



Geochemical Models



Geochemical Models

- Types of Models
 - Aqueous Speciation-Saturation
 - Mass Transfer
 - Inverse (Mass Balance)
 - Forward (Reaction Path)
 - Reactive Transport
- Available Codes in Common Use
- Examples in Mining Environments

Defining Some Terms

Aqueous speciation – the distribution of individual ions and ion pairs in water

Saturation – the state of an aqueous solution in chemical equilibrium with a particular solid phase

Undersaturation – phase is thermodynamically favored to dissolve

Supersaturation – phase is thermodynamically favored to form

Kinetics – the rates of geochemical reactions

Mass Transfer – moving mass between phases

Reactive Transport – coupling flow and chemical reactions

Aqueous Speciation-Saturation Models

Outline

- Purposes
- Theoretical Basis
- Geochemical Databases
- Input Data
- Output Data and Interpretation
- Some Programs in Common Use
- Uncertainties And Limitations

Aqueous Speciation-Saturation Models

Purposes

- Screen water-quality data – check **charge balance**
- Compute **individual ion activities** from analytical data
- **Aqueous speciation** for bioavailability and toxicity
- **Component molalities** needed as input for inverse (mass balance) and forward (reaction path) models
- **Saturation indices** indicate thermodynamic tendency of minerals to dissolve or precipitate

Aqueous Speciation-Saturation Models

Theoretical Basis

- Use total aqueous concentrations (e.g. mg/L) to compute:
 - Total molalities (m_i) (moles per kg H₂O)
 - Aqueous activities ($a_i = m_i \gamma_i$)
- Aqueous ion activity coefficients (γ_i) computed using:
 - Ion-association approach at low ionic strength
($I = 1/2 \sum m_i z_i^2 < 1.0$)
 - Specific-ion-interaction approach for brines ($I > 1.0$)
 - Pitzer's equations (e.g. PHRQPITZ)
 - Applicable only to species with explicit fit parameters
 - System Na-K-Ca-Mg-H-Cl-CO₃-HCO₃-CO₂-SO₄-H₂O
 - Plus limited data for Fe(II), Fe(III), Mn(II), Sr, Ba, Li, Al, B, Br

Aqueous Speciation-Saturation Models

Theoretical Basis (cont.)

- Multiple linear equations solved by numerical approximation (e.g. Newton-Raphson, continued fraction, etc.)
- **Redox equilibrium** assumed (erroneously) in many model
 - Should determine individual redox species where possible
 - e.g. determine Fe(II) and Fe(T) analytically, Fe(III) by difference
- **Saturation index (SI)** computed for each mineral in database:
SI = $\log (IAP/K_{sp})$, where IAP is the Ion Activity Product and K_{sp} is the equilibrium constant for the dissolution reaction.
 - e.g. for gypsum, $IAP = a(\text{Ca}^{2+})a(\text{SO}_4^{2-})a^2(\text{H}_2\text{O}) (= K_{sp} \text{ at equil.})$

SI < 0, solution is **undersaturated**, mineral will tend to dissolve

SI = 0, solution is **saturated** with mineral, apparent equilibrium

SI > 0, solution is **supersaturated**, mineral will tend to precipitate

Aqueous Speciation-Saturation Models

Geochemical Database

- Need **internally consistent database** with log K values (as $f(T,P)$) for minerals and aqueous species
 - Variation of log K's with temperature:
 - need data for enthalpy, entropy, and heat capacity of reactions
 - can make estimates, approximations if all data not available
 - Variation of log K's with pressure:
 - need data for molar volume of reaction
- **Limitations and uncertainties** inherent in database:
 - Temperature expressions may have limited range
 - Equilibrium constants may be poorly known
 - Constants for key species may be missing from database, leading to errors in computed single-ion activities.

Aqueous Speciation-Saturation Models

Input Data – Good quality required!

- Use **proper methods** of filtration, preservation, and dilution
- Measure **field parameters** (pH, Eh, D.O., temperature, alkalinity, specific conductance) at time of sample collection
- **Charge balance** must be within acceptable limits
 - Identify missing analytes or analytical problem
 - Some programs (e.g. PHREEQC) require achieving balance by adjusting concentration of a major ion prior to speciation
- Check **element ratios** and **time series** for anomalous analytical data
 - e.g. Zn/Cd, K/Na, Ca/Mg, Si/Al, Cu/Zn, Na/Cl, Cl/SO₄, etc.
- Check **measured vs. calculated**
 - Specific conductance, TDS, Eh (Fe³⁺/Fe²⁺)

Aqueous Speciation-Saturation Models

Output Data and Interpretation

- Individual ion activities, total molalities of elements
- Distribution of aqueous species among single ions and complexes
- Ion Activity Products and **Saturation Indices** for solid phases
- Which solid phases are likely to control solubility?
 - Phases that form at the field conditions, without kinetic barriers
 - Si: amorphous silica, not quartz
 - Al: poorly crystalline or amorphous Al-(OH)-SO₄ phases
 - Fe: ferrihydrite or Fe(III)-OH-SO₄ phases, not goethite, hematite

Aqueous Speciation-Saturation Models

Some Programs in Common Use

- **WATEQ4F** v. 2.63 (Ball and Nordstrom, 1991; updated 2004)
- **PHREEQC** v. 2.16.02 (Parkhurst and Appelo, 1999; updated 2009)
- **SpecE8** (Geochemist's Workbench, v. 8) (Bethke and Yeakel, 2009)
- **EQ3NR** v. 7.2 (Wolery 1992, updated 2005)
- **MINTEQA2** v. 4.03 (Allison et al. 1991; revised 2006)

