Reactive Transport Modeling of the Unsaturated Zone Hydrogeochemical System at Yucca Mountain, Nevada

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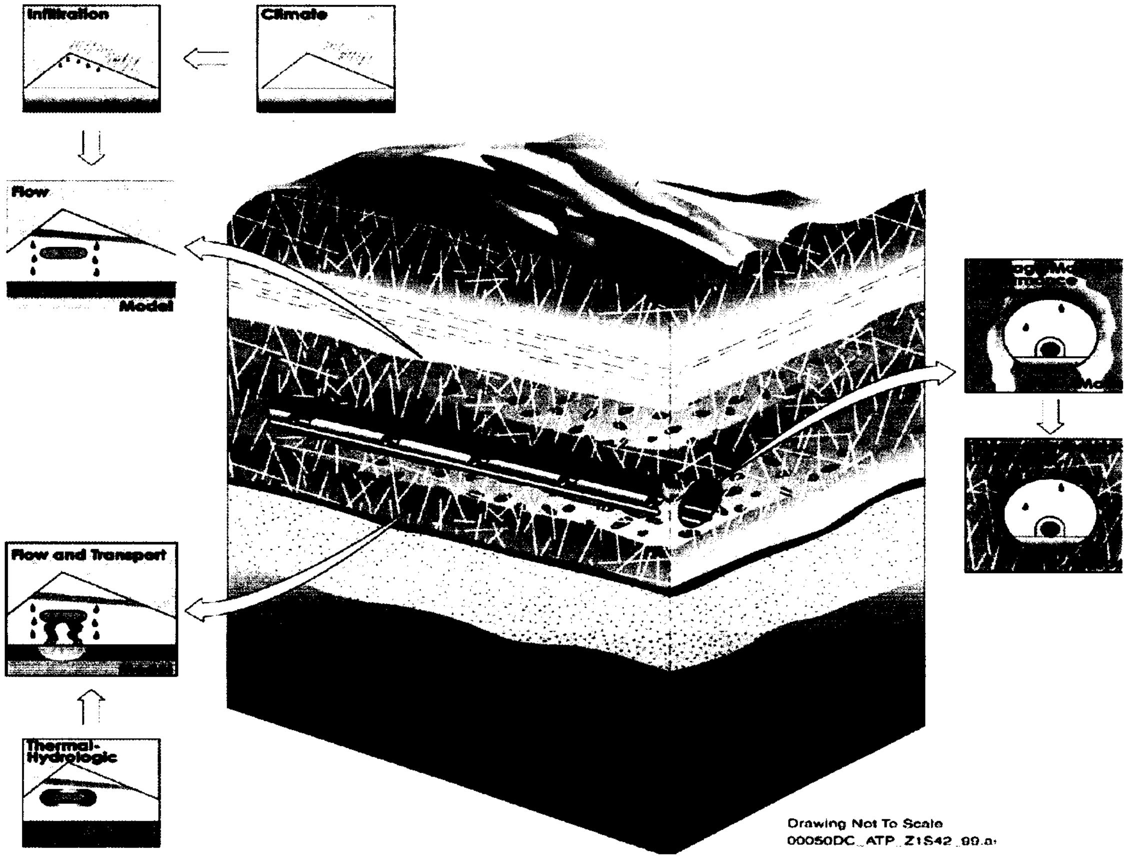
Background: Who and Why?

- Why are reactive transport simulations being developed?

  * The quantity and chemistry of in-drift water may affect the lifetimes of engineered materials.

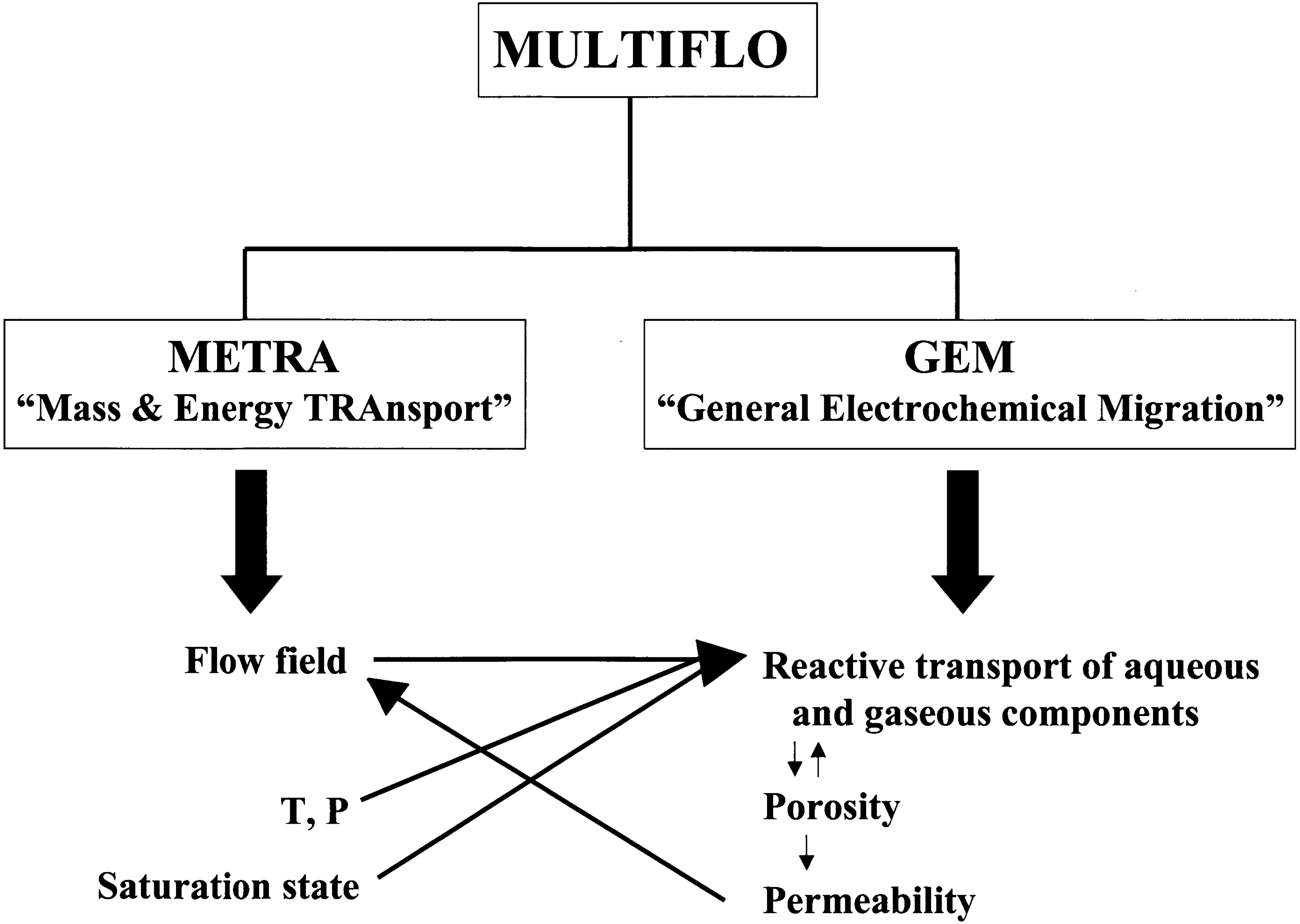
- Who is developing these models?

