

5.02

Modeling Low-temperature Geochemical Processes

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A model takes on the quality of theory when it abstracts from raw data the facts that its inventor perceives to be fundamental and controlling, and puts these into relation to each other in ways that were not understood before—thereby generating predictions of surprising new facts.

H. F. Judson (1980), *The Search for Solutions*

5.02.1 INTRODUCTION

Geochemical modeling has become a popular and useful tool for a wide number of applications from research on the fundamental processes of water–rock interactions to regulatory requirements and decisions regarding permits for

industrial and hazardous wastes. In low-temperature environments, generally thought of as those in the temperature range of 0–100 °C and close to atmospheric pressure (1 atm = 1.01325 bar = 101,325 Pa), complex hydrobiogeochemical reactions participate in an array of interconnected processes that affect us, and that, in turn, we affect. Understanding these complex processes often requires tools that are sufficiently sophisticated to portray multicomponent, multiphase chemical reactions yet transparent enough to reveal the main driving forces. Geochemical models are such tools. The major processes that they are required to model include mineral dissolution and precipitation; aqueous inorganic speciation and complexation; solute adsorption and desorption; ion exchange; oxidation–reduction; or redox; transformations; gas uptake or production; organic matter speciation and complexation; evaporation; dilution; water mixing; reaction during fluid flow; reaction involving biotic interactions; and photoreaction. These processes occur in rain, snow, fog, dry atmosphere, soils, bedrock weathering, streams, rivers, lakes, groundwaters, estuaries, brines, and diagenetic environments. Geochemical modeling attempts to understand the redistribution of elements and compounds, through anthropogenic and natural means, for a large range of scale from nanometer to global. “Aqueous geochemistry” and “environmental geochemistry” are often used interchangeably with “low-temperature geochemistry” to emphasize hydrologic or environmental objectives.

Recognition of the strategy or philosophy behind the use of geochemical modeling is not often discussed or explicitly described. Plummer (1984, 1992) and Parkhurst and Plummer (1993) compare and contrast two approaches for modeling groundwater chemistry: (i) “forward modeling,” which predicts water compositions from hypothesized reactions and user assumptions and (ii) “inverse modeling,” which uses water, mineral, and isotopic compositions to constrain hypothesized reactions. These approaches simply reflect the amount of information one has to work with. With minimal information on a site, a modeler is forced to rely on forward modeling. Optimal information would include detailed mineralogy on drill cores or well cuttings combined with detailed water analyses at varying depths and sufficient spatial distribution to follow geochemical reactions and mixing of waters along defined flow paths. With optimal information, a modeler will depend on inverse modeling.

This chapter outlines the main concepts and key developments in the field of geochemical modeling for low-temperature environments and illustrates their use with examples. It proceeds with a short discussion of what modeling is, continues

with concepts and definitions commonly used, and follows with a short history of geochemical models, a discussion of databases, the codes that embody models, and recent examples of how these codes have been used in water-rock interactions. An important new stage of development seems to have been reached in this field with questions of reliability and validity of models. Future work will be obligated to document ranges of certainty and sources of uncertainty, sensitivity of models and codes to parameter errors and assumptions, propagation of errors, and delineation of the range of applicability.

5.02.1.1 What is a Model?

A “model” has a relation to “reality,” but reality is experiential, and the moment we attempt to convey the experience we are seriously constrained by three limitations: our own ability to communicate, the capability of the communication medium to portray the experience, and the ability of the person receiving the communication to understand it. Communication requires the use of language and the use of percepts and concepts, and the process of perceiving, conceiving, and communicating is an abstracting process that removes us from the immediate experience. Any attempt to transform an experience into language suffers from this abstraction process so that we lose the immediate experience to gain some understanding of it. The problem is to transform existential knowledge to communicated or processed knowledge. To communicate knowledge, we must use a simplified and abstract symbolism (words, mathematics, pictures, diagrams, analogues, allegories, three-dimensional physical constructs, etc.) to describe a material object or phenomenon, i.e., a model. Models take on many forms but they are all characterized by being a simplification or idealization of reality. “... models include only properties and relationships that are needed to understand those aspects of the real system that we are interested in...” (Derry, 1999). Assumptions, both explicit and implicit, are made in model construction, because either we do not know all the necessary properties or we do not need to know them. Hopefully, models have caught the essential properties of that which they are attempting to portray so that they are useful and lead to new insights and to better answers for existing questions and problems.