Four acid mine waters



Leviathan Mine, CA, pH = 4.9



Leviathan Mine, CA, pH = 3.25



Note: Photo from Richmond Mine,
Drift A, 1990

Hornet and Richmond Mines,
Iron Mtn., CA pH = 1.1



Richmond Mine, Iron Mtn., CA
pH = 0.5

Input Data for Speciation- Saturation Modeling 4 acid mine waters

	AMD-A	AMD-B	AMD-C	AMD-D
Sample number	82WA109	82WA110	76WA103	90WA103
Water temperature (°C)	16.0	19.5	24.0	34.8
pH (field)	4.9	3.25	1.10	0.48
Constituent	(mg/l)			
Ca	44.7	82.2	240	183
Mg	13.5	23.6	720	821
Na	8.6	11.8	79.0	251
K	3.21	4.57	107	261
Cl	1.0	1.1	2.0	--- ¹
SO ₄	206	483	50,000	118,000
HCO ₃	---	0	0	0
SiO ₂	42.6	46.4	140	165
Ba	0.042	0.048	---	0.068
Al	5.06	19.8	1,410	2,210
F	0.30	0.52	2.0	---
Fe (total)	4.72	18.4	11,000 ³	20,300
Fe (II)	4.44	9.01	7,820	18,100
Fe (III) ²	0.28	9.39	3,180	2,200
Mn	1.26	3.04	11.0	17.1
Cu	0.09	0.23	360	290
Zn	0.04	0.15	1,860	2,010
Cd	.004	0.01	14.0	15.9
As (total)	0.01	0.02	---	56.4
As (III)	---	---	---	8.14
As (V) ⁴	---	---	---	48.3

TABLE 14.1—Chemical data for four acid mine water samples. [Samples AMD-A and AMD-B correspond respectively to samples 82WA109 and 82WA110 from the Leviathan mine, Alpine County, California (Ball and Nordstrom, 1989); sample AMD-C corresponds to sample 76WA103 from the Hornet and Richmond mines, Iron Mountain, Shasta County, California (Nordstrom, 1977); sample AMD-D corresponds to sample 90WA103 from the Richmond mine at Iron Mountain (Alpers and Nordstrom, 1991).]

Alpers and Nordstrom (1999)

¹---, not determined.

²Fe (III) computed as difference of Fe (total) and Fe (II).

³Value uncertain by up to 15%.

⁴As (V) computed as difference of As (total) and As (III).

Output from Aqueous Speciation-Saturation Modeling (WATEQ4F)

AMD-A

AMD-B

AMD-C

pH 4.9

pH 3.25

pH 1.1

Comparing Charge Balance

Analytical	2.5 %	2.7 %	-11.4 %
Speciated	2.4 %	4.9 %	3.9 %

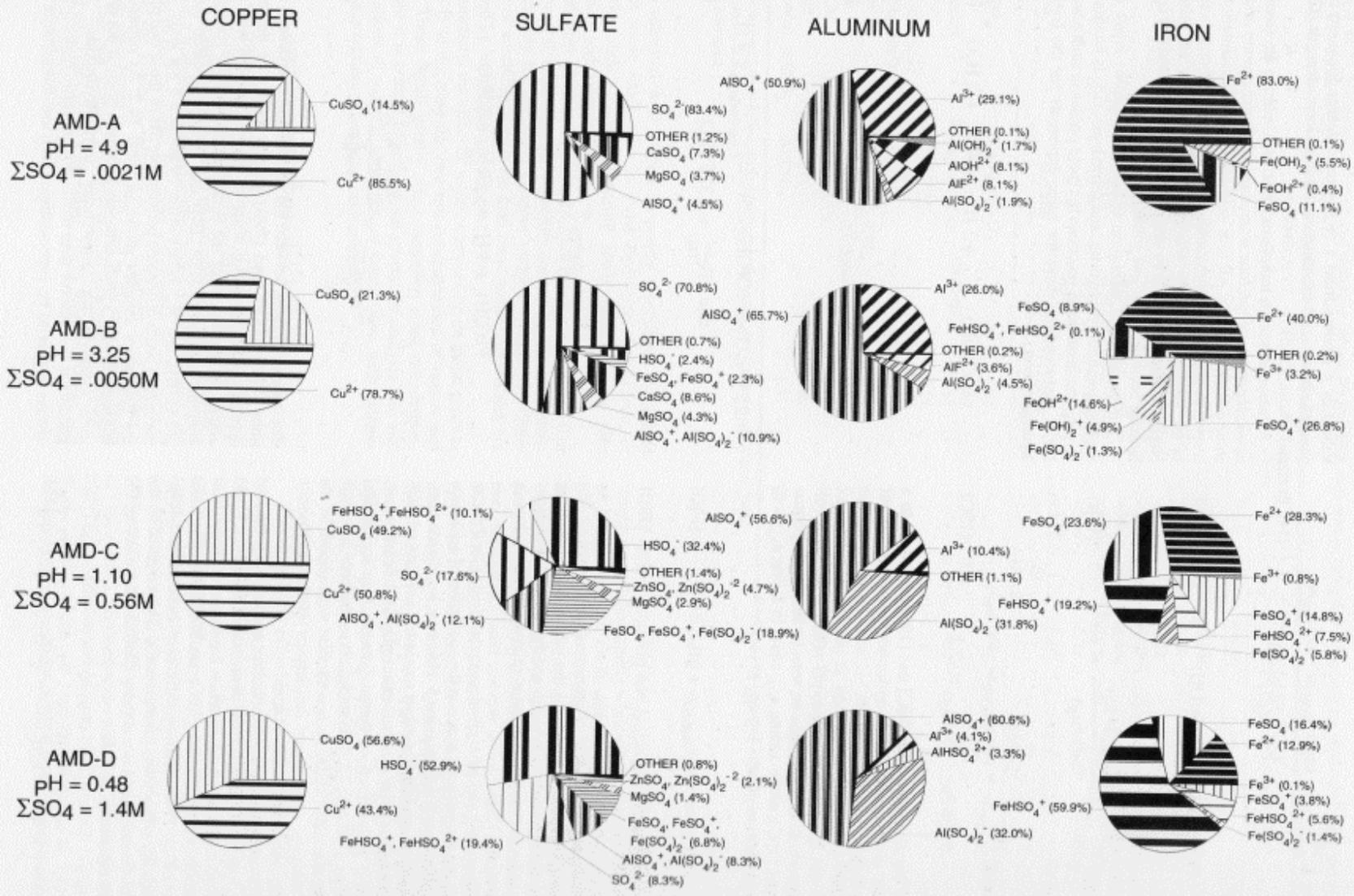
Comparing Specific Conductance

Measured	435 $\mu\text{S}/\text{cm}$	1100 $\mu\text{S}/\text{cm}$	40,000 $\mu\text{S}/\text{cm}$
Calculated	489	1173	50,000