  * U.S. Department of Energy, U.S. Nuclear Regulatory Commission



MULTIFLO Capabilities

* Heat, fluid, vapor transport in 1-, 2-, or 3-D
* Dual continuum models or equivalent continuum models
* Structured or unstructured grids
* Equilibrium, kinetic or mixed reactions for precipitation and dissolution
* Large numbers of minerals, primary and secondary aqueous species
* Diffusion and advection of aqueous and gaseous components
* Adsorption and ion exchange
* Permeability responds to mineral precipitation/dissolution



MULTIFLO

METRA
"Mass & Energy TRAnsport"

GEM
"General Electrochemical Migration"

Flow field

T, P

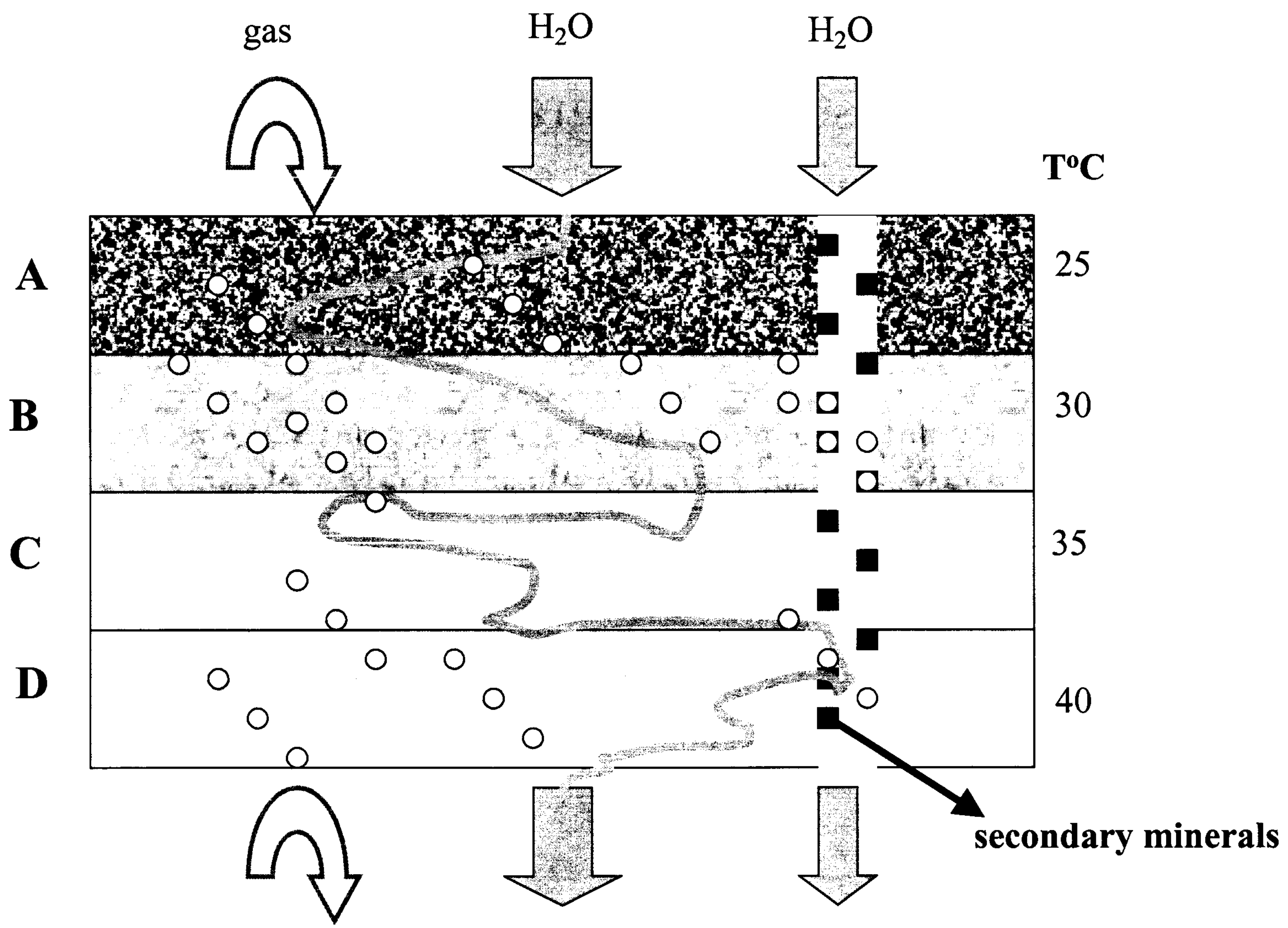
Saturation state

Reactive transport of aqueous and gaseous components

Porosity

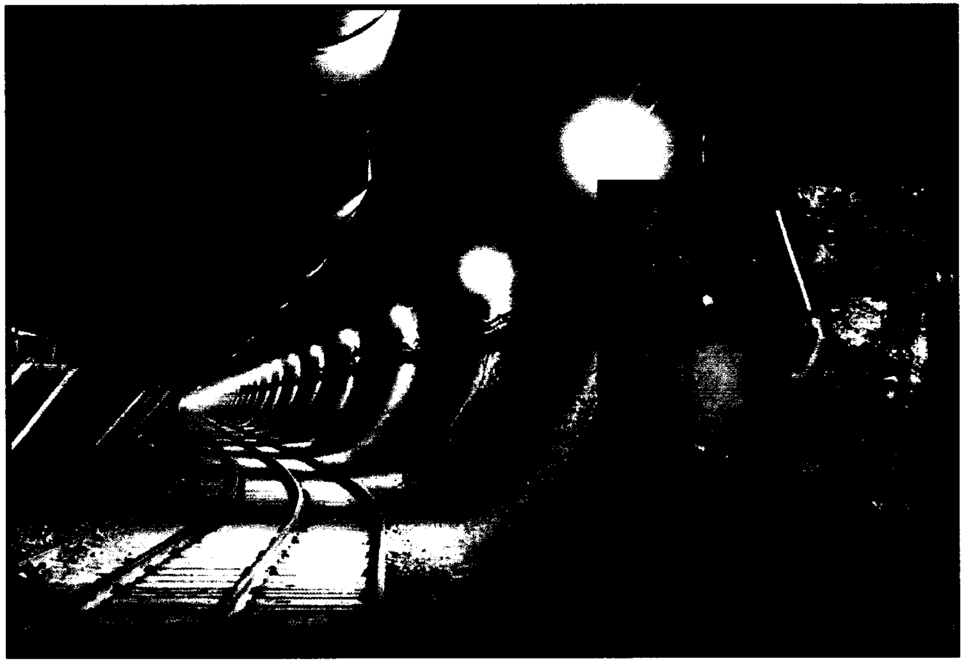
Permeability

Reactive Transport Using MULTIFLO: Specifying the Reaction System



Availability of Relevant Site-Specific Data

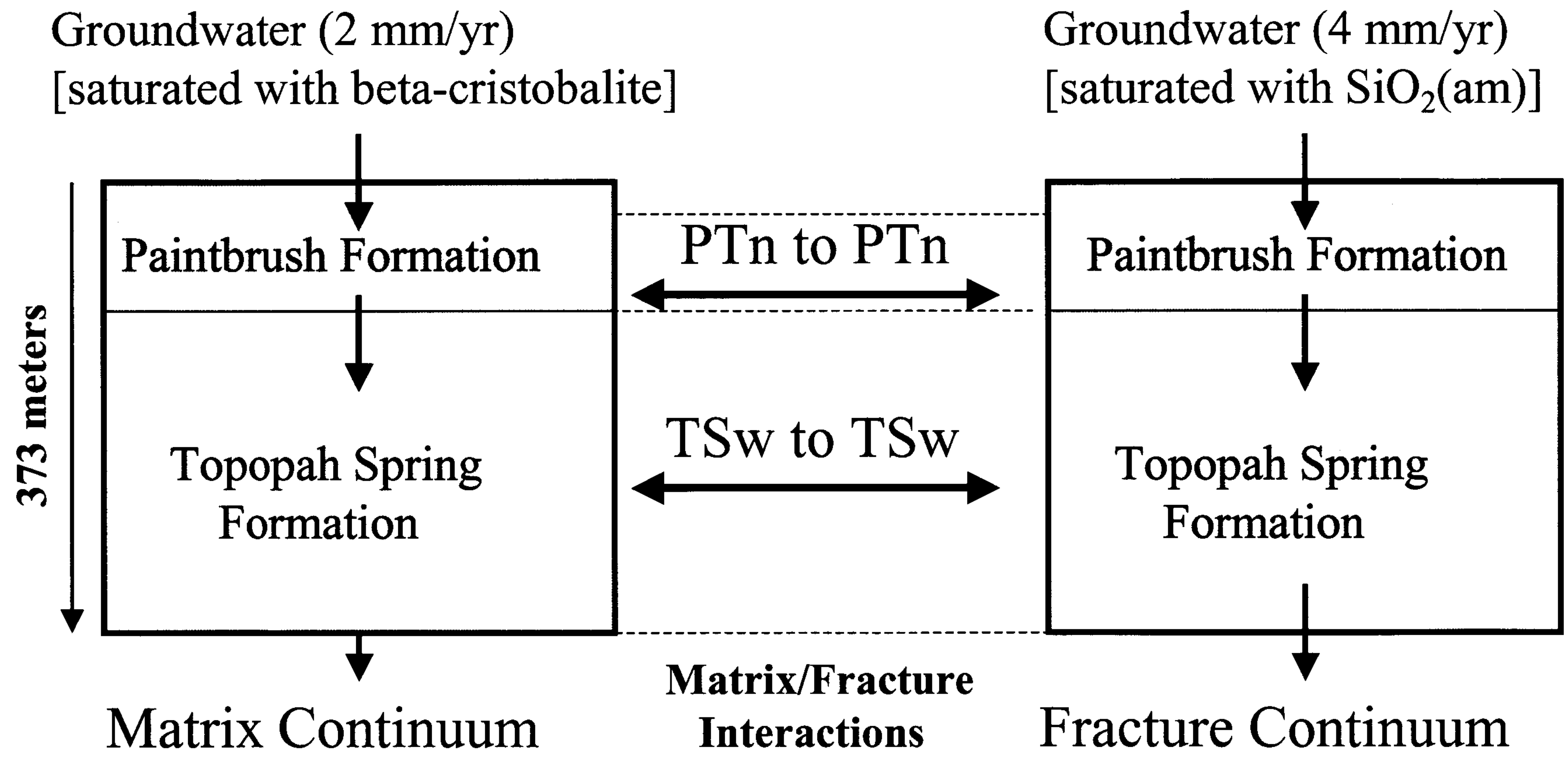
- **Site characterization data (ambient conditions)**: pore water chemistry, stratigraphy, hydrological and mineralogical properties of the rock units
- **Exploratory Studies Facility (thermal perturbation):** drift scale heater test (DST)



Hydrostratigraphic Units Included in Model Domain

