



U.S. Department of Energy  
Office of Civilian Radioactive Waste Management



# The In-Drift Chemical Environment During the Below-Boiling Period

Presented to:  
**Nuclear Waste Technical Review Board**

Presented by:  
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  - ◆ Greg Gdowski, Lawrence Livermore National Laboratory
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- **Thermal-Hydrologic-Chemistry evolution**
  - ◆ Nic Spycher, Lawrence Berkeley National Laboratory
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# Board Comments on Seepage Chemistry

- ***“The DOE’s analyses of water chemistries and their corrosive potential are extremely complex and suffer from empirical and theoretical weaknesses. Thus, the Board does not have a high degree of confidence in the DOE’s conclusion that any seepage water would be dilute or noncorrosive, because the methods used in the DOE’s analyses have significant technical uncertainties.”***  
**(Executive Summary, p. ii)**
- **In response to the Board, we present an overview of the processes affecting seepage water and evaporated brine chemistry and provide a high-level description of how these processes are addressed.**



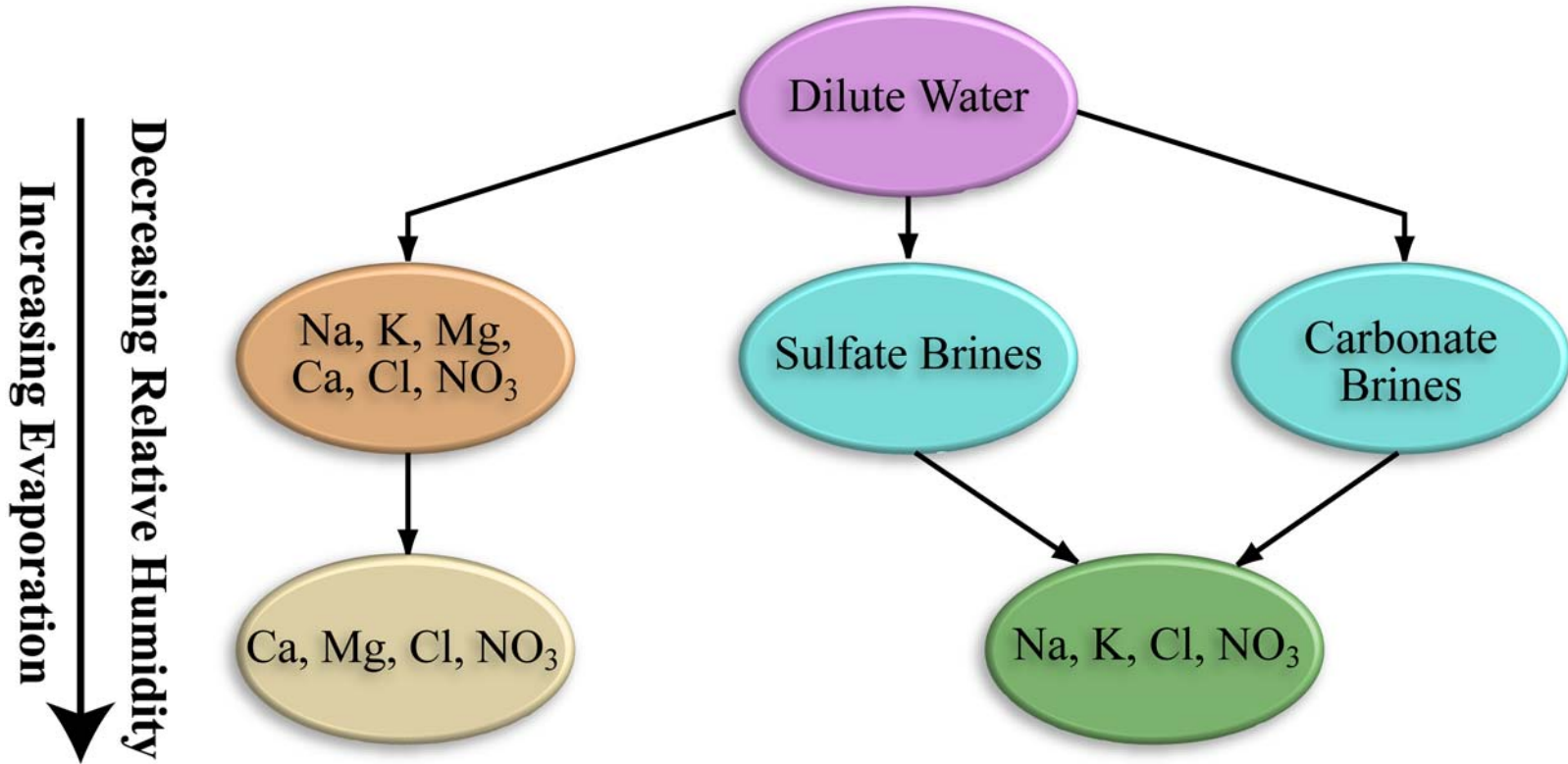
# Overview of Presentation

- **Definition of the below-boiling period**
- **What processes affect the chemistry of solutions that could contact the waste packages?**
- **What is the natural variability of ambient pore fluid compositions and how will this variability affect in-drift chemistry?**
- **How does the Thermal-Hydrologic-Chemical (THC) evolution affect the composition of potential seepage?**
- **How does evaporation in the drift affect the chemistry of solutions that could contact the waste packages?**
- **How is chemistry coupled to the Time-Temperature-RH histories of the emplacement drifts?**
- **Conclusions**



# Purpose of Evaluating Chemical Evolution of Fluids

**Aqueous solution types affect Alloy 22 waste package corrosion differently**

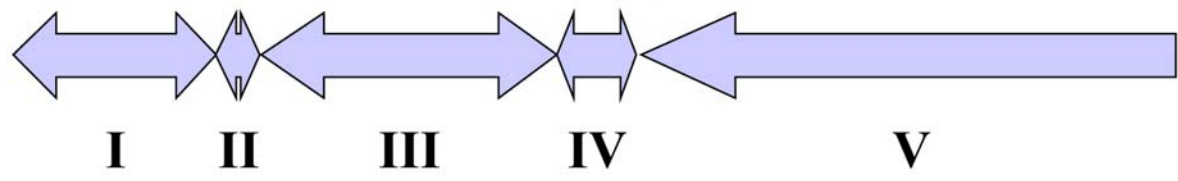
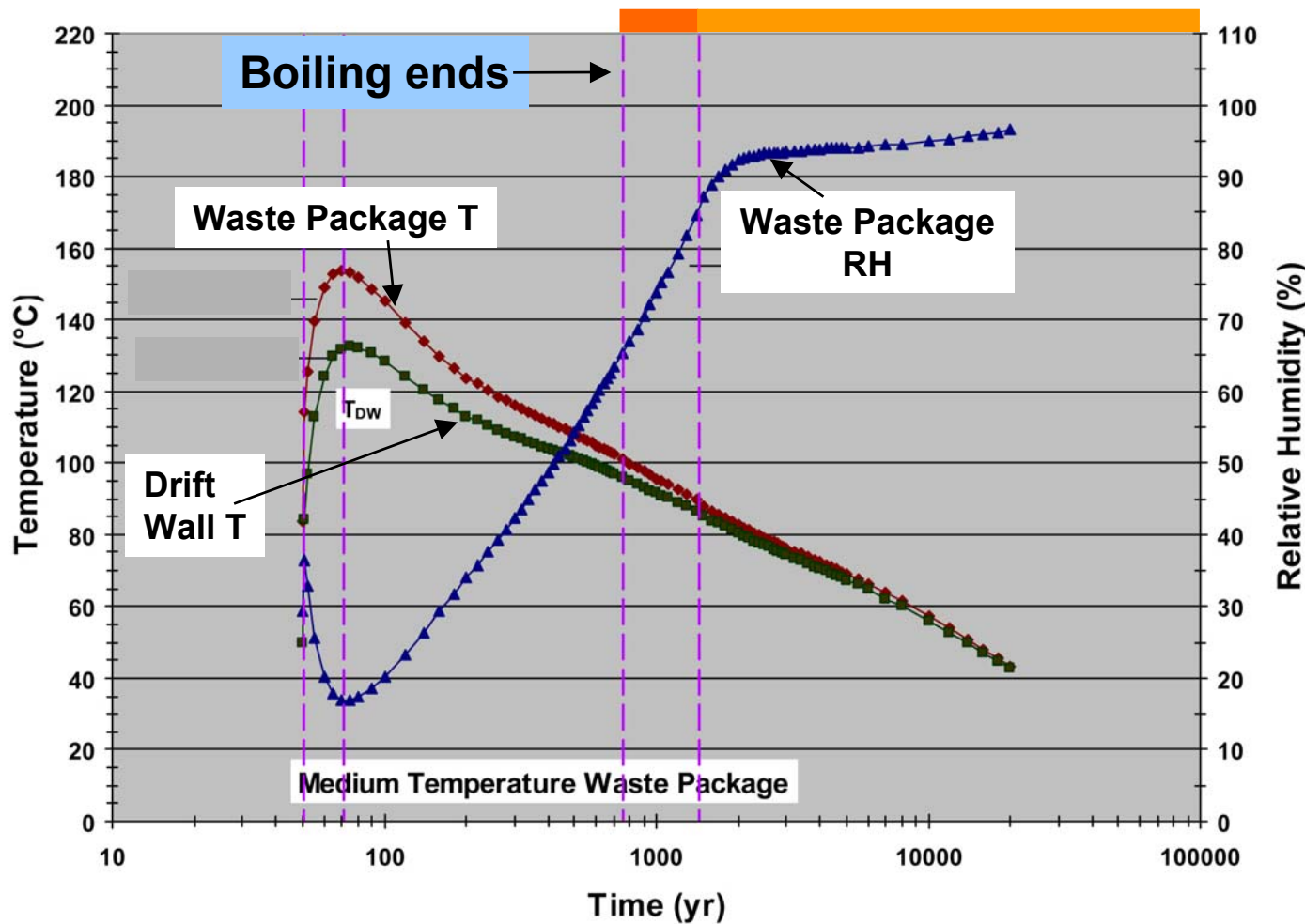


# In Which Cases Will the Chemistry of Seepage Water Be Relevant?

- **The chemistry of seepage water and its evaporative evolution inside the drift will be relevant only when seepage can occur**
  - **Seepage can only occur when the drip shield fails**
  - **Even in the absence of a drip shield, seepage can only occur in the case of a limited number of waste packages because of the efficiency of the capillary barrier**



# Definition of Below-Boiling Period



# What Processes Affect the Chemistry of Solutions in the Drift Environment?

- **Initial pore water chemistry**
- **Thermal-hydrologic-chemical (THC) processes in the rock**
- **Evaporative processes inside the drift**