Comparing Redox

Eh (field)	0.692 V	0.689 V	0.633 V
Eh for Fe(III)/Fe(II)	0.484	0.685	0.640

Aqueous Speciation of Four Acid Mine Waters



Alpers and Nordstrom (1999)

Output from Aqueous Speciation-Saturation Modeling (WATEQ4F) – Saturation Indices

Mineral	Formula	pH 4.9	pH 3.25
		SI ² AMD-A	SI AMD-B
Gypsum	CaSO ₄ •2H ₂ O	-1.48	-1.06
Barite	BaSO ₄	0.40	0.52
Melanterite	FeSO ₄ •7H ₂ O	-4.88	-4.46
Goethite	FeO(OH)	6.59	5.31
Ferric hydroxide [ferrihydrite ¹]	Fe(OH) ₃ ¹	0.70	-0.58
Jarosite	KFe ₃ (SO ₄) ₂ (OH) ₆	0.64	2.66
Alunite	KAl ₃ (SO ₄) ₂ (OH) ₆	5.91	-1.64
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	5.65	-3.01

Alpers and Nordstrom (1999)

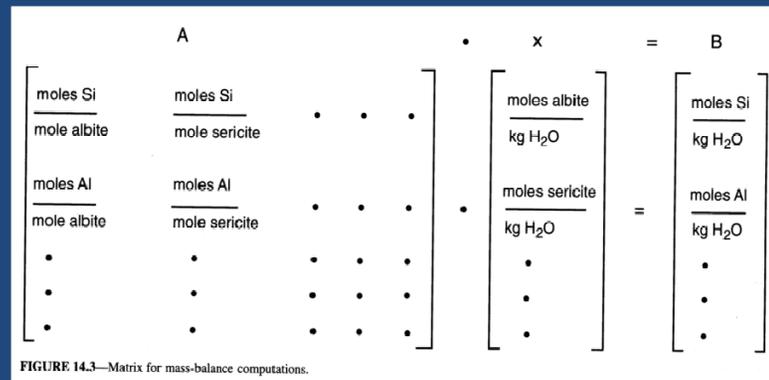
Aqueous Speciation-Saturation Models

Uncertainties and Limitations

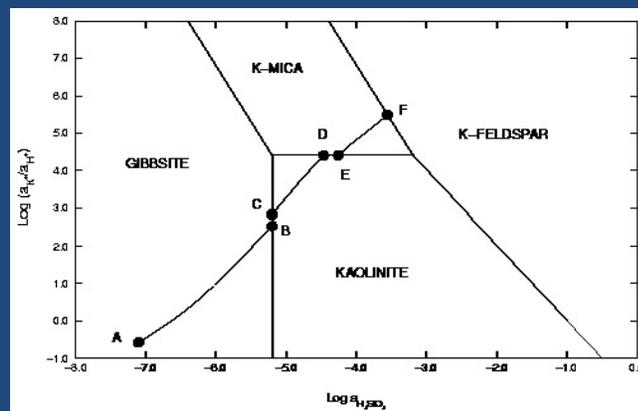
- Errors in analytical data
- Errors in thermodynamic data
- Limitations of aqueous model (e.g. ionic strength)
- Kinetic barriers to solubility control by some minerals
- Redox disequilibrium common in weathering environment, but key species often not measured
 - e.g. Fe(II)–Fe(III), As(III)–As(V), Cr(III)–Cr(VI)
 - Assumptions lead to uncertainties that should be quantified

Mass Transfer Models

□ Inverse (Mass Balance) Models



□ Forward (Reaction Path) Models



Inverse (Mass Balance) Models

Purposes:

- **identify processes** affecting water chemistry
- **quantify changes along flow path**
 - surface water or ground water
- **resolve mixing and water-mineral-gas reactions**
 - mineral precipitation and dissolution
 - ion exchange
 - stable isotope exchange
- **Based on stoichiometry** (elements, electrons, isotopes)
- **Consistency with thermodynamics** based on SI values
- **Consistency with kinetics** by avoiding unreactive phases

Inverse (Mass Balance) Models

Known: Mineral stoichiometry

Solve for:

Reaction coefficients

Known:

Water chemistry

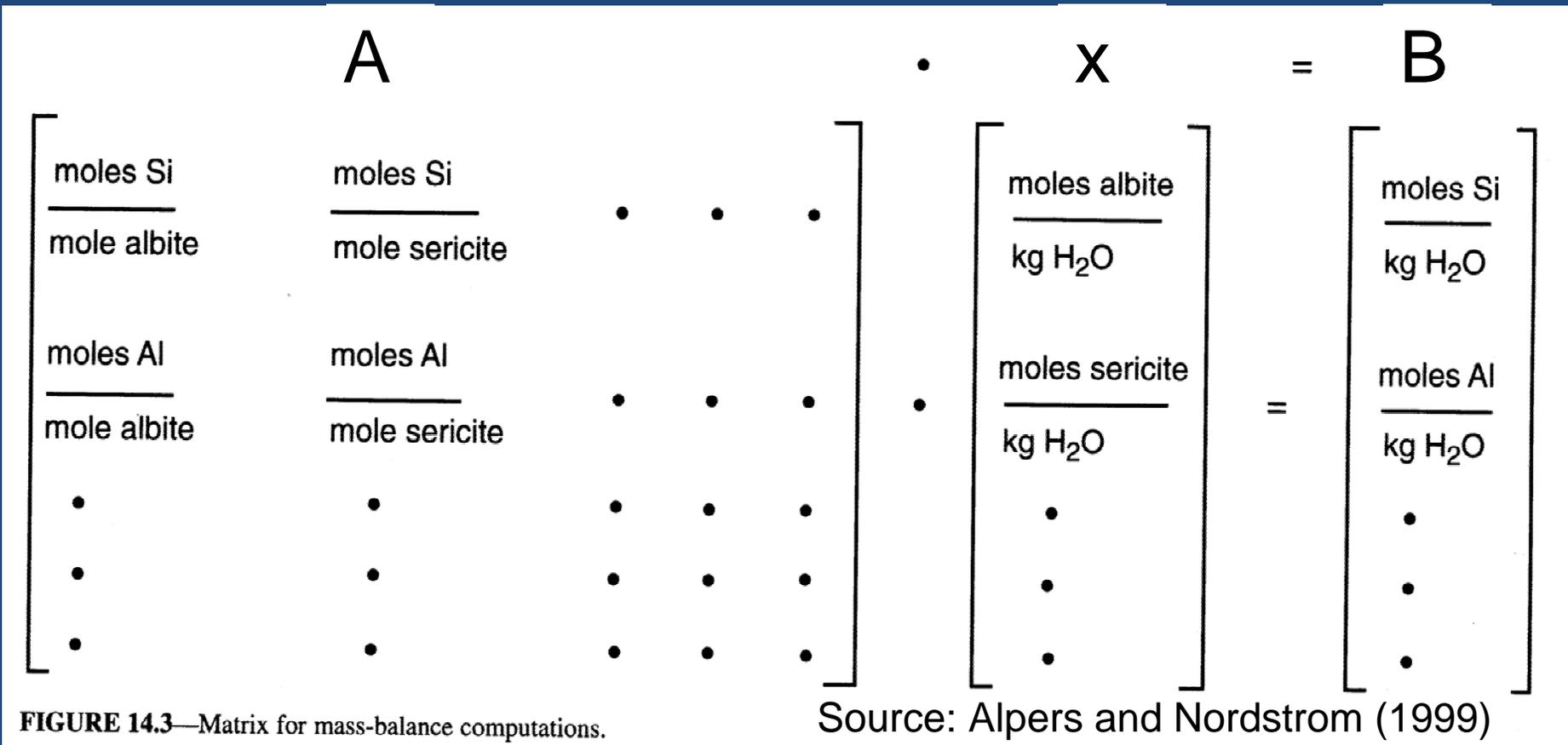


FIGURE 14.3—Matrix for mass-balance computations.

Source: Alpers and Nordstrom (1999)

Inverse (Mass Balance) Models

Input Data

- **Elemental molalities** in initial water(s) and final water
- **Saturation Indices** for possible reactants and products
- **Stoichiometric composition**, reactant and product phases
 - solid-solution compositions if possible (e.g. feldspars, micas)
 - possible ion-exchange reactions, gasses
- **Redox and stable-isotope data** may also be included
- Number of possible reactants/products may exceed number of known components in waters
 - possible exact solutions tested in combination

Inverse (Mass Balance) Models

Output Data and Interpretation

- **One or more non-unique solutions may be found** each consisting of:
 - **moles of minerals**, dissolved and (or) precipitated
 - **moles of gases** in-gassed or out-gassed
 - **moles of ion-exchange reactions**
 - **proportions of mixed solutions** (if appropriate)
- **Choosing most appropriate solution(s)** based on:
 - **proportions of reactant phases** in host material
 - **relative kinetics** of dissolution and precipitation
 - **hydrologic setting**
 - open vs. closed system with respect to gasses
 - mixing proportions consistent with flow model

Inverse (Mass Balance) Models

Some Programs in Common Use

- **BALANCE** (Parkhurst et al. 1982)
- **NETPATH** v.2 (Plummer et al. 1994)
 - Uses Saturation Indexes from WATEQ4F
 - Multiple combinations of unknown reactants & products
 - Mixing of up to 5 water compositions
- **PHREEQC** v. 2.16.02 (Parkhurst and Appelo, 1999; updated 2009)

TABLE 14.3—Minerals considered in mass-balance computation for Richmond mine water.

Mineral	Formula	Source ¹
Albite	$\text{Na}_{.96}\text{Ca}_{.04}\text{Al}_{1.04}\text{Si}_{2.96}\text{O}_8$	1
Sericite	$\text{K}_{.70}\text{Na}_{.12}(\text{H}_3\text{O})_{.16}\text{Al}_{1.91}\text{Mg}_{.06}\text{Fe}^{\text{II}}_{.02}(\text{Al}_{.9}\text{Si}_{3.1})\text{O}_{10}(\text{OH})_2$	2
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	
Epidote ²	$\text{Ca}_{1.96}\text{Fe}^{\text{II}}_{.88}\text{Mg}_{.05}\text{Al}_{2.05}\text{Si}_{3.04}\text{O}_{12}(\text{OH})$	2
Chlorite	$\text{Mg}_{2.95}\text{Fe}^{\text{II}}_{.88}\text{Al}^{\text{Oct}}_{1.82}\text{Al}^{\text{tet}}_{.81}\text{Si}_{2.82}\text{O}_{10}(\text{OH})_8$	2
Quartz	SiO_2	
Calcite	CaCO_3	
Pyrite	FeS_2	
Chalcopyrite	CuFeS_2	
Sphalerite	$\text{Zn}_{.933}\text{Fe}^{\text{II}}_{.062}\text{Cu}_{.005}\text{S}$	2
Melanterite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	

¹Sources: (1) Kinkel et al. (1956); (2) Reed (1984).