Hydrogeological Unit	Description	Hydrostratigraphy
Nonwelded Paintbrush Tuff, PTn	bedded tuff	(not included in model)
	Yucca Tuff	
	bedded tuff	
	Pah Canyon Tuff	
	bedded tuff	
	(non)welded, mod. welded vitric	ptn26
Topopah Springs Tuff, TSw	upper welded vitric	tsw31
	crystal rich, nonlithophysal	tsw32
	crystal rich lithophysal and crystal poor upper lithophysal	tsw33
	middle nonlithophysal, crystal poor	tsw34
	lower lithophysal, crystal poor	tsw35
	lower nonlithophysal, crystal poor	tsw36 tsw37
	lower welded vitric	tsw38
	lower mod. welded vitric	tsw39
	lower nonwelded vitric	(not included in model)
	bedded tuff	

Basic Model Structure



Groundwater (2 mm/yr)
[saturated with beta-cristobalite]

Groundwater (4 mm/yr)
[saturated with SiO$_2$(am)]

373 meters

Paintbrush Formation

Topopah Spring Formation

PTn to PTn

TSw to TSw

Paintbrush Formation

Topopah Spring Formation

Matrix Continuum

Matrix/Fracture Interactions

Fracture Continuum

Basic Model Properties

Code: MULTIFLO v. 1.5 (Painter et al., 2001)

Gridding: a 56 cell structured grid with a mixed upper boundary condition (i.e. specified gas pressure, temperature and liquid flux) and a gravity drainage lower boundary condition