Scientific models begin as ideas and opinions that are formalized into a language, often, but not necessarily, mathematical language. Furthermore, they must have testable consequences. The emphasis on testability, or falsifiability, is a fundamental attribute (Popper, 1934).

Greenwood (1989) stated that the word model should be reserved "... for well-constrained logical propositions, not necessarily mathematical, that have necessary and testable consequences, and avoid the use of the word if we are merely constructing a scenario of possibilities." A scientific model is a testable idea, hypothesis, theory, or combination of theories that provide new insight or a new interpretation of an existing problem. An additional quality often attributed to a model or theory is its ability to explain a large number of observations while maintaining simplicity (Occam's razor). The simplest model that explains the most observations is the one that will have the most appeal and applicability.

Models are applied to a "system," or a portion of the observable universe separated by well-defined boundaries for the purpose of investigation. A chemical model is a theoretical construct that permits the calculation of chemical properties and processes, such as the thermodynamic, kinetic, or quantum mechanical properties of a system. A geochemical model is a chemical model developed for geologic systems. Geochemical models often incorporate chemical models such as ion association and aqueous speciation together with mineralogical data and assumptions about mass transfer to study water-rock interactions.

A computer code is obviously not a model. A computer code that incorporates a geochemical model is one of several possible tools for interpreting water-rock interactions in low-temperature geochemistry. The computer codes in common use and examples of their application will be the main focus of this chapter. It is unfortunate that one commonly finds, in the literature, reference to the MINTEQ model or the PHREEQE model or the EQ3/6 model when these are not models but computer codes. Some of the models used by these codes are the same so that a different code name does not necessarily mean a different model is being used.

5.02.2 MODELING CONCEPTS AND DEFINITIONS

5.02.2.1 Modeling Concepts

Many different forms of models are utilized, usually dictated by the objectives of research. *Conceptual models* are the most fundamental. All of us have some kind of concept of water-rock interactions. For a groundwater interacting with the aquifer minerals during its evolution, one might conceive that most minerals would be undersaturated in the area of recharge but that some minerals (those that dissolve fastest) would become saturated at some point down gradient, having reached their equilibrium solubility

(a state of *partial equilibrium*). The conceptual model can be formalized into a set of mathematical equations using chemical principles, the *mathematical model*, entered into a computer program, the *code*, and predictions made to test the assumptions (and the databases) against the results from real field data. This exercise helps to quantify and constrain the possible reactions that might occur in the subsurface. Mathematical equations for complex interacting variables are not always solved exactly and, therefore, systems of numerical approximations, or *numerical models*, have been developed. Alternatively, an experiment could be set up in the laboratory with columns made of aquifer material with groundwater flowing through to simulate the reactions, the *experimental model* or *scale model*. Having obtained results from a mathematical or scale model, some unexpected results often occur which force us to change our original conceptual model. This example demonstrates how science works; it is an ongoing process of approximation that iterates between idea, theory, observational testing of theory, and back to modifications of theory or development of new theories.

5.02.2.2 Modeling Definitions

In low-temperature geochemistry and geochemical modeling, it is helpful to define several words and phrases in common use.

Aqueous speciation. The distribution of dissolved components among free ions, ion pairs, and complexes. For example, dissolved iron in acid mine drainage (AMD) can be present as $\text{Fe}_{(\text{aq})}^{2+}$ (free ferrous iron), $\text{FeSO}_{4(\text{aq})}^0$ (ion pair), $\text{Fe}_{(\text{aq})}^{3+}$ (free ferric iron), $\text{Fe}(\text{OH})_{(\text{aq})}^{2+}$, and $\text{FeSO}_{4(\text{aq})}^+$ species. These species are present in a single phase, aqueous solution. Aqueous speciation is not uniquely defined but depends on the theoretical formulation of mass action equilibria and activity coefficients, i.e. it is model dependent. Some aqueous speciation can be determined analytically but operational definitions and assumptions are still unavoidable.

Phase. Commonly defined as a uniform, homogeneous, physically distinct, and mechanically separable part of a system. Unfortunately, mineral phases are often not uniform, homogeneous, or mechanically separable except in theory. Sophisticated microscopic and spectroscopic techniques and operational definitions are needed to define some mineral phases.

