

Geochemical Modeling and Its Applications to Groundwater Resources and Quality

A NGWA Webinar
January 18, 2017

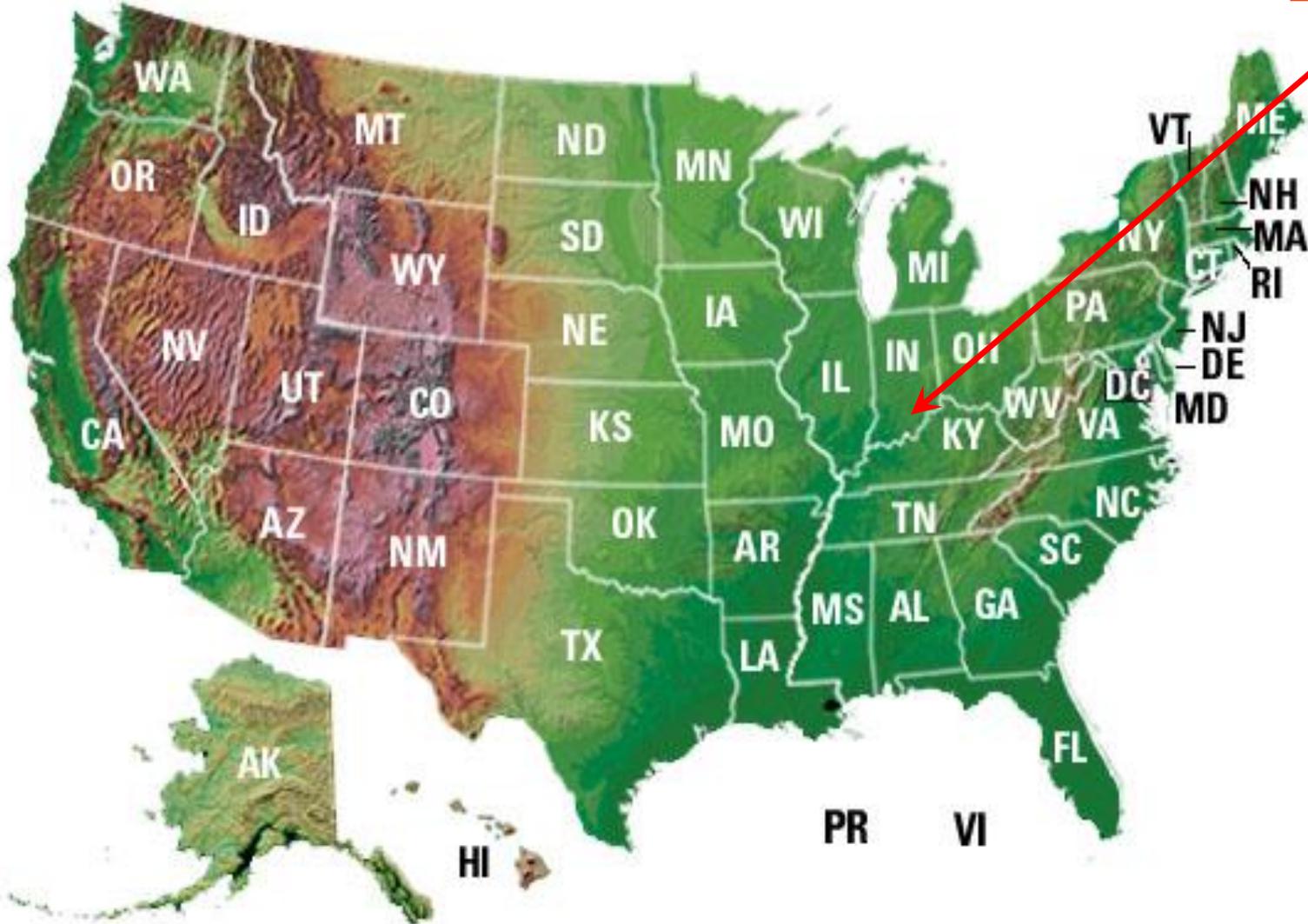
Professor Chen ZHU



www.indiana.edu/~hydrogeo

Indiana University is one of the BIG TEN

**Bloomington,
Indiana, USA**



Great
music
school

Indiana University
Bloomington, Indiana,
USA



Introduce myself:

Chen Zhu, Professor at Indiana University

- ❖ Ph.D., Johns Hopkins, Geochemistry & hydrogeology
- ❖ M.Sc., University of Toronto, geochemistry
- ❖ B. Eng, Chengdu College of Geology, China
- ❖ Post-doctoral fellowship, Woods Hole Oceanographic Institution

- ❖ Five years as Senior Geochemist, GeoTrans, Inc. (part of now Tetra Tech)

**Book by Cambridge
University Press
May, 2002**

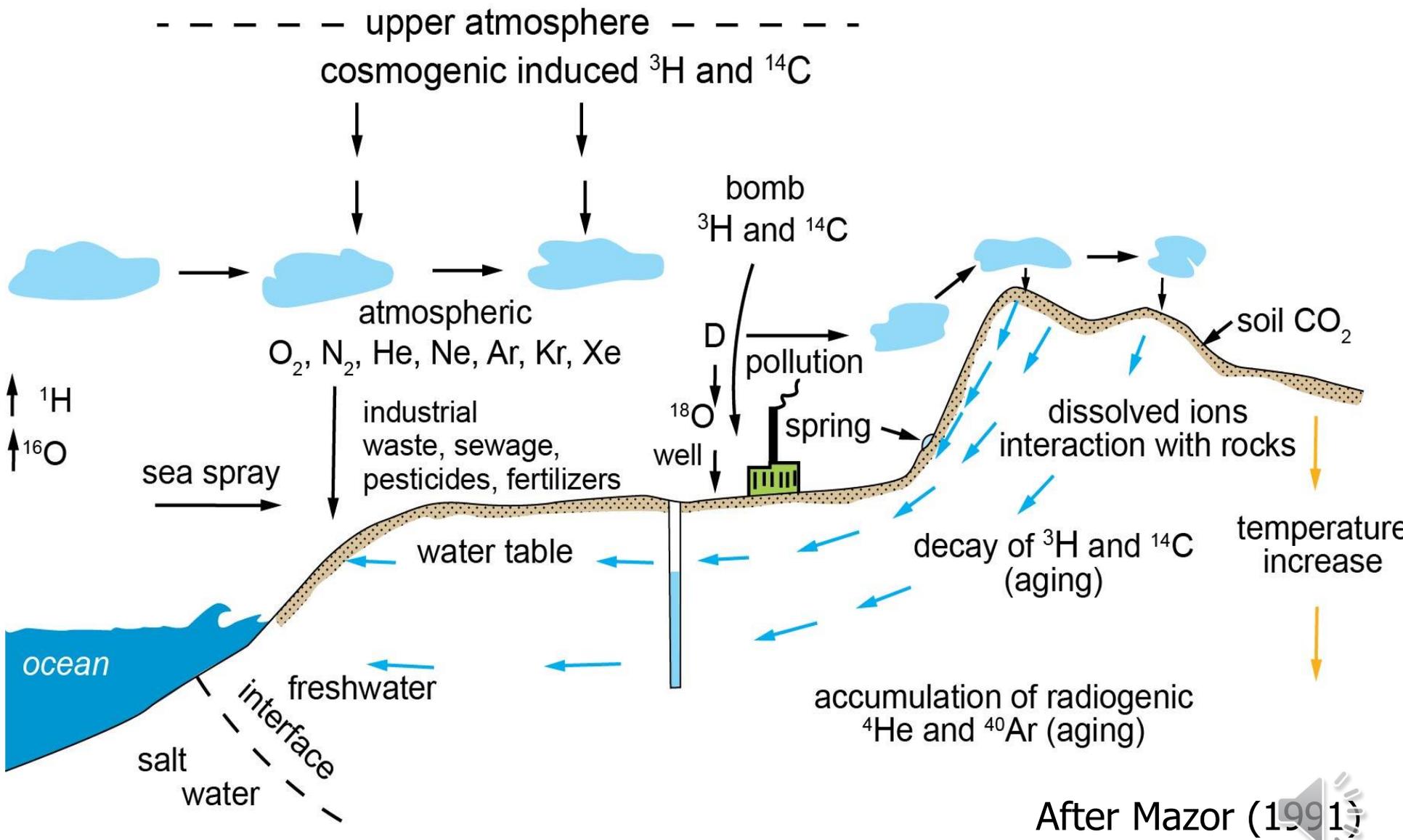
**sold over 200 copies
Adopted as textbook
in USA, Canada,
Poland, South Africa
etc**

Environmental Applications of
Geochemical Modeling

Chen Zhu and Greg Anderson



Chemical processes in the hydrologic cycle



Why to use geochemical models?

- ❖ **Predicting the future**
- ❖ **Complicated processes, coupling of processes, feedback of different processes**

Water Quantity: To use chemical and isotope tracers to quantify fluxes across reservoirs in the hydrologic cycle;

Water Quality: To determine the concentrations and speciation of chemicals in water. Sources and fate of contaminants;

Bear Creek Uranium Mill Tailing site, Wyoming



Figure 6.2. Plan view of the mine site and tailings impoundment.

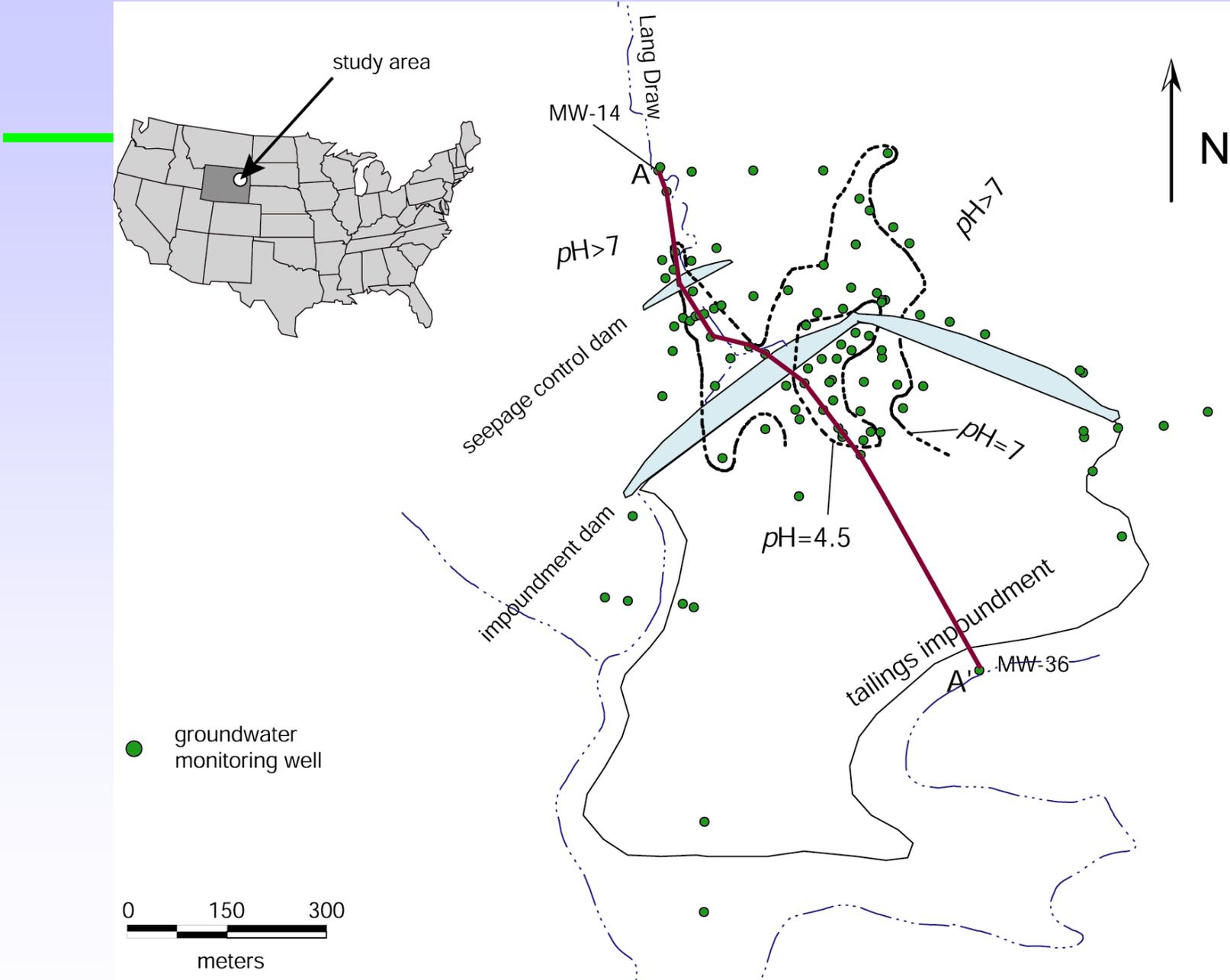
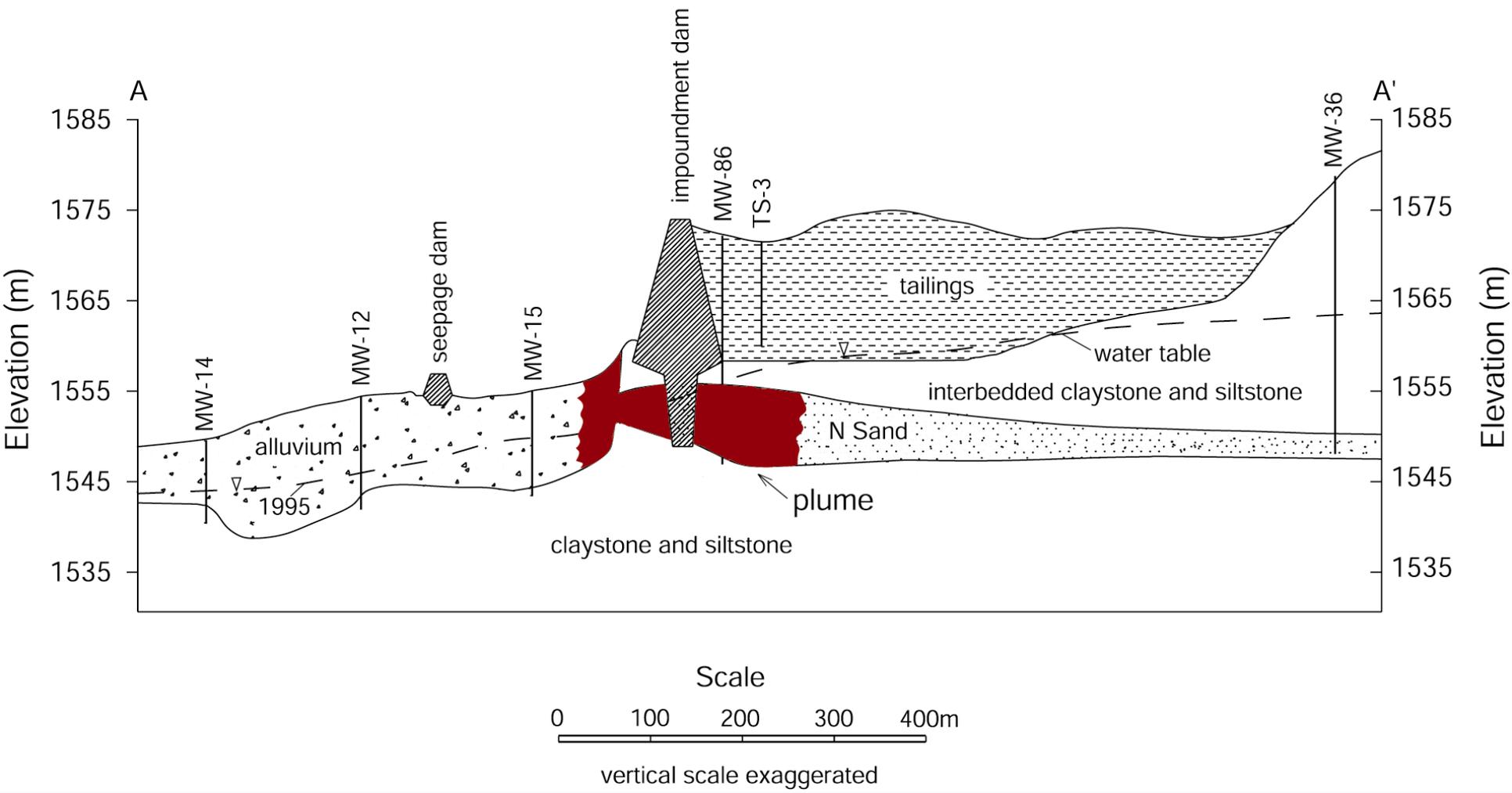


Figure 6.3. Cross-section A—A' from Figure 6.2. Water level was recorded on January 5, 1995.



The role of geochemical modeling

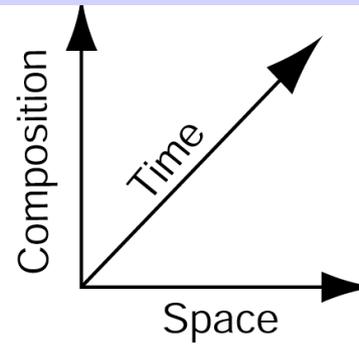
Overall

- ⇒ **Prediction of chemical concentrations and speciation in space and time**
- ⇒ **Time coordinate**
- ⇒ **Spatial coordinate**

Types of geochemical models

- ❖ **Speciation-solubility models**
- ❖ **Surface adsorption models**
- ❖ **Reaction-path models**
- ❖ **Inverse mass balance models**
- ❖ **Coupled reactive transport models**

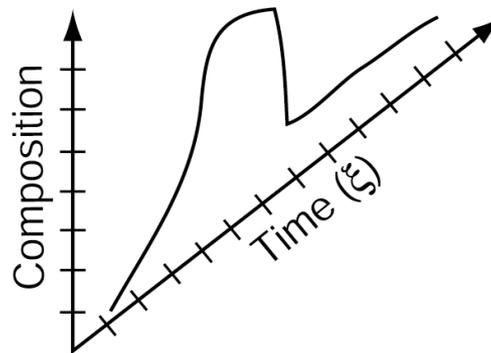
Figure 2.3. Different levels of complexity of geochemical models. After Raffensperger (1996).



