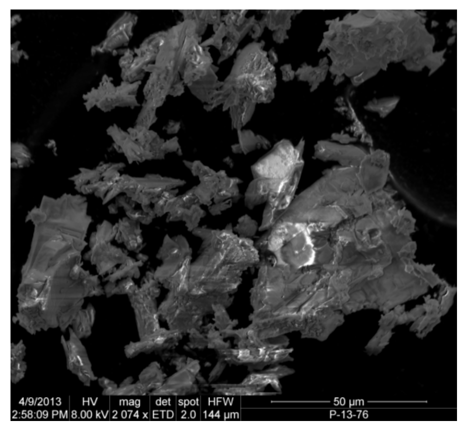
Brine migrates towards the heat source by dissolution of the salt matrix. It creates a network of dissolution channels of about 10 μm diameter that extend along the migration path

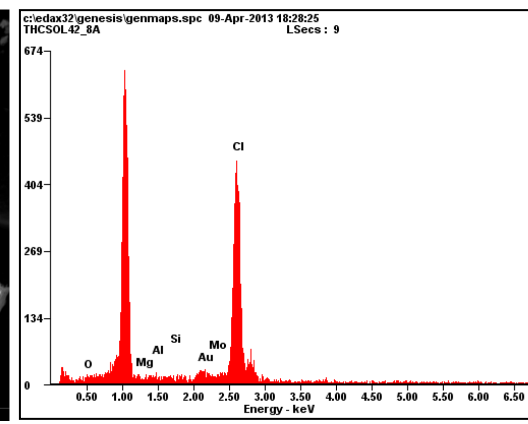
Salt is deposited along the migration channels at crystal edges

The composition of the salt deposited evolves from a Mg/Ca/Na mixture at the start of the migration pathway to a pure NaCl salt at the end of the migration channel