²Epidote formula included for reference only; phase not included in preferred mass-balance solution for water sample AMD-D.

Alpers and
Nordstrom
(1999)

Results of Inverse Modeling

Iron Mtn. mine water, pH = 0.5



TABLE 14.4—Reaction coefficients for mineral dissolution and precipitation, and gas fluxes for the formation of water sample AMD-D (data in Table 14.1), based on mass-balance computations using mineral formulas in Table 14.3.

	Reaction coefficient (mol/kg _{H₂O})	Formula weight (g/mole)	Reactive mass (g/kg _{H₂O})	Percent of total reactants (wt%)
Reactants				
Pyrite	.9816	120	117.8	
Chalcopyrite	.0051	184	0.9	
Sphalerite	.0385	96	3.7	
Total Sulfides			122.4	48
Calcite	.0047	100	0.5	
Albite	.0119	263	3.1	
Sericite	.0111	389	4.3	
Chlorite	.0132	567	7.5	
Kaolinite	.0063	258	1.6	
Total Gangue			17.0	7
O ₂ gas	3.5421	32	113.3	45
Total Reactants			252.7	100
Products				
Melanterite	.5759	152 ¹	87.5	
Silica (amorphous)	.1162	60 ¹	7.0	
CO ₂ gas	.0047	40	0.2	
Total Products			94.7	37
Net Total (reactants-products)			158.0	63

¹Melanterite and amorphous silica formula weights without waters of hydration; H and O not included in mass balance.

Alpers and Nordstrom (1999)

Some Secondary Minerals, Richmond Mine, Iron Mountain, CA



Melanterite stalactites,
Richmond Mine (pH = -0.7)



Jarosite – amorphous silica stalactites,
Richmond Mine (pH = 2.0)

Inverse (Mass Balance) Models

Uncertainties and Limitations

- Critical Assumptions
 - Initial and final water samples from **same flow path**
 - **Steady-state** chemical gradients
- Deduced Reactions Must Be Feasible
 - Can get multiple, **non-unique solutions**
 - Professional judgment needed to **rule out unlikely solutions**
 - Best to **confirm reactants and products with field observations**
 - Apply **thermodynamic test** using Saturation Indices
 - Consideration of **kinetics** of mineral dissolution and formation

Forward (Reaction Path) Models

Principles

- Predict results of hypothetical water-mineral-gas reactions
- **Irreversible reactions** applied to an initial solution
 - usually 1 kg H₂O of known composition
- At each step of **reaction progress**:
 - Solution speciation, Saturation Indices computed
 - Precipitation of supersaturated minerals
- Relative kinetic rates determine proportions of reactants

Forward (Reaction Path) Models

Closed vs. Open Systems

- **Closed:** secondary products available for dissolution
 - Reaction path follows stability boundaries of solid phases
- **Open:** secondary products "removed" from system
 - Reaction path crosses stability boundaries of solid phases

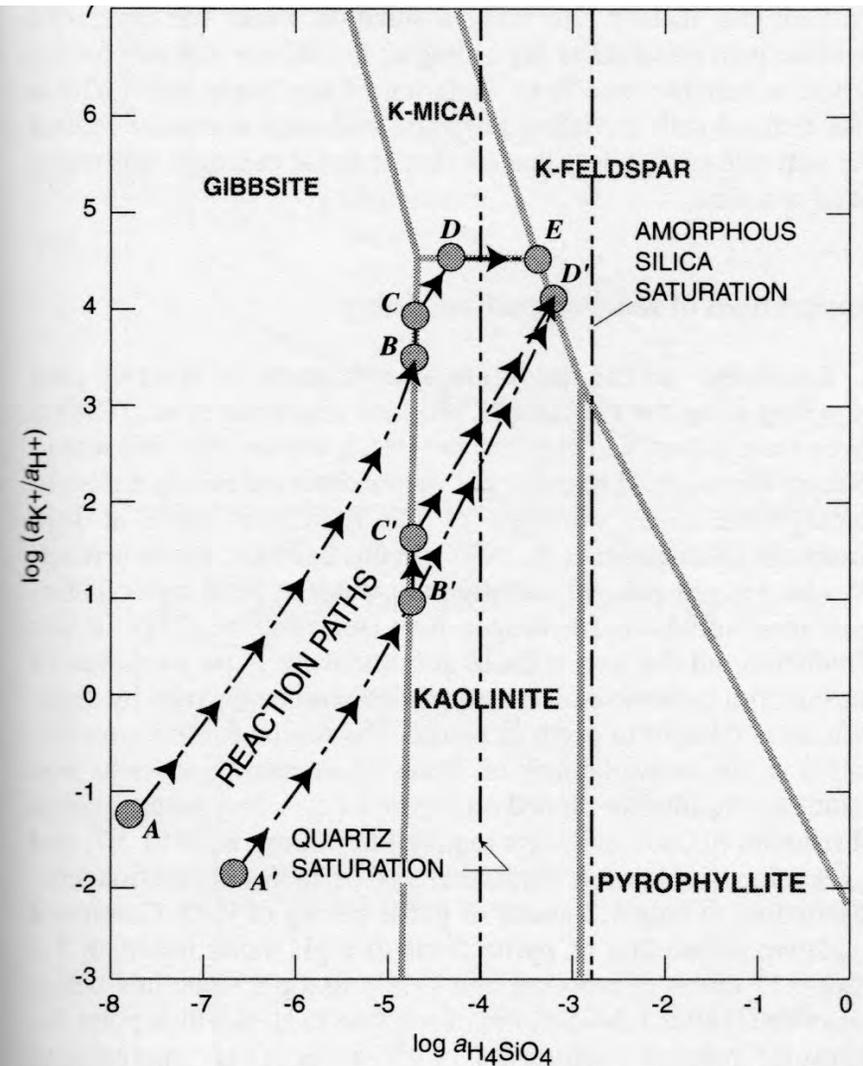


FIGURE 14.4—Equilibrium aqueous activity diagram for potassium versus silica at 25°C and 1 bar, showing a comparison of closed-system reaction paths (ABCDE and A'B'C'D') and an open-system path (A'B'D') for the dissolution of K-feldspar; after Helgeson (1974) and reproduced with permission from Manchester University Press.