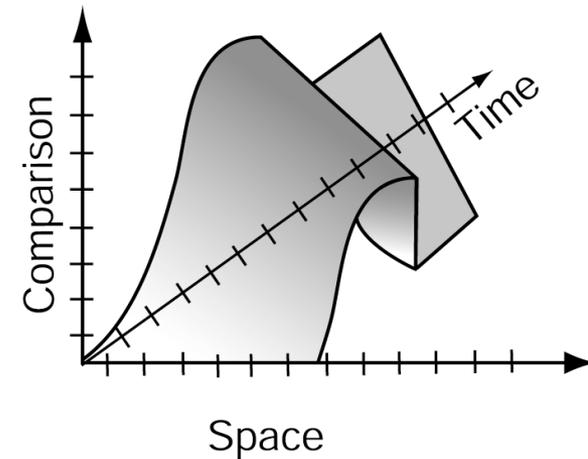
Batch calculations



Reaction-path calculations



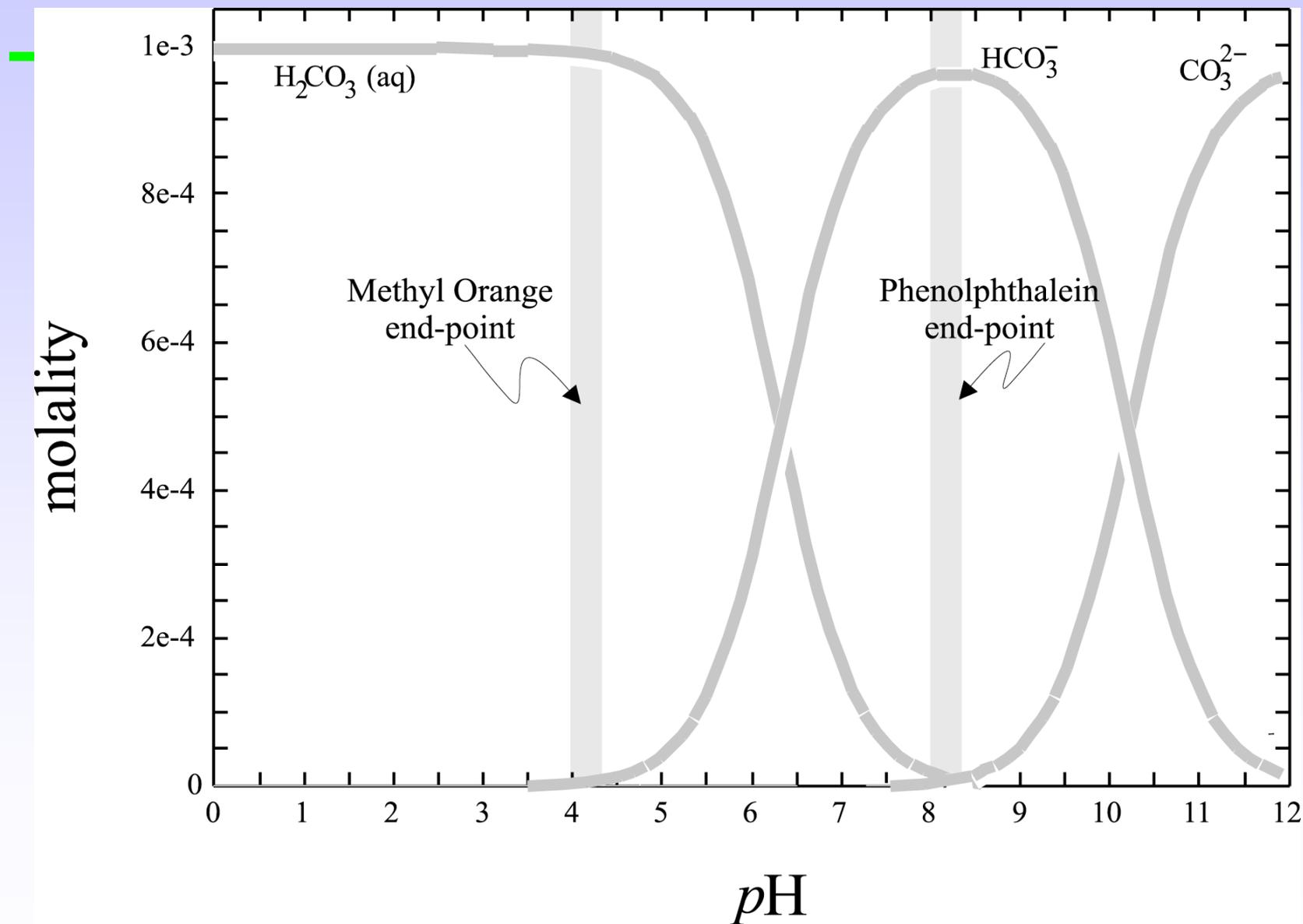
Reactive transport calculations



Types of Geochemical Models

- ❖ **1. Speciation-solubility model**
 - ◆ **What are the concentrations and activities of ionic and molecular species in an aqueous solution?**
 - ◆ **What are the saturation states with respect to various minerals in the system, and hence the directions of reactions that might occur toward achieving equilibrium?**
 - ◆ **What is the stable species distribution on surfaces or ion-exchangers that is at equilibrium with the aqueous solution?**
- ❖ **Closed, static, batch, or beaker type system or a snap shot in a dynamic system**
- ❖ **Read Anderson & Crerar (1993) and Bethke (1996) for equilibrium constants and free energy minimization approaches**

Figure 3.1. Molalities of H_2CO_3 , bicarbonate, and carbonate ions as a function of pH, for a total concentration of 10^{-5} m.



Types of Geochemical Models (continued)

- ❖ **2. Reaction Path Models**
 - ◆ A sequence of equilibrium states involving incremental or step-wise mass transfer between phases
 - ◆ Incremental addition or subtraction of a reactant
 - ◆ Increase or decrease of T , P .
- ❖ **Simulate processes versus speciation-solubility only calculations that simulate equilibrium states**
- ❖ **Chemical equilibrium and kinetics + mass balance principles**
- ❖ **Read Helgeson (1968), Helgeson et al. (1969)**

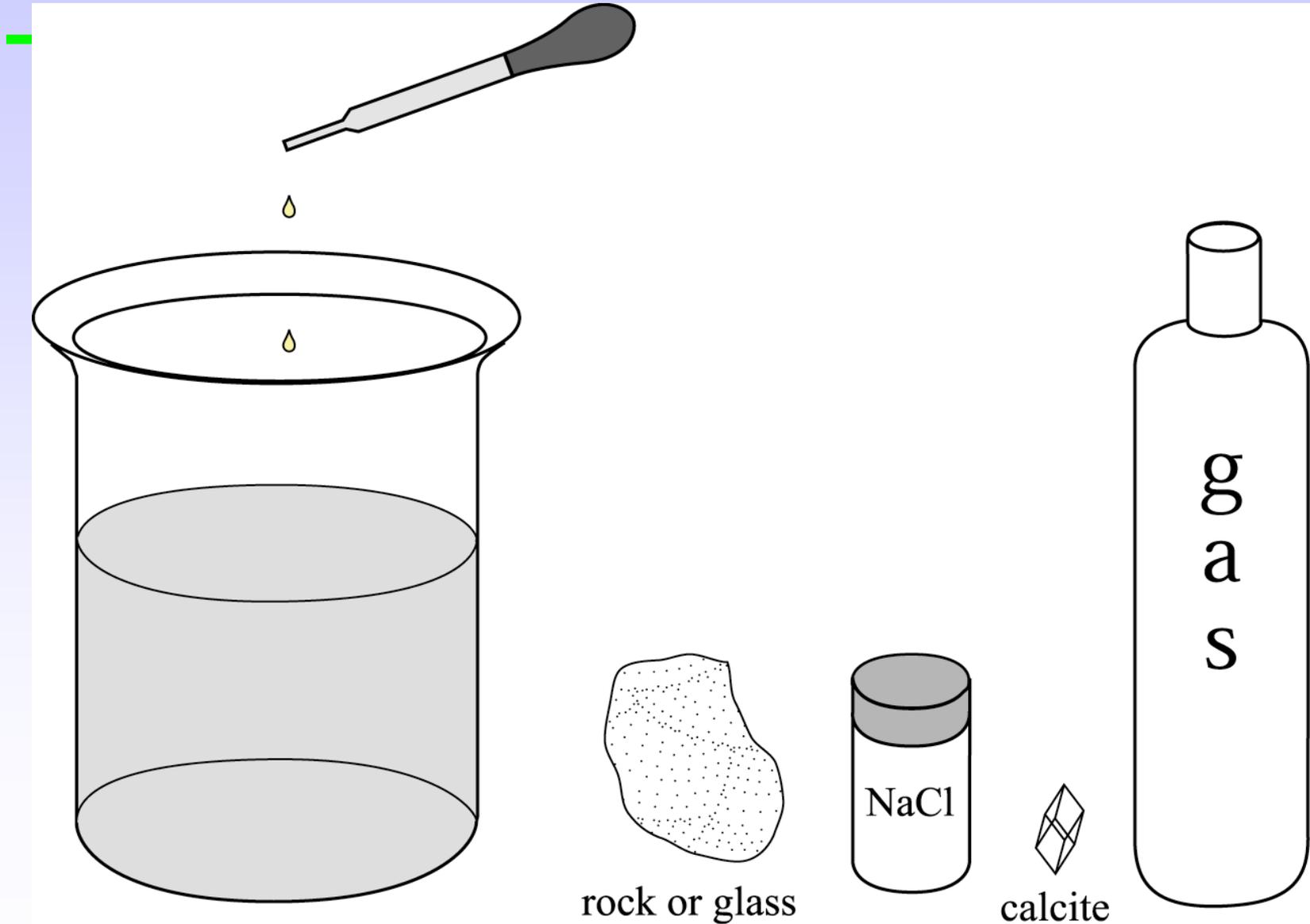
Types of Geochemical Models (continued)

❖ Reaction Path Models

◆ Titration model

- after each aliquot of the reactant, the aqueous solution is re-equilibrated by precipitating or dissolving a solid or gas phase or phases.
- The reactant can be a mineral, a chemical reagent, a glass, a gas, another aqueous solution, a "rock", or anything for which the chemical stoichiometry can be defined.
- Evaporation is considered as a negative titration of water.

Figure 2.4. Schematic representation of a mixing or titration model.



Types of Geochemical Models (continued)

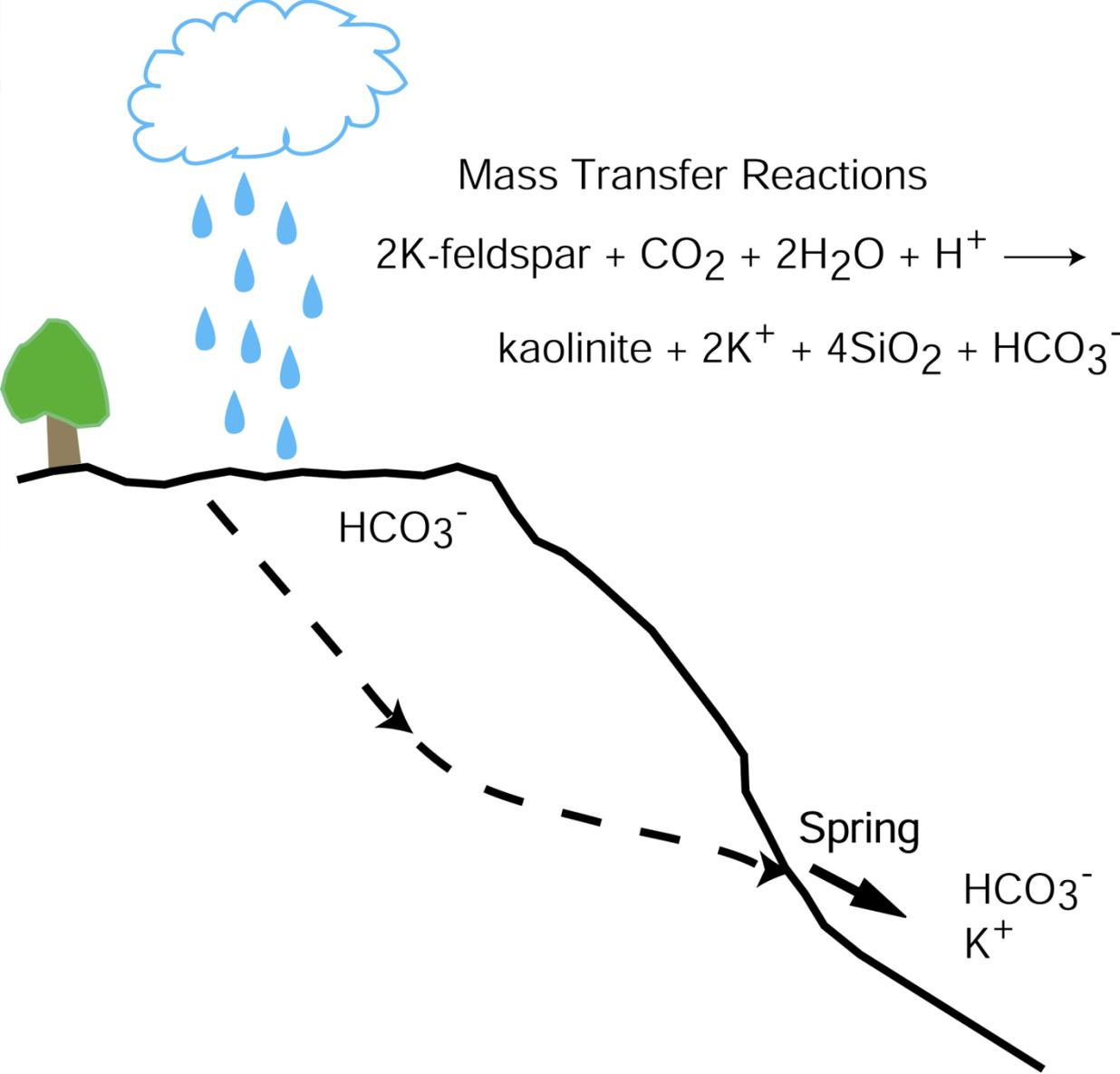
❖ 3. Inverse Mass Balance Models

- ◆ Initial water + reactants → final water + products

- ❖ Based on principles of mass balance only;

- ❖ Thermodynamics and equilibrium not considered

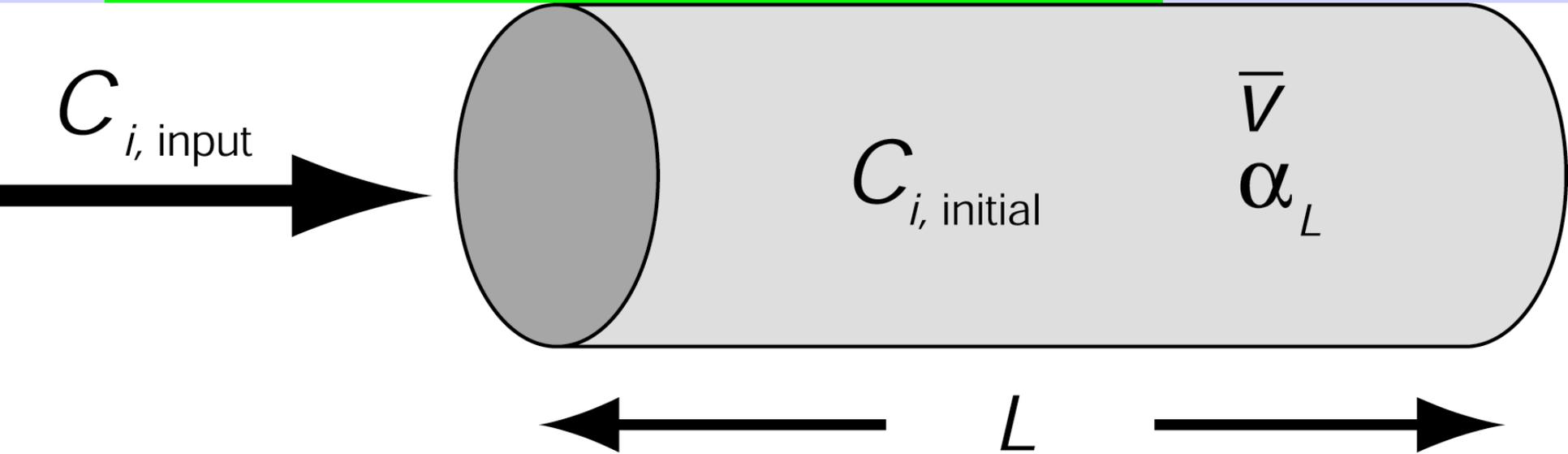
Figure 2.6. Schematic representation of the inverse mass balance model.



Types of Geochemical Models (continued)

- ❖ **4. Coupled Mass Transport Models**
 - ◆ **Partial differential equations describing physical transport processes**
 - ◆ **Algebraic equations describing chemical equilibrium and kinetics**
 - ◆ **Heat conduction**
 - ◆ **Fluid flow**

Figure 2.7. Schematic diagram of a one-dimensional reactive transport model.



State of geochemical modeling

- ❖ **Geochemical modeling useful**
- ❖ **Grossly under used**
- ❖ **Limitations mostly from kinetics and surface adsorption**
- ❖ **Model is useful in integrating data, quantifying processes**

The “rule of three” for geochemical modeling

- ❖ **A computer code**
- ❖ **A thermodynamic, kinetic, and surface property database**
- ❖ **Chemical and physical measurements of the system of concern**

PHREEQC

http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/

- ❖ **U.S. Geological Survey, public domain**
- ❖ **C Language**
- ❖ **Three versions**
 - ◆ **phreeqc-interactive, will be used in class**
 - ◆ **Batch win32**
 - ◆ **Windows by Vincent Post**
- ❖ **Manual in PDF format**
- ❖ **Databases**
- ❖ **Example input files (18)**

MINTEQA2

<http://www2.lwr.kth.se/English/OurSoftware/vminteq/>

- ❖ **U.S. Environmental Protection Agency (EPA), public domain**
- ❖ **Fortran Language**
- ❖ **Three versions**
 - ◆ **MS-DOS version by EPA, free**
 - ◆ **Visual MINTEQ by the Swedish, free, will be used in class**
 - ◆ **MINTEQA2 for Windows by Allison, at cost**
- ❖ **Manual in PDF format**
- ❖ **Visual MINTEQ has guides in html format**

Part 2: database

- ❖ **LLNL.dat: Jim Johnson, EQ3/6**
- ❖ **Minteq.dat: Minteq**
- ❖ **MINteqv.4.dat: ver. 4.02 of MINTEQA2**
- ❖ **Waterq4f.dat: From Ball and Nordstrom (1990)**
- ❖ **Pitzer.dat: with Pitzer equation**

Internal consistency of thermodynamic data

(Nordstrom and Munoz, 1986)

- ◆ Data are consistent with thermodynamic relationship (the basic laws and their consequences)
- ◆ Common scales are used for T, energy, atomic mass, and fundamental physical constants
- ◆ Conflicts among measurements have been resolved
- ◆ The mathematical model is used to fit different data sets
- ◆ The same chemical model is used to fit different data sets
- ◆ Appropriate consideration has been given to starting point in applying item 1
- ◆ Appropriate choice of standard states has been made, and the same standard states have been used for all similar substance

Book by Cambridge
University Press

Environmental Applications of **Geochemical Modeling**

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5.9.3 Who Produced the Model?

The common perception among environmental practitioners, that a modeling program produces a model, is not correct. *It is always the modeler, not the computer code, that produces a model.* In environmental practice, this misconception, and sometimes misrepresentation, borders on deception of the public, regulators, or clients because most popular modeling codes are distributed by regulatory or federal agencies and therefore carry an air of authority.

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in fact we make a distinction between computer programs and models. A model is produced by a human being aided by computer programs. He or she must choose what data to use, what computer program options are appropriate, and must select the results which seem reasonable, and reject those which do not.



Code \neq Model

database (maybe) = model(s)

- ❖ **Code = appliance (David Sherman)**
 - ◆ **Oven: bake fish, beef, or sweet potato**
- ❖ **Input file is your model design**
- ❖ **"Databases" imply models**
 - ◆ **Activity coefficient models (ion association vs ion interactions, Davis vs. B-dot)**
 - ◆ **Aqueous speciation (Tagoriv and Schott (2001) for Al or Shock et al. (1989) or Pokrovskii and Helgeson (1995))**



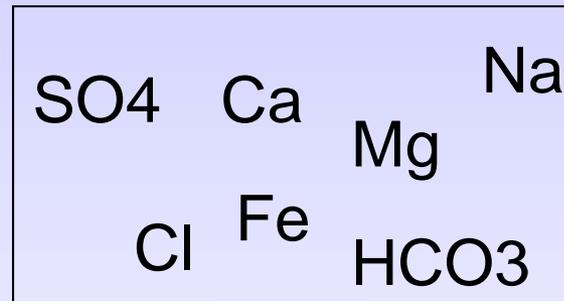
1. Speciation – solubility modeling

- ❖ Solving a set of mass balance and mass action equations
- ❖ Need an activity coefficient model
- ❖ A number of computer codes available: Eq3/6, PHREEQC, MINTEQ family, Geochemist's Workbench[©], etc

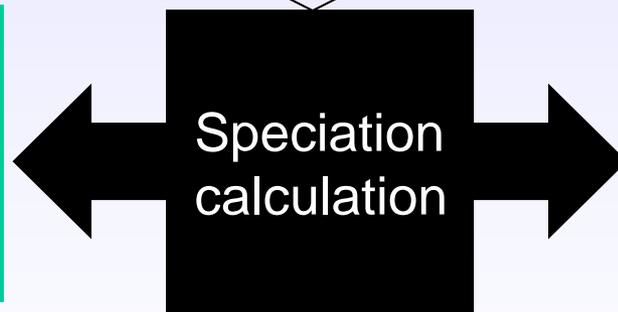
- ❖ Snap shot of the state of the chemical system at a point in time
- ❖ Building blocks for more advanced process modeling

Speciation and Solubility Modeling

Water chemical analysis



Saturation Indices



Species distribution

Thermodynamic database

Speciation-solubility model

- ❖ **What are the concentrations and activities of ionic and molecular species in an aqueous solution?**
- ❖ **What are the saturation states with respect to various minerals in the system, and hence the directions of reactions that might occur toward achieving equilibrium?**
- ❖ **Closed, static, batch, or beaker type system**

What is a speciation calculation?