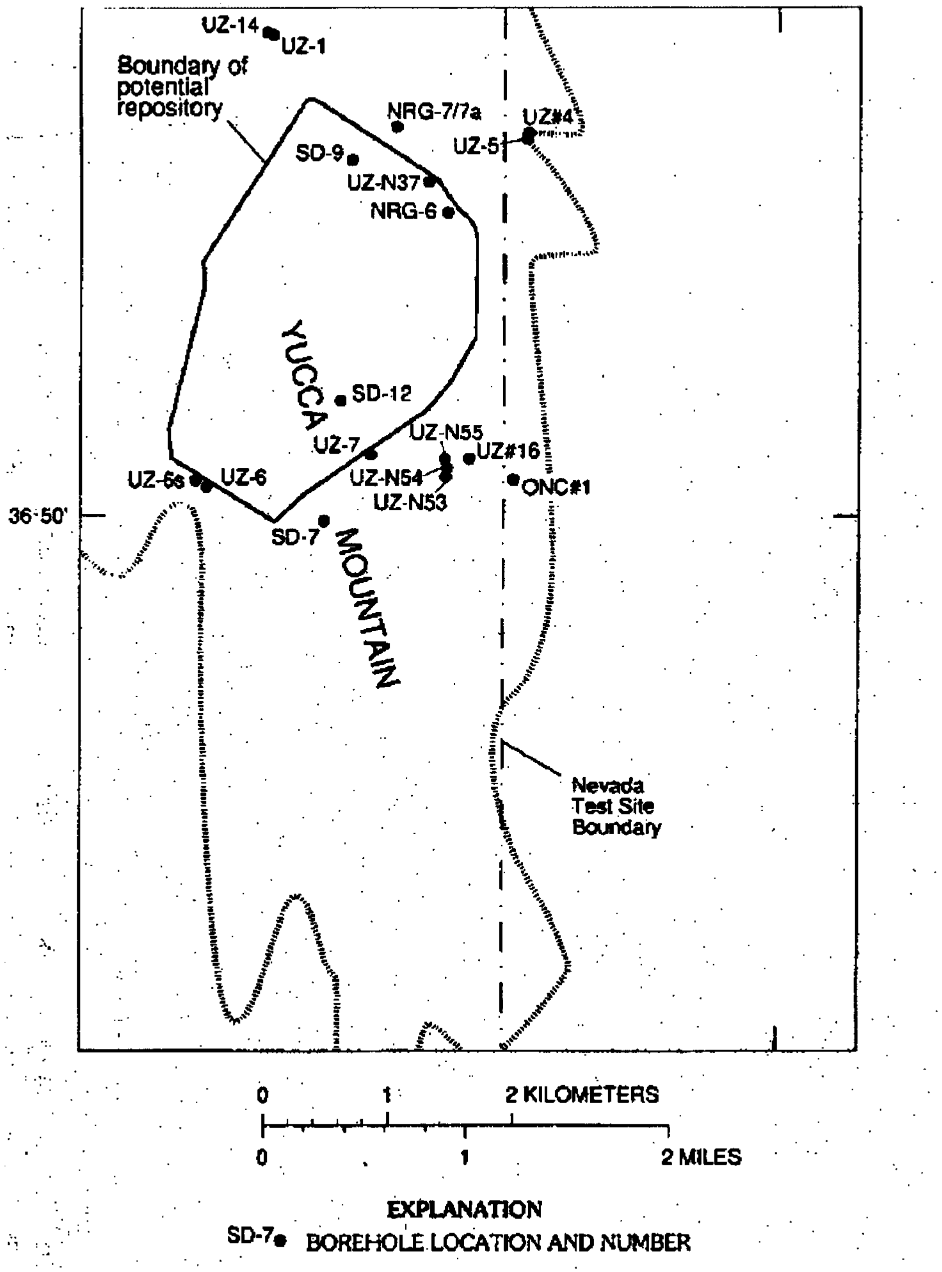
Groundwater flow:

* Darcy's law coupled with constitutive relationships
* van Genuchten function with Mualem assumption for moisture retention and relative permeability
* the active fracture model (Liu et al., 1998)
* parameter values adopted from CRWMS M&O (2001).

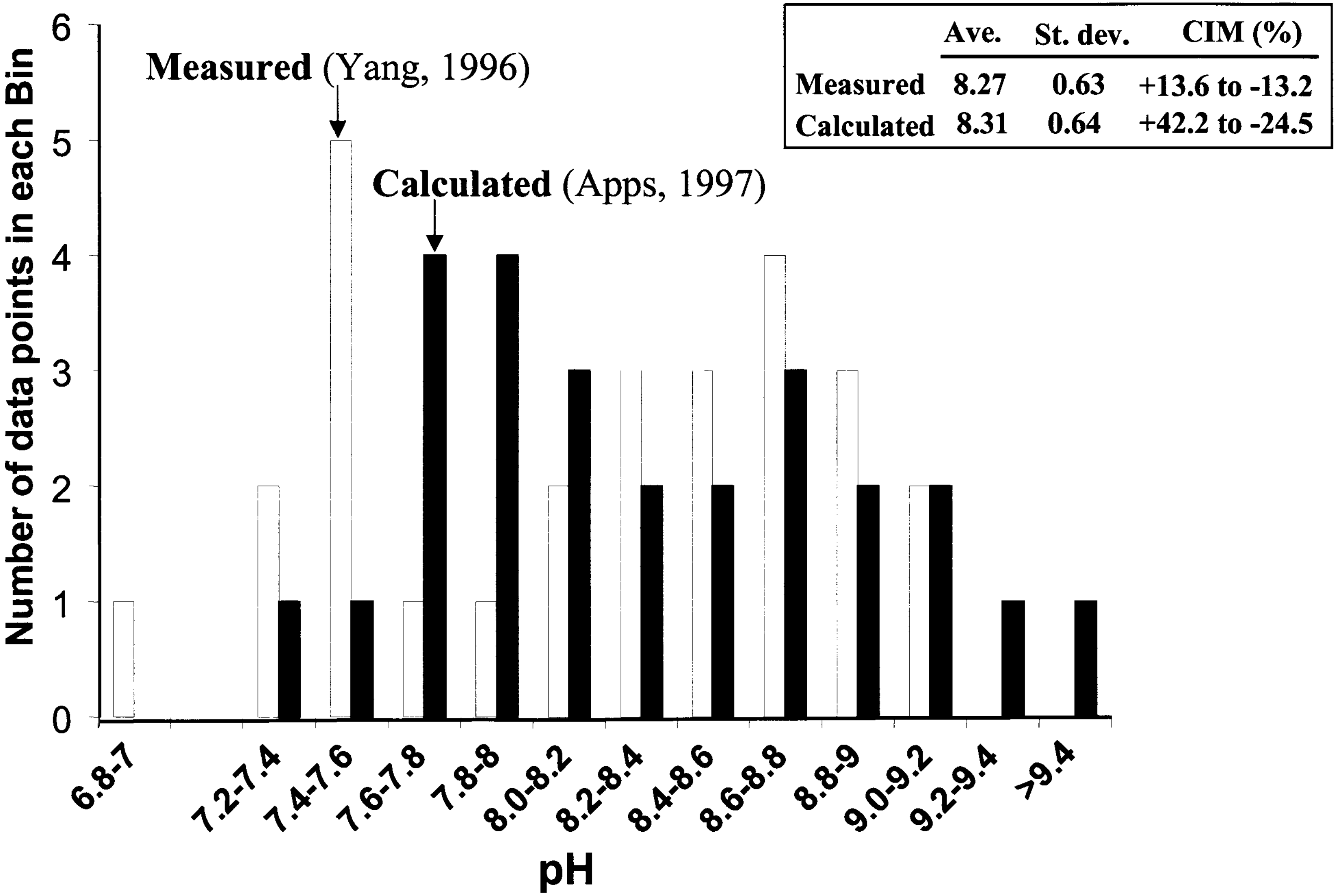
Geochemical Model: The model considers:

* dissolved species and gas: Cl^-, Ca^{2+}, H^+, HCO_3-, $CO_2(aq)$, CO_3^{2-}, $SiO_2(aq)$, $HSiO_3^-$, $Al(OH)_4^-$, Na^+, K^+, OH^-, and Al^{3+}, and $CO_2(g)$
* kinetically reactive phases: low albite, calcite, rhyolitic glass, amorphous silica, and endmember Na, Ca, and K-smectites
* infiltrating and initial water compositions: revised analytical data described in Browning et al. (2000).