# Variability of Pore Water Chemistry



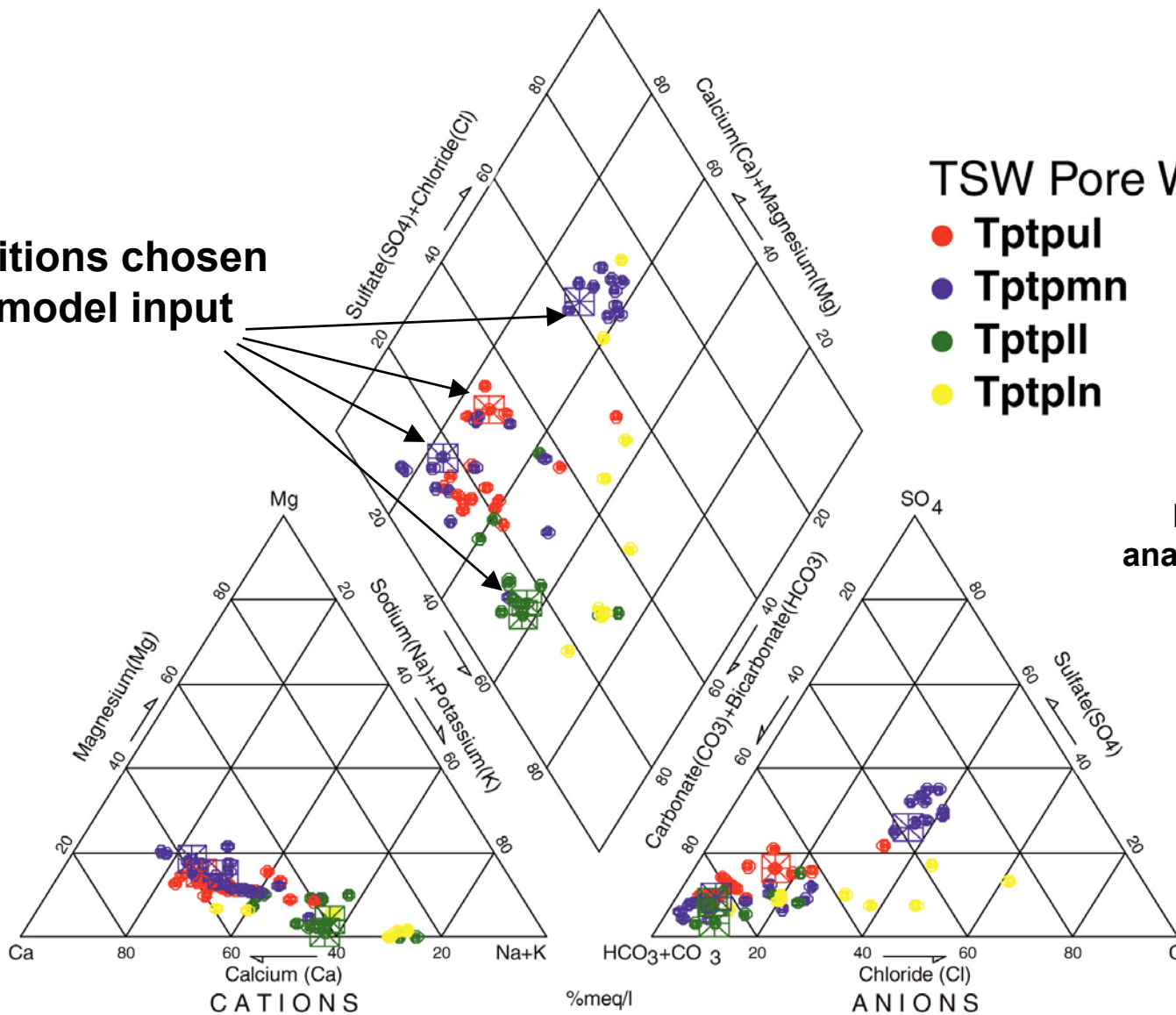
# What is the natural variability of pore water compositions in the ambient system?

- **Samples of pore fluids have been collected and analyzed from all potential repository units**
- **Pore waters show a substantial range of major cation proportions ( $\text{Ca}^{+2}$  and  $\text{Na}^{+}$ ) and important anions ( $\text{Cl}^{-}$ ,  $\text{NO}_3^{-}$ ,  $\text{SO}_4^{-2}$ ,  $\text{CO}_3^{-2}$ )**
  - **$\text{Ca}^{+2}$  generally becomes less abundant with depth due to calcite precipitation and ion exchange with  $\text{Na}^{+}$**
- **$\text{NO}_3^{-}/\text{Cl}^{-}$  ratios, important for metal corrosion, are variable**
- **Pore water compositions used as boundary/initial conditions for THC simulations span the range in the ambient system**

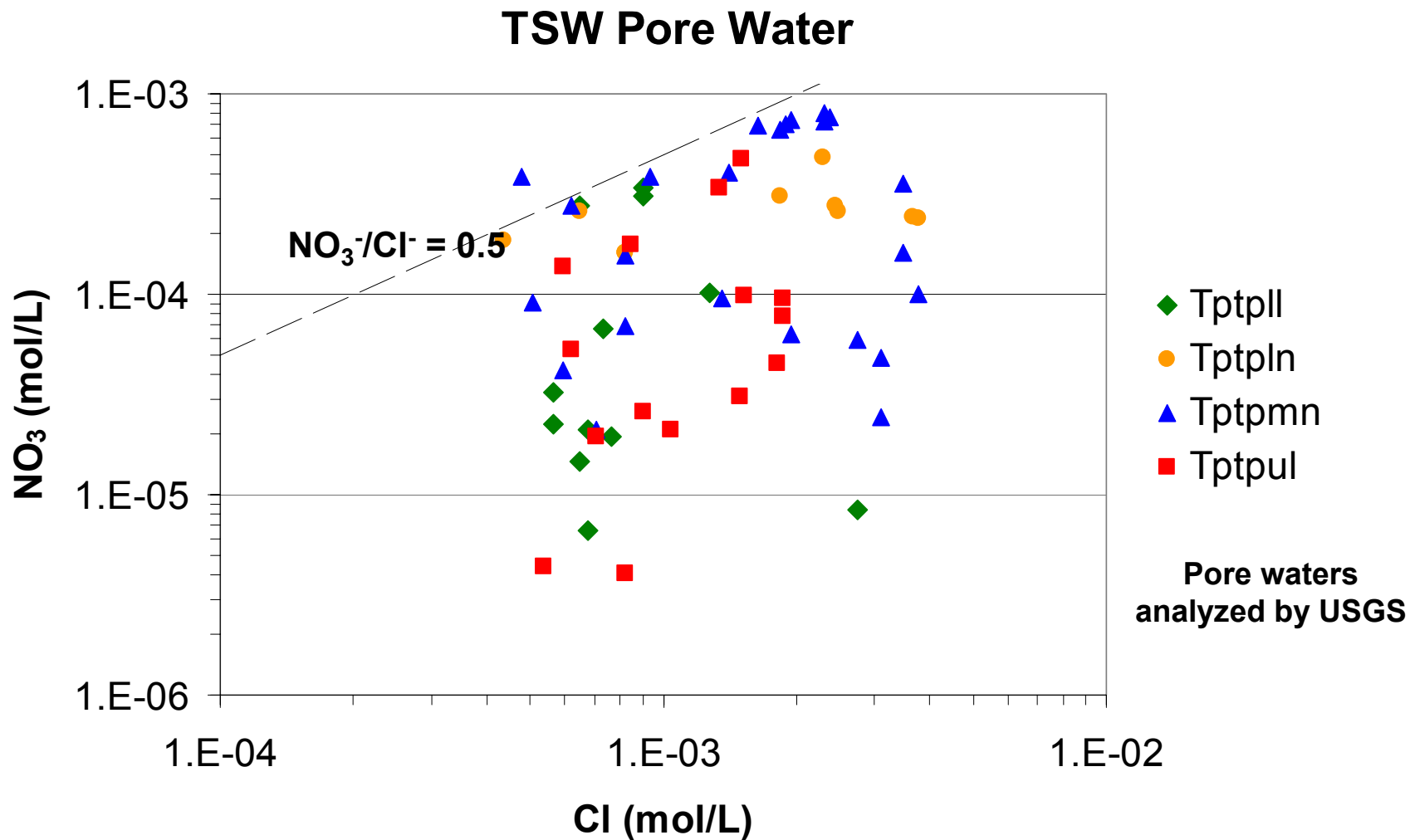


# Range of Pore Waters from Repository Horizons

Compositions chosen for THC model input



# Nitrate to Chloride Ratios in Pore Fluids



# Effect of THC Processes on Seepage Chemistry

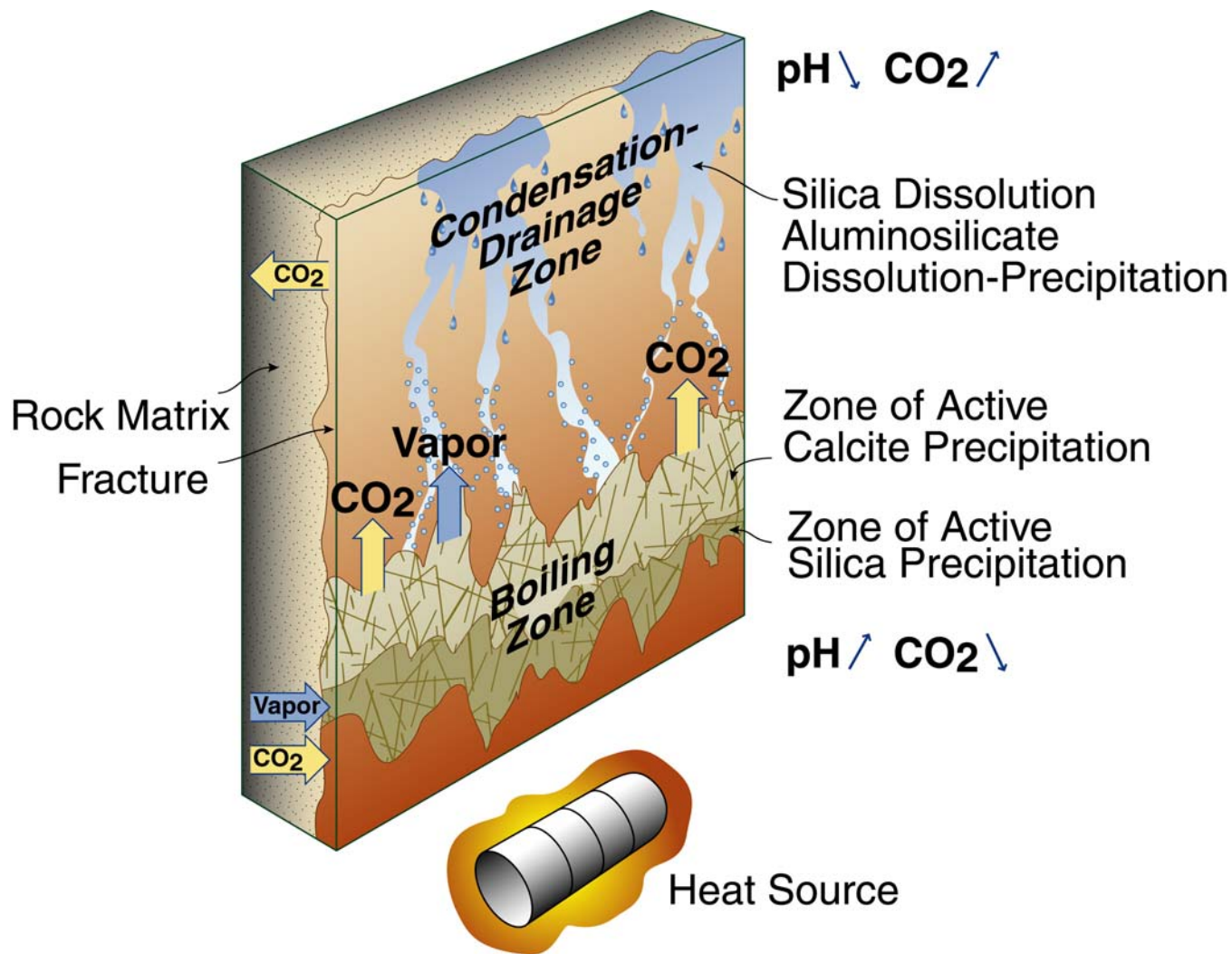


# Thermal-Hydrologic-Chemical (THC) Evolution of Fracture Fluids in the Rock

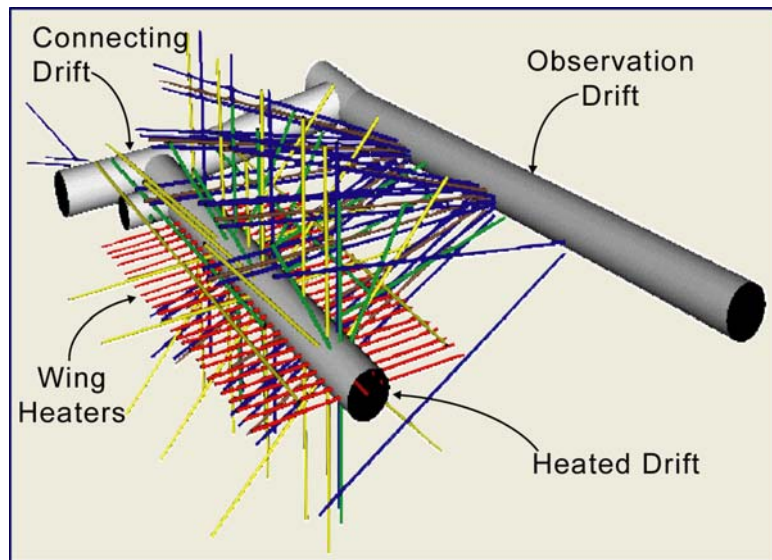
- **Purpose of THC modeling**
  - Propagate range of ambient pore water compositions through the THC processes to determine chemistry of potential seepage
- **Conceptual approach**
  - Capture coupled effects of solution-mineral-gas reaction, gas-liquid transport, and heat transport
- **Validation**
  - Drift-Scale Test
  - Laboratory experiments