❖ **Input:**

- ◆ pH
- ◆ pe
- ◆ Elemental Concentrations

❖ **Equations:**

- ◆ Mass-balance—total calcium = sum of the calcium species
- ◆ Mass-action—activities of products divided by reactants = equilibrium constant
- ◆ Newton-Raphson Iteration
- ◆ Activity coefficients—function of ionic strength and ion properties

❖ **Output**

- ◆ Molalities, activities of all aqueous species
- ◆ Saturation indices



Figure 6.2. Plan view of the mine site and tailings impoundment.

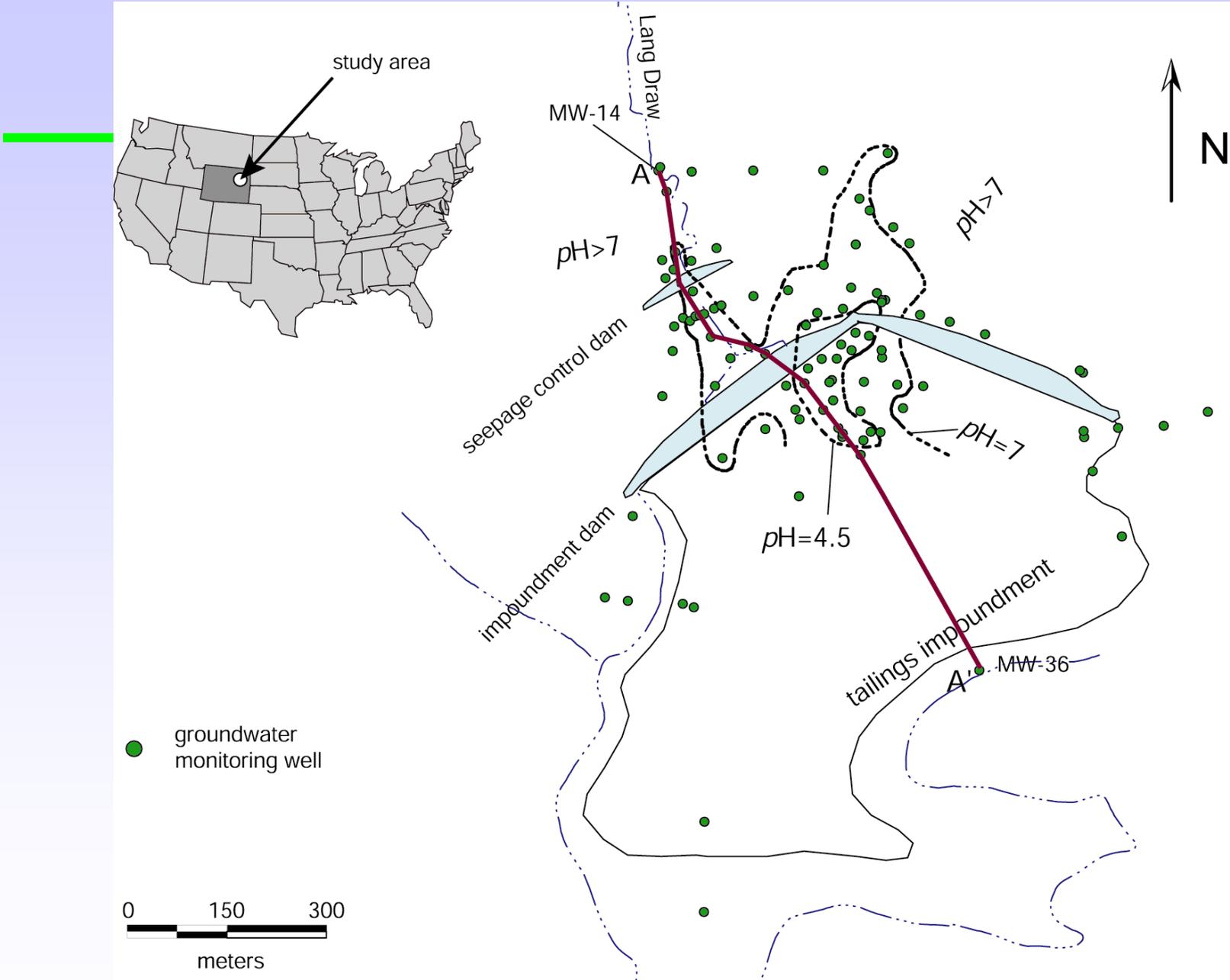
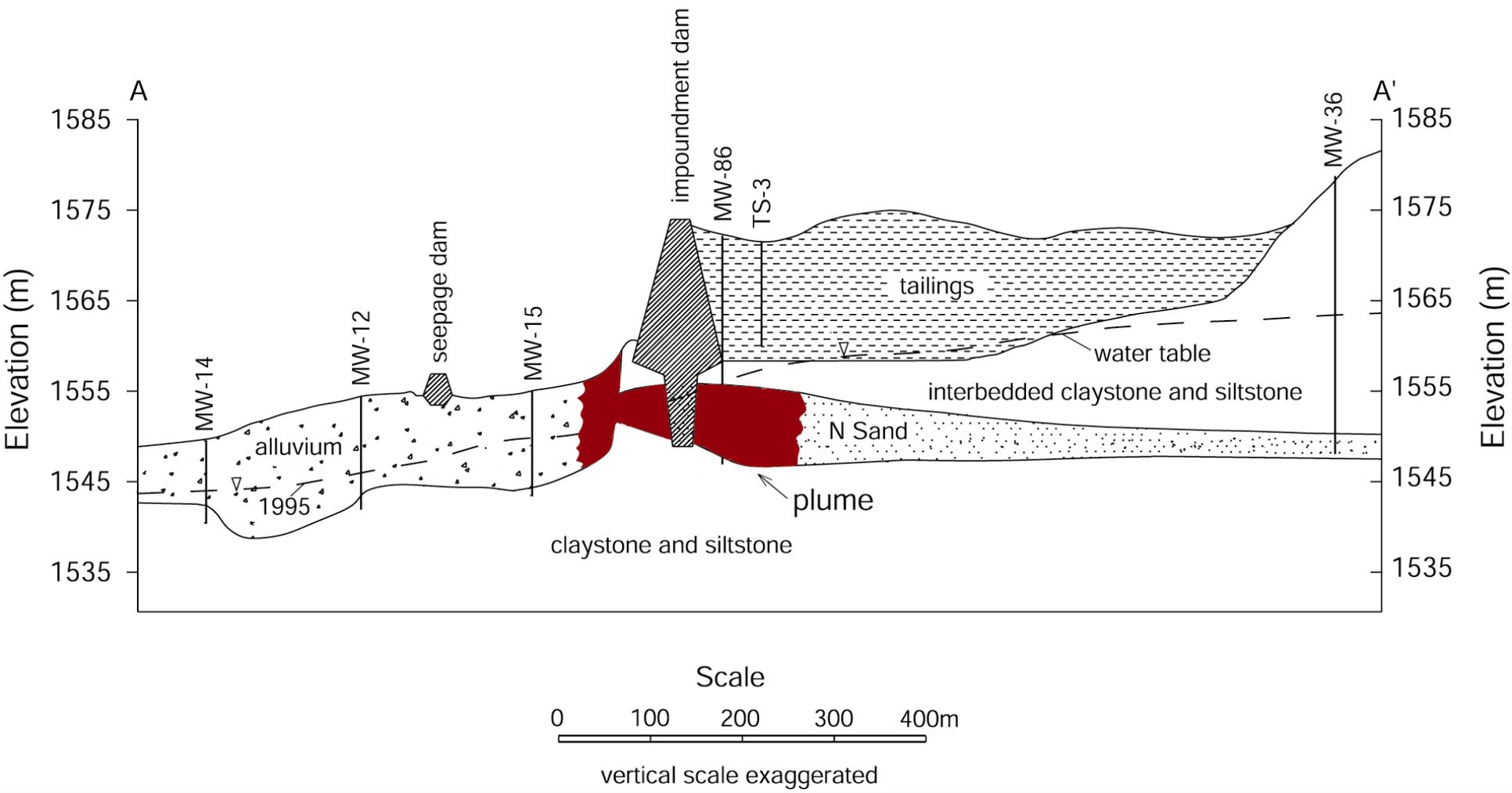


Figure 6.3. Cross-section A—A' from Figure 6.2. Water level was recorded on January 5, 1995.



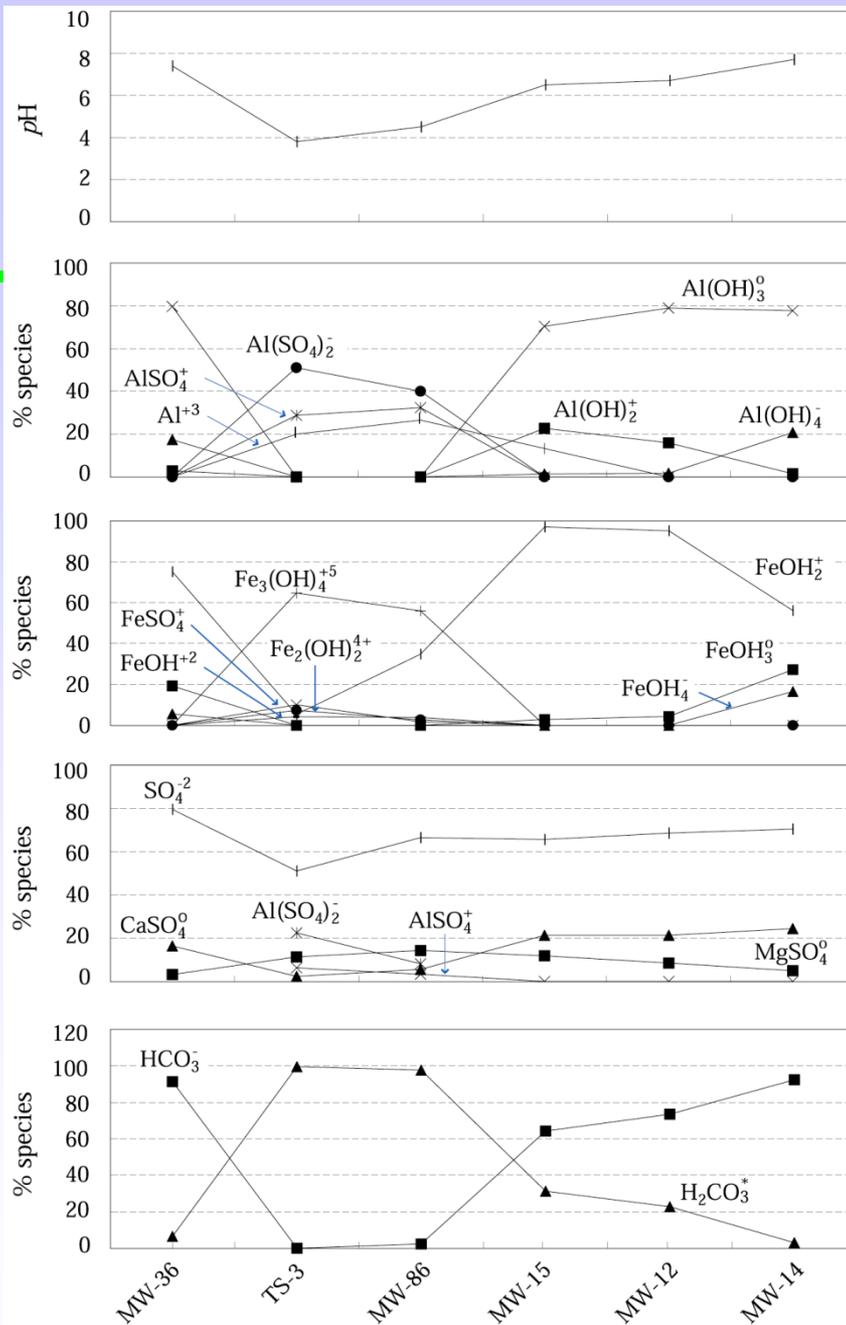


Figure 6.4. Changes of species distribution in groundwater samples from Cross-section A—A' of Figure 6.3.

Figure 6.5. Saturation Indices for carbonate minerals from MINTEQA2.

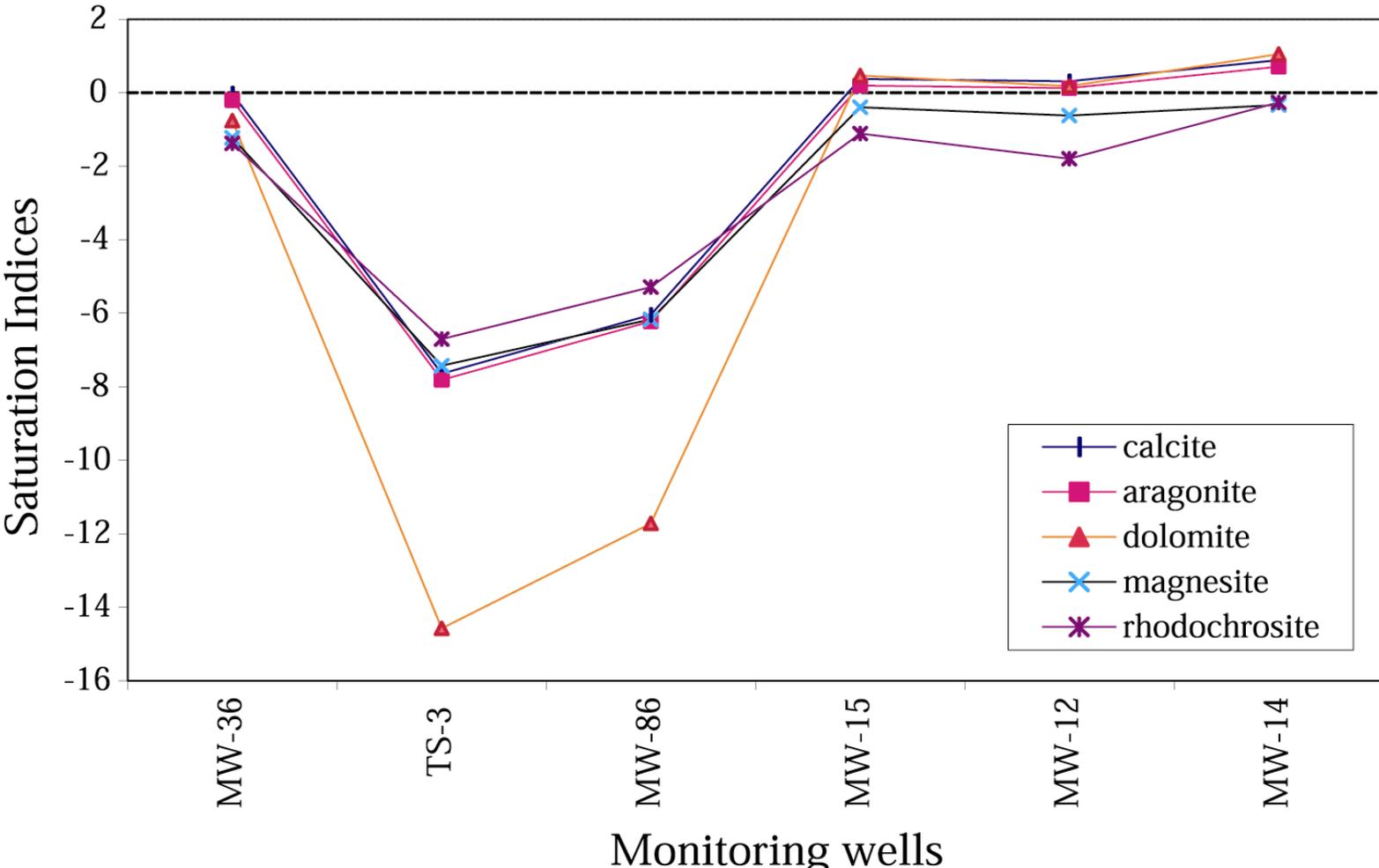
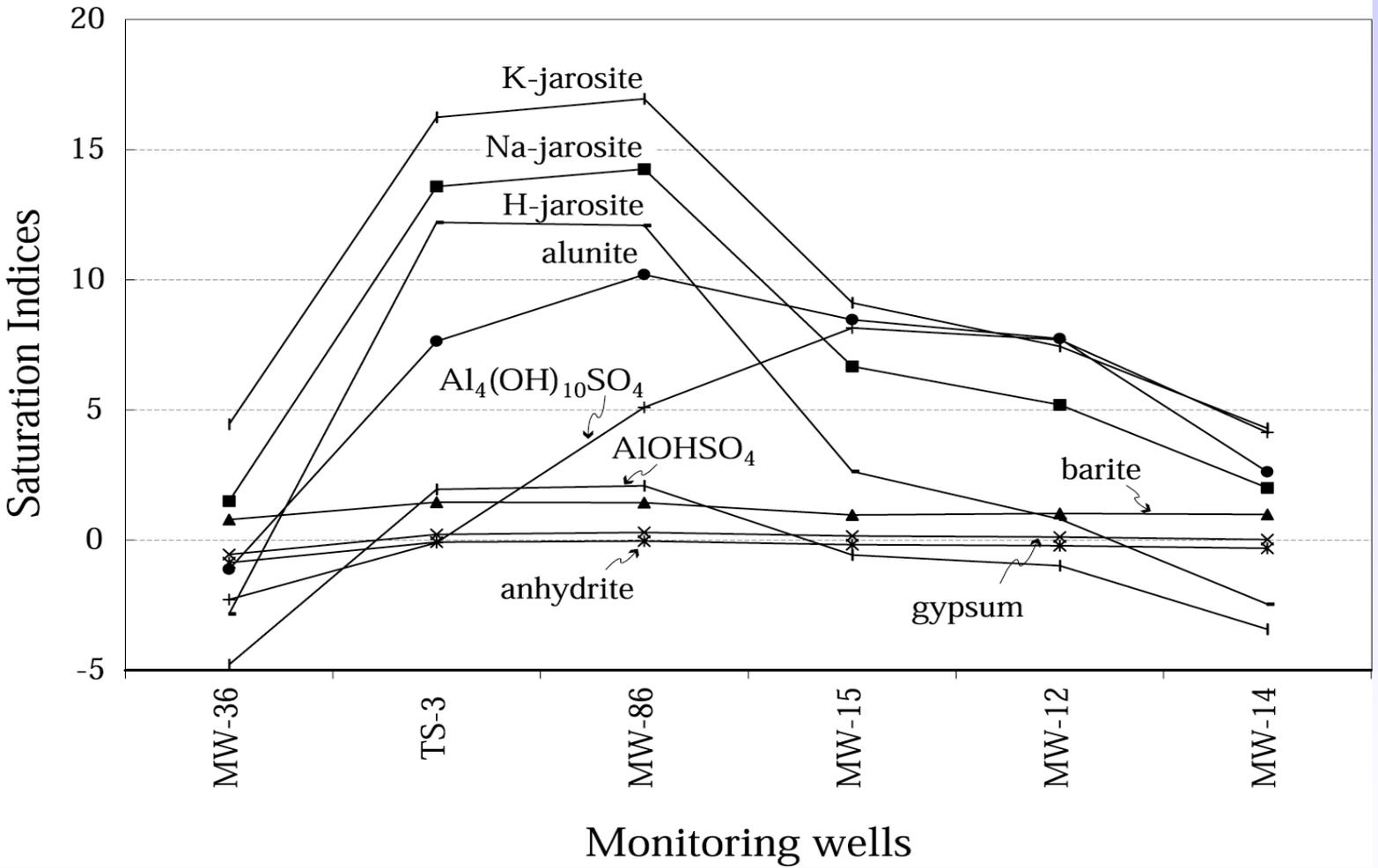
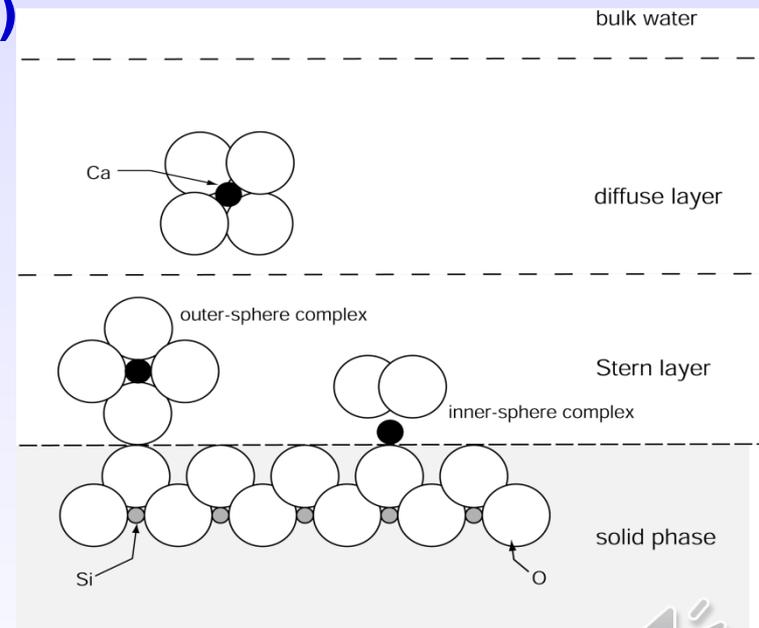


Figure 6.6. Saturation Indices for sulfate minerals from MINTEQA2.



