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Evolution of Concentrated Brine Composition at Elevated Temperatures

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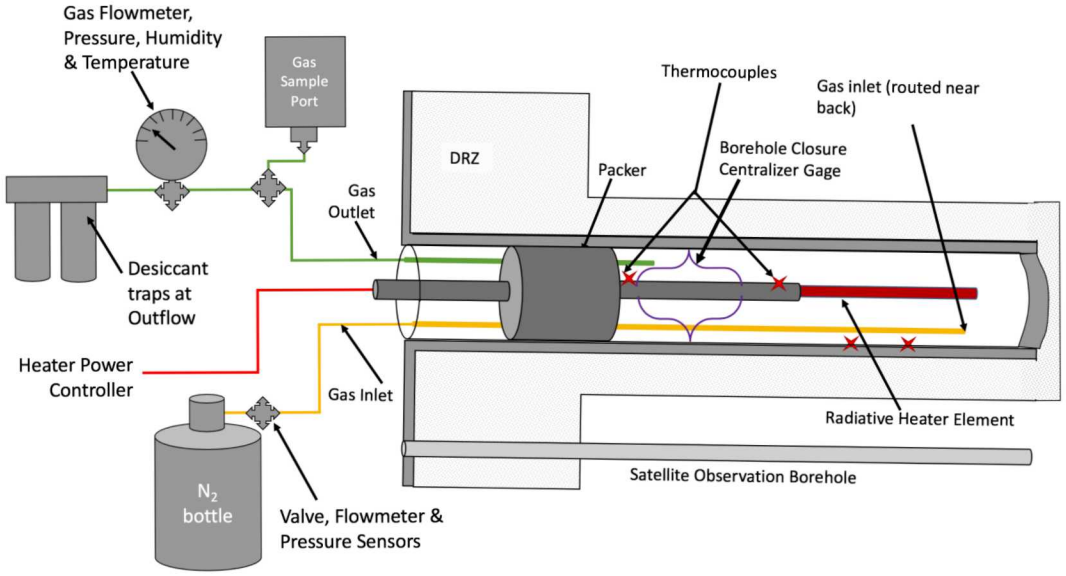
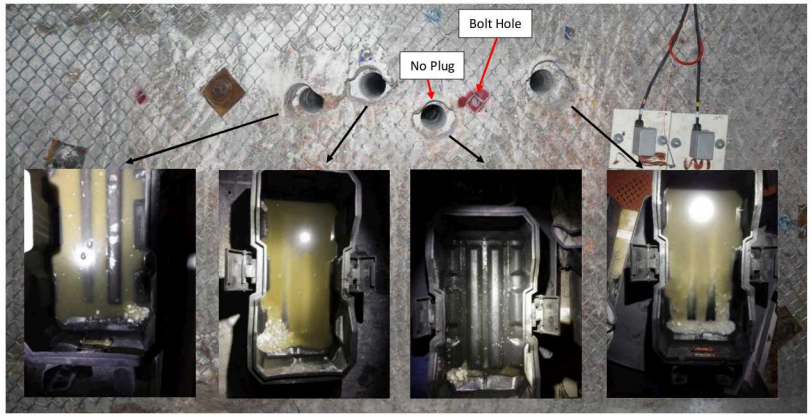
Motivation

- **Salt is a viable geologic media for the disposal of radioactive waste**
  - However, disposing of heat generating waste still requires further research for long-term safety case predictions
- **Borehole heater test currently being conducted at the Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico, under DOE-Nuclear Energy**
  - Collaboration between three National Labs: Sandia, Los Alamos, and Lawrence-Berkeley



Connection to Brine

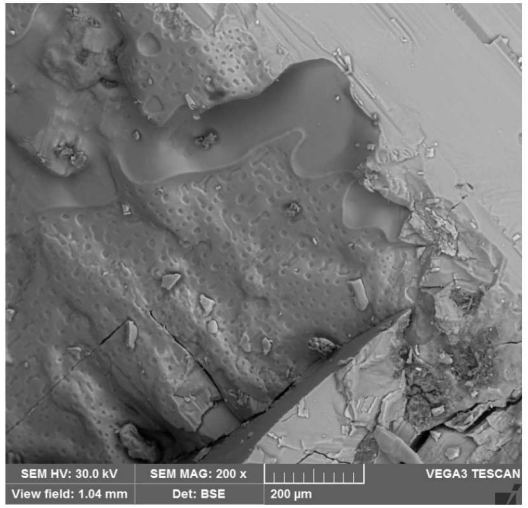
- **Bedded salt (specifically WIPP) can have a fair amount of brine in the formation**