Alpers and Nordstrom (1999)

Forward (Reaction Path) Models

- User-defined reaction path models
 - e.g. PHREEQC, PHRQPITZ
 - User must pre-select phases that form
- Path-finding models
 - e.g. EQ6, React (Geochemist's Workbench)
 - Program determines identity of phases that form

Forward (Reaction Path) Models

Database: Same as Aqueous Speciation-Saturation models

Input Data:

- **Initial water composition**, from Speciation-Saturation model
 - choice of aqueous model [ion association, specific ion-interaction (Pitzer)]
- **Irreversible reactions** involving minerals and (or) gasses
 - relative kinetic rates among minerals, or rate laws
- **Reversible reactions**: minerals that may precipitate
 - suppress minerals with kinetic barriers to formation
- **Temperature, pressure** conditions
 - can vary as a function of reaction progress or time (some codes)
- Define **step size** for reaction progress

Forward Model of Pyrite Oxidation by O₂ Using PHRQPITZ



Alpers and Nordstrom (1991, 1999)

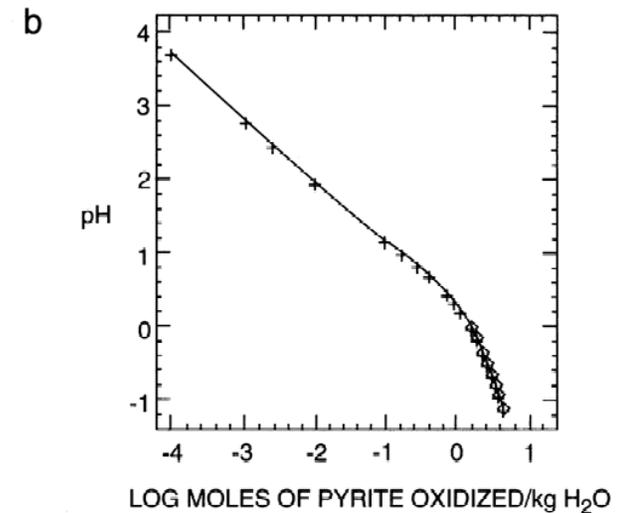
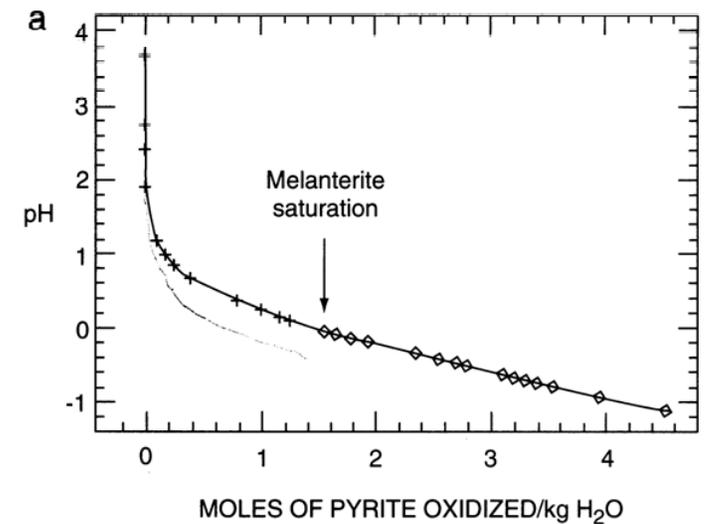
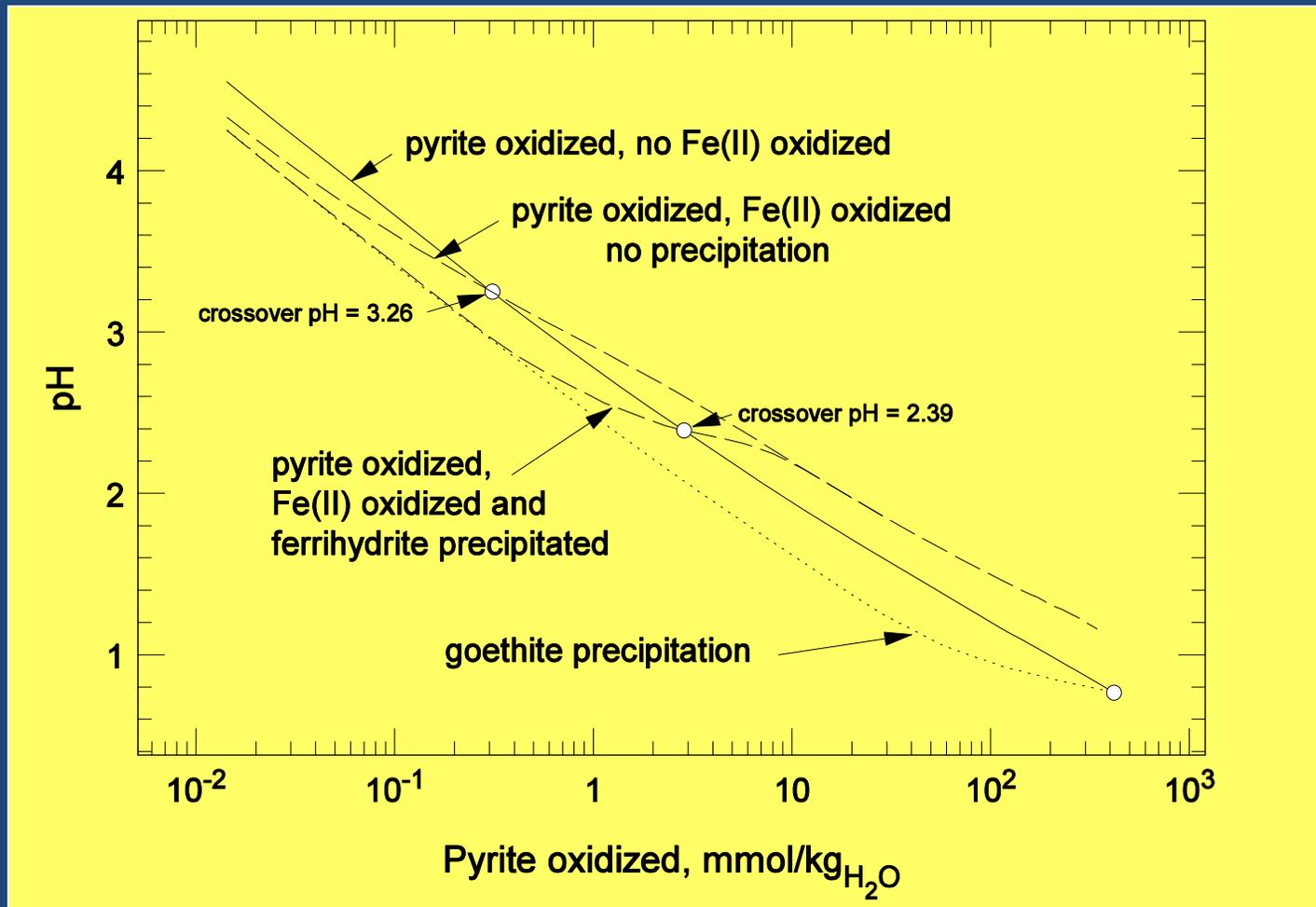