Phase speciation. The distribution of components among two or more phases. In a wet soil, iron can be present in at least three phases: as the X-ray amorphous oxyhydroxide, ferrihydrite; as goethite; and as dissolved aqueous iron.

Mass transfer. The transfer of mass between two or more phases, for example, the precipitation and dissolution of minerals in a groundwater.

Reaction-path calculation. A sequence of mass transfer calculations that follows defined phase (or reaction) boundaries during incremental steps of reaction progress.

Mass transport. Solute movement by mass flow of a fluid (could be liquid, gas, or mixture of solid and liquid and/or gas).

Reactive transport. Mass transfer combined with mass transport; commonly refers to geochemical reactions during stream flow or groundwater flow.

Forward geochemical modeling. Given an initial water of known composition and a rock of known mineralogy and composition, the rock and water are computationally reacted under a given set of conditions (constant or variable temperature, pressure, and water composition) to produce rock and water (or set of rocks and waters). In forward modeling the products are inferred from an assumed set of conditions (equilibrium or not, phases allowed to precipitate or not, etc.) and thermodynamic and/or kinetic data are necessary.

Inverse geochemical modeling. Given a set of two or more actual water analyses along a flow path that have already reacted with a rock of known mineralogy, the reactions are inferred. In inverse modeling the reactions are computed from the known field conditions (known water chemistry evolution and known mineralogy) and assumed mineral reactivity. Inverse modeling is based on mass or mole balancing, and thermodynamic and kinetic data are not necessary although saturation indices provide useful constraints. Relativistic kinetics (i.e. relative mineral reaction rates) are deduced as part of the results.

5.02.2.3 Inverse Modeling, Mass Balancing, and Mole Balancing

A key concept to interpreting water–rock interactions is mass balancing between water chemistry data, mineral/gas transformations, and biological uptake or release. The mass-balance concept is a means of keeping track of reacting phases that transfer mass during fluid flow. It is an integral part of the continuity equation for steady-state and transient-state flow conditions. Formalizing mass balances for solutes during fluid flow is simple if the solutes are conservative but more complex when reactions take place. For applications to the environment, different types of mass balances have been used and these require some explanation.

Three types of mass-balance approaches will be discussed. In its simplest form, mass balancing is

utilizing the law of conservation of mass that reflects that any partitioning of mass through a system must sum to the total. The first type of mass-balance approach, catchment mass balances (or mass fluxes), use “input–output” accounting methods to identify overall gains and losses of solutes during the flow of water from meteoric inputs to stream outflow at a specified point (Bormann and Likens, 1967; Likens *et al.*, 1977). Pačes (1983, 1984) called this the integral mass-balance approach:

$$[\text{Mass rate}_{\text{in}} - \text{mass rate}_{\text{out}}] \pm \text{mass rate}_{\text{internal}} = \text{rate of accumulation/depletion} \quad (1)$$

In difference form

$$\frac{\Delta m_{\text{trans}}}{\Delta t} + \frac{\Delta m_{\text{int}}}{\Delta t} = \frac{\Delta m_{\text{tot}}}{\Delta t} \quad (2)$$

where $\Delta m_{\text{trans}}/\Delta t$ is the difference in rate of mass (of some component) transported into and out of the system via fluid flow, $\Delta m_{\text{int}}/\Delta t$ is the rate of mass produced or removed from the fluid by internal chemical reaction, and $\Delta m_{\text{tot}}/\Delta t$ is the total rate of change in mass for a component in the fluid. Steady-state conditions are often assumed so that the accumulation/depletion rate becomes zero and the difference between input and output for a component becomes equal to the internal processes that produce or remove that component. These mass rates of change are usually obtained as integral mass fluxes (computed as discharge times concentration).

For catchments in which input from precipitation and dry deposition can be measured and the output through a weir or similar confining outflow can be measured, the difference in solute flow averaged over an appropriate period of time provides an accounting of solutes gained or lost. Overviews and summaries of essential concepts of catchment mass balances have been presented by Drever (1997a,b), Bassett (1997), and Bricker *et al.* (Chapter 5.04). The input–output mass balance treats the catchment as a black box, but knowledge of biogeochemical processes, use of lab experiments, additional field data, and well-controlled small-scale field-plot studies can help to identify the dominant processes causing the gain or loss of a particular solute. Load (or mass flux) calculations for a river or stream use the same type of accounting procedure.