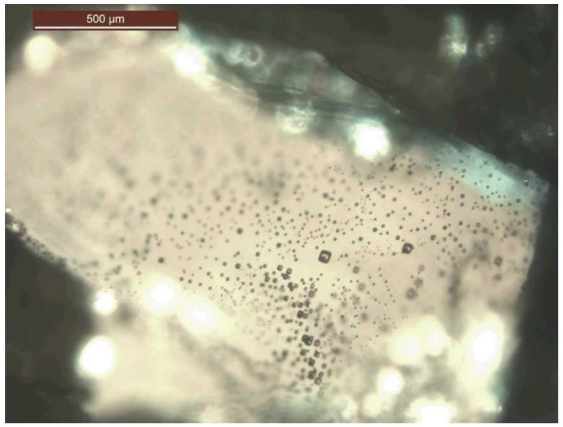


- **Impacts of brine on performance of repository**
  - Waste package corrosion effects
  - Limit closure of brine-filled cavities
  - Transport of radionuclides to the far field

- **Main goal of the Heated Borehole Field Test is to improve the understanding of brine availability and evolution of brine chemistry in bedded salt when heated**

Fluids in Salt



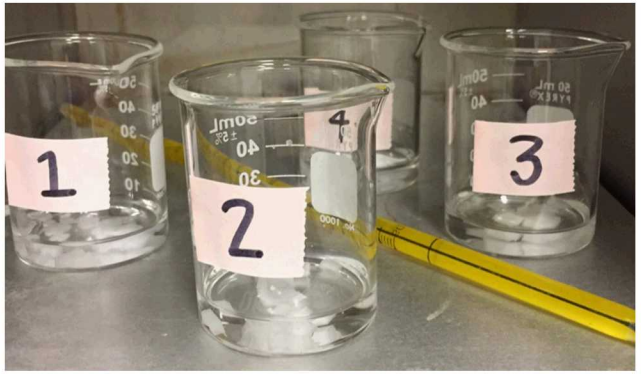


- **Three main types of fluid in salt:**
  - Intergranular water (between grains)
  - Intragranular water (fluid inclusions inside grains)
  - Hydrated minerals
    - Clays (5-18% H_2O by weight)
    - Gypsum (21% H_2O by weight)
    - Polyhalite (6% H_2O by weight)
- **Water sources respond differently to heat**
  - Brine between grains flows first (ambient)
  - Fluid inclusions move/break due to temperature
  - Clays dehydrate at ≤100° C
  - Gypsum dehydrates 75 – 175° C
  - Polyhalite dehydrates ≥300° C

- **<u>Want to discern contributions from these brine sources through time at different temperatures</u>**

Laboratory Experiments

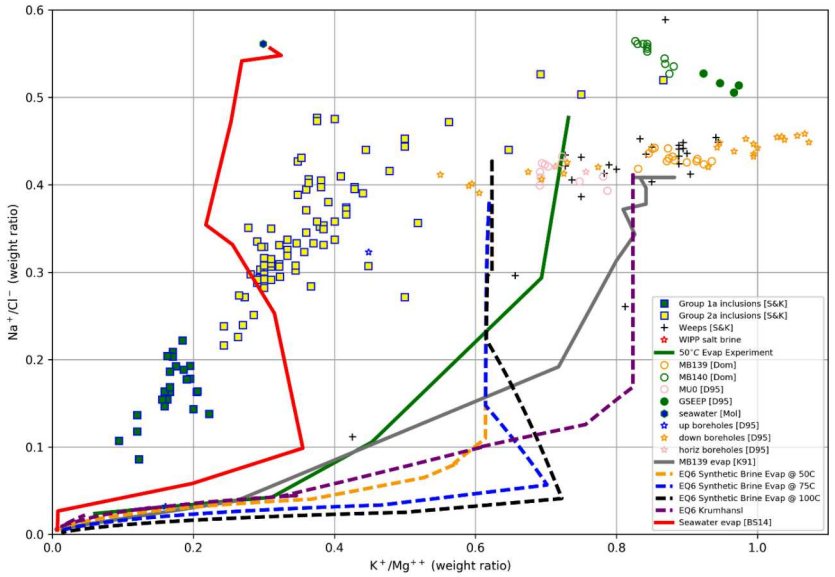
- **Laboratory brine evaporation experiments support possible outcomes from the field test**
- **Conducted brine analysis on multiple brine types and evaporation experiments at varying temperatures of 50°C, 75°C, and 100°C**
  - Analyze liquid chemistry
  - Analyze precipitant composition
  - Perform EQ3/6 geochemical models
  - Compare to historical samples