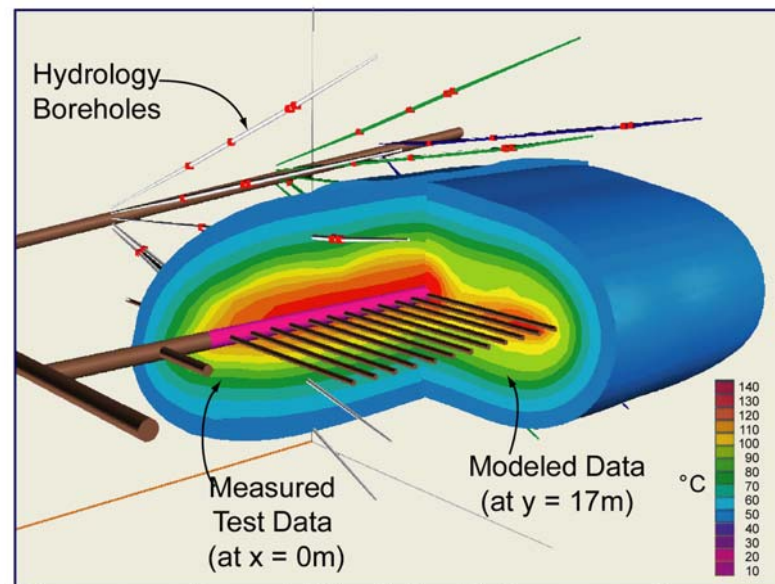
# Conceptual Model for THC Processes



# Model Validation - Drift-Scale Test



**Schematic of Drift Scale Test**



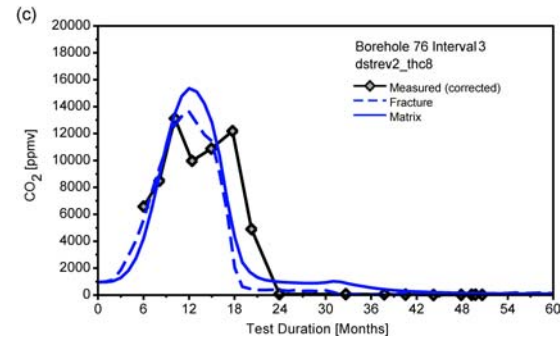
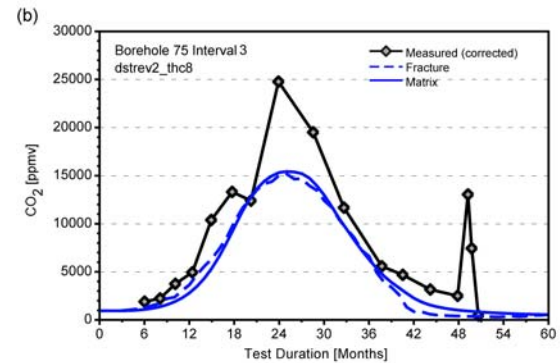
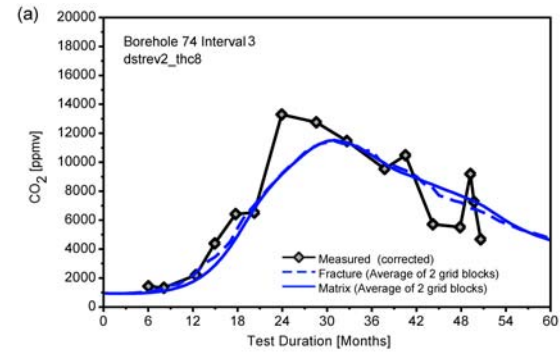
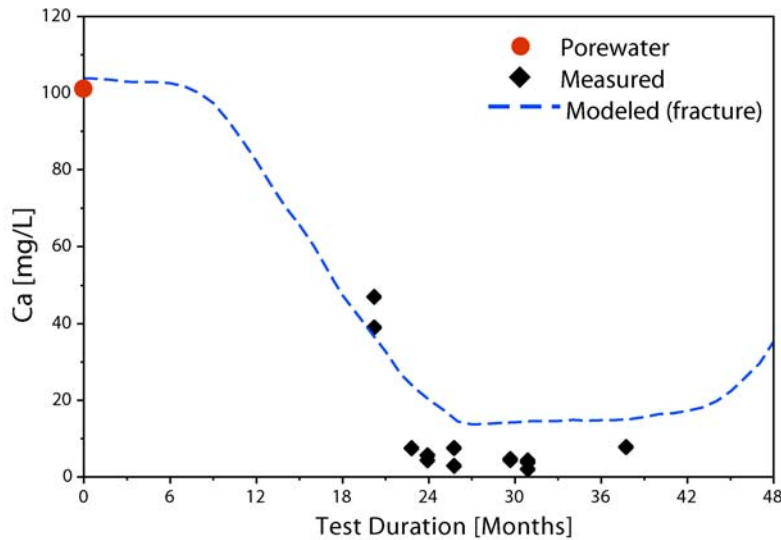
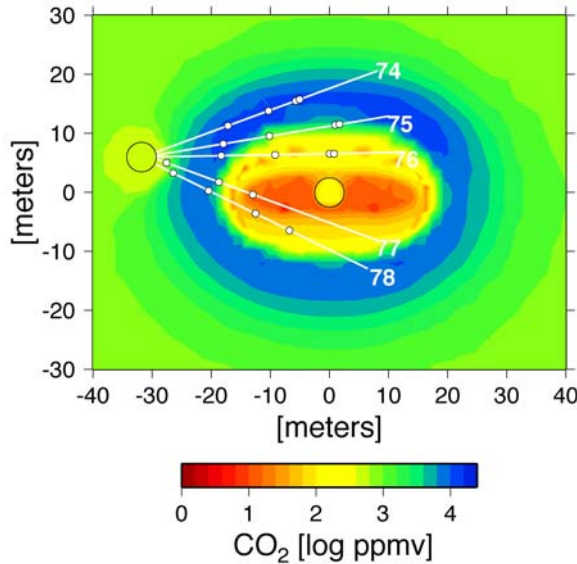
**Measured and Modeled Temperatures**



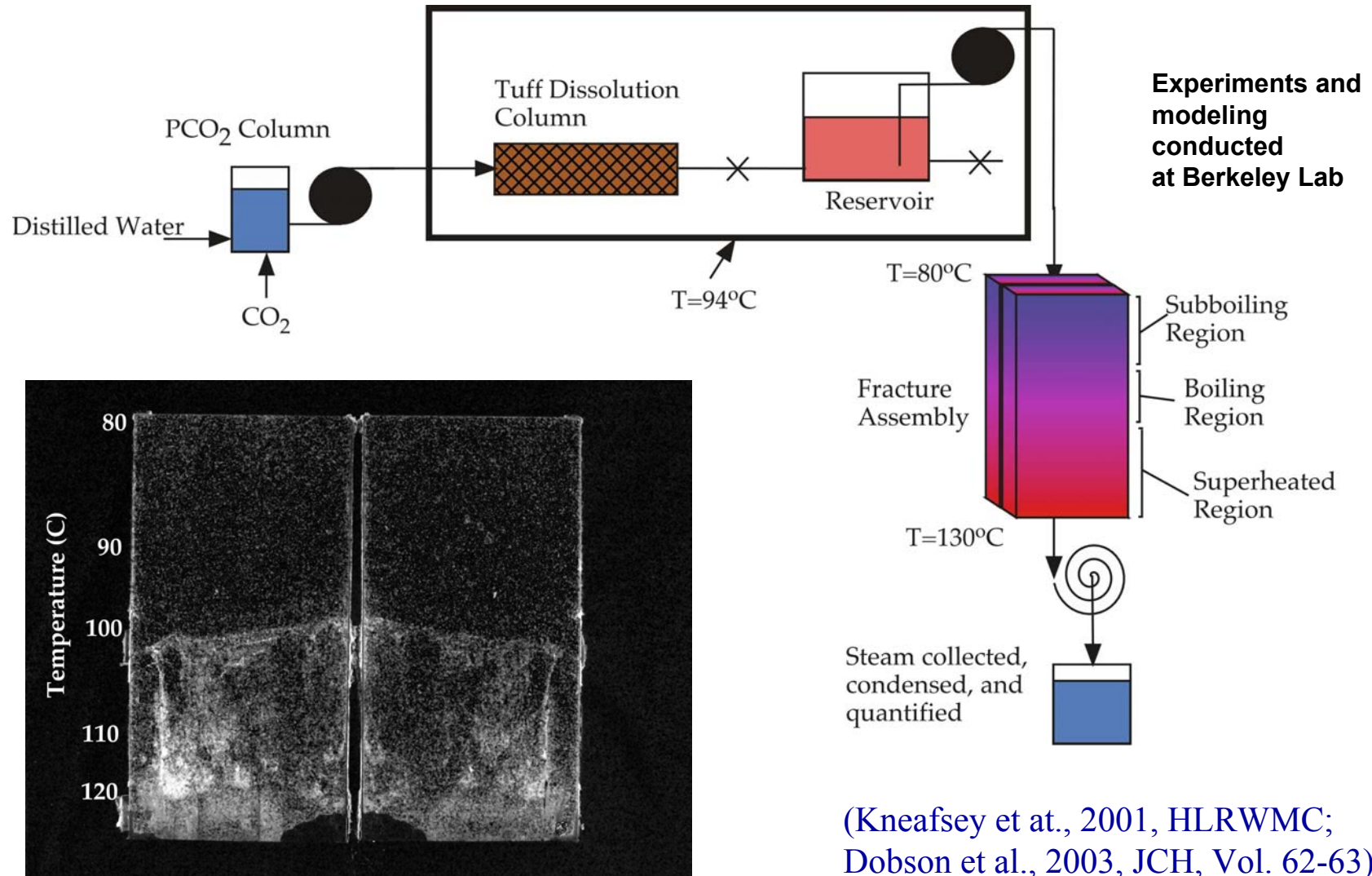


# Model Validation - Drift-Scale Test

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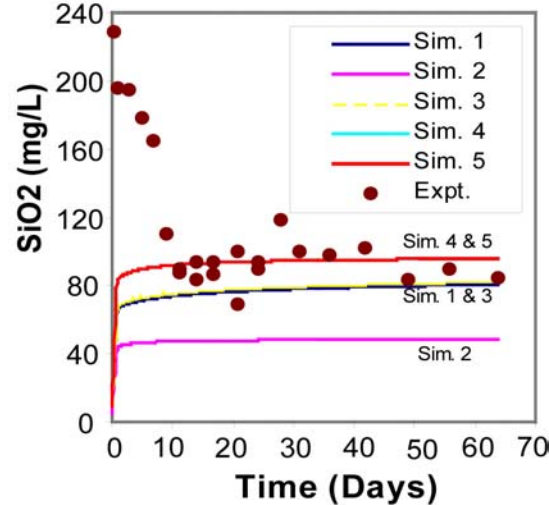
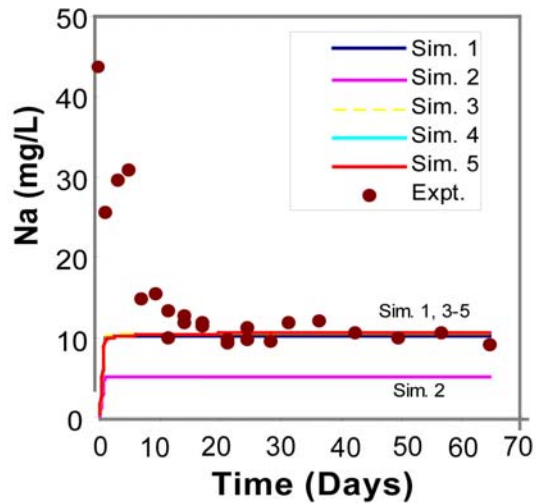