Borehole Locations at Yucca Mountain, NV



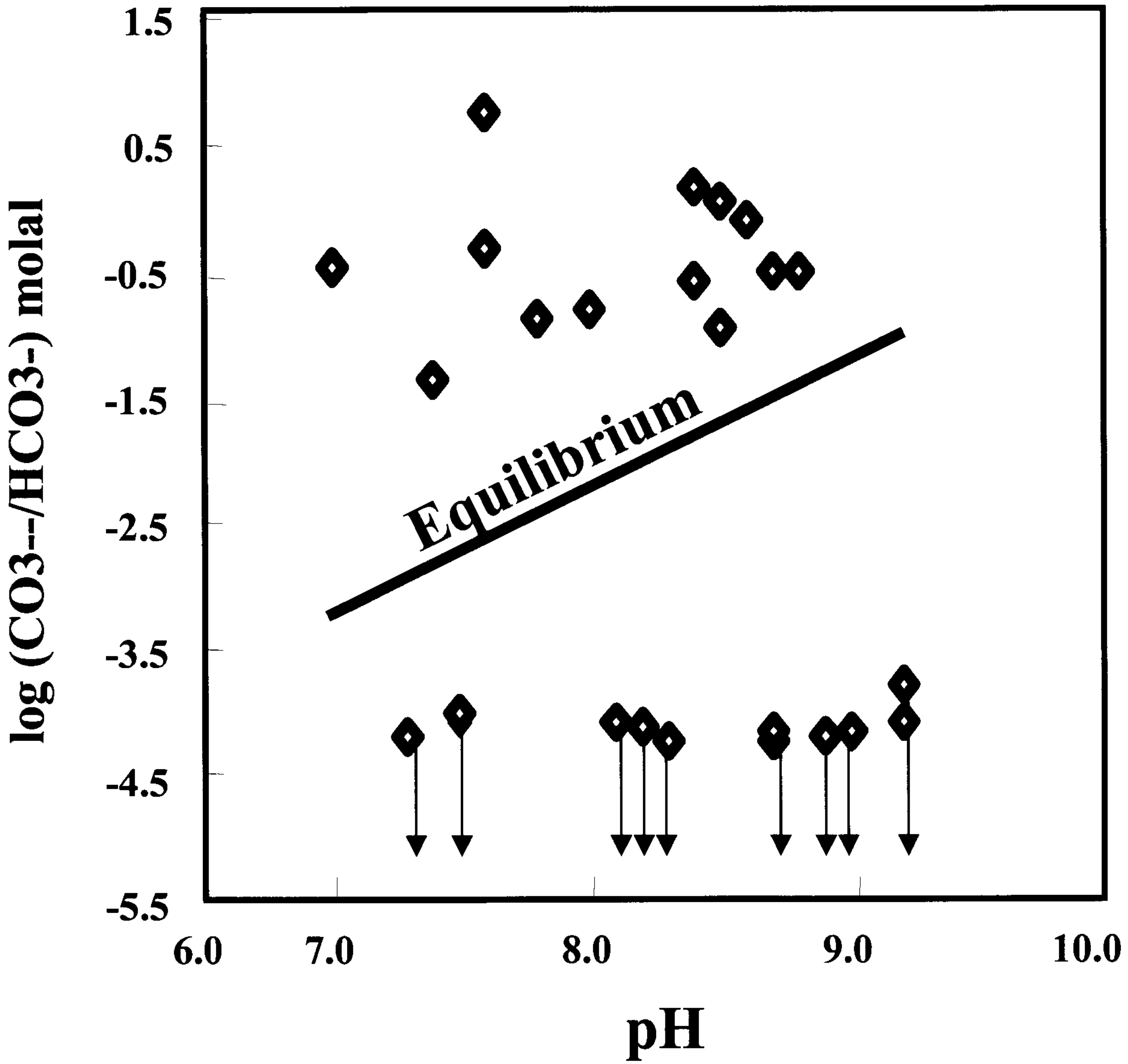
Uncertainties in Measured and Calculated Compositions of Pore Waters Extracted from Boreholes at Yucca Mountain



	Ave.	St. dev.	CIM (%)
Measured	8.27	0.63	+13.6 to -13.2
Calculated	8.31	0.64	+42.2 to -24.5

Analytical vs. Equilibrium Aqueous Speciation

(Data from Yang et al., 1996; figure from Browning et al., 2000)



Equilibrium Condition

$$HCO3^- \rightleftarrows CO_3^{2-} + H^+$$

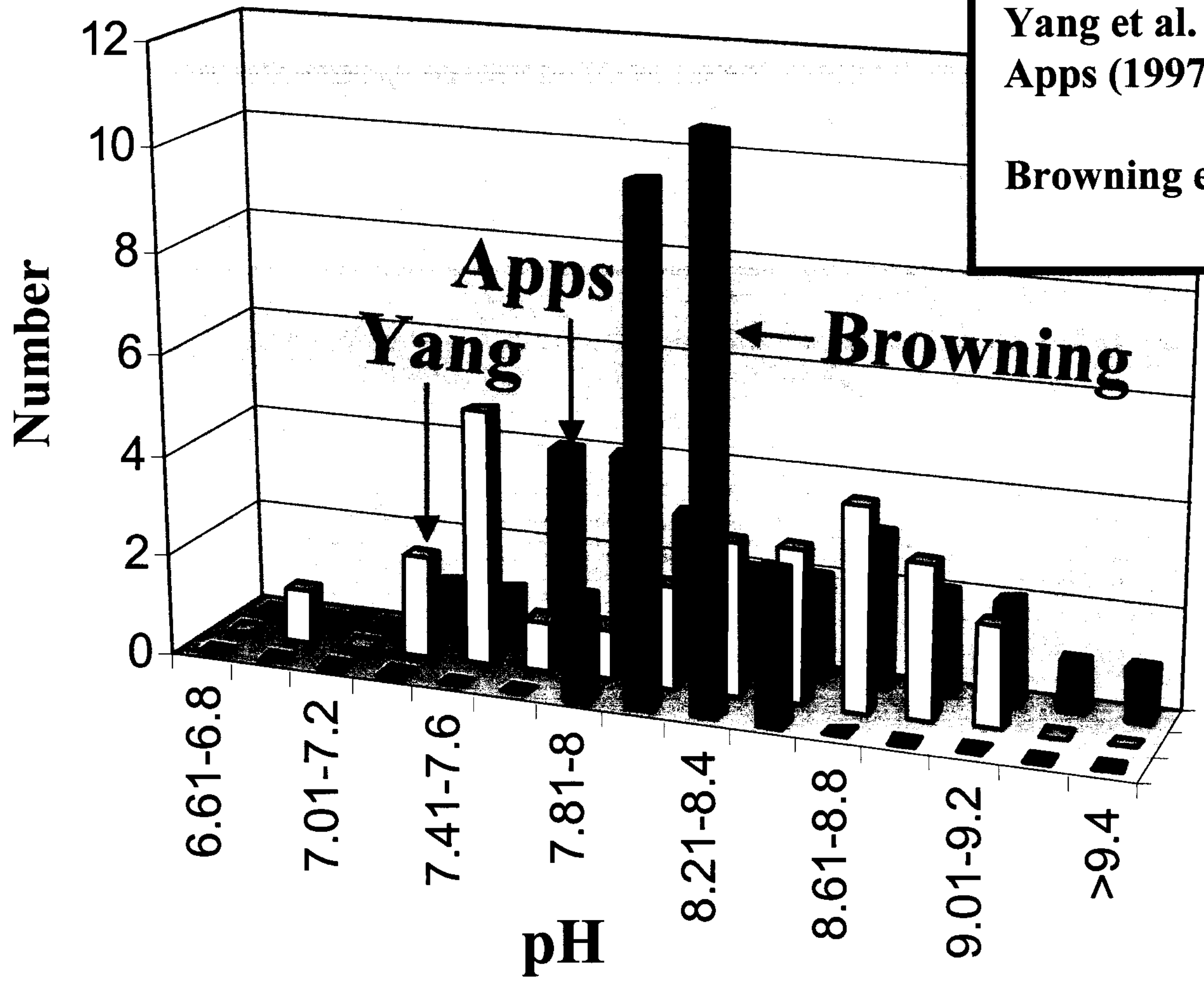
$$K = \frac{aCO_3^{2-}\ aH^+}{aHCO3^-}$$