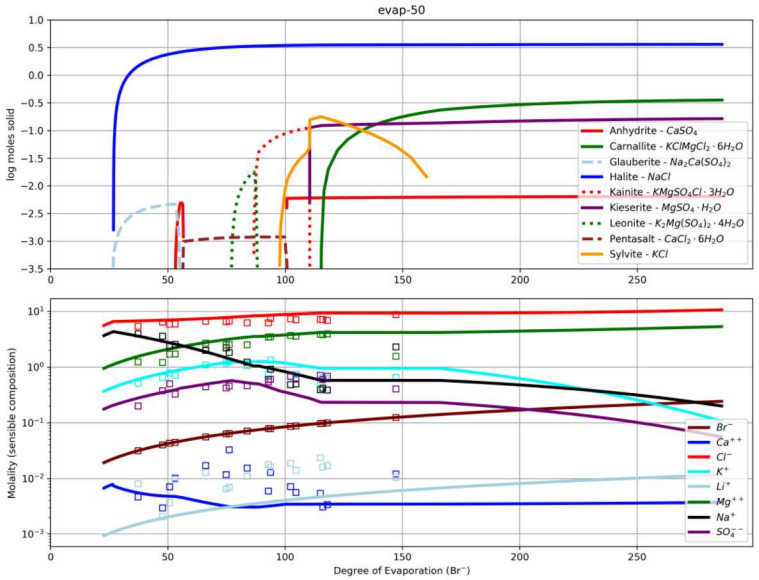


Experimental and Analysis Techniques

- **Prepare brine solutions**
  - Type 1: Dissolve WIPP salt in water until saturated
  - Type 2: Modified Synthetic Salado WIPP GWB brine
- **Heat brine in vacuum oven and sample periodically**
- **Analyze Liquid**
  - Ion Chomatography (IC)
  - Ion Coupled Plasma-Optical Emission Spectrometry (ICP-OES)
- **Analyze Precipitants**
  - X-ray Fluorescence (XRF)
  - Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDS)
  - IC and ICP-OES of redissolved precipitated solids
- **Complexities**
  - High dilution required for liquids
  - Need to cross section solids for internal composition on SEM-EDS