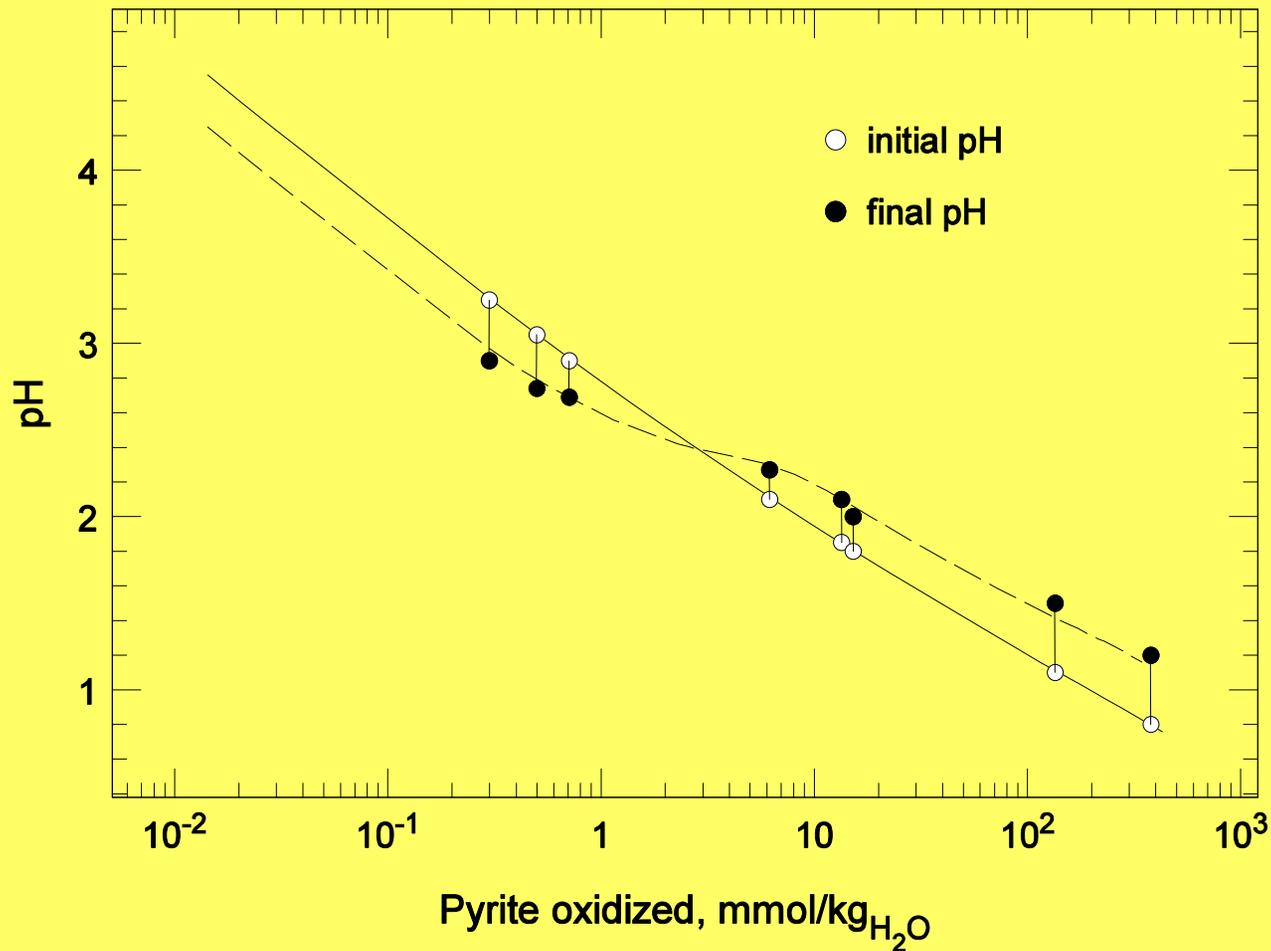
FIGURE 14.5—Forward simulation using program PHRQPITZ of pyrite oxidation, with melanterite precipitation at negative pH; from Alpers and Nordstrom (1991). (a) Linear horizontal scale; (b) Logarithmic horizontal scale, showing non-ideal solution behavior at negative pH values.