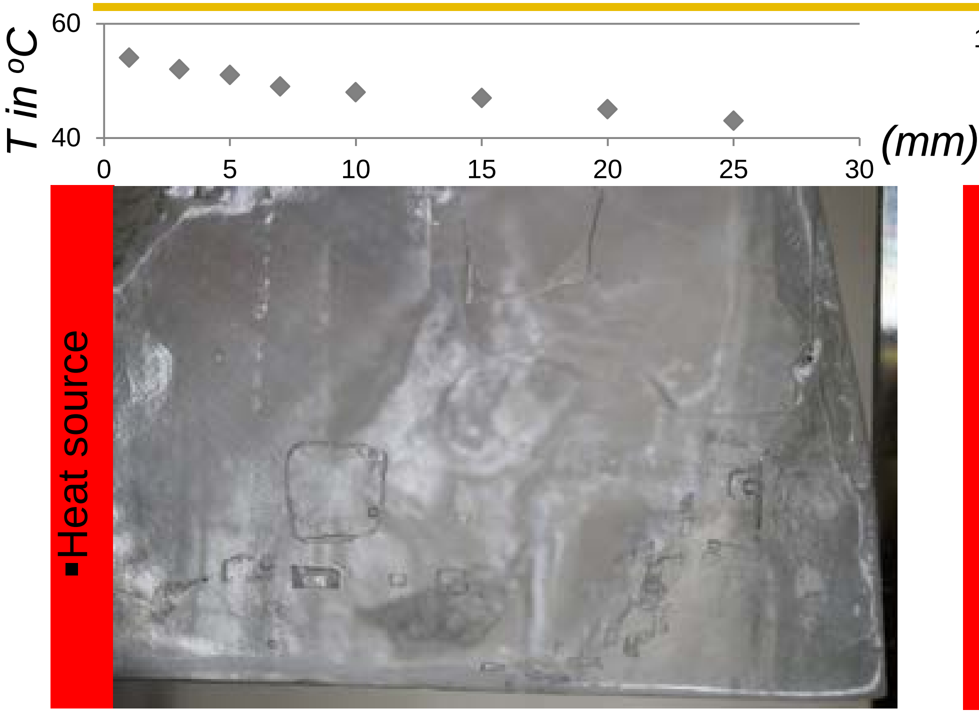


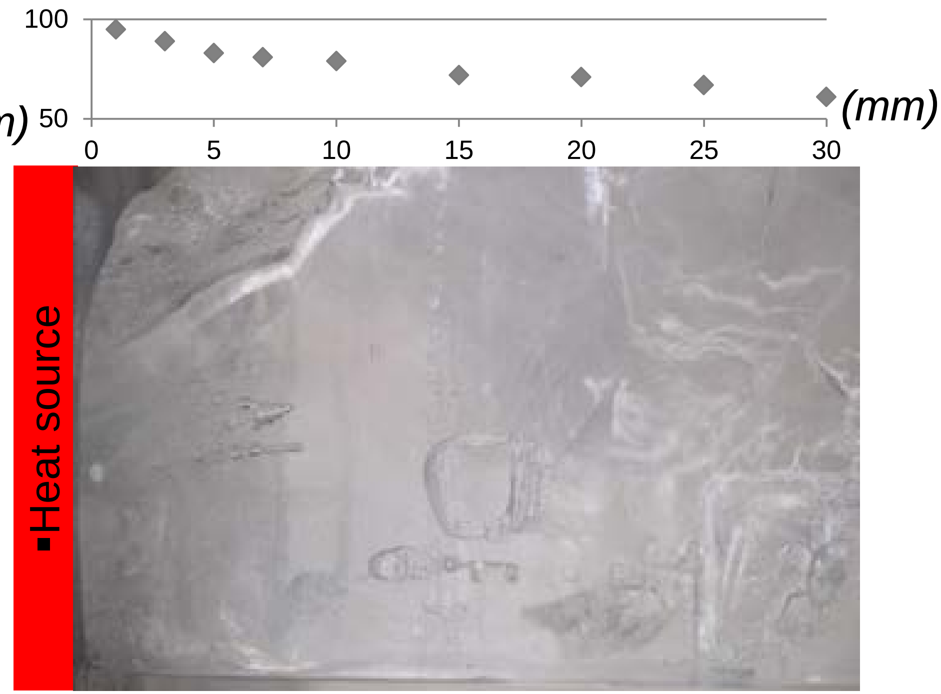




SEM/EDS analysis of salt crystals deposited along the migration pathway

Two Phase Inclusion Migration under Temperature Gradients(30 days)

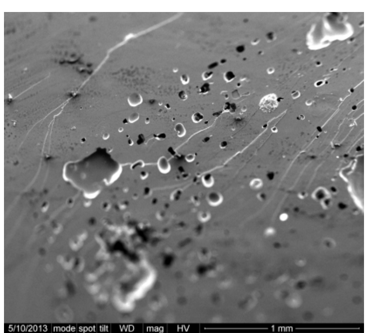


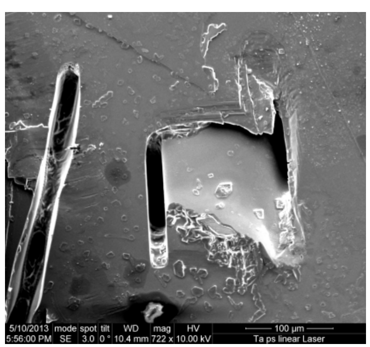


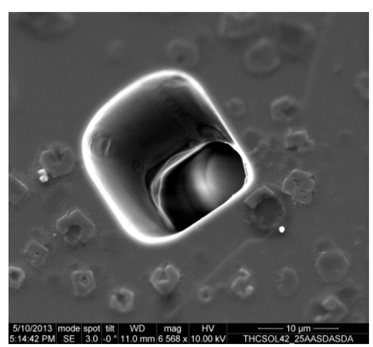
- *Brine migration is induced by vey low temperatures of < 40 ^{o}C*
- *Brine moves towards the heat source while the gas bubble moves towards the cold end of the salt (Anthony and Cline, 1972)*
- *Inclusions are able to travel across crystal cleavage planes*
- *The rate of brine migration is mainly influenced by the temperature gradient*

Brine Migration Pathways - Two Phase Inclusions

- *In two phase inclusions, brine migrates towards the heat source but a fraction of the moisture is driven by gas towards the cold salt*
- *Migration occurs through a network of 10 μm channels that expand along the temperature gradient*