Modeling Methodology: EQ3/6

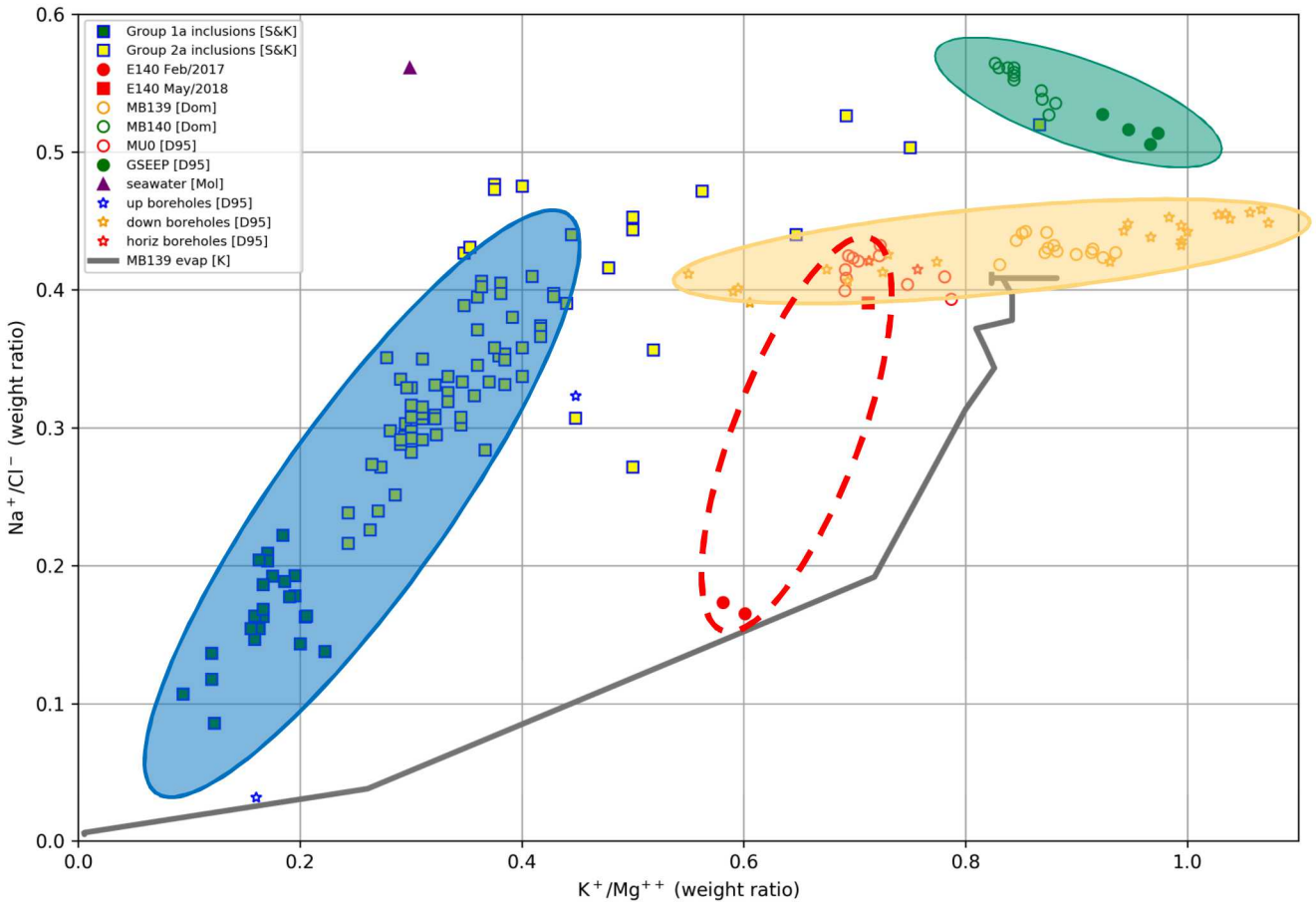




- **EQ3/6 is a geochemical simulator with Pitzer capabilities being used to predict:**
  - Evolution of brine during evaporation
  - Precipitant expected in the heated borehole
  - Better understand contributions from each possible brine components present in the salt
- **Laboratory experiments provided validation datasets for modeling of brines under controlled experimental conditions at a range of relevant temperatures**
- **Outcomes of the model were displayed as:**
  - Mass ratio plots of various elements
  - Degree of evaporation based on conservative ions (Li^+, Br^-, Mg^{++})