# Model Validation - Laboratory Experiments



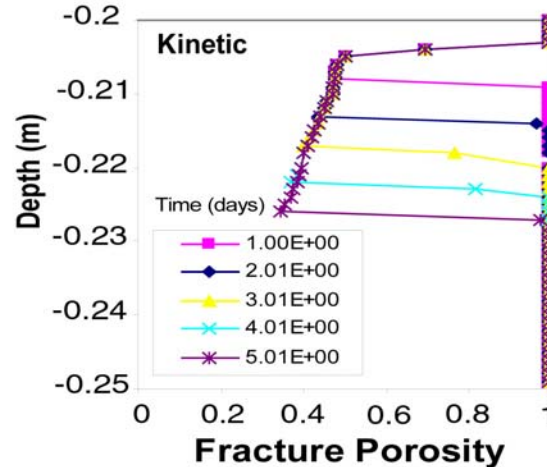
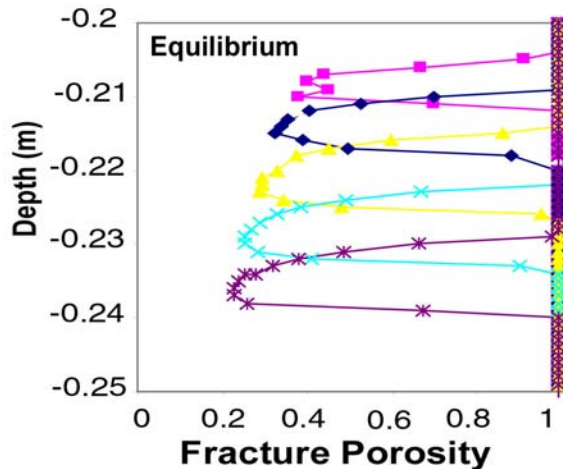
# Validation with Plug Flow Experiment

## Tuff Dissolution Plug-Flow Experiment



**Solution chemistry in effluent is captured with modeling**

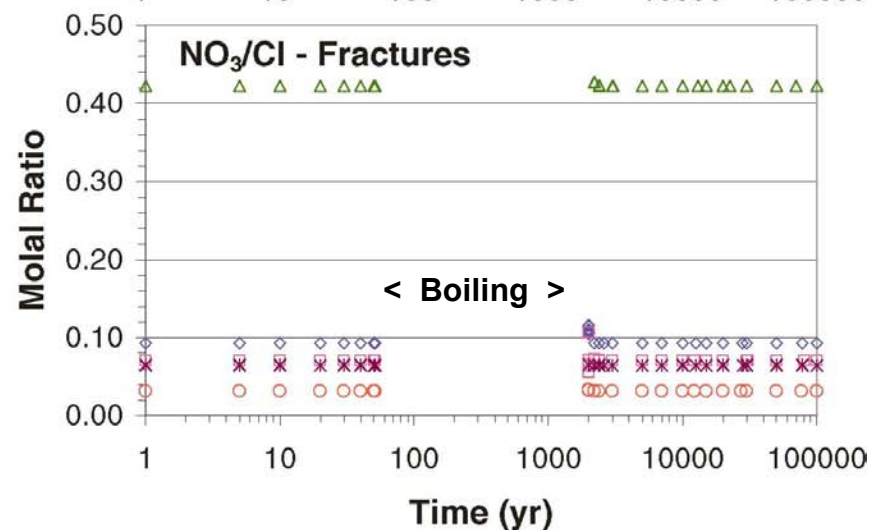
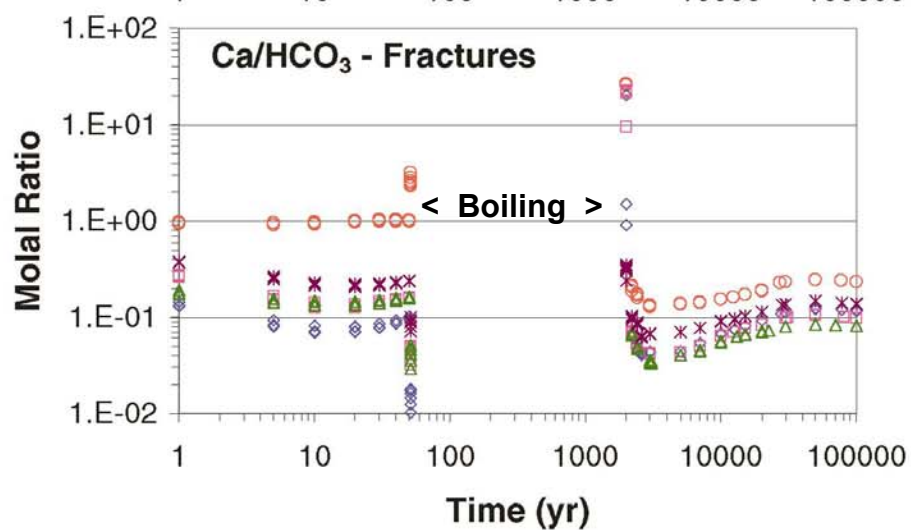
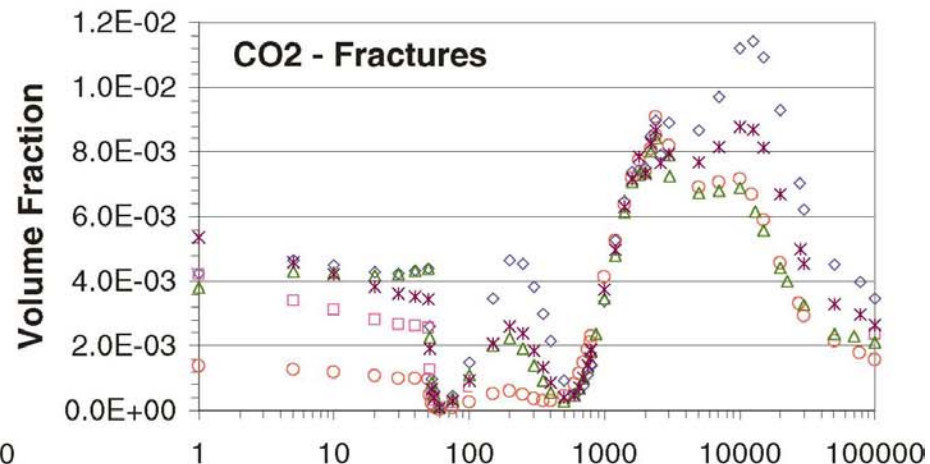
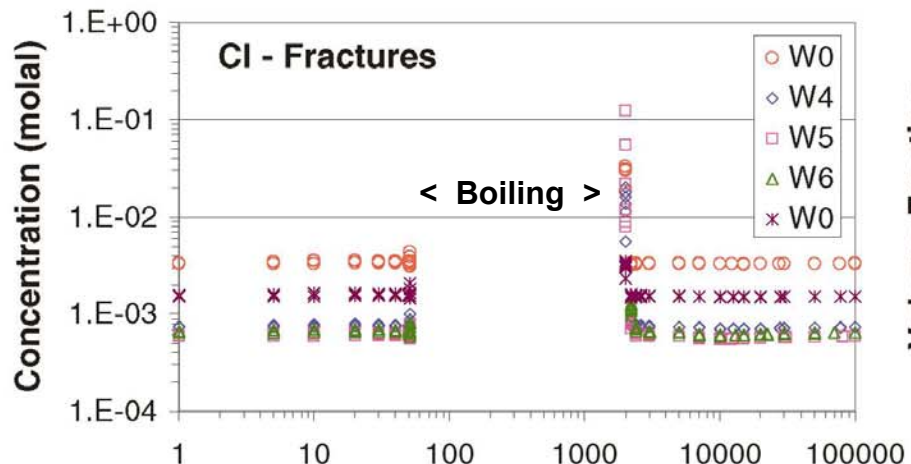
## Fracture Sealing Experiment



**Propagation of fracture sealing is captured with modeling**



# THC Model Predictions Provide Potential Seepage Compositions



# In-Drift Chemical Processes

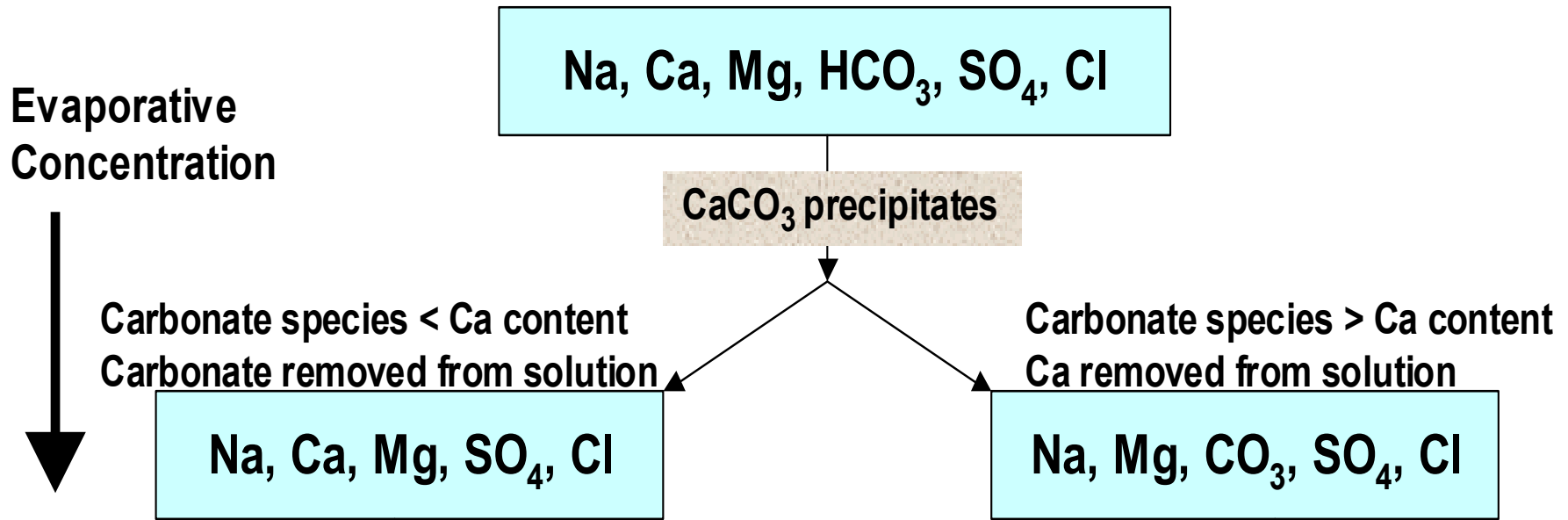


# What processes inside the drifts affect the chemistry of seepage fluids?

- **Temperature difference between drift-wall and waste package creates gradient in RH**
  - **Where seepage occurs, drift wall RH ~100%**
  - **Drips move to lower RH inside drift, driving evaporation and concentration of seepage water**
  - **Initial solution composition along with T and RH determine the reaction path**
  - **Concentration of fluids leads to mineral precipitation and depletion of solution in components**