Dissolved salt is deposited along the migration channels at crystal edges

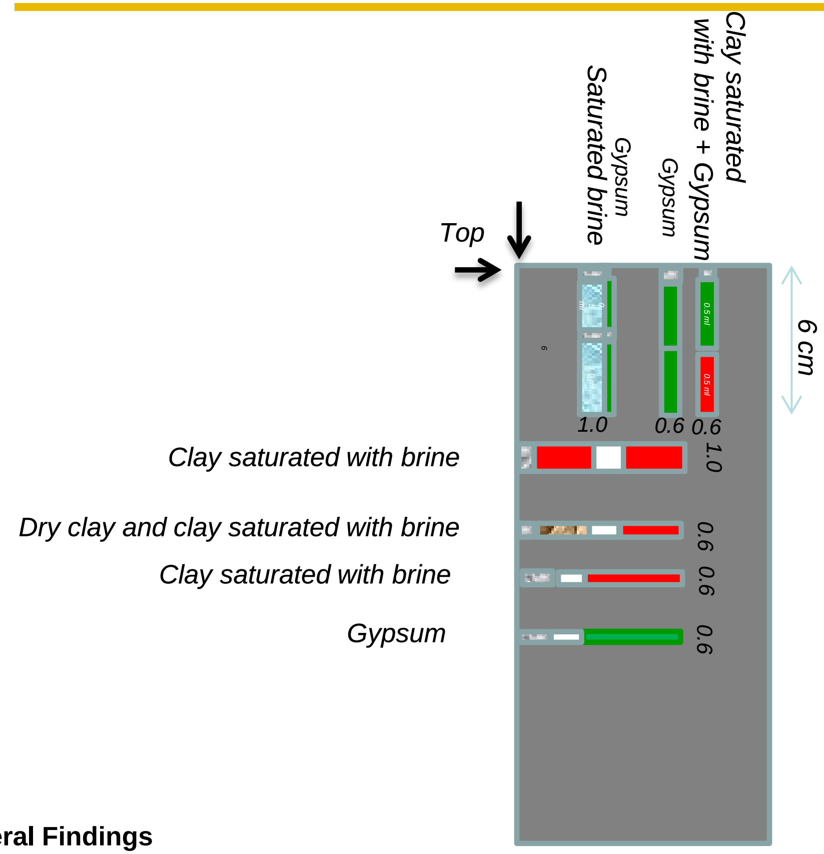
The salt deposited along the migration channels becomes NCl enriched