Modeling Surface Adsorption

- ❖ Adsorption onto mineral surfaces generally is the process controlling the concentration of most metal contaminants
 - ◆ Concentrations of contaminants (e.g., Pb, As) are at the ppm to ppb level (not controlled by solubility)
 - ◆ The subsurface has large surface areas
- ❖ Fe and Mn oxyhydroxides commonly play a major role even when constituting a minor fraction of the bulk rocks, soils, or sediments
- ❖ Tied to the redox cycle

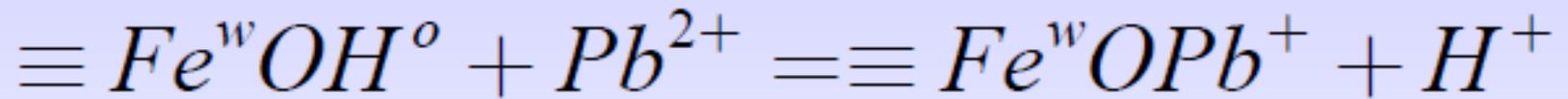


Significance of surface adsorption in environmental studies

- ❖ **Low concentrations of pollutants**
- ❖ **Large surface areas in porous media**
- ❖ **Trace elements or contaminants not controlled by mineral solubility, but by surface adsorption**
- ❖ **Dissolution and precipitation reactions are thought to be controlled by surface reactions**

Surface complexation models

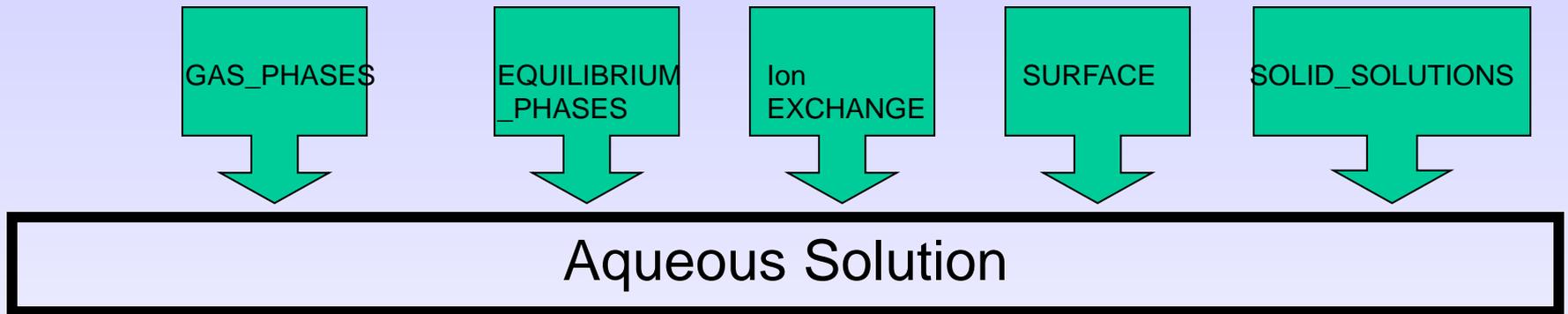
❖ Adsorption onto hydrous ferric oxides (HFO)



$$K = \frac{[\equiv FeOPb^+]a_{H^+}}{[\equiv FeOH^o]a_{pb2+}} e^{(\Delta ZF\Psi/RT)}$$

- Law of mass action, $\Delta_r G$ activity, $\log K$
- Analogous to aqueous complex formation
- Electrostatic correction term later

Equilibrium phase modeling



Types of Geochemical Models (continued)

❖ Reaction Path Models

- ◆ A sequence of states involving incremental or step-wise mass transfer between phases
- ◆ Incremental addition or subtraction of a reactant
- ◆ Increase or decrease of T, P.

❖ Simulate processes versus speciation-solubility calculations that simulate equilibrium states

❖ Chemical equilibrium and kinetics + mass balance principles

❖ Read Helgeson (1968), Helgeson et al. (1969)

Fig. 2.4. Schematic representation of a mixing or titration model.

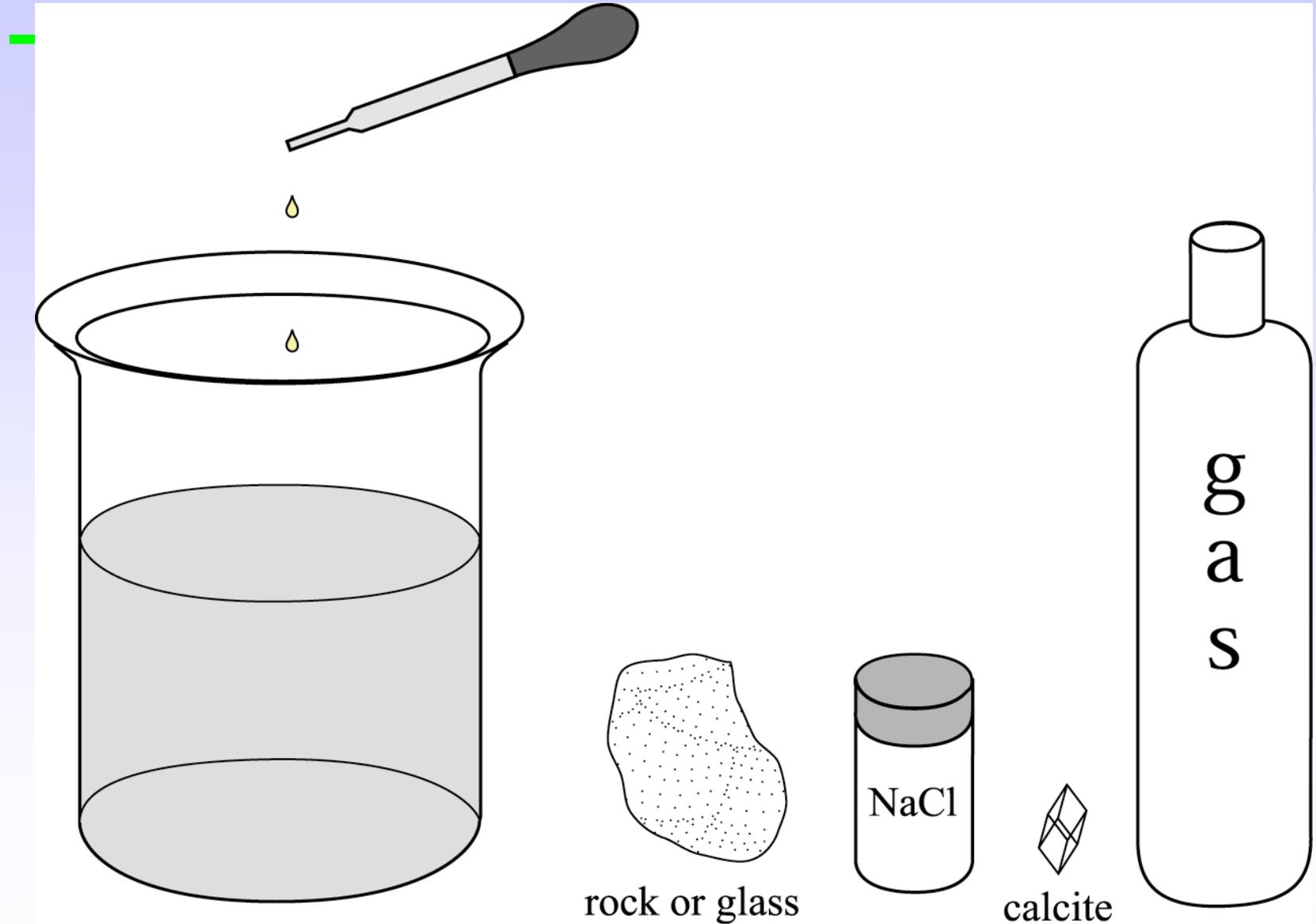


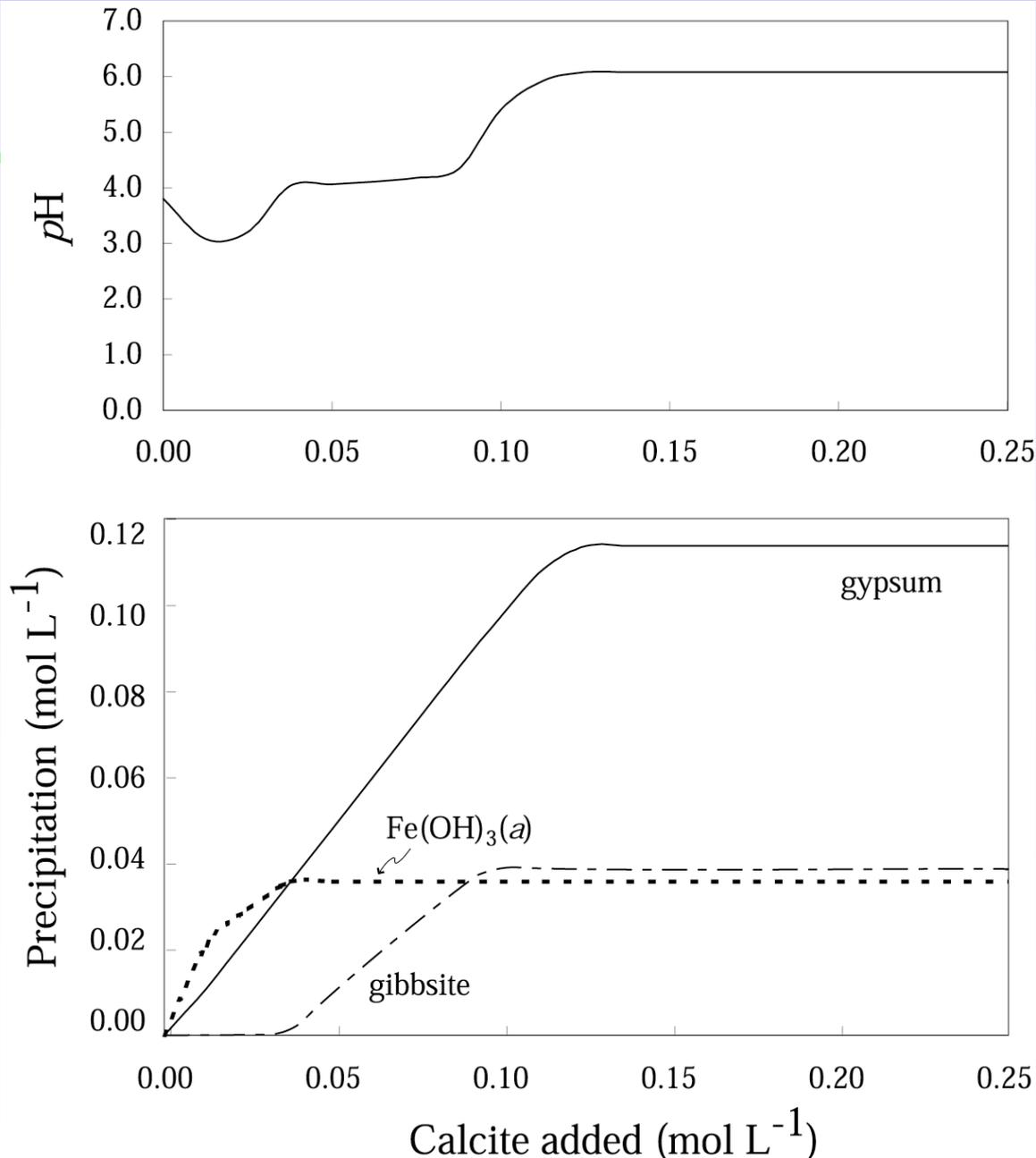
Table 8.2

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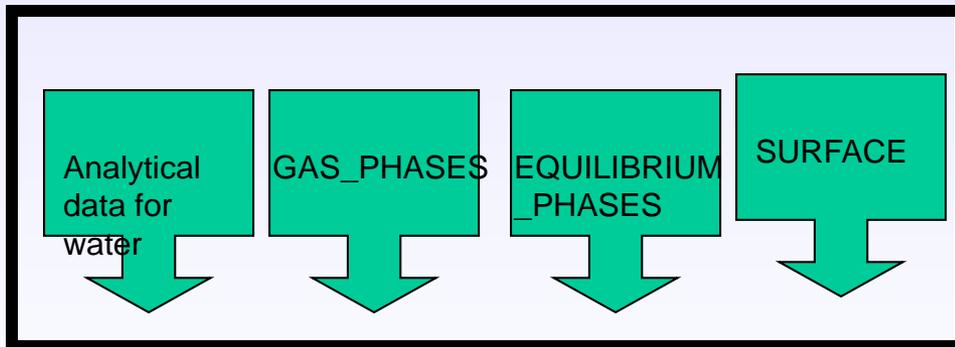
```
TITLE Titrate TS-3 with calcite
SOLUTION 1 TS-3
  pH      3.8
  unit    mg/l
  temp    16.0
  Na      389.    charge
  K       60.
  Ca      310.
  Mg     1000.
  Cl      550.
  C(4)    5.
  S(6) 16500.
  Fe(3) 1950.
  Al     1020.
  Mn(2)  66.3
  Si     40.5
EQUILIBRIUM_PHASES 1
  Gibbsite      0.0  0.0
  Fe(OH)3(a)    0.0  0.0
  calcite       0.0  0.0
  gypsum        0.0  0.0
  CO2(g)
REACTION 1 Add calcite to the acid groundwater
  Calcite      1.0
  0.25        moles in 20 steps
SELECTED_OUTPUT
  -file      ts3.pun
  -a        H+
  -si calcite
  -equilibrium_phases  gypsum Fe(OH)3(a) gibbsi
END
```

- Simulate limestone treatment of AMD
- Simulate reactions, albeit without flow, when AMD encounter calcite in soils and aquifers

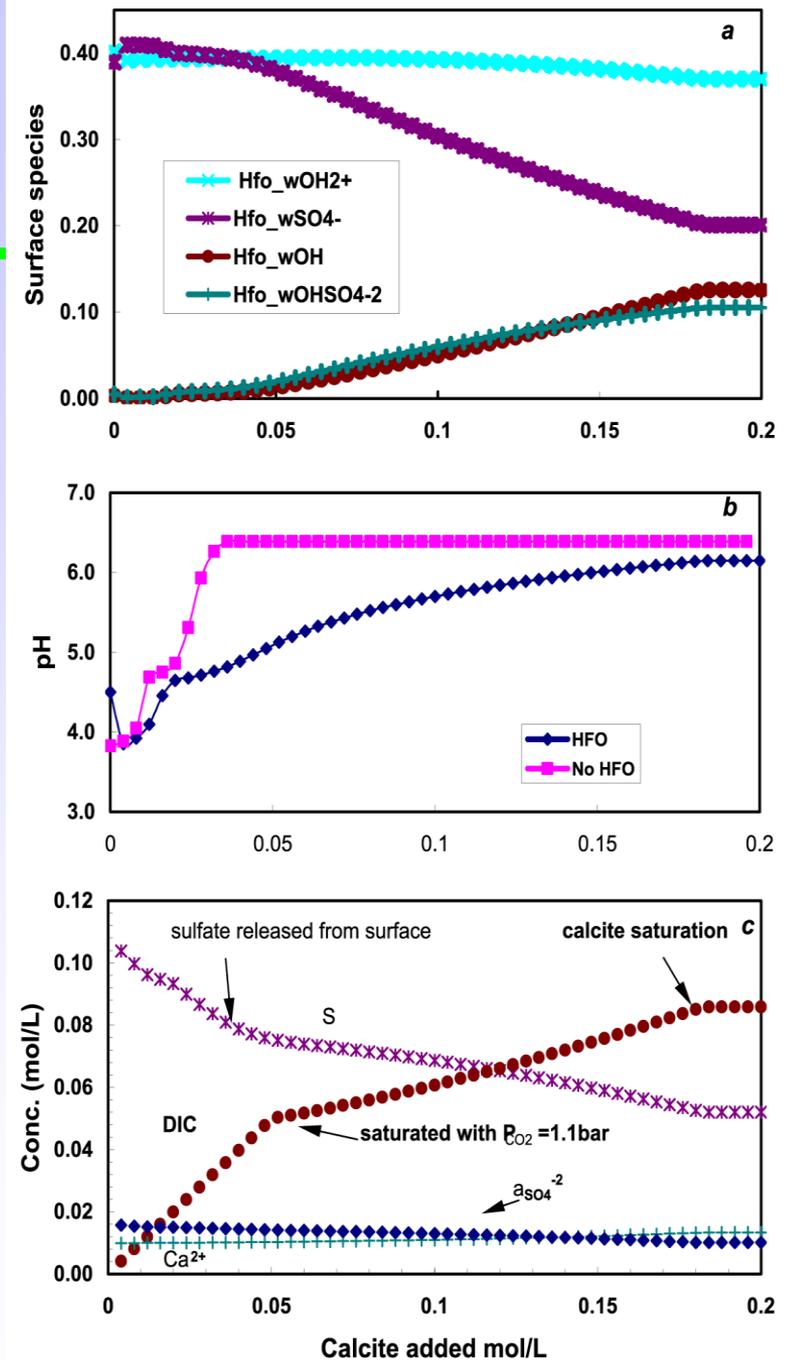
Figure 8.4. Results of titration of calcite into TS-3 water.