# Evaporative Reaction Path Described with Chemical Divide Theory



# Integrated Approach to Evaluating Chemical Evolution of Fluids due to Evaporation

- **Experimental investigations**
  - Detailed evaporation studies of solutions
  - Literature data on salt solubilities and deliquescence
  - Heterogeneous studies of multi-phase salt systems
- **Modeling investigations**
  - Thermochemical model for multicomponent salt-brine systems
  - Pitzer database to deal with activity corrections at high ionic strength
  - Comparisons of model with data are used to validate the modeling approach

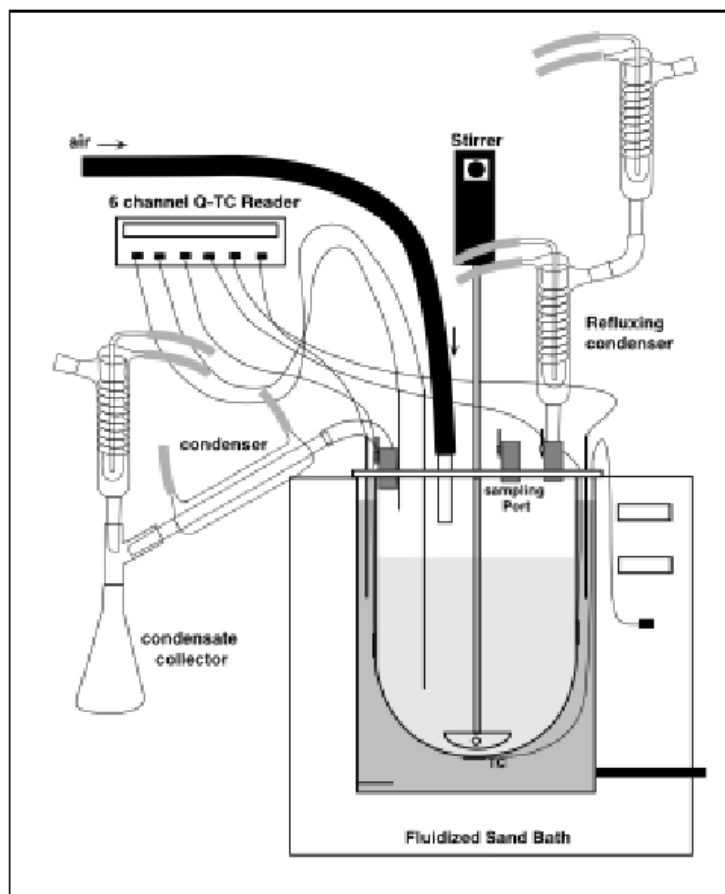




# Experimental Studies of In-Drift Chemical Processes

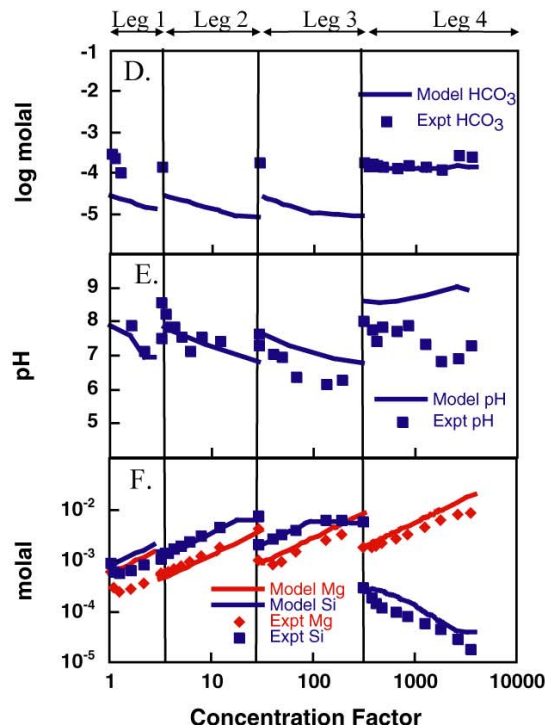
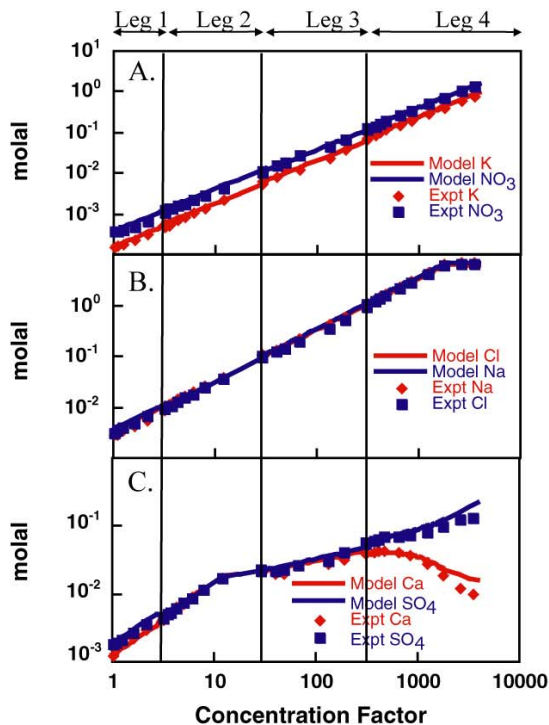


# Environmental Chamber for Evaporation Experiments

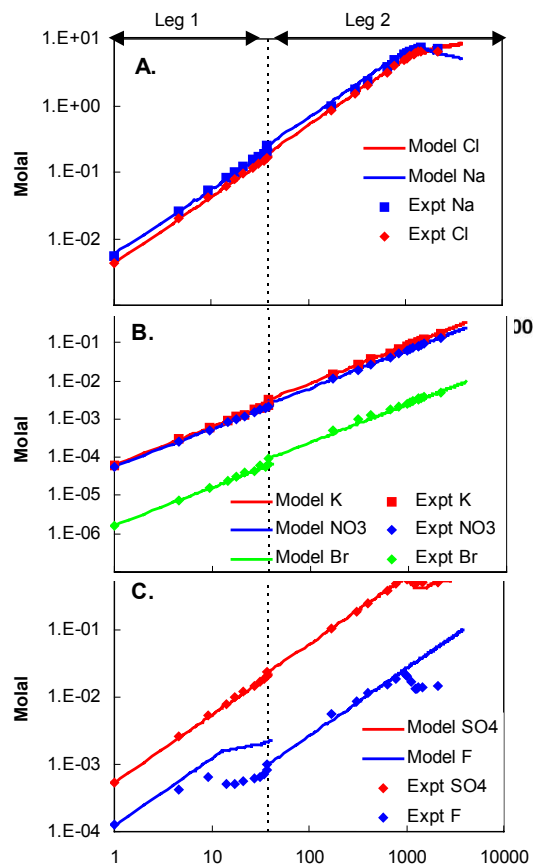


# Good Agreement Between Experiment and Model for the Evaporation at 95°C

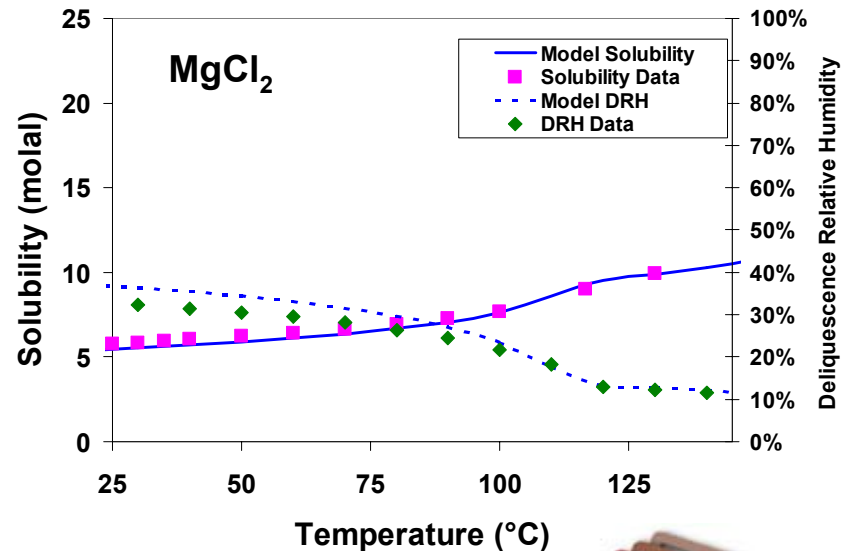
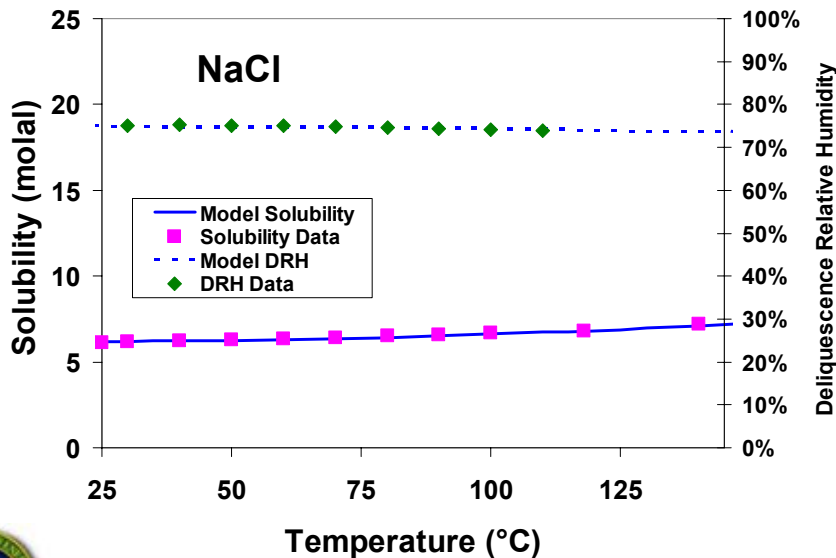
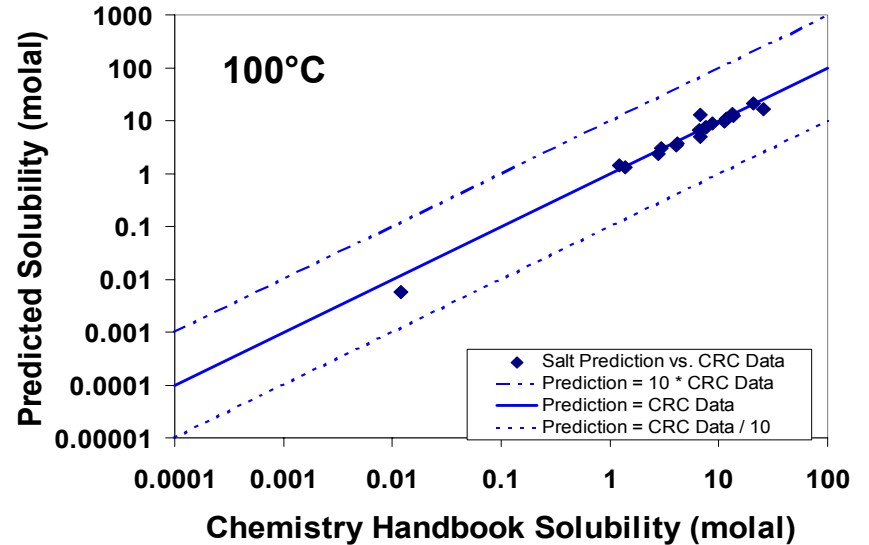
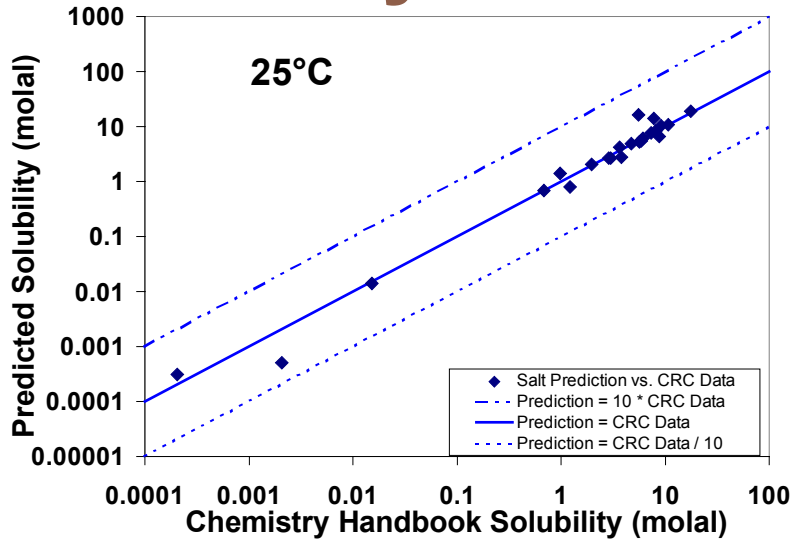
## Sulfate-type water