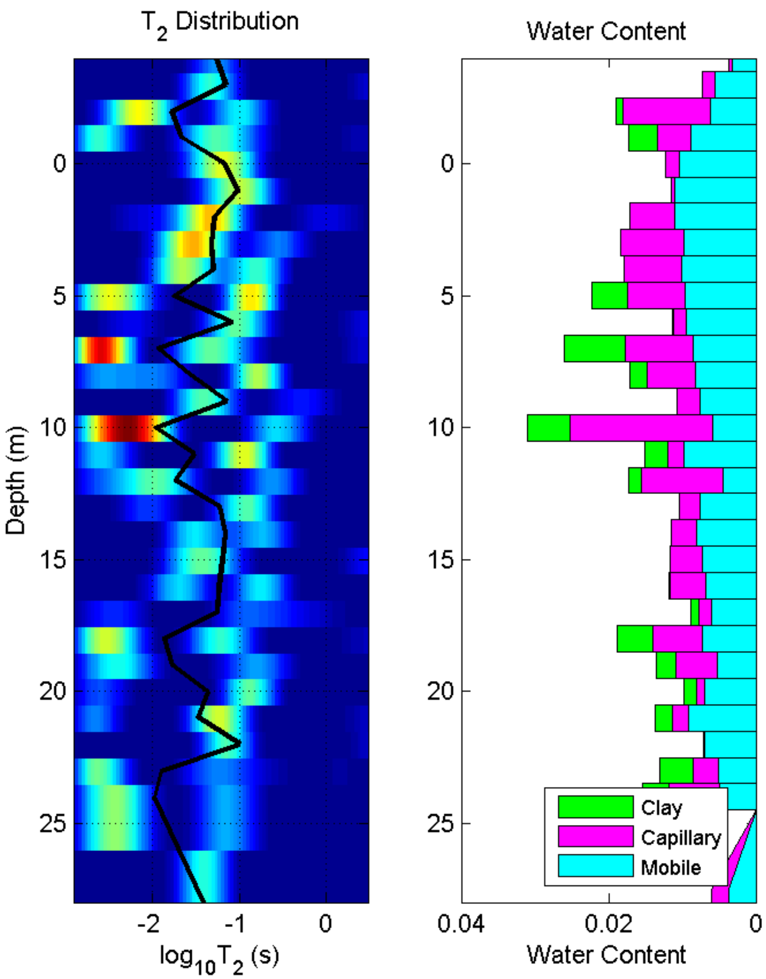
Preliminary Tests of Imaging Techniques

- **Low-field NMR Analysis- Good correlation, not yet calibrated for quantification**

- **Neutron Tomography – Good imaging of brine inclusions, resolution needs refinement.**

Low-field NMR Analysis of Salt Core





General Findings

•Volumetric water content estimates on order of 1-2% along entire length of core (lateral resolution ~8cm)

•Longest signals on order of T2=300ms

–Shorter than anticipated for brine –(high dissolved Fe?)

•Short signal components on order of T2=2-10ms also detected

–Likely associated with saturated clay –(loosely packed?)

Brine Migration Results

- There is low coupling between the heat source and salt. As a result of this low coupling and the low heat conductivity of salt, temperatures in crushed and intact salt drop very rapidly away from the heat source
- Temperatures of < 40 ^{o}C can induce brine migration
- Brine contained in small inclusions moves towards the heat source regardless of the type of inclusion (i.e., full inclusions, two phase inclusions)
- In two phase inclusions a fraction of the moisture is driven away from the heat source by the gas toward cold salt
- Brine migration occurs through a network of μm size channels that extend along the temperature gradient pathway
- The rate of the migration is influenced by the size of the inclusion and the temperature gradient in the salt
- Brine migration pathways do cross crystal planes
- The brine becomes enriched in NaCl as it migrates towards the heat source and deposits Mg rich salt along the migration channels

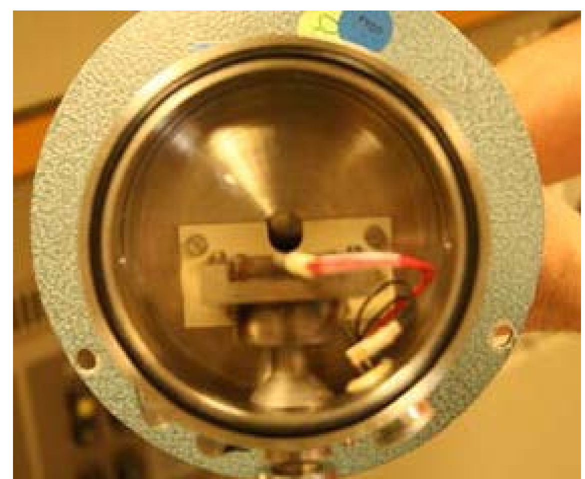
Mineral Dehydration/Transformation

- **Clays : potential water loss - rehydration, phase change to mica**

- **Sulfates: significant water / volume loss, phase change to anhydrite**

R&D Capabilities at Los Alamos National Laboratory

- **High Pressure / Temperature Lab**
  - < 400 ºC, < 600 bar
  - Few such labs running in the U.S.
  - Present work – UFD EBS, CO_2 sequestration, geothermal tracers
- **XRD environmental chamber**
  - < 300 ºC, controlled atmosphere
- **Capabilities for analyzing heat induced brine migration in salt.**
  - < 300 ºC, optical scale, continuous video