Measured and Calculated Distributions of pH

(Borehole UE-25, UZ#16)

Approaches:

Yang et al. (1996): Analytical data
Apps (1997): calcite equilibrium
no charge balance
Browning et al. (2000): fix pCO_2
balance on H^+



Revised matrix pore water compositions constrain the boundary/initial conditions in our model

Groundwater Component	Revised SD-9 Composition
pH	8.04
Ca (mg/L)	22.7
Na (mg/L)	53
SiO_c(aq) (mg/L)	48.6
K (mg/L)	8
Al (mg/L)	1.3e-5
HCO_3^- (mg/L)	115.3
CO_3^{2-} (mg/L)	0.64
Cl (mgL)	60

Reactive transport predictions have three substantial sources of uncertainty that are difficult to quantify: code limitations, unrepresentative conceptual models, and uncertain parameter values

→ confidence in reactive transport models should be improved by successful applications

→ calibration of parameter values within plausible ranges of uncertainty is generally needed to accurately represent the observable system

(from Browning et al., 2003)

Uncertain thermodynamic and kinetic parameters were calibrated to reflect observed trends at Yucca Mountain

Three calibration criteria were defined:

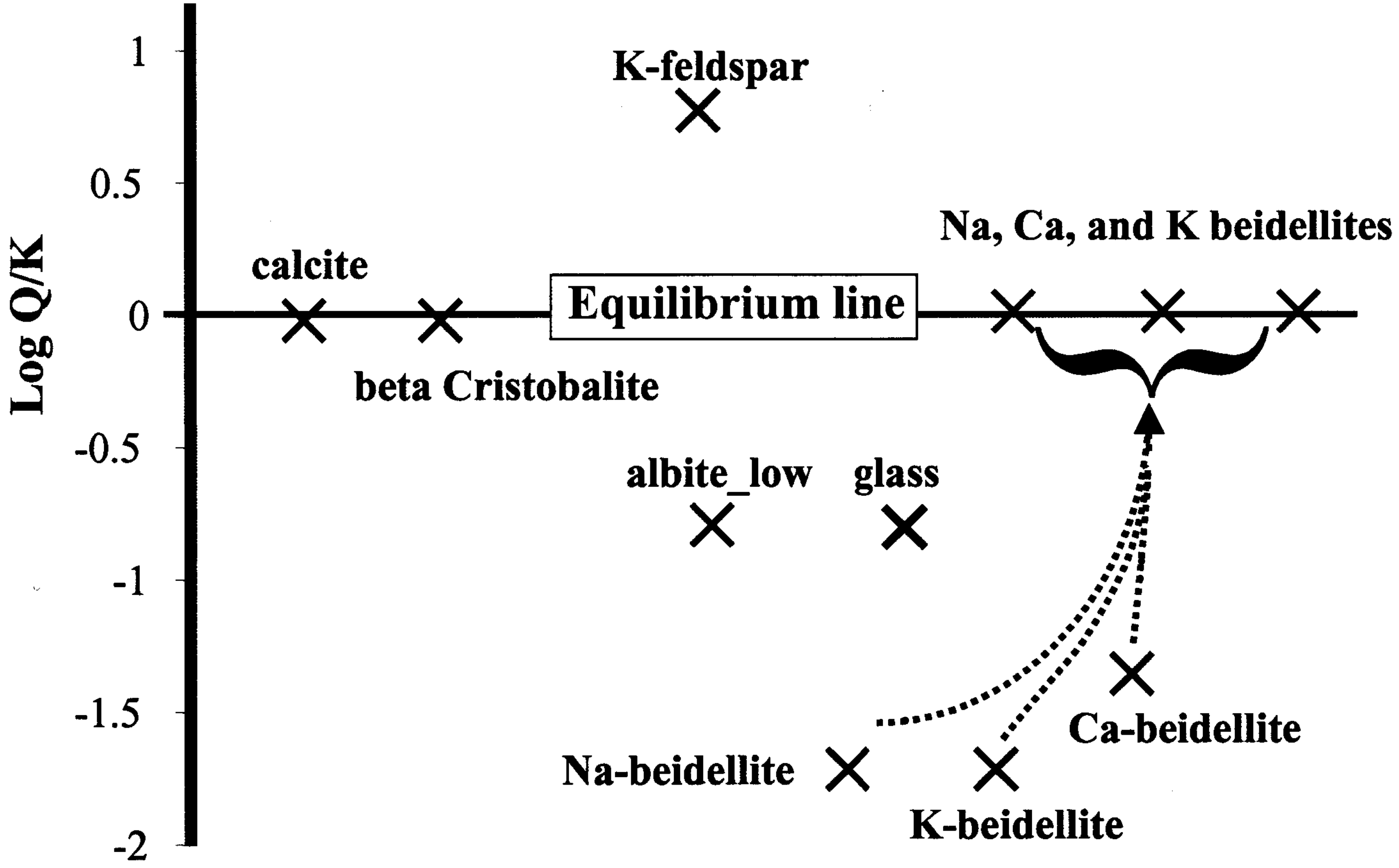
1 agreement between observed and simulated multicomponent matrix pore water compositions in PTn.

2 feldspars and glass dissolve, while clays and calcite precipitate.

3 where data are lacking, silica concentrations with depth must be bounded by observed analytical range.