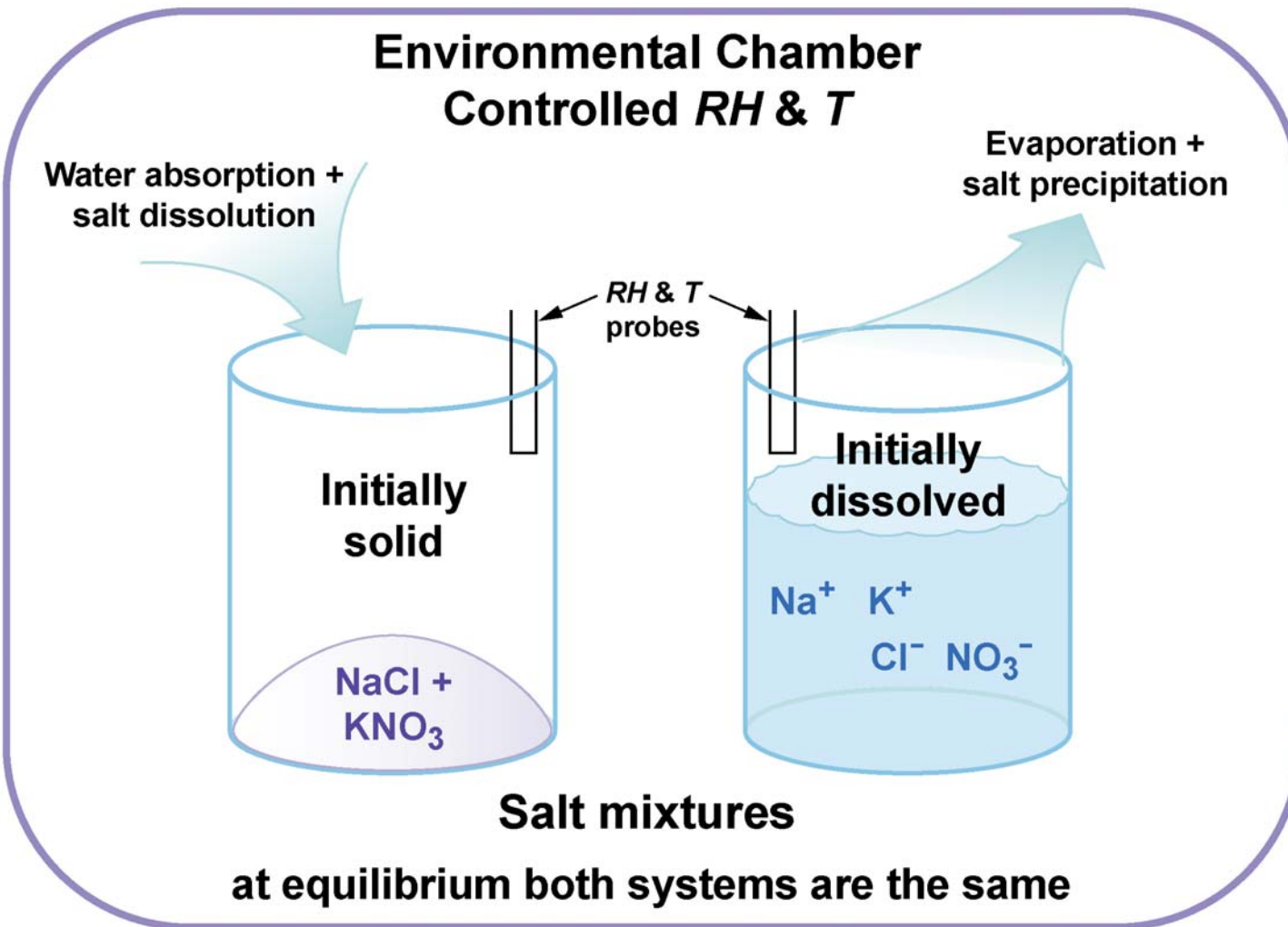
## Carbonate-type water



# Comparison of Evaporative Model Against Solubility Data at Various Temperatures

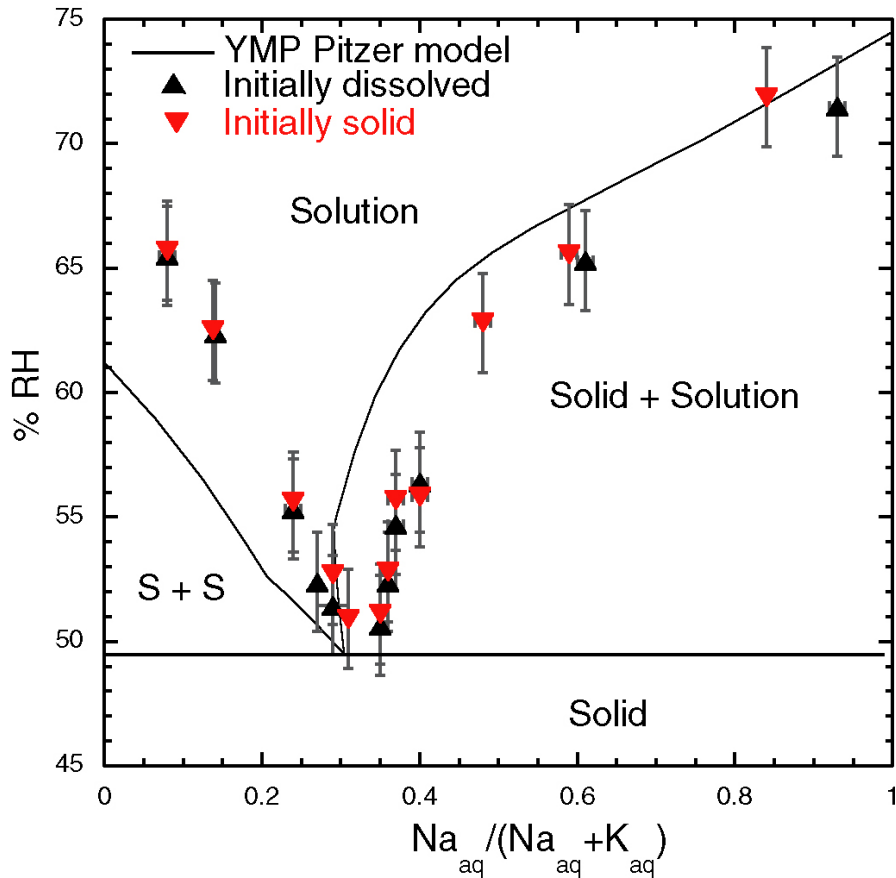


# Approach to Investigating Multicomponent Salt Systems

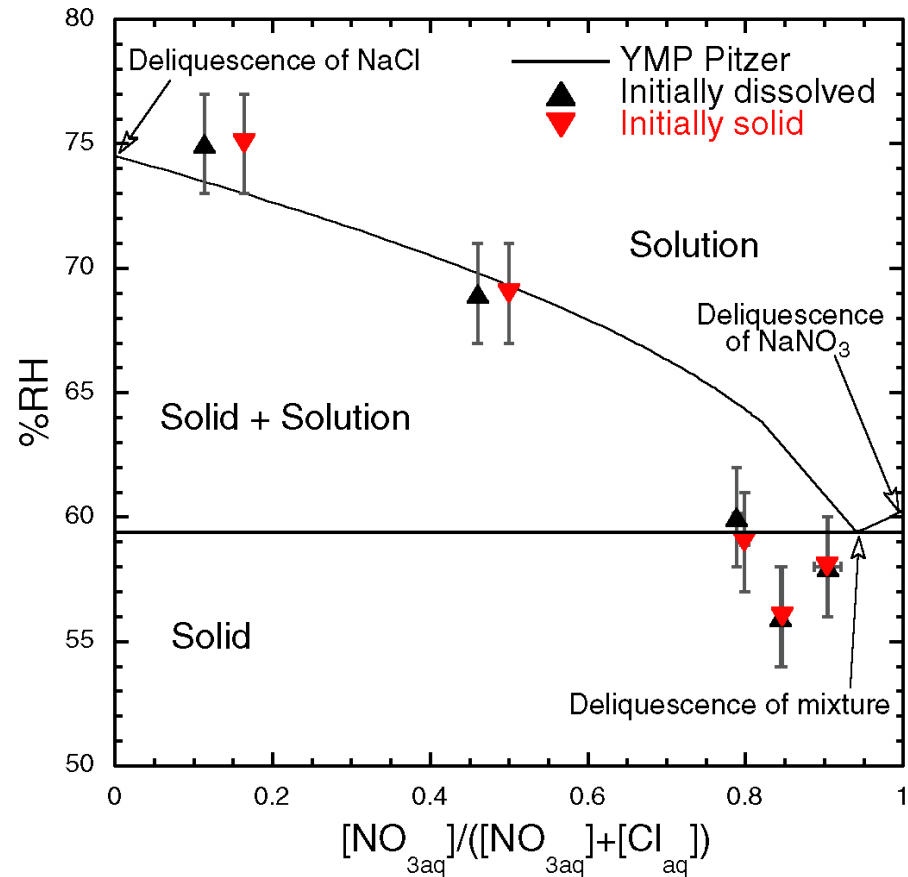


# Validation of YMP Thermochemical Model at 90°C

## NaCl-KNO<sub>3</sub>



## NaCl-NaNO<sub>3</sub>



# Key Results of In-Drift Chemistry Analyses



# Summary of Key Results

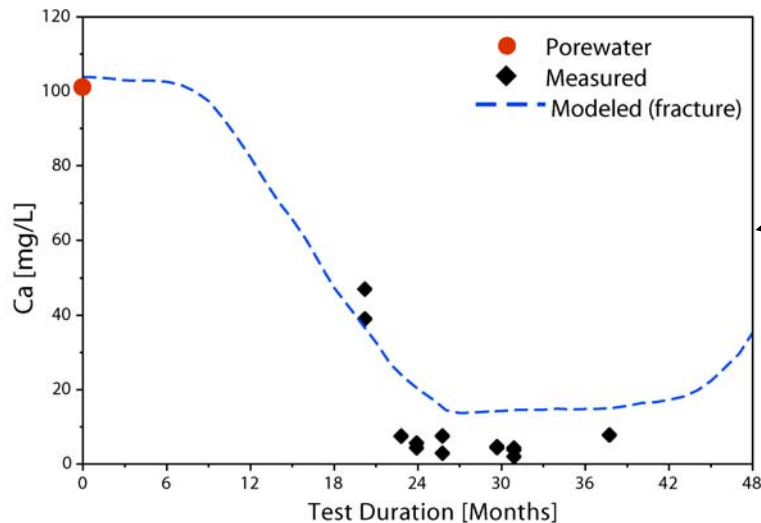
- **CaCl<sub>2</sub> brines unlikely to form during below-boiling period**
  - Dilution and mineral reaction associated with THC processes in the rock reduce Ca<sup>+2</sup>
  - Ca<sup>+2</sup> further reduced during evaporation by mineral precipitation
- **Evaporation of seepage water leads to very large decreases in fluid mass**
- **Time-Temperature-RH histories for drifts coupled to evaporative chemical evolution**