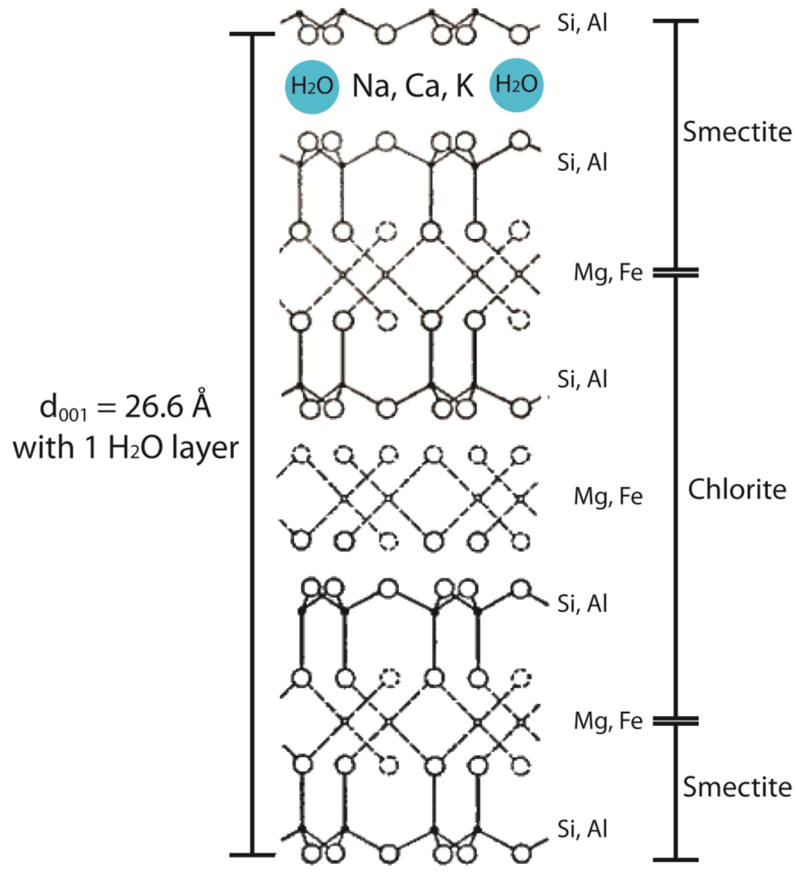


Insoluble Minerals in WIPP Salt

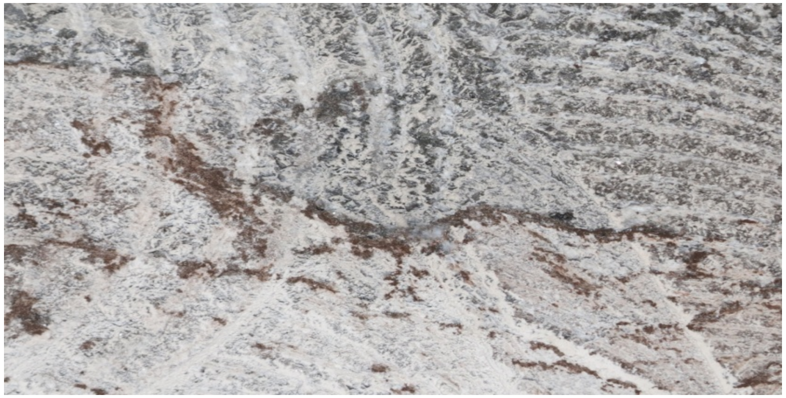
- **Orange Salt-*Residue***
- **Corrensite** **$(Mg,Al)_9(Si,Al)_8O_{20}(OH)_{10}*4H_2O$**
- **Quartz-SiO_2**
- **Magnesite-$MgCO_3$**
- **Muscovite-$KAl_2(Si_3Al)O_{10}(OH)_2$**
- **Hematite-Fe_2O_3**
- **Anhydrite-$CaSO_4$**
- **Both Rocks dominated by halite**