(from Browning et al., 2003)

Calibration of Thermodynamic Data



(from Browning et al., 2003)

Calibration of Kinetic Data

Rate Law: $R = k^{*}A_s^{*}\ a(H^+)^x\ {}^{*}(Q/K - 1)$

k = rate coefficient

A_s = specific reactive surface area

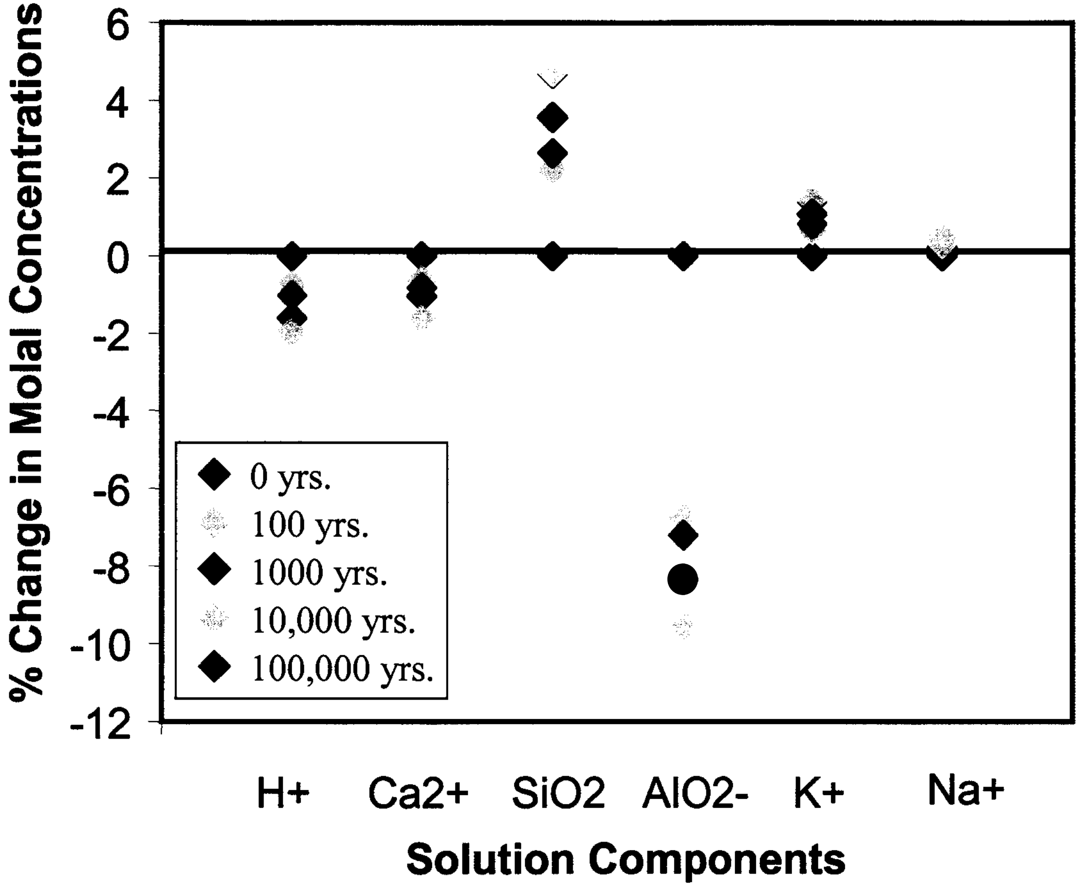
$a(H^+)^x$ = hydrogen activity term

$(Q/K - 1)$ = chemical affinity

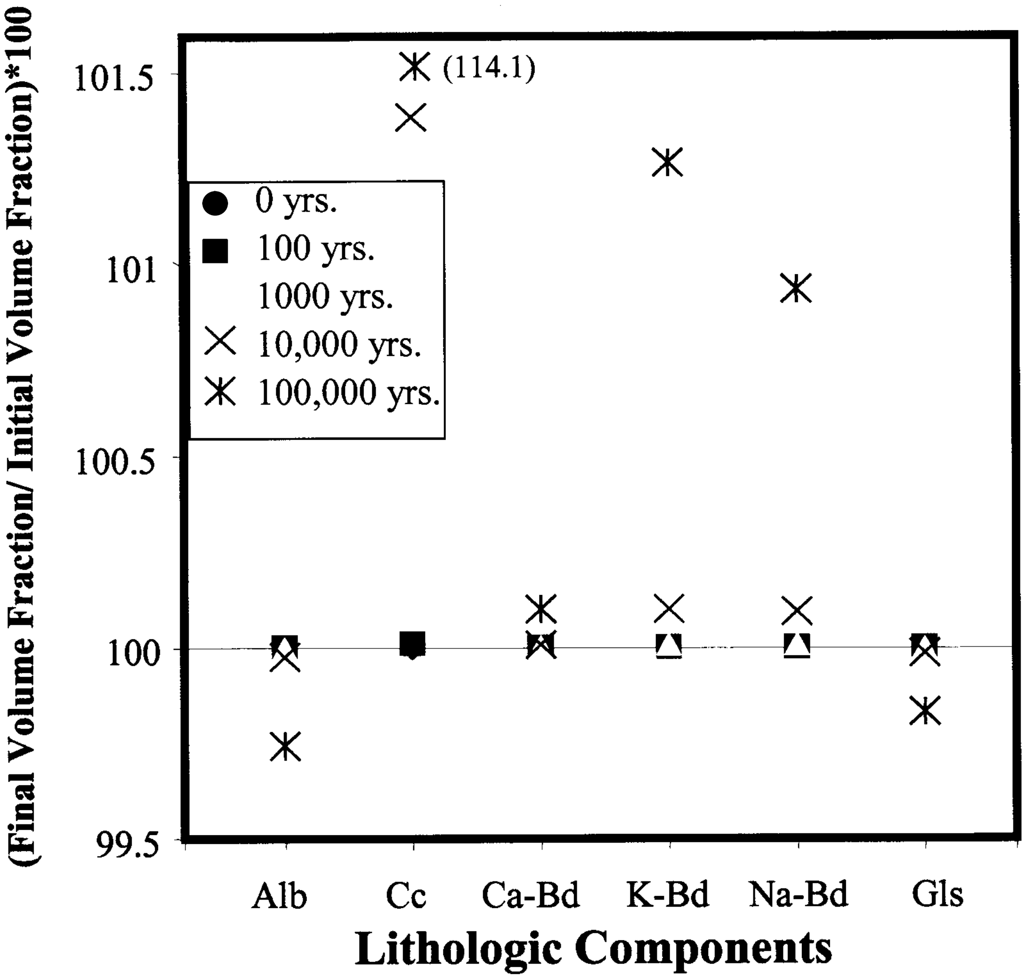
* defined maximum relative rates for individual minerals.

* estimated absolute rates for the set of minerals by calibrating surface area values for individual minerals.