PHREEQC – Forward Model – Pyrite Titration in Water



From Nordstrom (2004) Modeling low-temperature geochemical processes, Treatise of Geochemistry

Confirmation of PHREEQC Modeling Result with Field Data – Final pH Measured in Lab after Fe(II) Oxidation



Nordstrom (2004) Treatise of Geochemistry

Forward (Reaction Path) Models

Output Data and Interpretation

- Reaction paths
 - solution composition as a function of reaction progress
 - quantities of secondary minerals formed
 - composition of solid-solutions formed (some codes)
- Time of reaction
 - kinetic rate laws
 - relative reaction rates

Example of Forward Model

(based on
results of
inverse
model)

Alpers and
Nordstrom (1999)

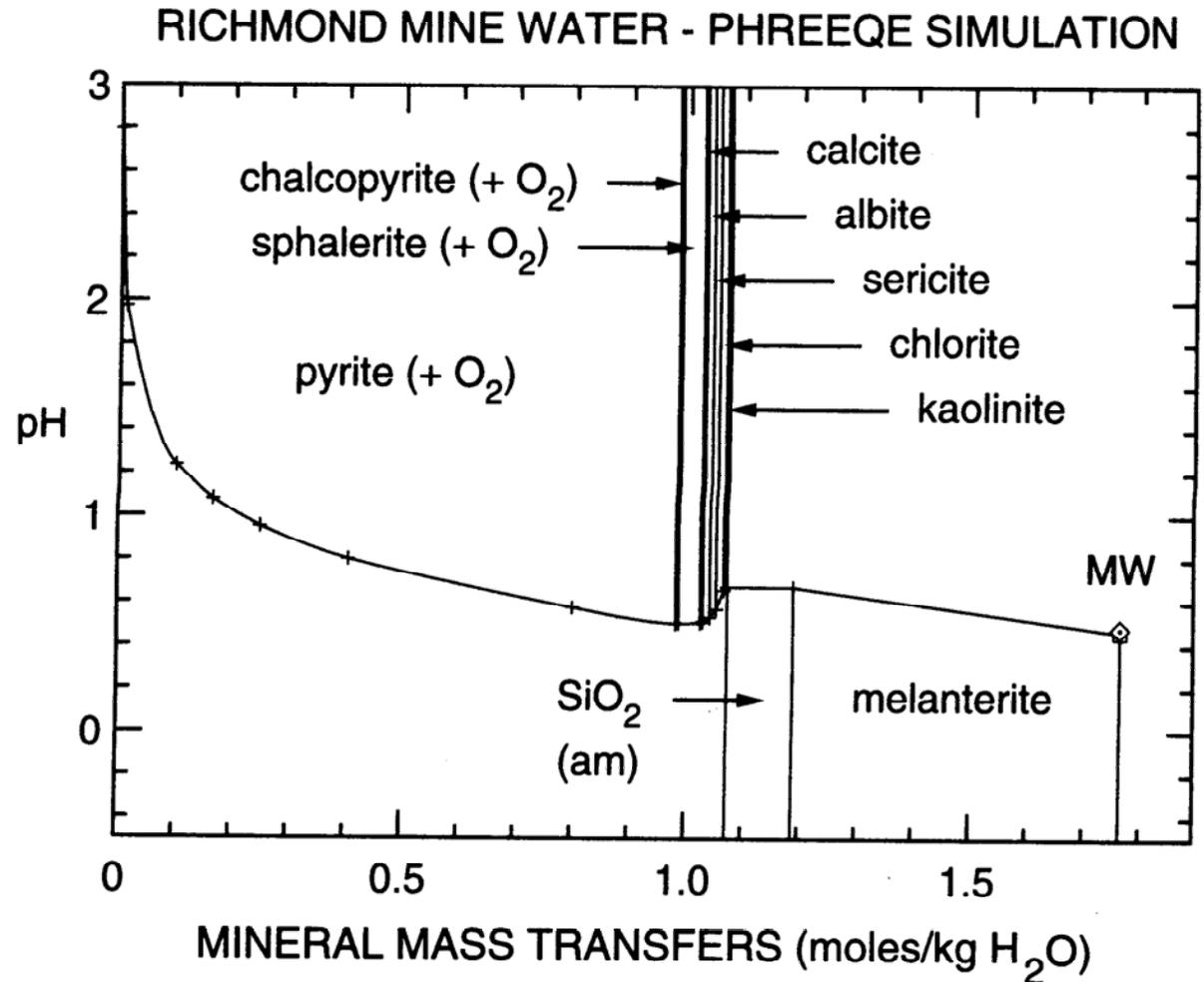


FIGURE 14.6—Forward simulation using program PHREEQE of mineral dissolution using reaction coefficients in Table 14.4; from Alpers and Nordstrom (1991).

	INVERSE MODELING	FORWARD MODELING
Theoretical basis	Mass balance , Stoichiometry, Consistency with SI's ensures thermodynamic reasonableness	Mass transfer , Irreversible thermodynamics
Role of kinetics	Time scales from hydrologic model or ^{14}C	Either assume relative rates, or use rate laws
Input data	Initial and final water compositions , must know mineralogy	Initial water composition only
Output	Proportions of reactants and products , accounting for observed changes in water chemistry along flow path	Prediction of consequences of hypothesized reactions, Reaction paths
Chemistry	Steady-state gradient	Transient and steady-state
Applications	Geochemical processes in aquifers, surface waters; Mixing proportions in ground waters	Designing experiments Inaccessible systems Ore deposit genesis Consequences of remediation

Reactive Transport Models

- Transport Processes
 - Advection
 - Hydrodynamic Dispersion
 - Diffusion
 - Reactions on Mineral Surfaces
 - Adsorption
 - Ion exchange
 - Mineral Dissolution and Precipitation
 - Thermodynamic model
 - Kinetic rate expressions
 - Biochemical Processes
 - Radioactive Decay