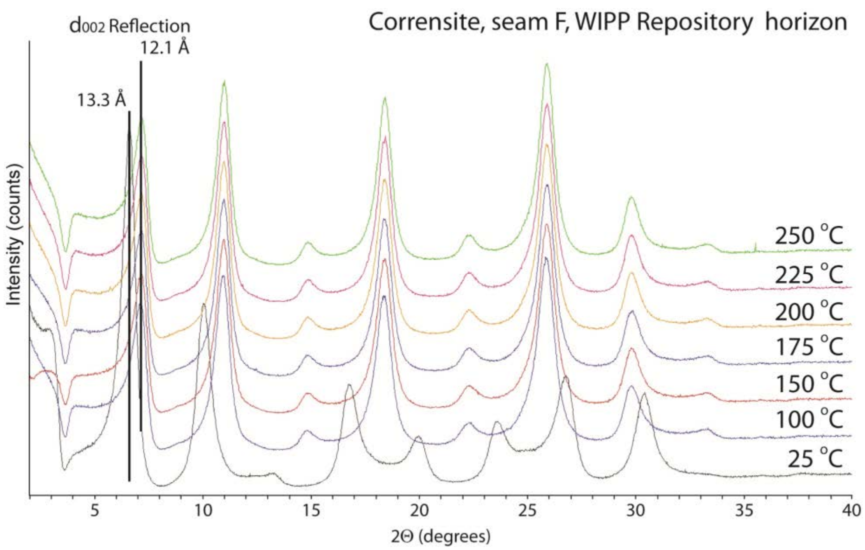
- ***White Salt-Residue***
- ***Corrensite-$(Mg,Al)_9(Si,Al)_8O_{20}(OH)_{10}*4H_2O$***
- ***Quartz-SiO_2***
- ***Magnesite-$MgCO_3$***
- ***Muscovite-$KAl_2(Si_3Al)O_{10}(OH)_2$***
- ***Hematite-Fe_2O_3***
- ***Anhydrite-$CaSO_4$***
- ***Microcline-$KAlSi_3O_8$***
- ***Calcite-$CaCO_3$***
- ***Bassanite-$CaSO_4*0.5H_2O$***

Corrensite Crystal Structure

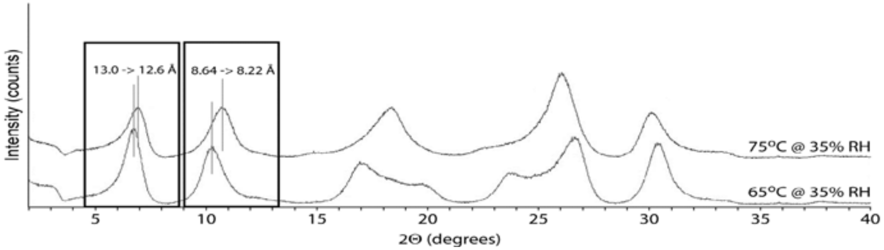


Corrensite Results





- Dehydration between 65-75ºC at 35% RH
- Loss of interlayer water
- Reversible
- Brine saturated at 300 ºC, corrensite stable