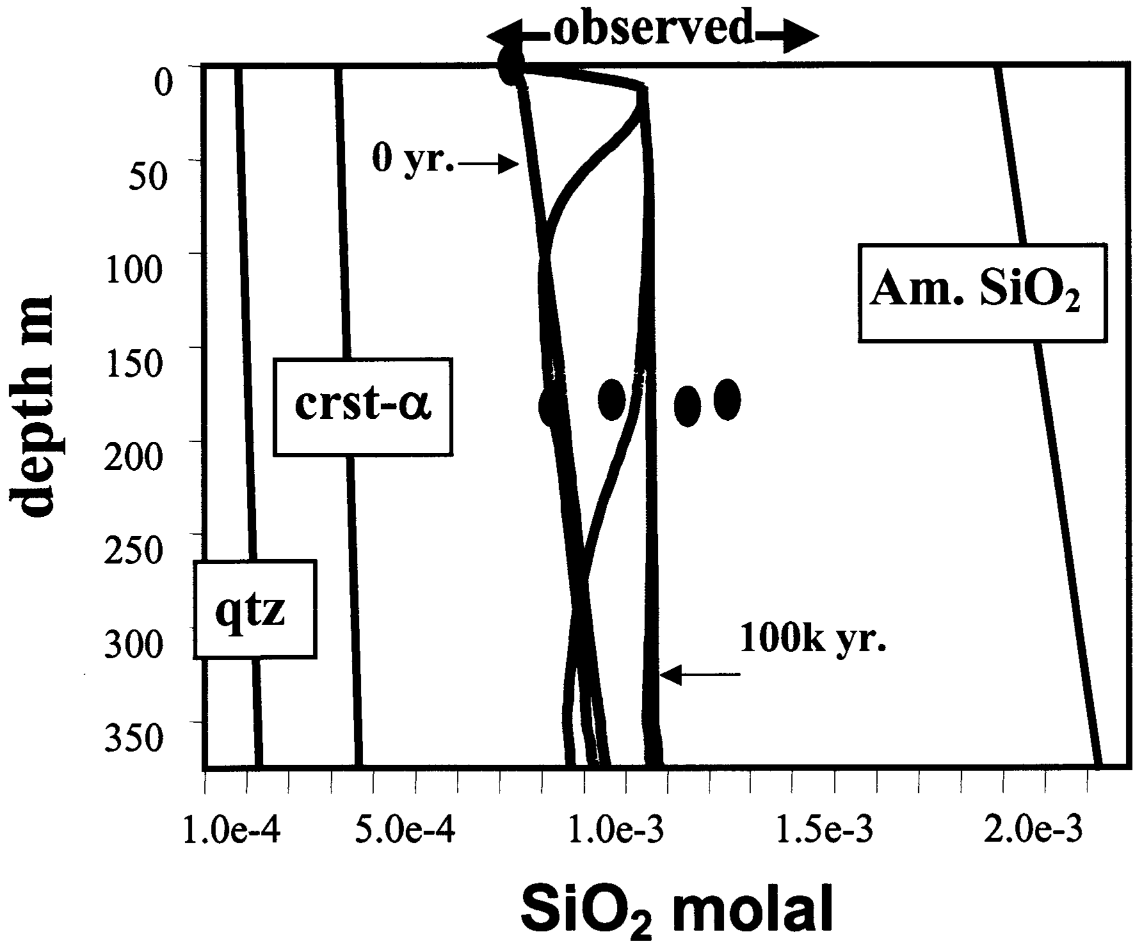
Satisfaction of First Calibration Criterion



Satisfaction of Second Calibration Criterion



Satisfaction of Third Calibration Criterion and Partial Model Validation



Calibrated Thermodynamic & Kinetic Parameters

Relative reaction rates are defined by our conceptualization of ambient YM conditions.

- *Absolute* reaction rates are constrained by the calibration criteria.

- Calibrated surface areas are consistent with in situ surface area measurements of natural permeable glass deposits (Bourcier et al., 2000).

Rate constant (K_{ml}) and calibrated specific reactive surface areas (S_m) for glass

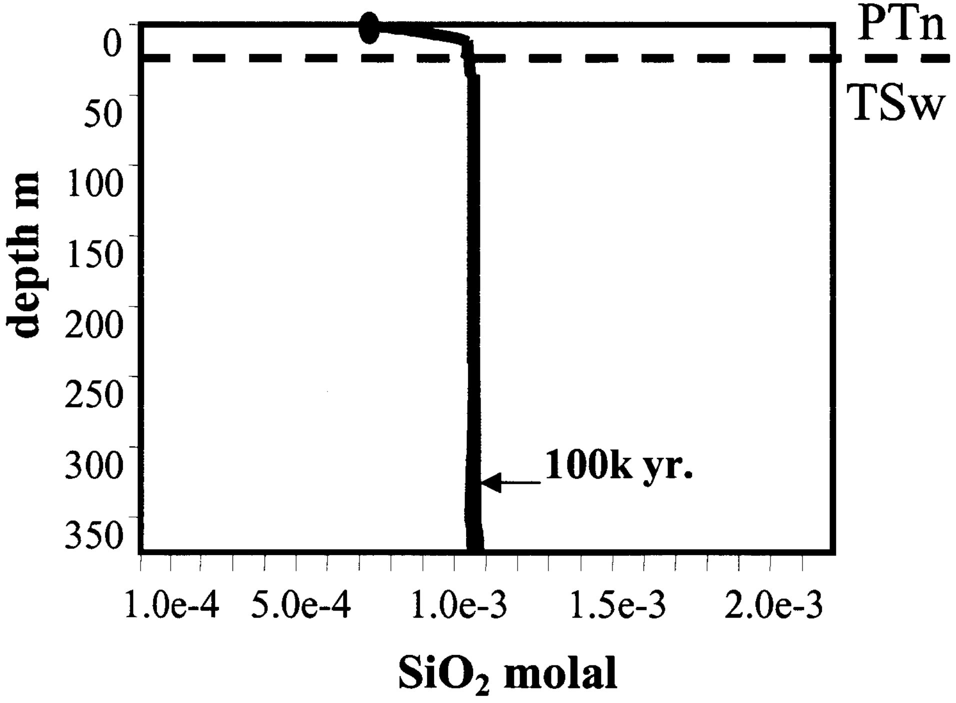
Parameter type (hydrostratigraphic unit)	Units	Value
K_{ml} (ptn26-tsw39)	moles/cm^2*s	9.3e-18
S_m (ptn26)	cm^2/cm^3	2.64
S_m (tsw31)	cm^2/cm^3	0.013
S_m (tsw32)	cm^2/cm^3	0.622
^aS_m (tsw33-37)	cm^2/cm^3	n/a
S_m (tsw38)	cm^2/cm^3	0.021
S_m (tsw39)	cm^2/cm^3	0.013

Insights: Controlling Water-Rock-Gas Reactions

Changes in simulated solution composition in the unsaturated zone above the repository horizon are largely related to glass dissolution reactions, as in:

$$\text{Glass} + 1.345\text{Al(OH)}_4^- + 1.366\text{H}^+ + 1.214\text{SiO}_2\text{(aq)} = 2.689\text{H}_2\text{O} + 0.3515\text{Beid-Na} + 0.3327\text{Beid-K} + 0.0103\text{Ca}^{2+}$$

Glass is a major phase both above (PTn) and below (CHn) the repository horizon (TSw), but is generally absent throughout the TSw units, suggesting that solution compositions at the depth of the potential repository are inherited from percolating waters, rather than being controlled by in situ chemical reactions.



Model Results

- Increased confidence in our ability to accurately represent complex hydrogeochemical processes at YM using reactive transport models.

- A set of calibrated thermodynamic and kinetic data for major phases present in the geologic units above the potential repository horizon that:
  - * improve our understanding of the ambient hydrogeochemical system at Yucca Mountain.
  - * may constrain the initial and boundary conditions of thermally perturbed models of Yucca Mountain.

References

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