Titration of calcite to pore water + Fe(OH)₃ with adsorbed acidity



Zhu et al., 2002, *Ground Water*

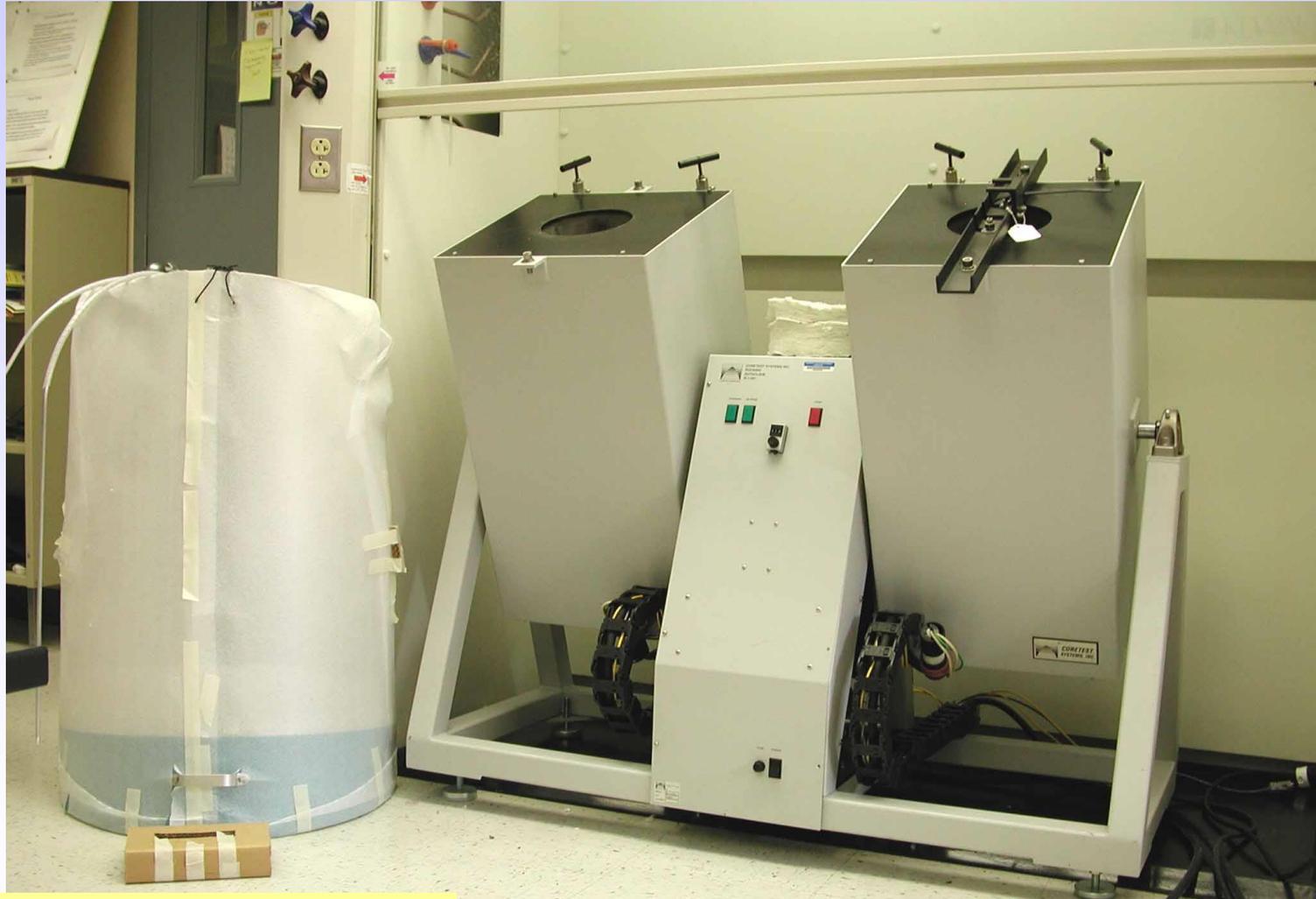


Chap. 11 Kinetics Modeling – put reaction on a time scale

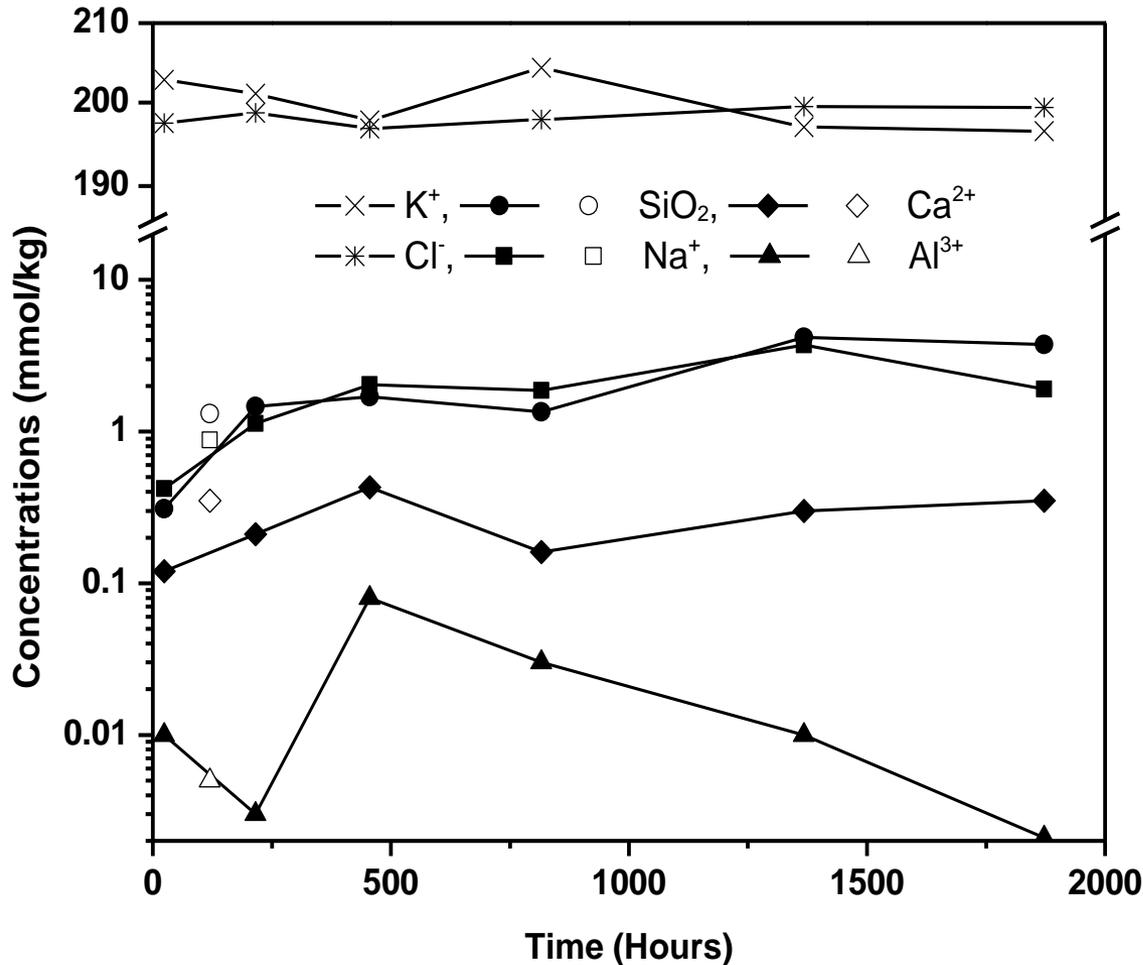
Experiment of feldspar hydrolysis

Dual furnace rocker autoclave for gas/water/rock interaction experiments

In situ
sampling
solution



Time-series solution chemistry for major and trace elements (200 °C, 300 bars)



Modeling kinetics with PHREEQC

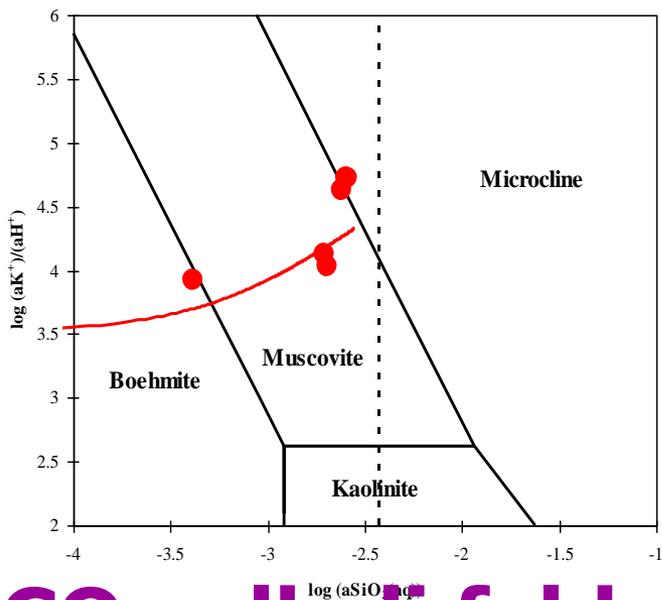
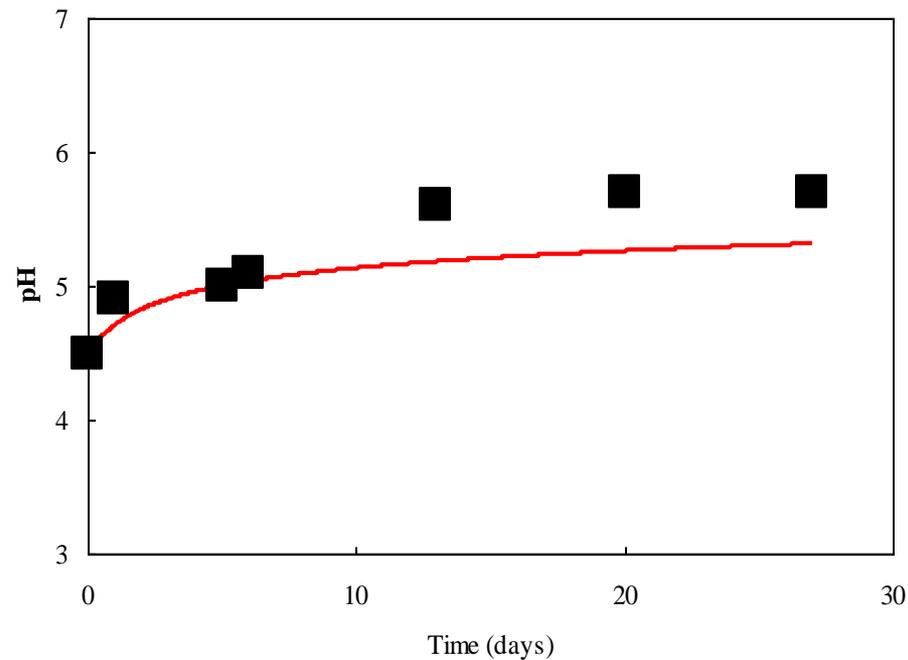
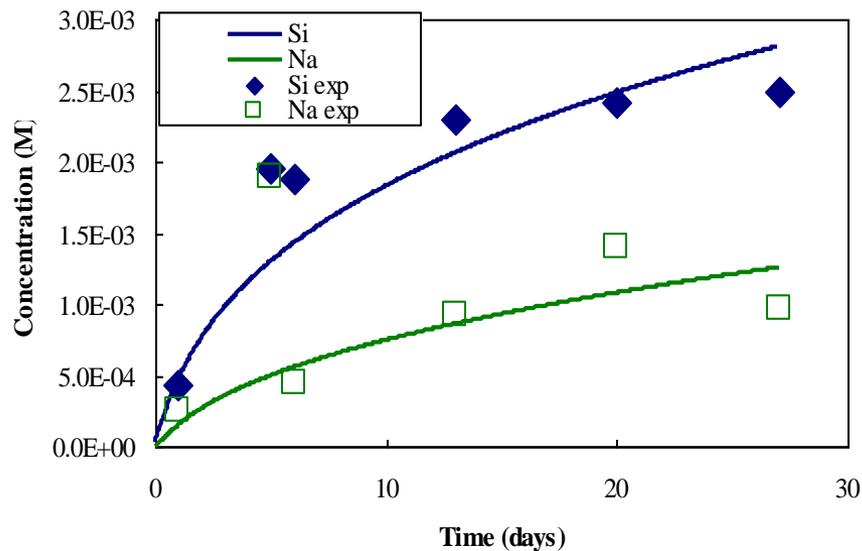
❖ PHREEQC Keywords

◆ Kinetics

- Keyword call for kinetic calculation
- Pass parameters to RATES

◆ Rates

- The Basic function
- Completely programmable



$k^*_{clay}/k^*_{feldspar} \ll 1$

CO₂-alkali feldspar-brine experiments at 200 °C 300 bars, 50 mM CO₂, 0.2M KCl

General Rate Law (Lasaga, 1981)

$$R_j = k_j S_j a_{H^+}^{n_{H^+}} g(I) \prod_a a_i^{n_i} f(\Delta G_r)$$

- ❖ R_j is the rate of dissolution of the j th mineral ($\text{mol m}^{-2} \text{ s}^{-1}$)
- ❖ k_j the respective rate constant
- ❖ S_j the reactive surface area
- ❖ a_{H^+} -- activity of hydrogen in the aqueous solution
- ❖ $g(I)$ accounts for possible ionic strength dependence of the rates
- ❖ $\prod_a a_i^{n_i}$ catalytic and inhibitory effects of all aqueous species e.g., Al
- ❖ ΔG_r stands for the Gibbs free energy of the reaction
- ❖ $f(\Delta G_r)$ accounts for the variation of the rate with the deviation from equilibrium

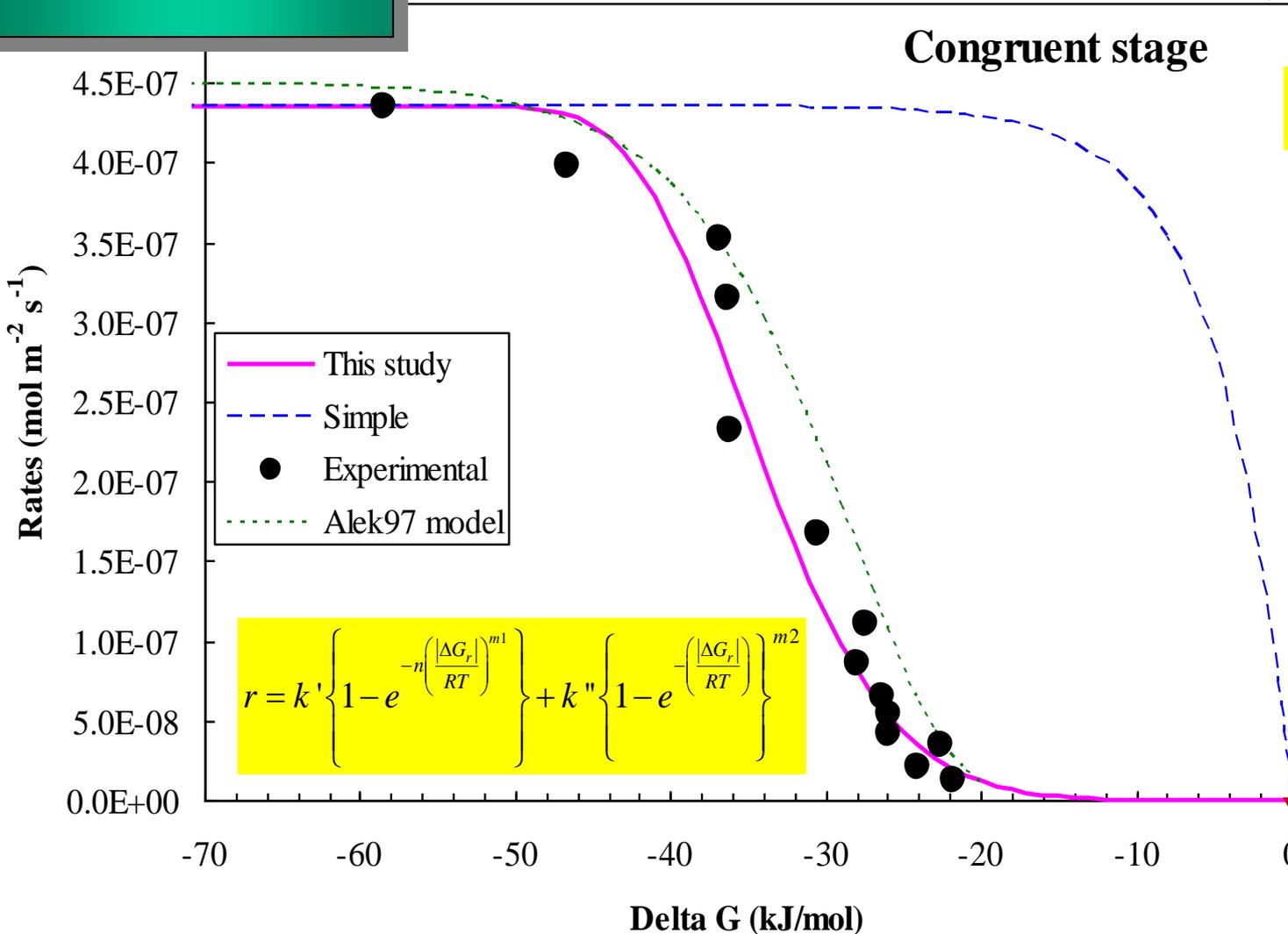
$f(\Delta G_r)$ - the thermodynamic drive

Far from eqbm

Albite dissolution at 300 °C, pH 9

Congruent stage

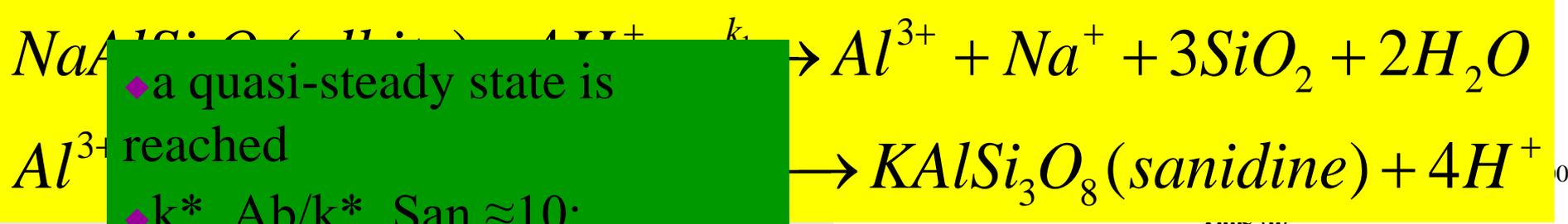
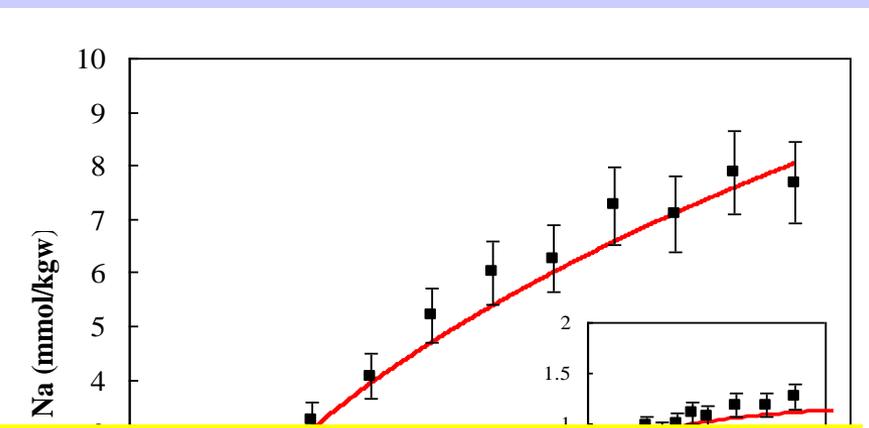
$$r_1 = k_1 S_1 (1 - e^{\Delta G_r / RT})$$