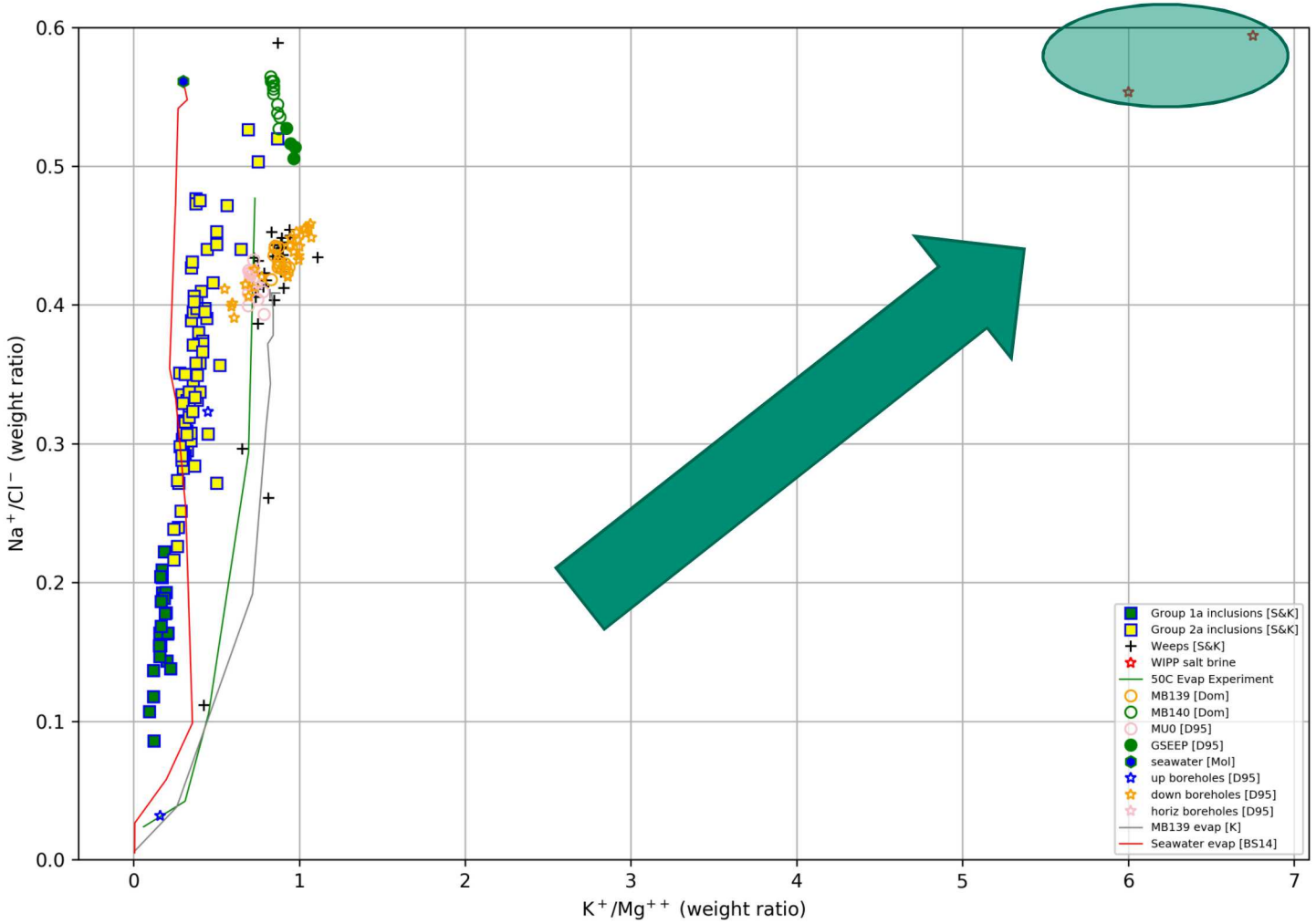
Previous Brine Studies

- **Many studies related to the evaporation of seawater, but few on the evolution of WIPP brines or brines of similar composition**
- **Experimental methodology similar to approaches by Krumhansl et al (1991) and McCaffery et al (1987)**
- **Krumhansl et al (1991):**
  - Analyzed composition of various WIPP brines from different locations and marker beds
  - Conducted an evaporation study with sourced WIPP brine over seven months
    - However, humidity and temperature were not measured or controlled, and certain aspects of the experiment are unclear