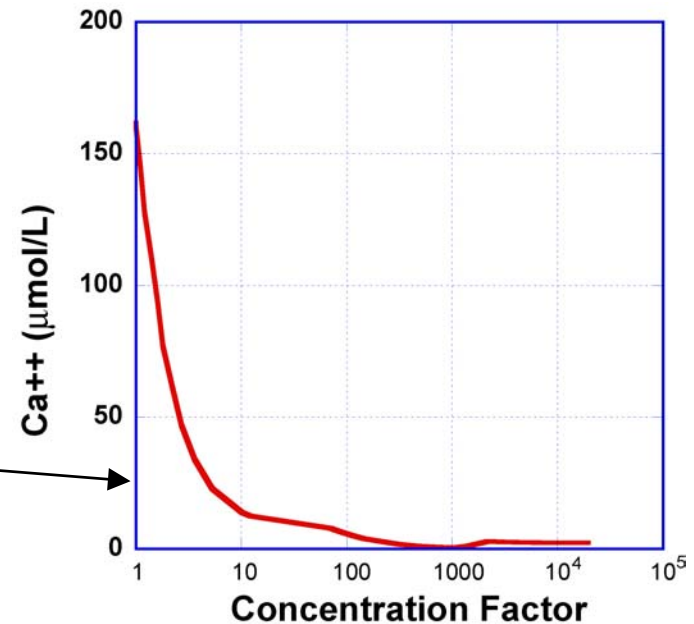
# CaCl<sub>2</sub> Seepage Brines Unlikely to Form

## Borehole 59—Drift Scale Test

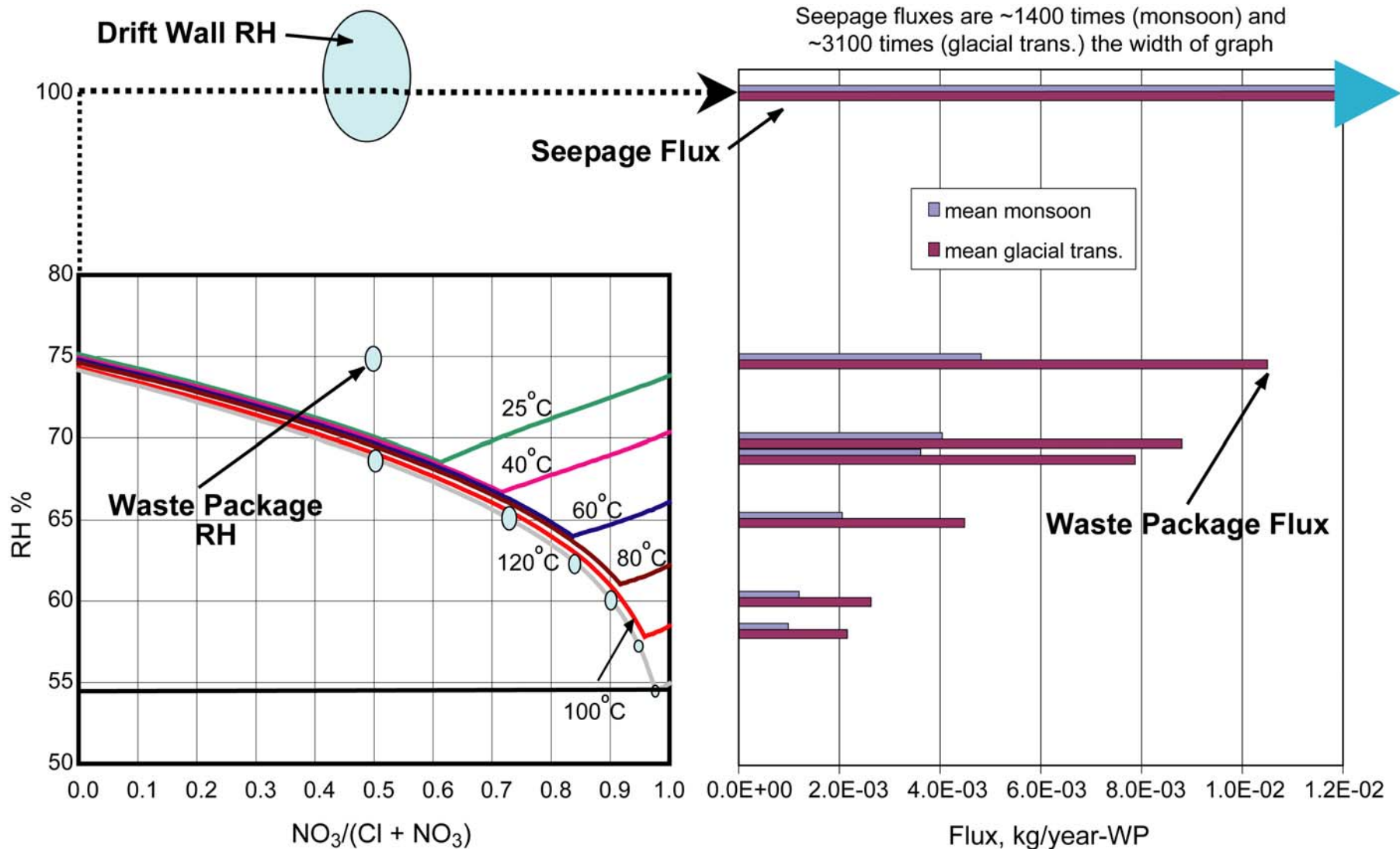


**Ca<sup>2+</sup> decreases in potential seepage fluid due to dilution and mineral precipitation**

**Ca<sup>2+</sup> decreases further due to mineral precipitation (especially calcite and fluorite) during evaporation**

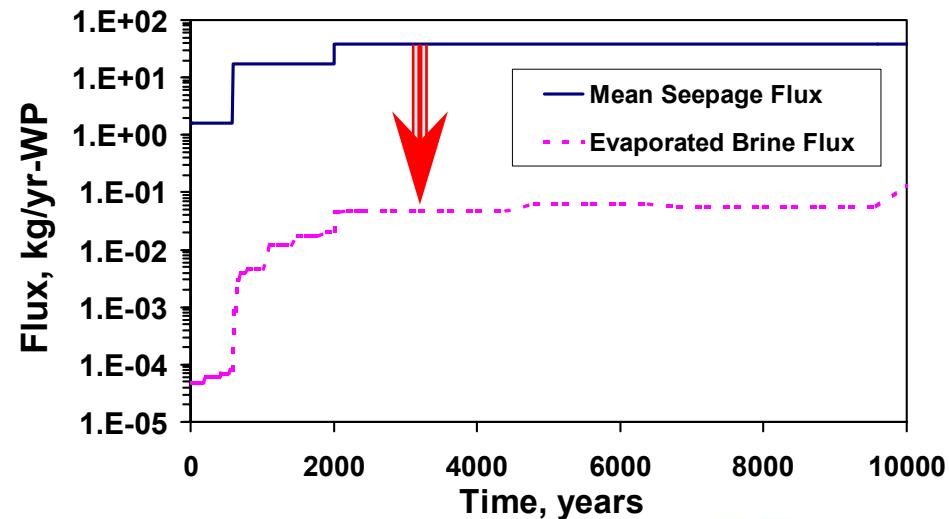
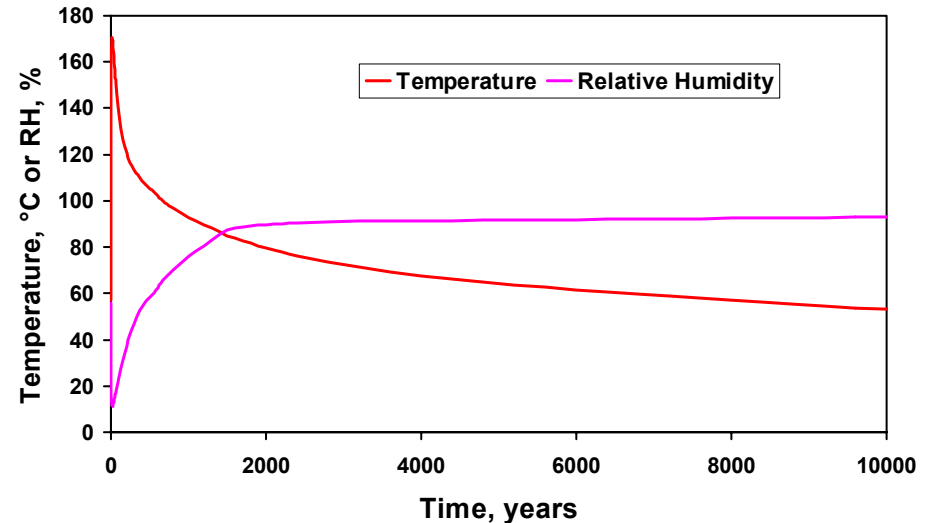


# Evaporation Vastly Reduces the Fluid Mass

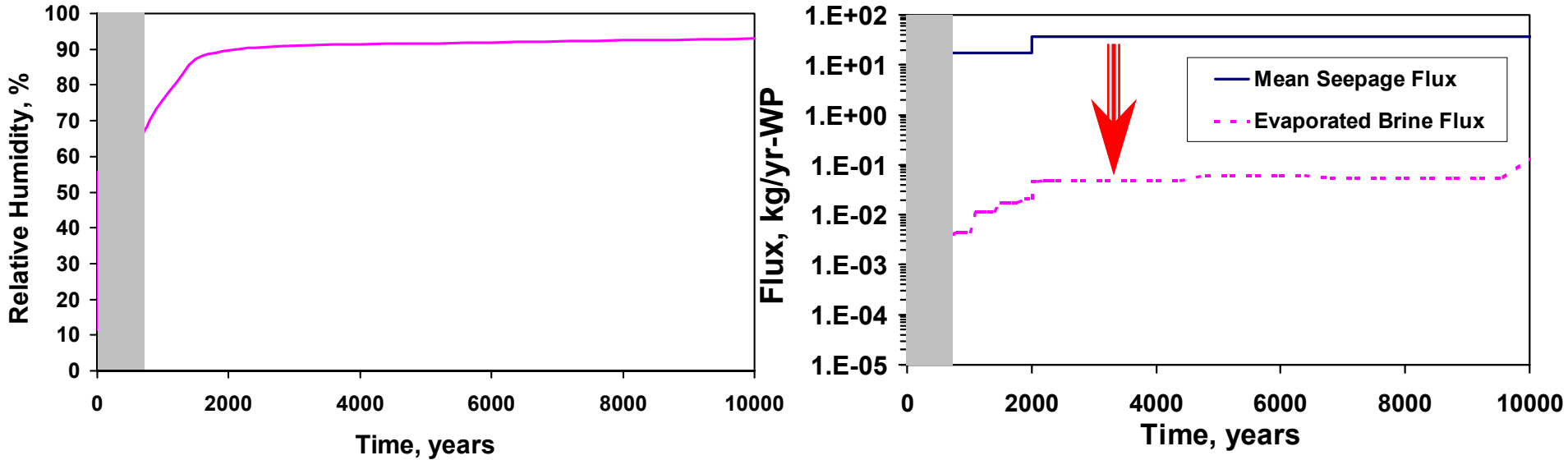


# Evaporation Reduces Fluid Fluxes Through Time

- Calculate the evaporative fluid mass reduction using the waste package history
  - RH is dominant control
- Seepage fluids evaporate extensively, leaving only ~1/500 to 1/10,000 of the original fluid mass
- Evaporated brine flux is ~1 - 100 grams/yr-WP