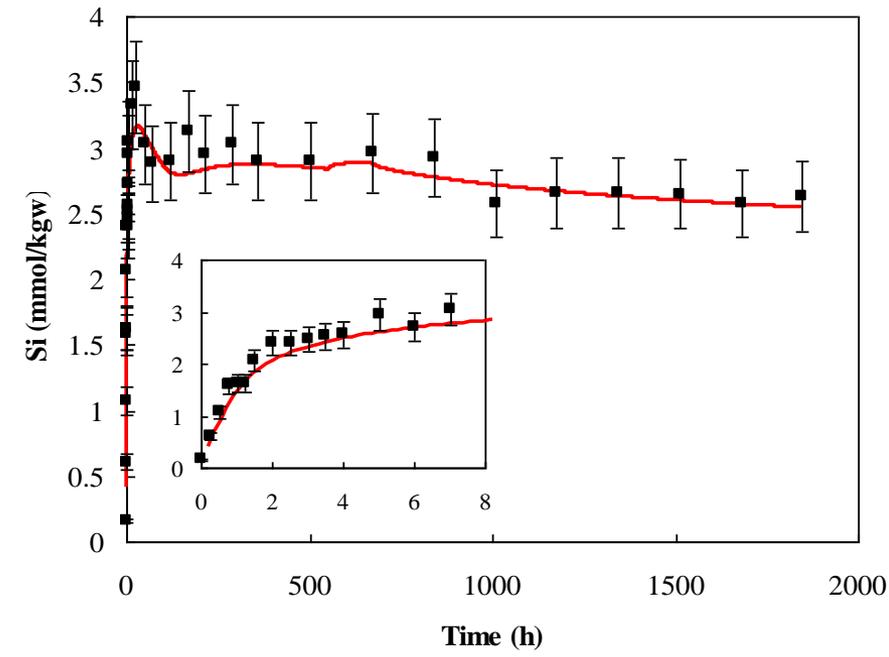
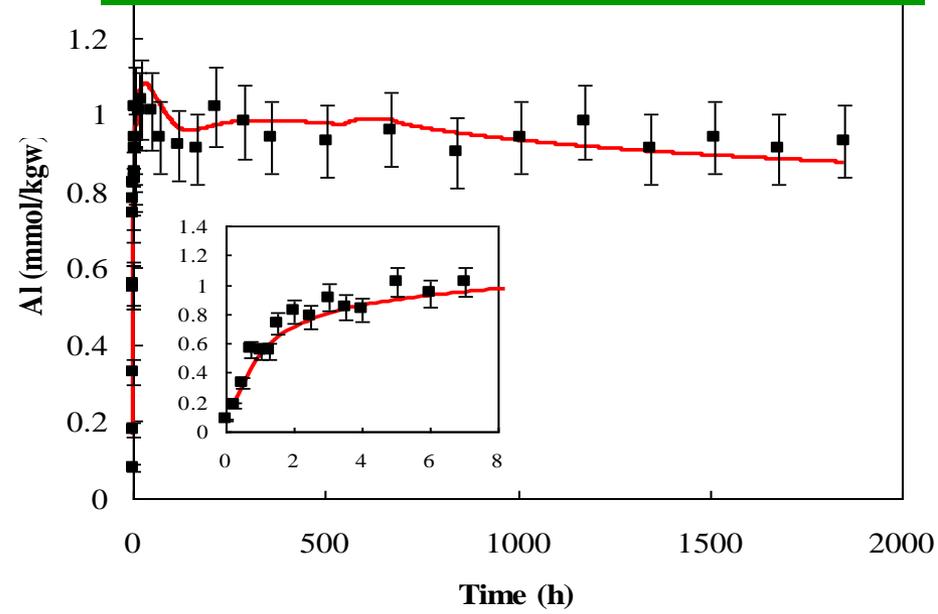
- Transition State Theory
- Linear
- Simple

equilibrium

Albite dissolution – sanidine precipitation, 300 °C, pH 9, Alekseyev et al. (1997)

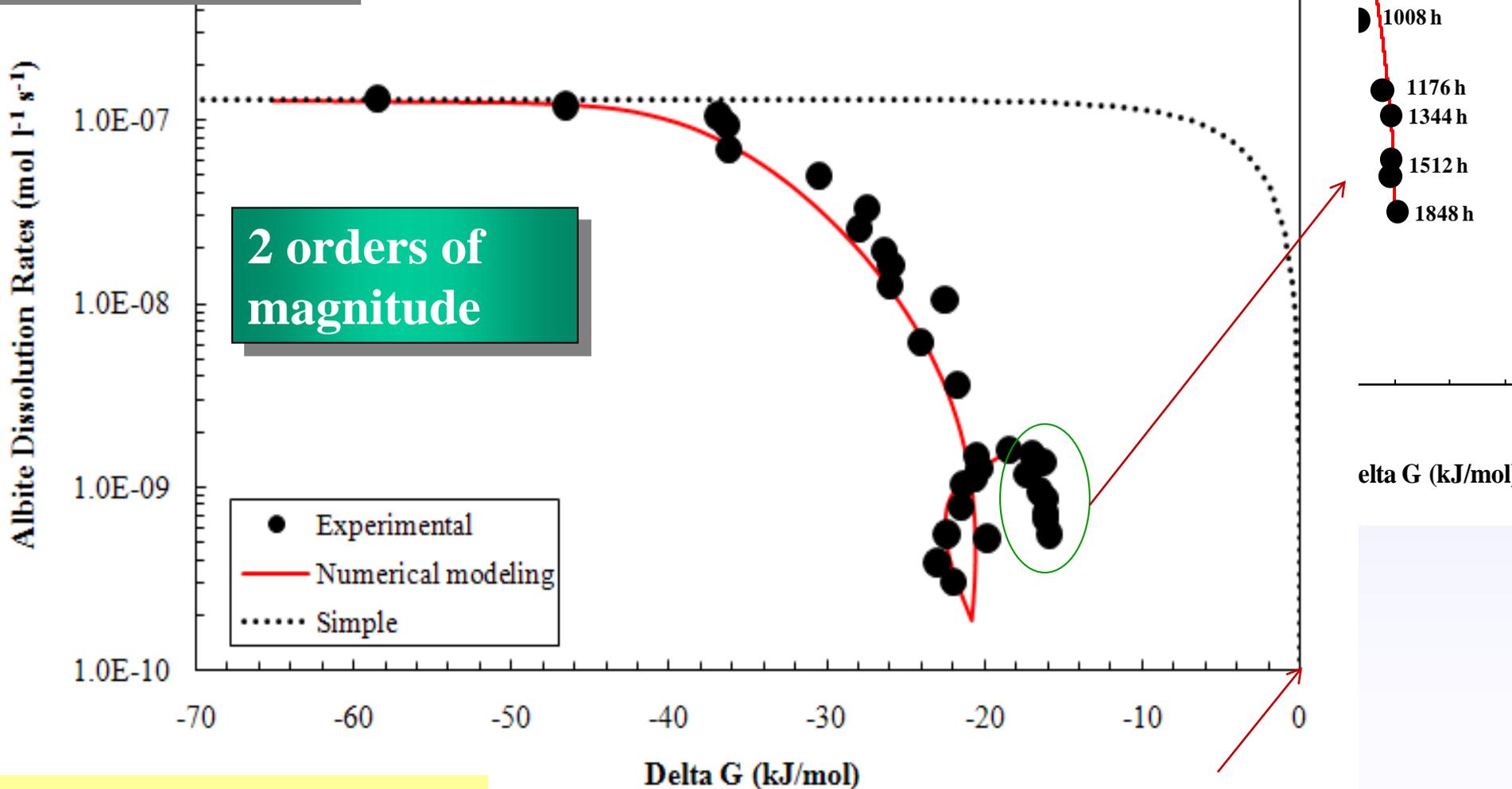


◆ a quasi-steady state is reached
 ◆ $k^*_{Ab}/k^*_{San} \approx 10$;
 $k^* = k \times S_A$

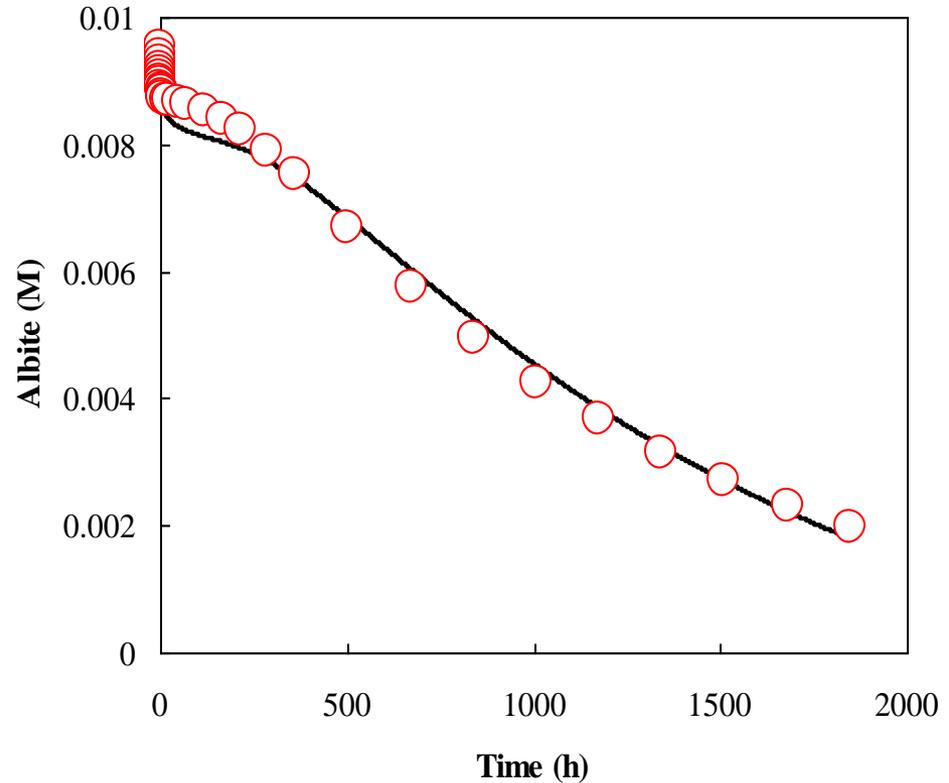
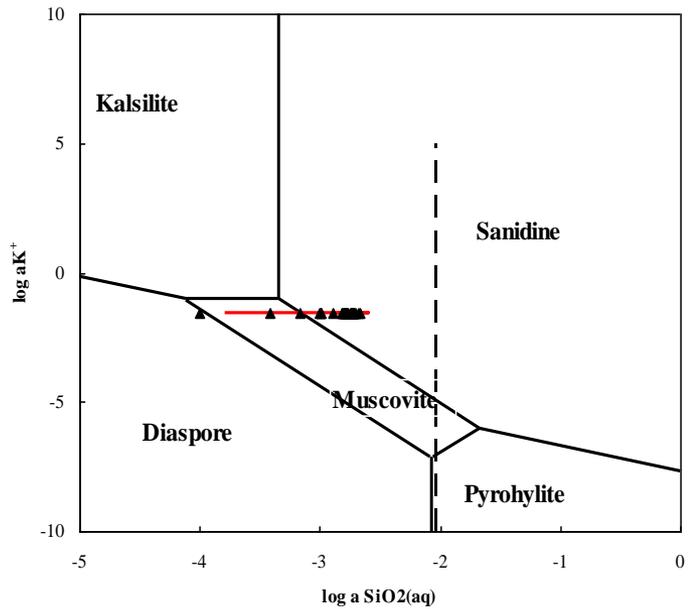
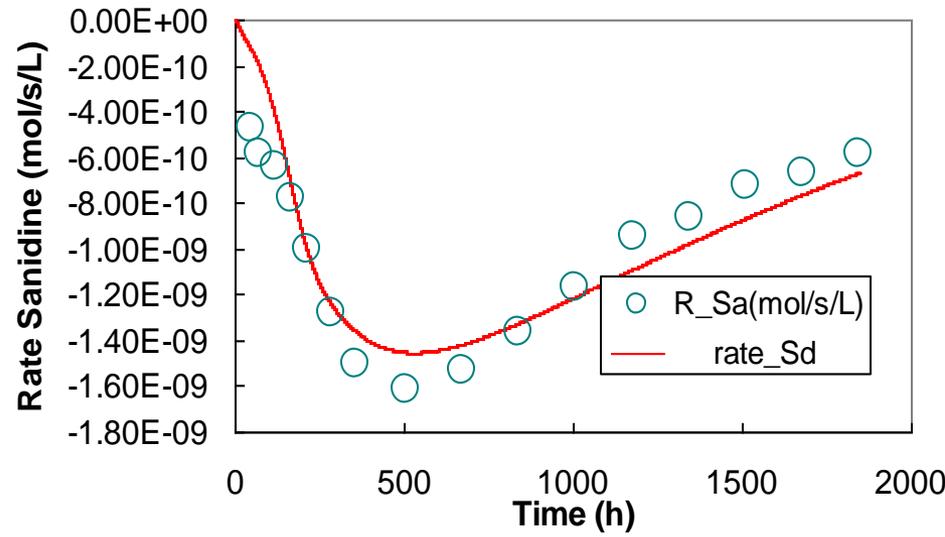
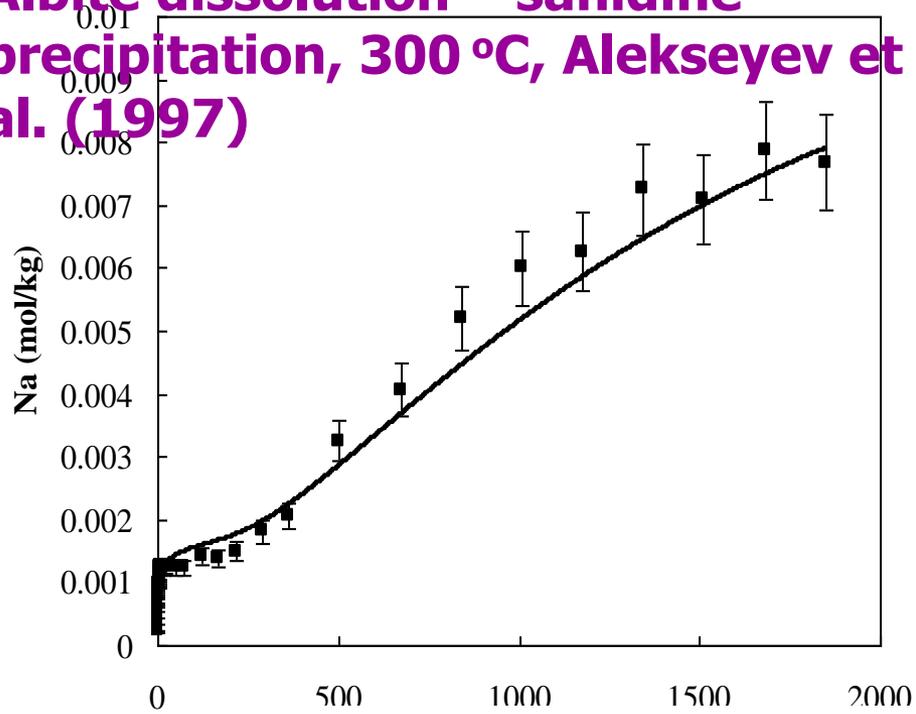


Albite dissolution and sanidine precipitation (Alek9)

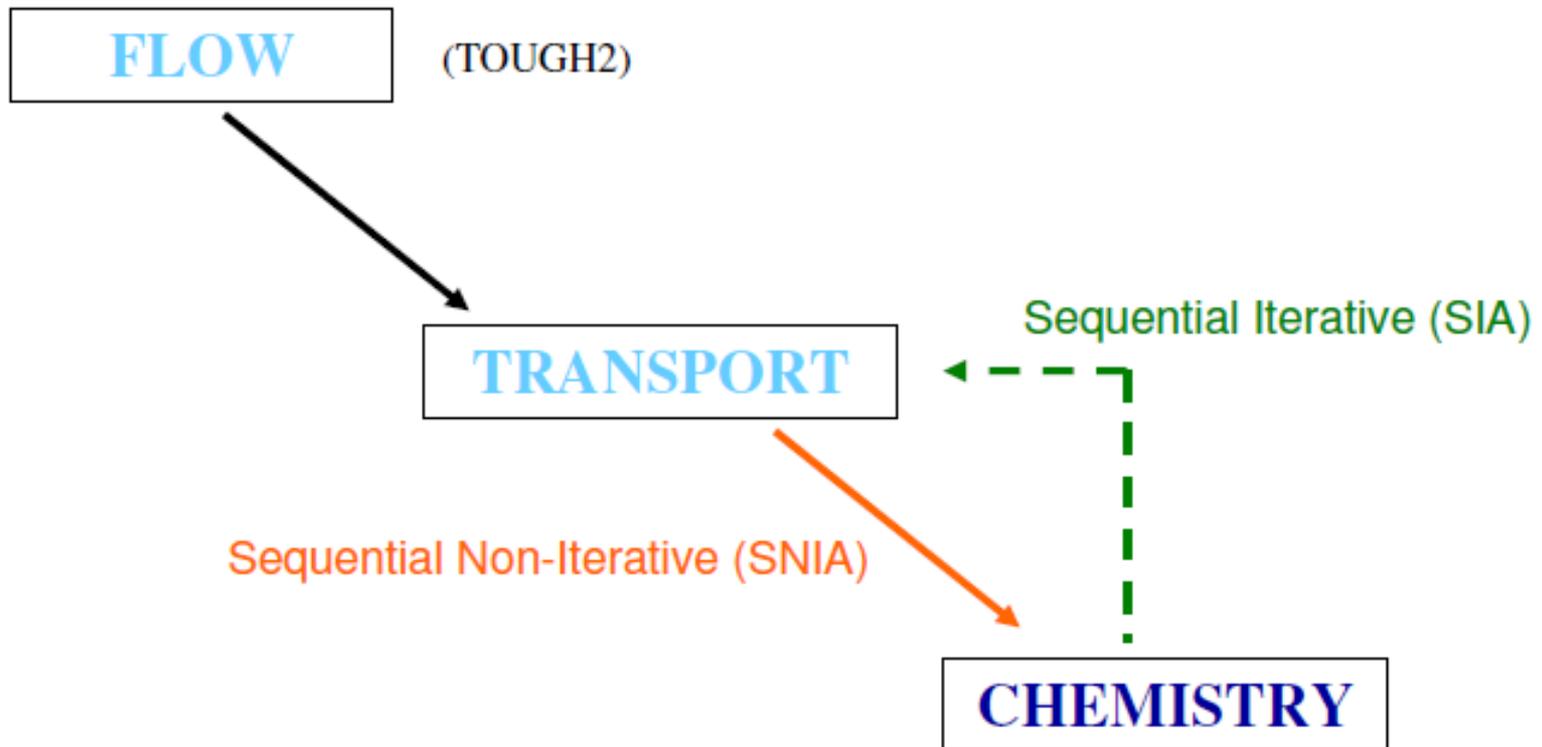
Far from eqbm



Albite dissolution – sanidine precipitation, 300 °C, Alekseyev et al. (1997)



Reactive Transport Computational Approach



Multicomponent Chemical System

- Multicomponent Reactions (water must be present)
 - Aqueous Species
 - Minerals
 - Gases
 - Exchange Species
 - Surface Complexes (v2.0 beta)
- Aqueous Speciation: equilibrium (v2.0 beta with kinetics)
- Surface Complexation/Exchange: equilibrium
- Mass Transfer:
 - Minerals: equilibrium or kinetic constraints
 - Gases: equilibrium
- External Thermodynamic Database: reaction stoichiometries, equilibrium constants, activity coefficient data, etc.