Blue = WIPP fluid inclusions
Yellow = near Marker Bed 139
Green = near Marker Bed 140
Red = Recent samples from drift borehole
Gray = Krumhansl evaporation experiment

Brine from Dissolved WIPP Salt?



- Attempted a simple approach to dissolve WIPP salt in DI water until saturated
- Dissolved WIPP salt is not the same as brine collected at WIPP
  - SO_4^{2-}, K^+, Mg^+ & Br^- : too low
  - Na^+ & Cl^- : too high

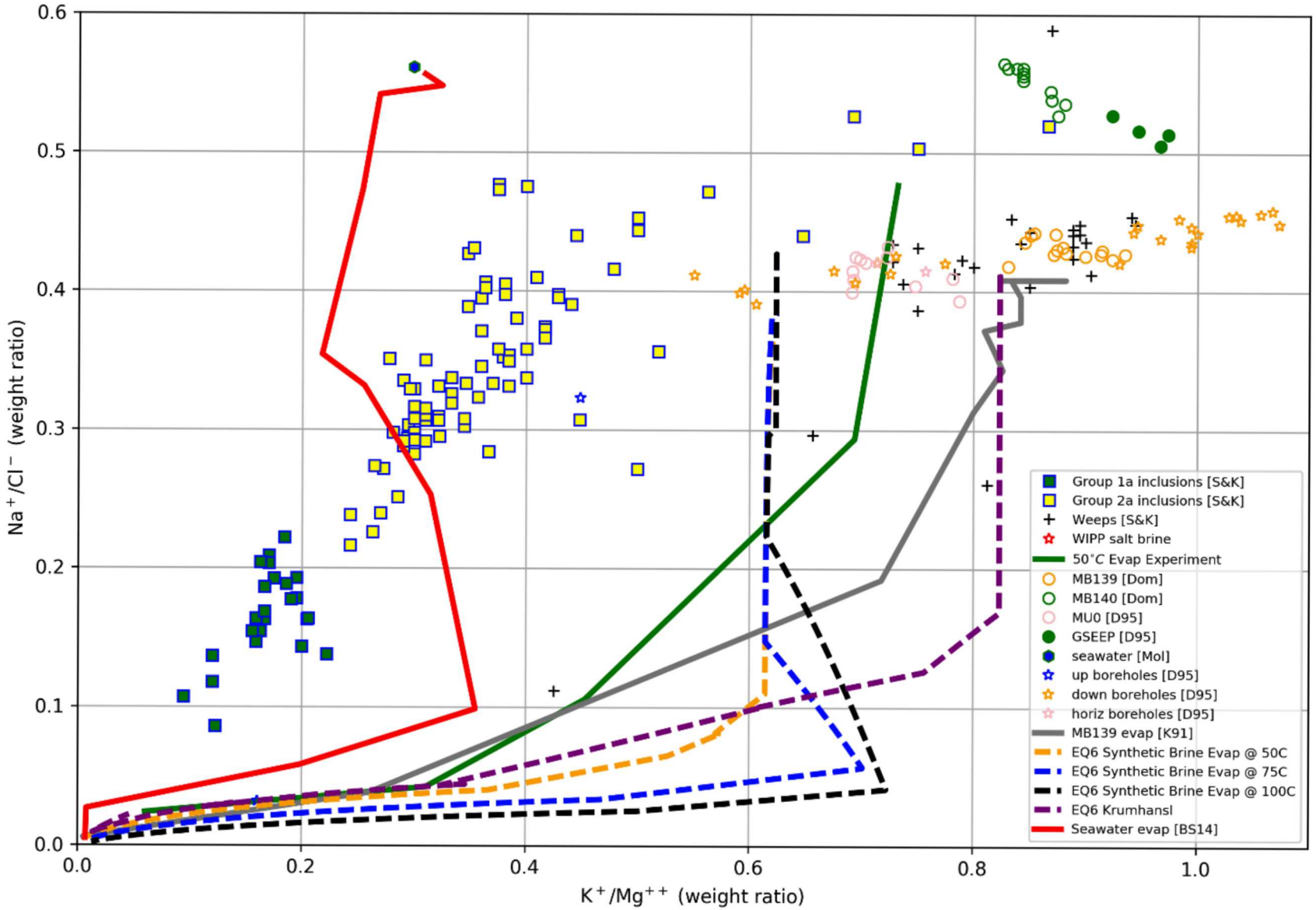
- **Takeaway:** Can see differences in brine sources from analysis!