Sulfate Stabilities at Elevated Temperatures

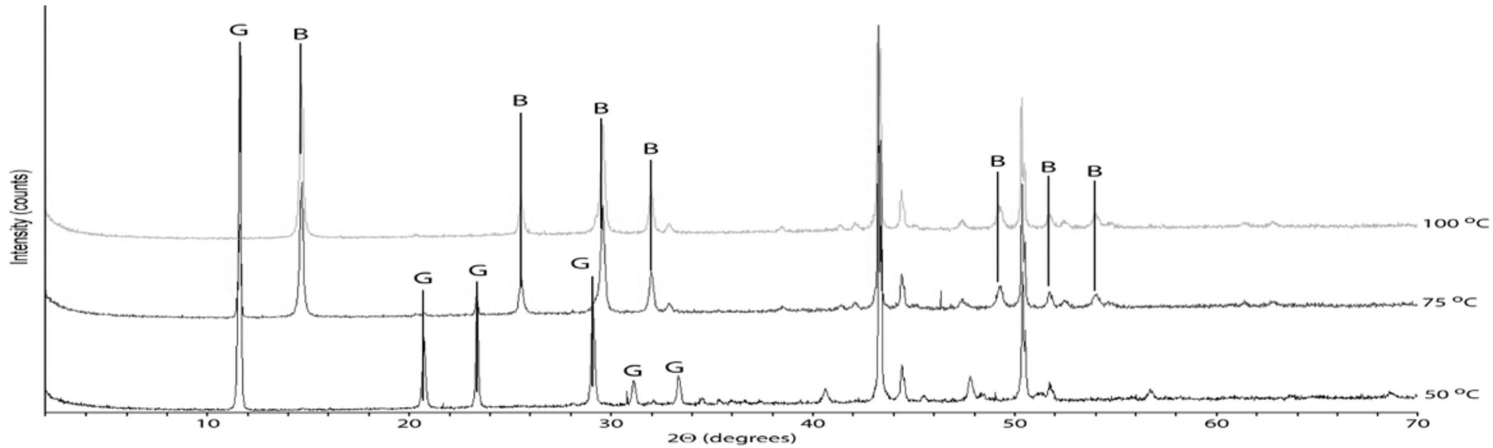
Two step reaction with metastable phase

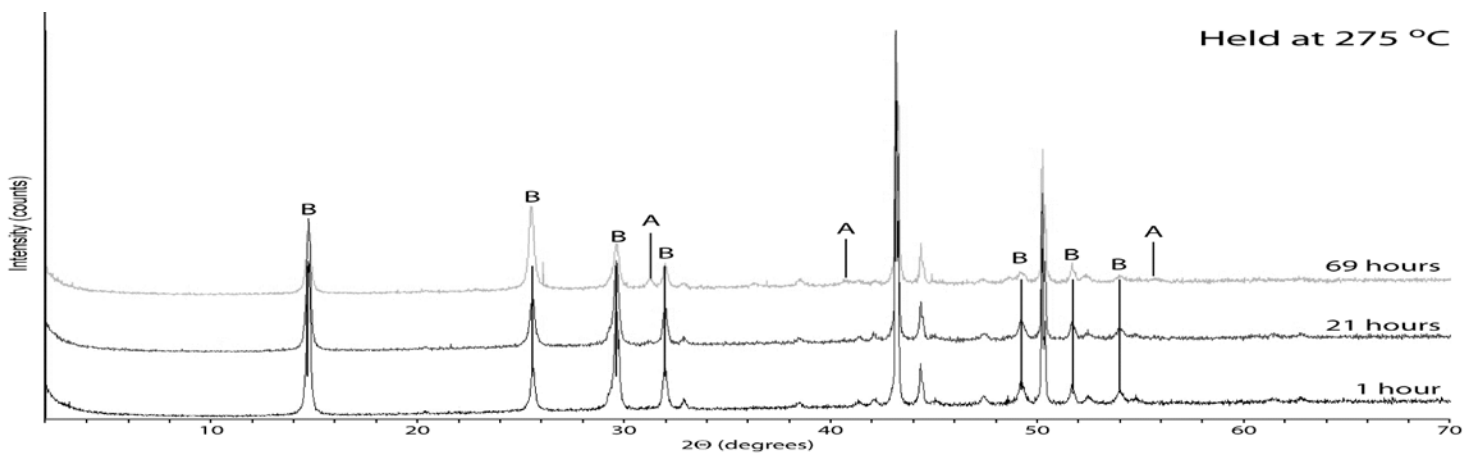
- Gypsum ($CaSO_4$ $2H_2O$) to bassanite ($CaSO_4$ $0.5H_2O$) to anhydrite ($CaSO_4$)
- Gypsum to bassanite transformation at 76 ^oC (Freyer, 2000). Bassanite to anhydrite (Shcherban and Shirokikh, 1971) at 100 to 140 ^oC.