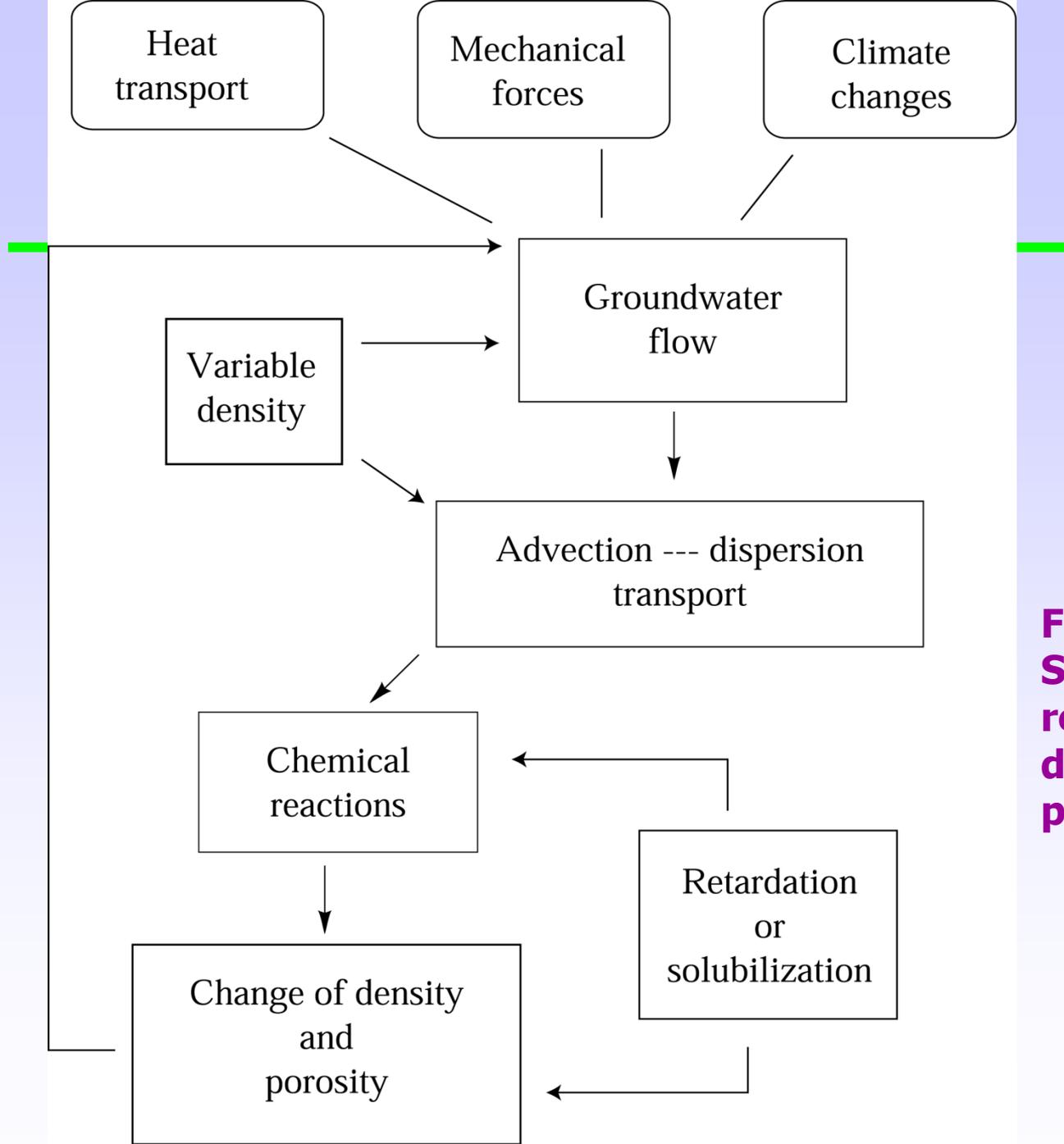
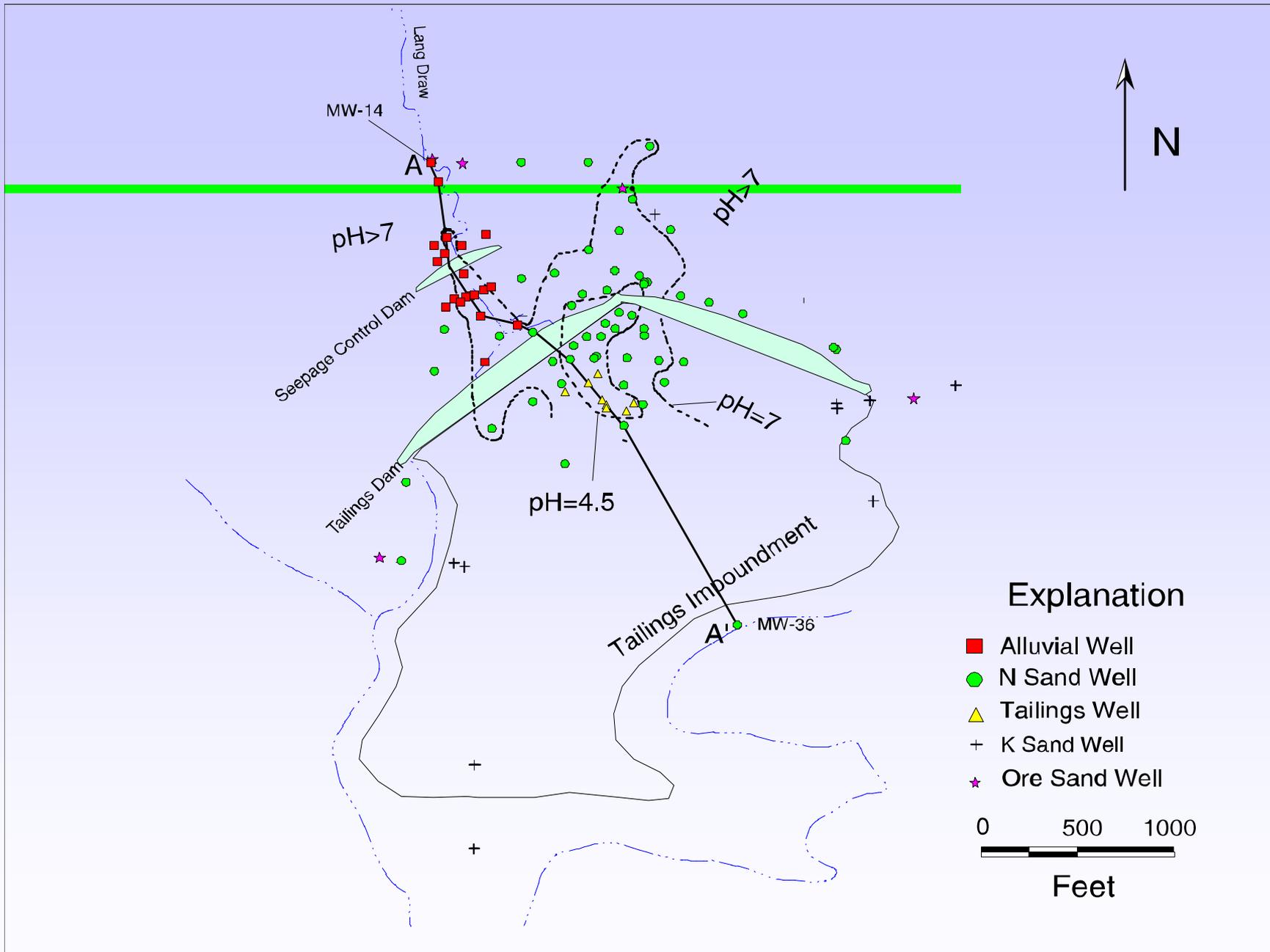


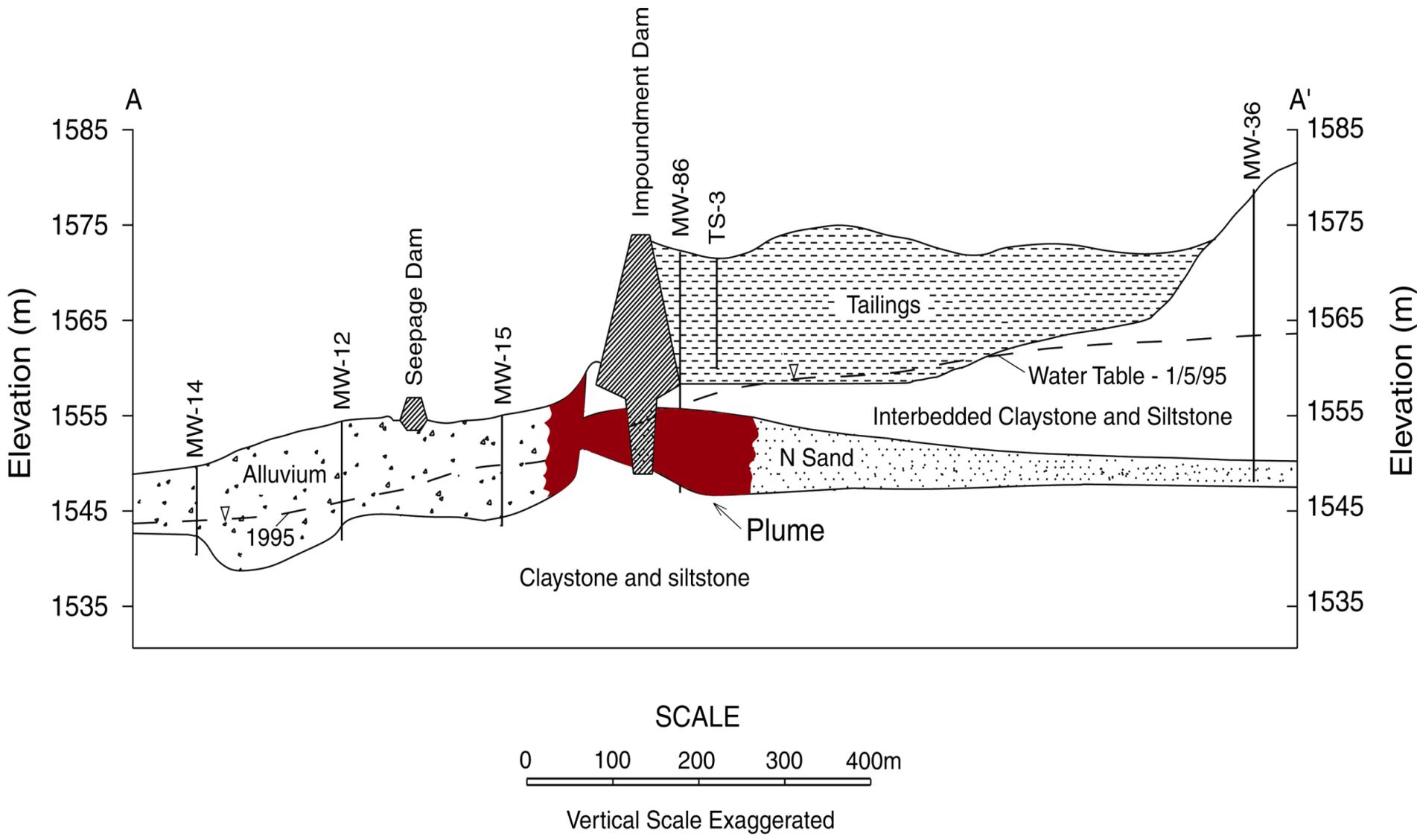
Figure 2.1.
Schematic
representation of
different
processes.



Tailings Fluids

- ❖ pH 1.5 ~ 3.5
- ❖ Contaminants: As, Be, Cd, Cr, Pb, Mo, Ni, Se, ^{226}Ra , ^{228}Ra , ^{230}Th , U
- ❖ Fe 2,000 mg/L, Al ~1,000 mg/L, SO_4^{2-} ~20,000 mg/L



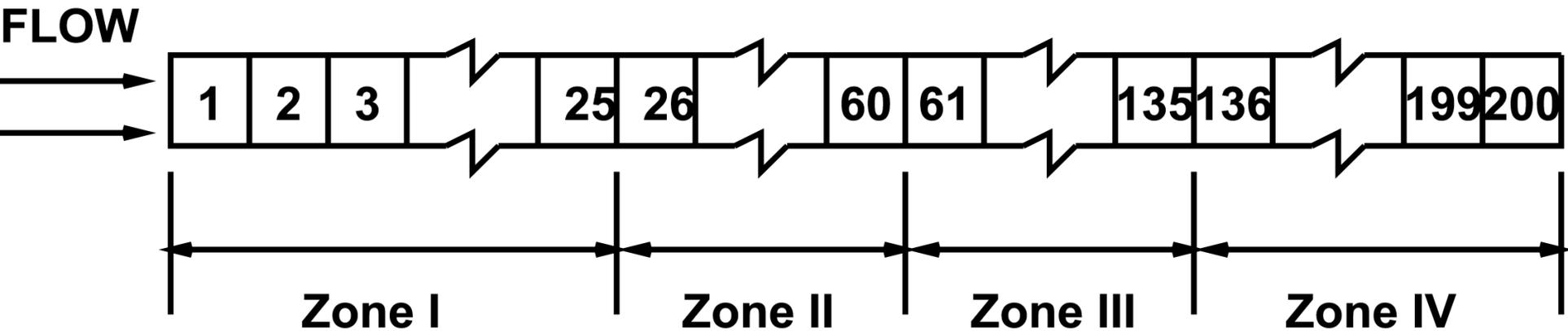


Model to Evaluate Remediation Alternatives

- ❖ “Cover and attenuate” reclamation plan
- ❖ Approval from NRC
- ❖ Will it work?

- ❖ Concentration distribution in time and space
- ❖ 1D coupled reactive transport model, with PHREEQC

Discretization of the simulated domain



Flow and transport model parameters

- **Uniform Darcy velocity 15 m/yr**
- **Porosity 30%**
- **Dispersivity 10 m**
- **Cauchy flux boundary**
 - **first 5 years infiltration of tailings fluid**
 - **another 200 years flushing by uncontaminated upgradient water**

Reaction Model

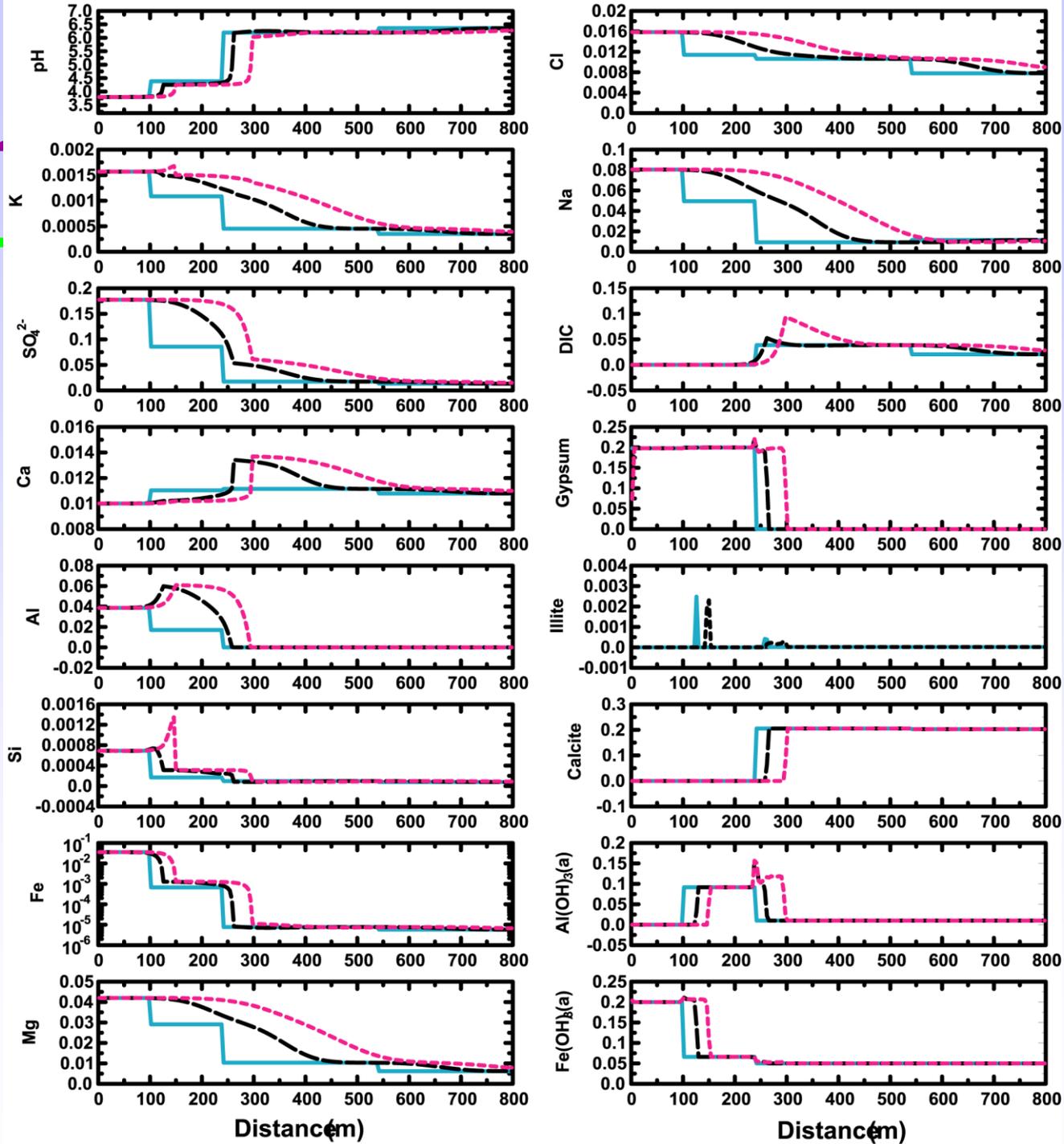
- **11 Components: H, Ca, Mg, Cl, C, Al, S, Fe, Na, K, and Si**
- **6 Minerals: $\text{Al}(\text{OH})_3(\text{a})$, $\text{Fe}(\text{OH})_3(\text{a})$, calcite, gypsum, $\text{SiO}_2(\text{a})$, and illite**
- **Surface adsorption: Dzombak and Morel's double diffuse layer model**
- **Successive pH buffer reactions with calcite, $\text{Al}(\text{OH})_3(\text{a})$, and $\text{Fe}(\text{OH})_3(\text{a})$**

Initial and Boundary Conditions

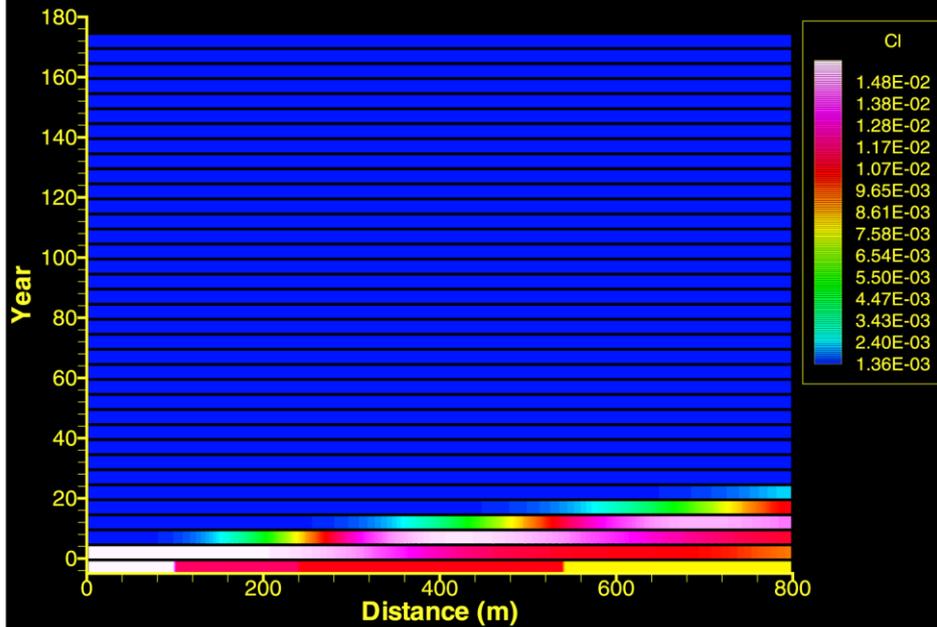
- ❖ **1994 pore fluid measurements**
- ❖ **Bulk mineral analysis and postulations**