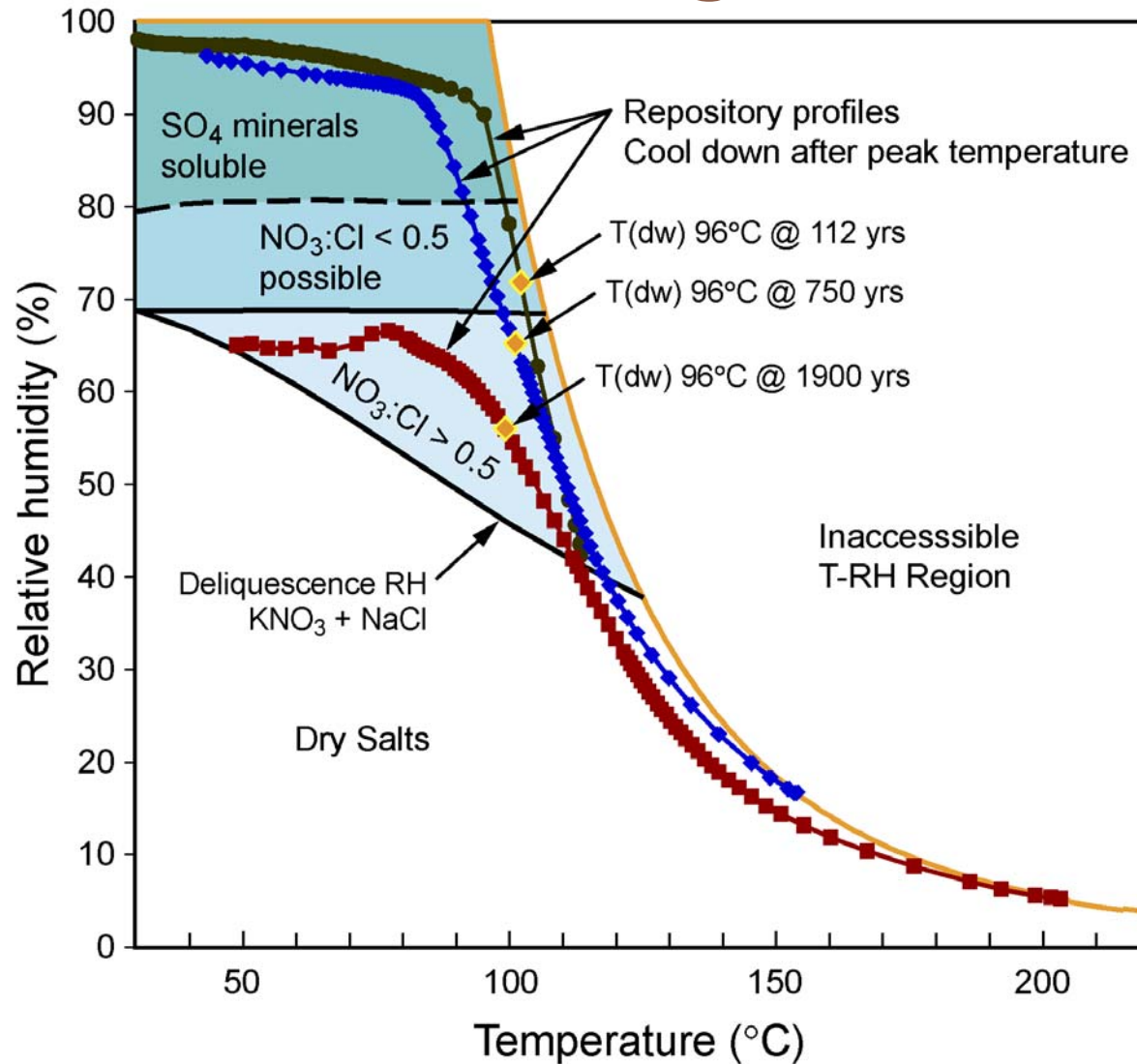
# Time-Temperature-RH History Coupled to In-Drift Chemical Processes



Time years	Seepage Compositions			Brine Compositions		
	Cl millimolal	NO <sub>3</sub> millimolal	NO <sub>3</sub> /Cl mole ratio	Cl molal	NO <sub>3</sub> molal	NO <sub>3</sub> /Cl mole ratio
650	0.73 to 3.3	0.13 to 0.31	0.07 to 0.42	7.2	5.9	0.81
1500	0.73 to 1.3	0.13 to 0.31	0.10 to 0.42	7.0	4.1	0.59
5200	0.73 to 1.3	0.13 to 0.31	0.10 to 0.42	3.2	0.58	0.18
9200	0.60 to 3.3	0.04 to 0.10	0.03 to 0.09	2.7	0.15	0.06



# Summary of Possible Brine Chemistry for Below-Boiling Period



# Conclusions

- **Although the evolution of seepage water chemistry is complex, DOE has developed a scientifically defensible, integrated approach that couples chemistry to the Time-Temperature-RH history of the drifts**
- **The approach considers**
  - **The natural variability of pore water chemistry**
  - **Modifications to pore and fracture water chemistry as a result of THC processes**
  - **Evaporative concentration and resulting mineral precipitation**
- **The approach is implemented through a combination of experimentation and modeling**



# Conclusions

- **The analysis indicates that seepage will not result in  $\text{CaCl}_2$  brines during the below-boiling period because of precipitation of Ca mineral phases**
- **In hotter waste packages during the below-boiling period, thermodynamic controls result in favorable  $\text{NO}_3/\text{Cl}$  ratios**
- **Evaporated brine fluxes are on the order of 1-100 ml/WP/year**
- **In the expected case where very little seepage on waste packages occurs due to the effectiveness of drip shields and the capillary barrier, the foregoing discussion on seepage chemistry is irrelevant**



# Backup Slides





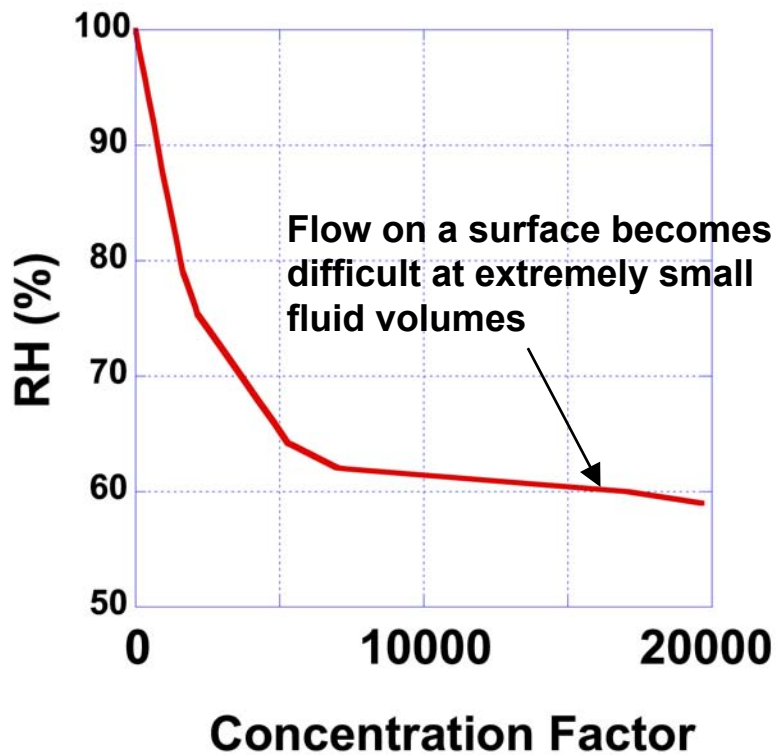
# Flow Separation of Nitrate and Chloride

- **Flow separation of nitrate and chloride is possible because the nitrate salts are more soluble than the Na and K chloride salts**
  - NaCl and KCl could precipitate while  $\text{NO}_3^-$  in solution flows away, thus leaving a residual salt rich in chloride
  - Chloride salts could then deliquesce at higher RH
- **Flow separation of nitrate and chloride requires very high degrees of evaporation (~10,000 times), implying that fluid volumes are very small**
  - Natural capillarity of waste package surface will limit flow of nitrate-rich solution at such high concentration factors

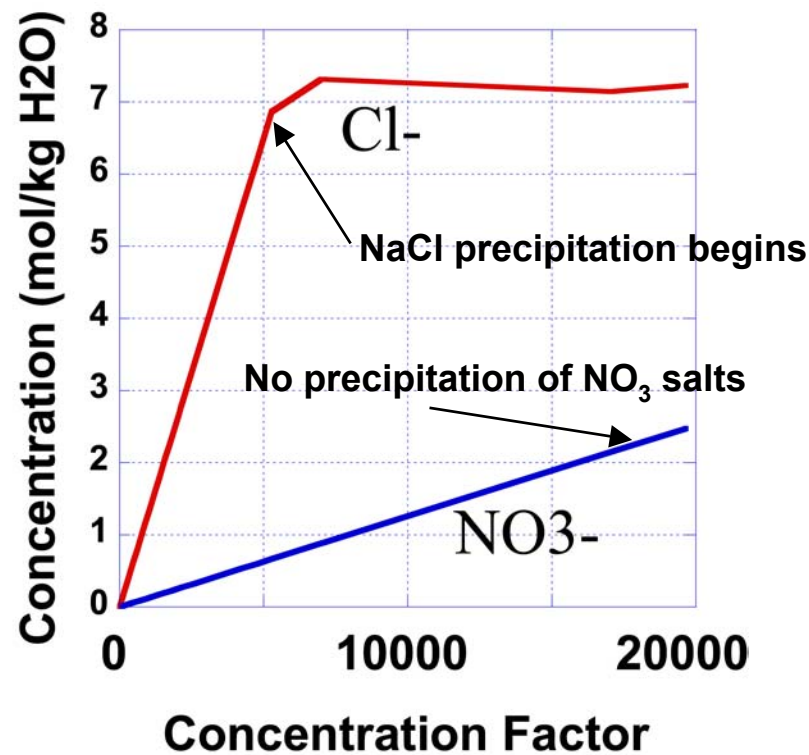


# Is Flow Separation Possible for a NaCl Seepage Water?

Low RH values correspond to high degrees of concentration and low fluid volumes



$\text{NO}_3/\text{Cl}$  ratios increase if flow separation does not occur



# THC Fluid Evaporation: Brine Composition for Hot Location