One step reaction

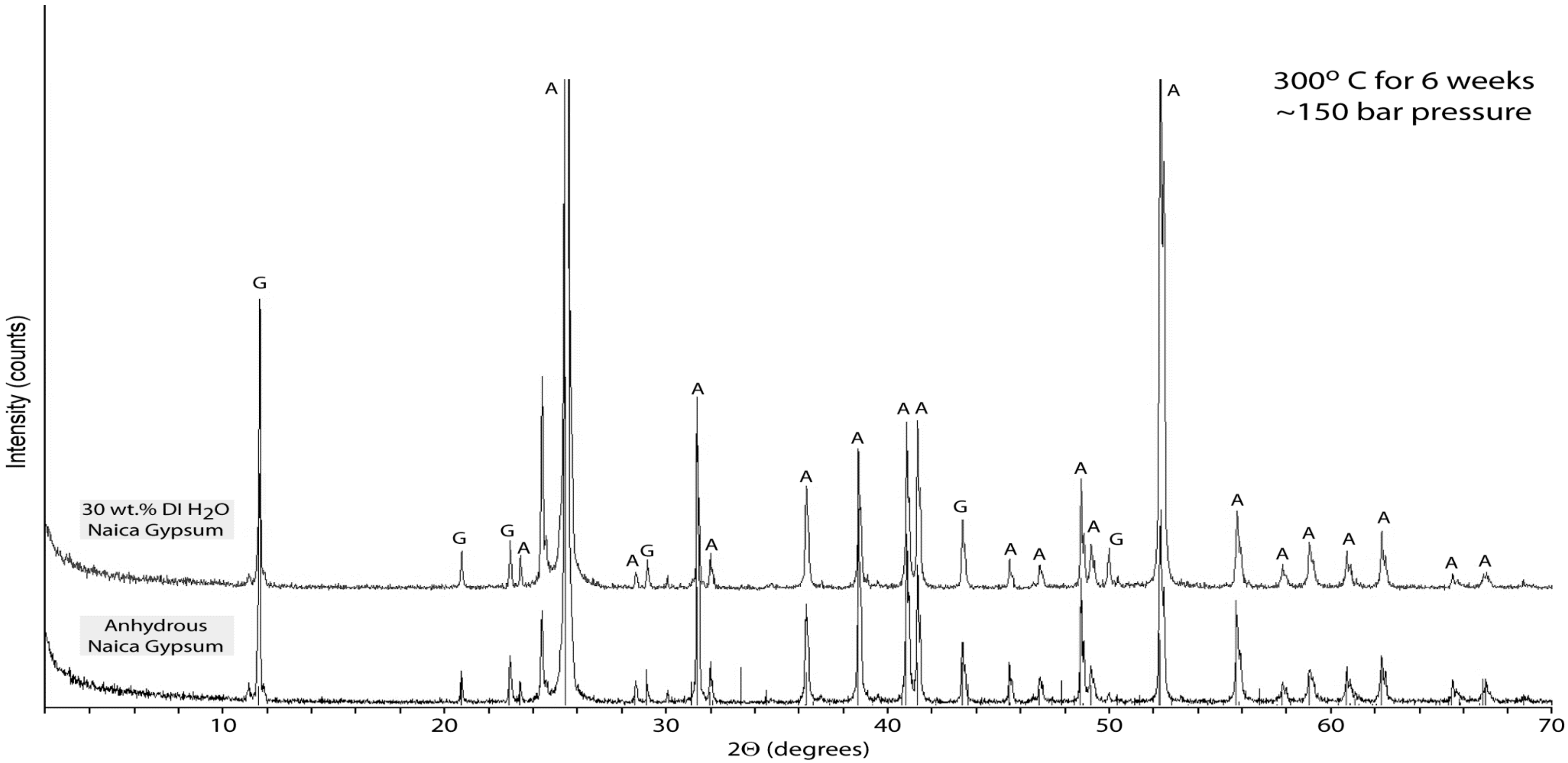
- Gypsum ($CaSO_4$ $2H_2O$) to anhydrite ($CaSO_4$) (180 ^oC)
- Either reaction series creates a large water release (21% wt. loss) and volume reduction (~40%). Water loss from structure and volume contraction may induce fractures.

Gypsum to Bassanite Transition at 75 ºC, Bassanite to Anhydrite 275 ºC





Gypsum to Anhydrite - Sealed Capsules



Clay / Sulfate Phase Transition Conclusions

CLAY

- Corrensite releases interlayer water at 75 ºC, stable to 300 ºC

Sulfate

- Gypsum to Bassanite at 75 ºC, Gypsum gone at 100 ºC
- Bassanite to Anhydrite at 275 ºC and low RH, reaction slow
- Gypsum to Anhydrite at 300 ºC (6 weeks, saturated), minor remnant Gypsum remains
- Robertson and Bish (2013) note that sulfate dehydration reactions are very sluggish and quite dependant on RH
- Further research needed to constrain both one stage and two stage reaction temperatures at repository conditions.

Research Plans

- **Multi-crystal (intact, crushed), clay-rich salt at range of temperatures**
- **Upscale - Perform brine migration studies at core scale**
- **Couple migration rates observed at single crystal scale to the core scale**
- **Examine brine migration in a salt core subjected to a temperature gradient and confining pressure**
- **Resolve gas migration mechanism**
- **Refine neutron tomography, NMR techniques**

- **Refine clay hydration-dehydration / sulfate phase transition (single, dual) parameters (T, RH)**
- **Identify mineral phase reaction onset and completion at appropriate salt repository P,T conditions.**
- **Integrate with THM model efforts**

End of Presentation

Acknowledgments

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Thank You

Questions?

Finito

Grazie mille.

Avete domande?