- ❖ **Third-type or Cauchy boundary condition at both ends**
- ❖ **Five years infiltration and 200 years flushing by clean groundwater**

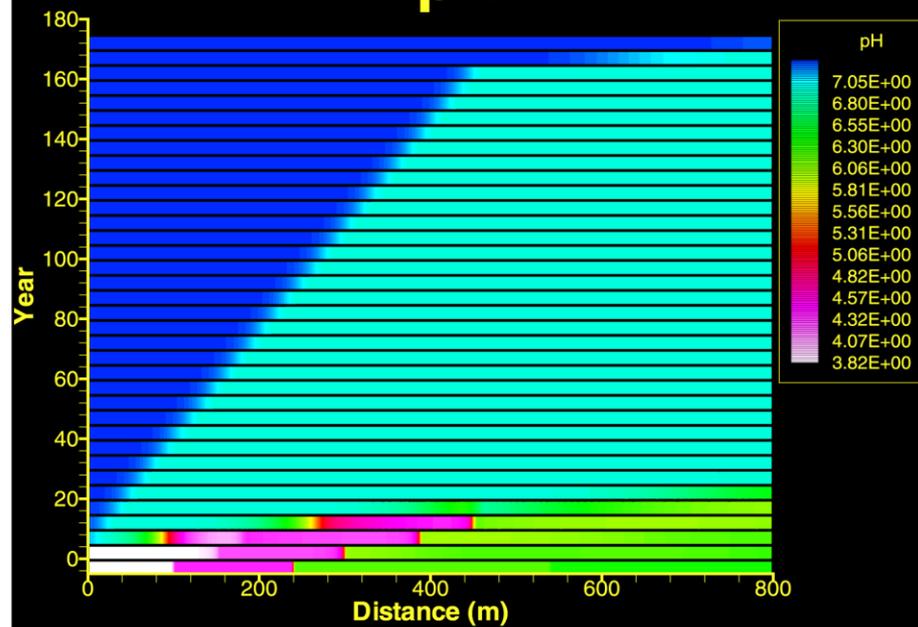
Cor



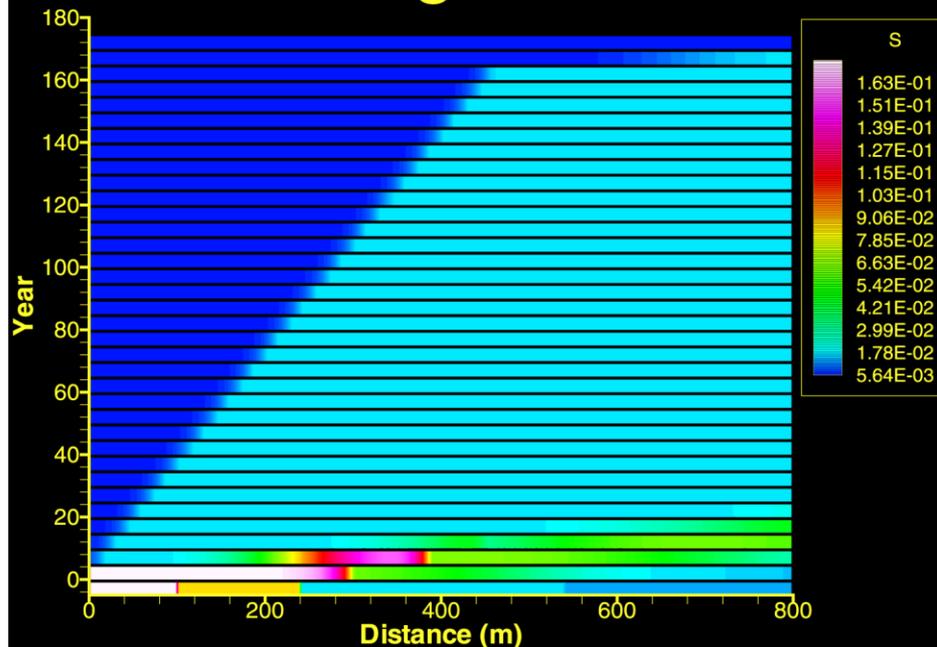
Cl



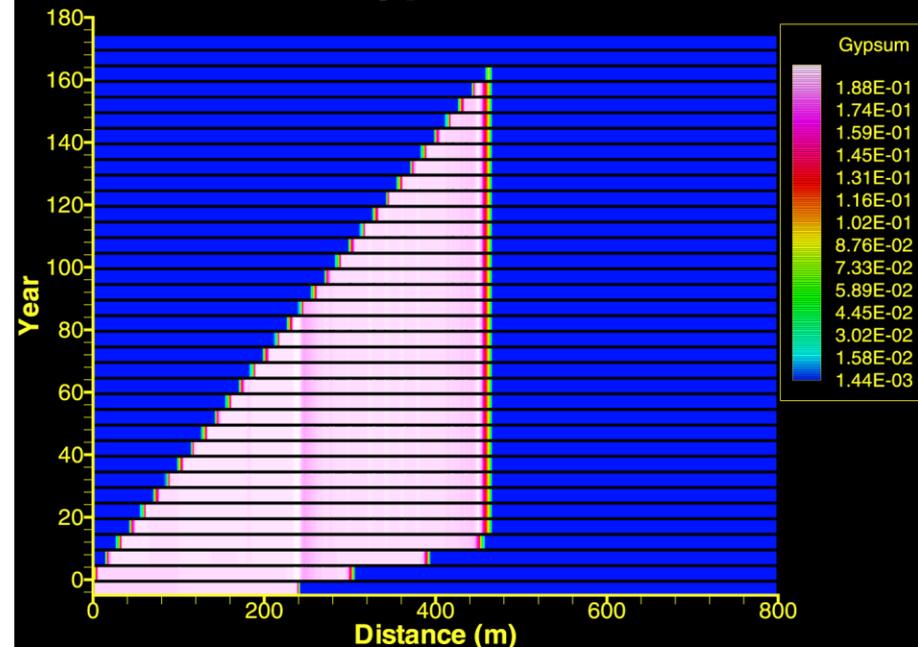
pH

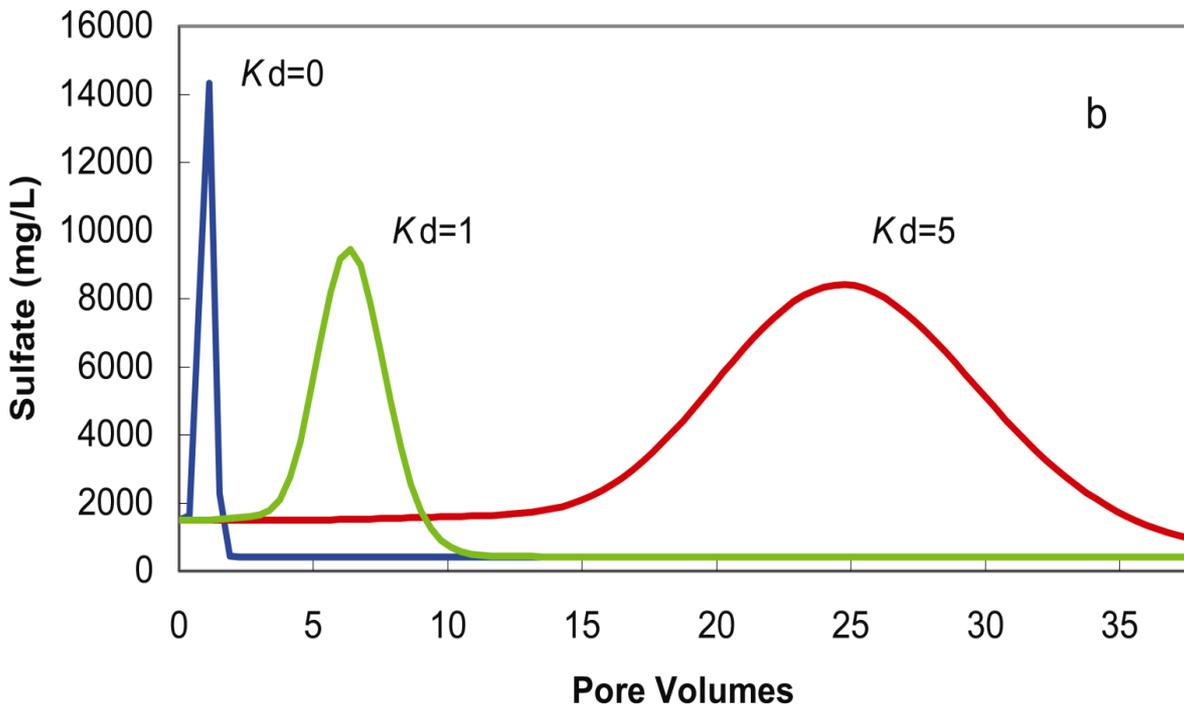
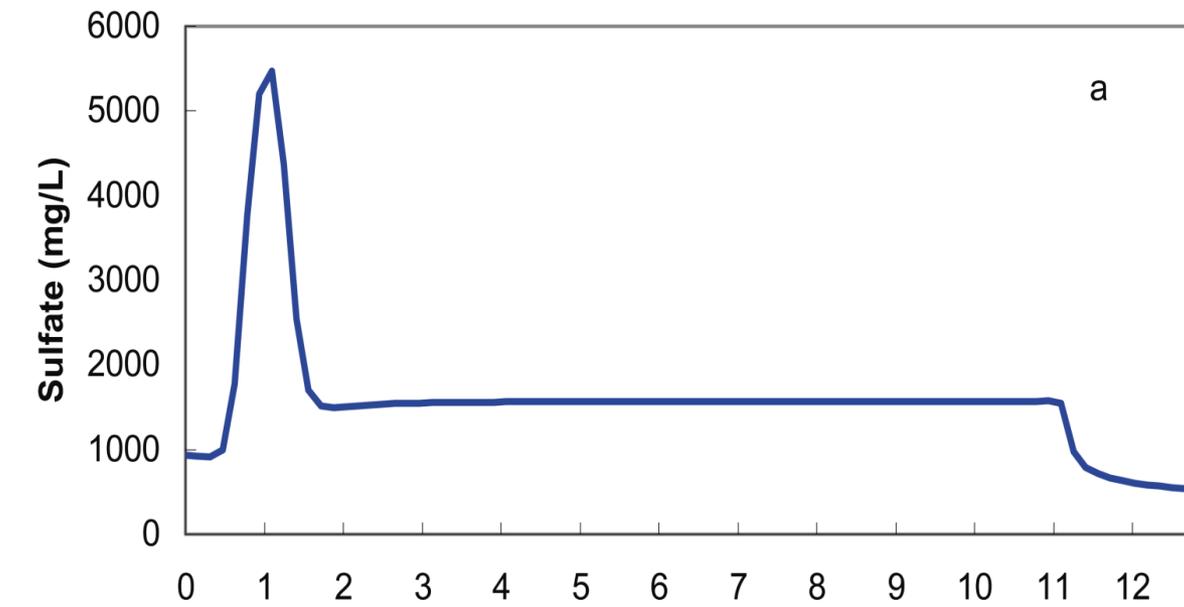


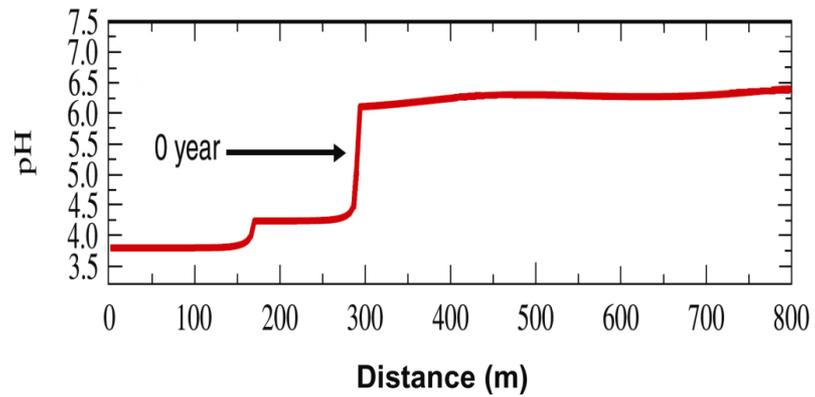
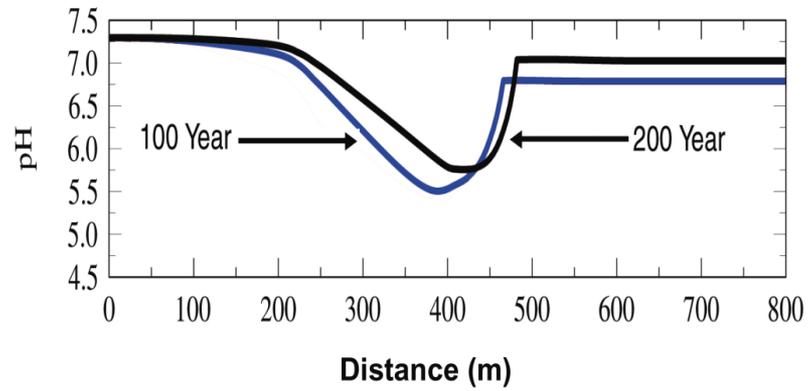
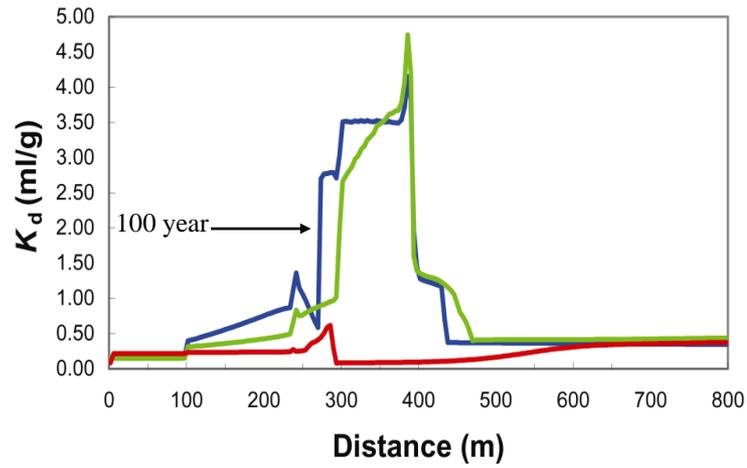
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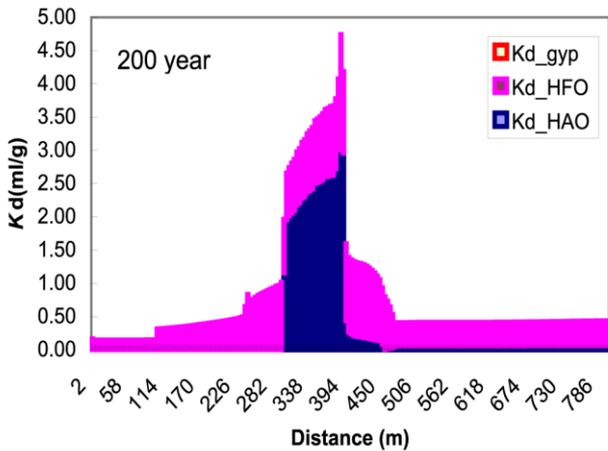
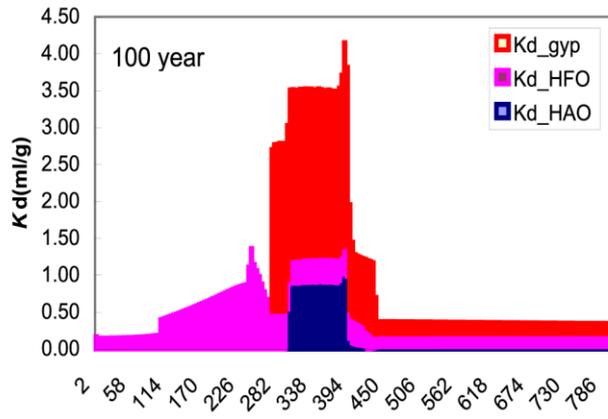
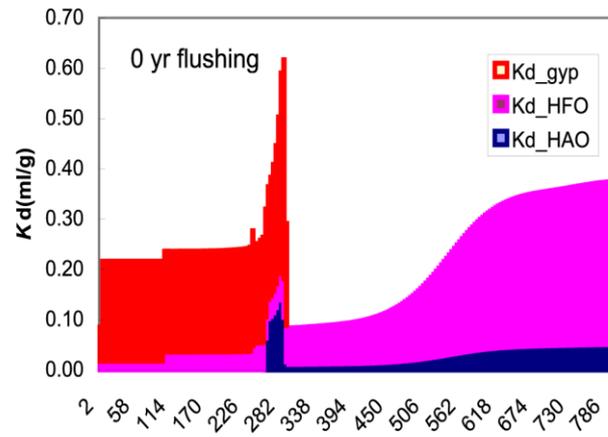


Gypsum









Summary and Conclusions

- **Simulated reactive mass transport of the natural attenuation of an acid groundwater plume at a uranium mill tailings site under a reclamation scenario**
- **In different time-space domains, the transport of reactive constituents is dominated alternatively by chemical reactions or physical processes**
- **Geochemical evolution of the contaminated aquifer produces multiple concentration waves**

Geochemical Modeling and Its Applications to Groundwater Resources and Quality

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Geochemical modeling was transformed from expert only exercise to nearly everyone's tool

Example calculations

❖ Carbon sequestration

- ◆ Liu, Faye (Yifei), P. Lu, C. Zhu, Y. Xiao (2010) Coupled reactive transport modeling of CO₂ Sequestration in the Mt. Simon Sandstone Formation, Midwest U.S.A. *The International Journal of Greenhouse Gas Control*, DOI: 10.1016/j.ijggc.2010.08.008.
- ◆ Strazisar, B. R., Zhu, C., and Hedges, S. W. (2006) Preliminary modeling of the long-term fate of CO₂ following injection into deep geological formations. *Environmental Geosciences* v.13, no.1, 1-15.

❖ Acid mine drainage

- ◆ Zhu, C., A case against K_d -based transport model: Natural attenuation at a mill tailings site. *Computer & Geosciences* v. 29, 351-359, 2003.
- ◆ Zhu, C., Hu, F. Q., and Burden, D. S., Multi-component reactive transport modeling of natural attenuation of an acid ground water plume at a uranium mill tailings site. *Journal of Contaminant Hydrology* v. 52, no. 1-2, 85-108, 2001.
- ◆ Zhu, C., and Burden, D. S., Mineralogical compositions of aquifer matrix as necessary initial conditions in reactive contaminant transport models. *Journal of Contaminant Hydrology* v. 51, no. 3-4, 145-161, 2001.
- ◆ Zhu, C., G. Yeh, and R. K. Waddell (1996) A new approach to modeling metal contaminant transport associated with mining wastes, *Proceedings of Tailings & Mining Waste '96*, January 16-19, 1996, Colorado State University, Fort Collins, Colorado, pp. 341-250.

❖ Naturally occurring radioactive materials (NORM)

- ◆ Zhu†, C., Coprecipitation in the barite isostructural family: 2. Numerical simulations of precipitation kinetics and reactive transport. *Geochimica et Cosmochimica Acta* v. 68, no. 16, 3339-3349, 2004.