Modified Synthetic Brine

- Followed an existing approach and recipe from Xiong, 2008 to create a G-Seep WIPP brine
- Used different proportions of salts to math the expected MU-0 brine better

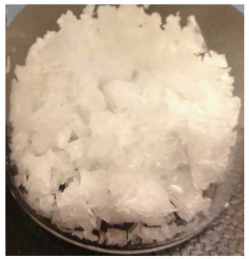
Salt	g/L solution GWB (Xiong, 2008)	g/L solution MU-0 brine
NaCl	179.61	177.08
KCl	34.84	29.45
LiCl	0.19	0.21
$Na_2B_4O_7*10(H_2O)$	15.06	12.91
$CaCl_2*2(H_2O)$	2.03	1.04
NaBr	2.74	1.96
$MgCl_2*6(H_2O)$	207.05	180.44
Na_2SO4	25.23	24.02

Results: Evaporation Studies with Model Predictions

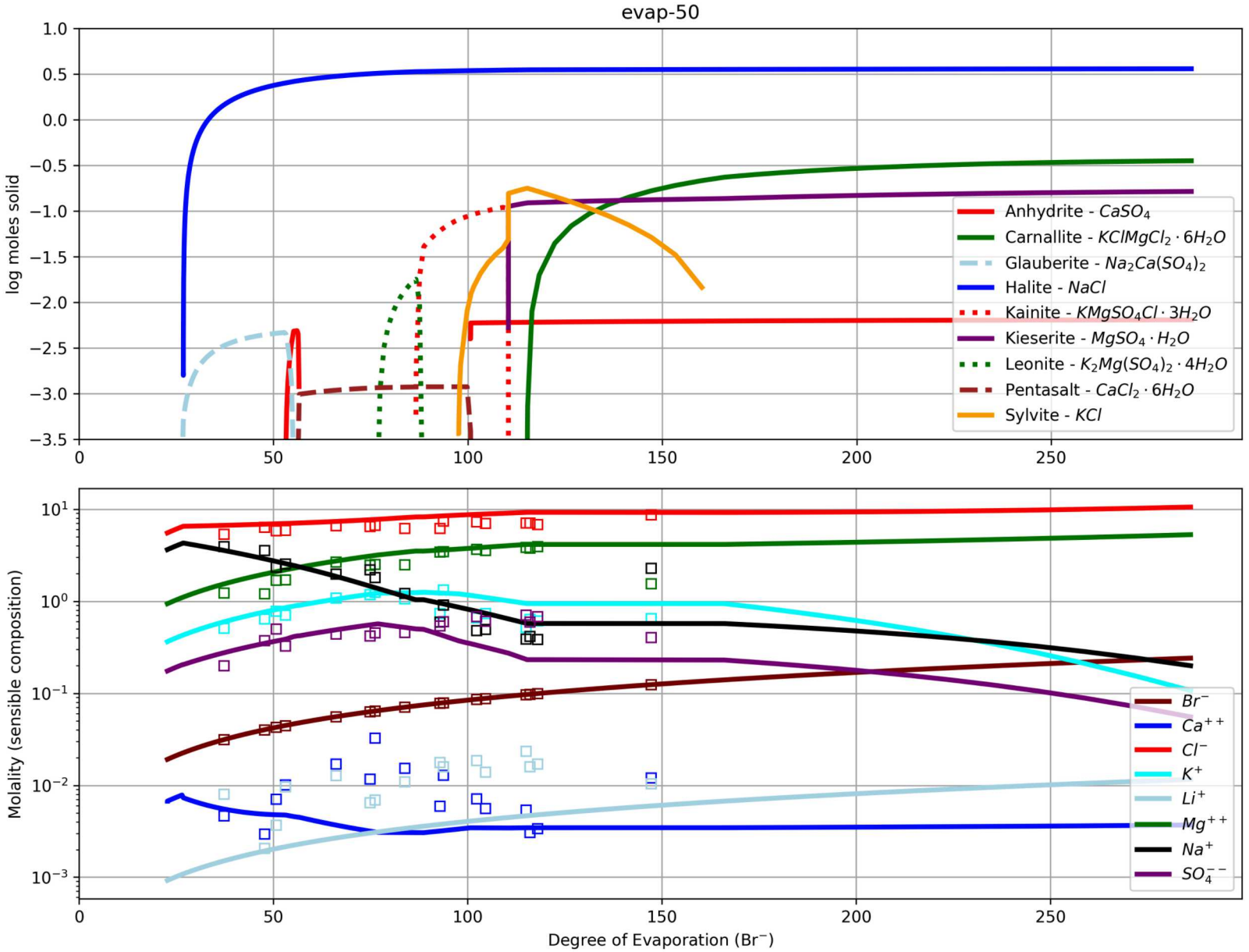


Results: EQ3/6 Predictions for 50°C Evaporation

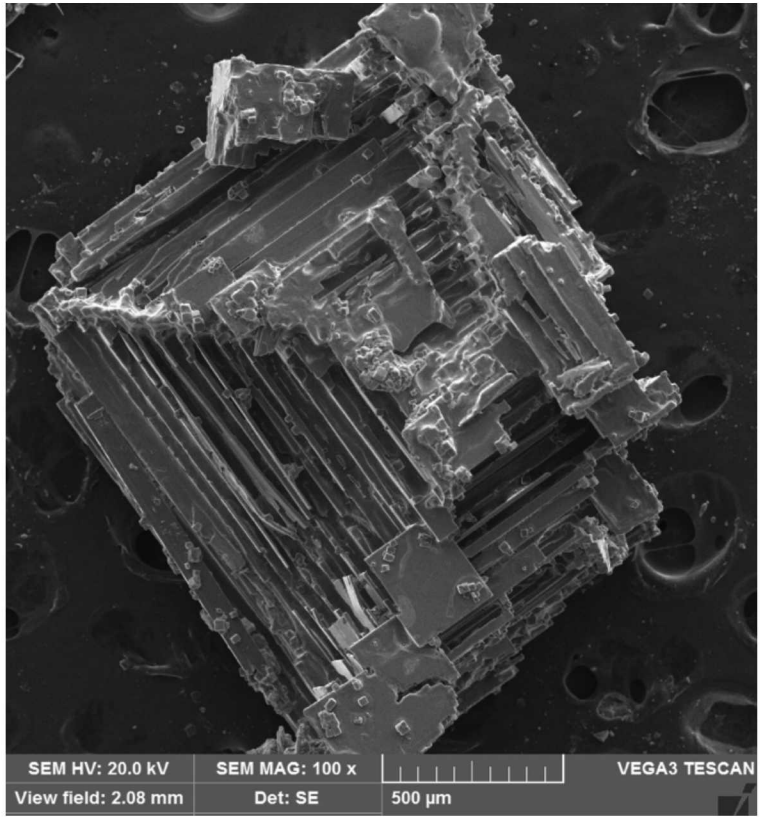
Solids



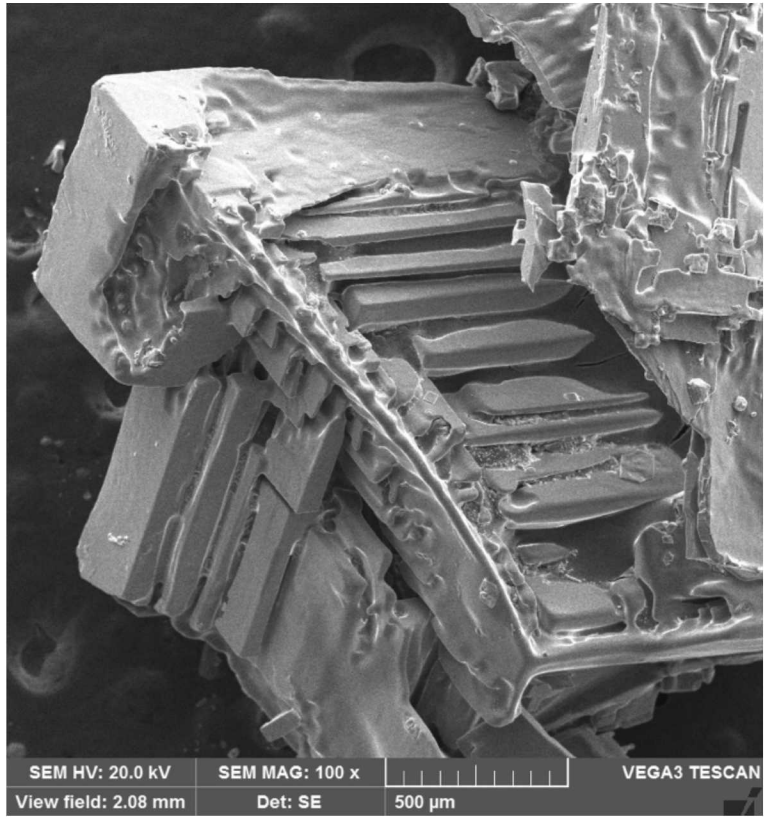
Liquid



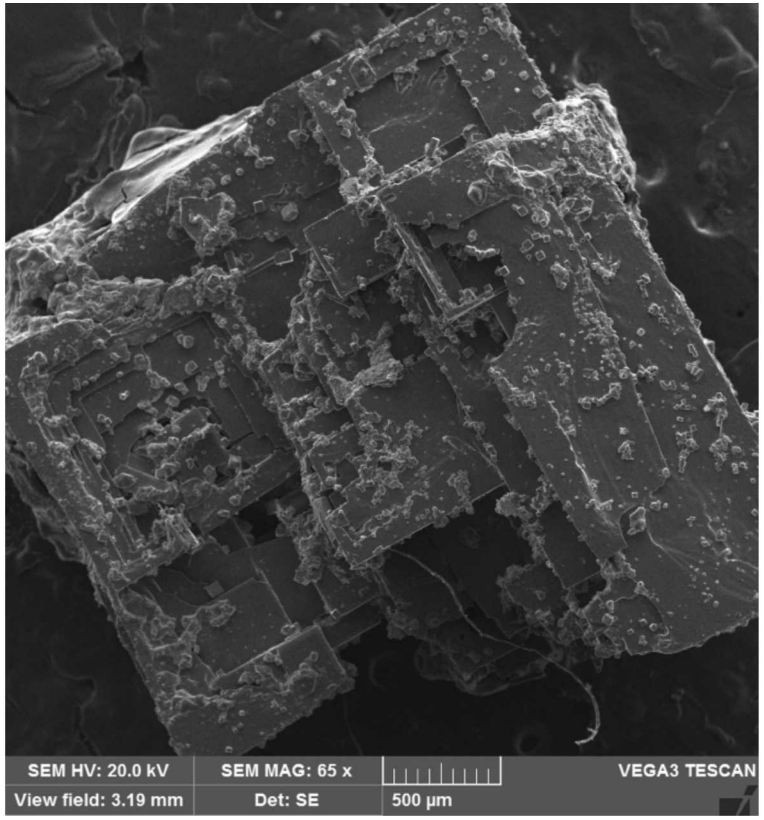
Results: SEM



50°C



75°C



100°C

Future Work

- Multiple quantitative comparisons will be made between modeling results and laboratory data to improve simulations and accuracy, and better understand the geochemical systems
- Mineral phases observed in experiments will be further investigated and compare quantitatively to predicted phases at all three temperatures.
- Quantify and assess the importance of uncertainty of both laboratory measurements and numerical model predictions.
  - Helps identify the level of match expected between numerical model and field observations, given their inherent uncertainties
- Collect and analyze field samples during the borehole field test for their composition and degree of evaporation
- Effort into estimating pH accurately, and possible measurements of specific gravity and electrical conductivity