A second type of mass-balance approach is quantitative incorporation of mass balances within a reactive-transport model and could be applied to groundwaters, surface waters, and surface-water-groundwater interactions. Pačes (1983, 1984) calls this the local mass-balance approach. There are numerous examples and explanations of this approach (e.g., Freeze and Cherry, 1979; Domenico and Schwartz, 1990).

A third type of mass-balance approach is to leave the physical flow conditions implicit, assume steady-state flow along a flow line in an aquifer, and account for observed chemical changes that occur as the groundwater flows from recharge to discharge (Plummer and Back, 1980). This approach was introduced formally by the classic paper of Garrels and Mackenzie (1967), who calculated mass balances derived from springwater data in the Sierra Nevada Mountains of California. The modeler begins with aqueous chemical data along a flow path in an aquifer (or catchment) of known mineralogy and accounts for changes in solute concentrations by specified reaction sources and sinks. The analytical solution is achieved by solving a set of simultaneous linear equations known as mole balancing:

$$\sum_{j=1}^j b_p \alpha_p^i = \Delta m_i = m_{i(\text{final})} - m_{i(\text{initial})} \quad (3)$$

in which m_i is the number of moles of element/component i per kilogram of water, α_p^i is the stoichiometric coefficient of element i in phase p , b_p is the mass transfer coefficient of the p th phase, and j is the number of phases (Plummer *et al.*, 1983). Because groundwaters are frequently mixtures of different water quality types, mixing fractions can also be employed in the matrix array. Redox chemistry can be included through conservation of electrons and water balance can be used to simulate evaporation. Plummer (1984) has called this type of modeling the inverse method, because it proceeds in a reverse manner to that of forward modeling, i.e., it backs out the probable reactions from known data on water chemistry, isotopes, and mineralogy. Parkhurst (1997) simply refers to it as mole balancing. Semantics aside, this model is developed for water–rock interactions from “a set of mixing fractions of initial aqueous solutions and mole transfers of minerals and gases that quantitatively account for the chemical composition of the final solution” (Parkhurst, 1997).

Two papers point out the fundamental nature of mole balancing for interpreting groundwater chemistry. Plummer (1984) describes attempts to model the Madison Limestone aquifer by both forward and inverse methods. Two valuable conclusions from this paper were that information gained from mole balancing was needed to provide relativistic reaction rates for forward modeling and that even with these rates, the well-water compositions could not be closely matched, whereas they can be exactly matched with inverse modeling. Furthermore forward modeling required much more effort and contained more uncertainty. Similar conclusions were reached by Glynn and Brown (1996) in their

detailed study of the acidic plume moving in the Pinal Creek Basin. They found that the best approach was to pursue a series of mole-balance calculations, improving their modeling with each re-examination of the phases and reactions considered. Then they took their refined mole-balance results and made further improvements by forward modeling. Inverse modeling, however, was a key to their successful interpretation. The complex nature of interpreting a dispersed contaminant plume and the associated mineral dissolution front required the use of reactive-transport modeling. The reactive-transport modeling, however, would have been much more uncertain without the inverse modeling at the front end.

It has been pointed out that inverse modeling assumes advective, steady-state flow and that “reaction inversion” does not occur (Steeff and Van Cappellen, 1998). Although these are important issues, they are often not serious limitations. These assumptions are not a firm requirement for the system being studied, it is only essential that the consequences of assuming them for non-steady-state flow (with or without dispersion) do not have a significant effect on the results of the calculation. For example, it can be argued that over a long enough period of time or for a large enough aquifer, steady-state conditions never truly apply. Indeed, steady state is an approximation of the physical and chemical state of an aquifer system that works well for many, if not most, aquifers. As Zhu and Anderson (2002) pointed out, the most important criterion is that the same parcel of water has traveled from point A to point B. They also state that chemical steady state is sufficient but not necessary “because the underlying mathematical equations to be solved... are the integrated forms of mass conservation (Lichtner, 1996).” At the Iron Mountain mines (Alpers *et al.*, 1992), high concentrations of sulfate (tens of grams per liter) and metals (grams per liter) discharge from two major portals. The groundwater has advective and nonadvective (dispersive and convective) properties, and the variable effluent flows would indicate transient state. The chemistry, however, is still dominated by oxidation of sulfide minerals and acid dissolution of aluminosilicate minerals, and a mass-balance calculation will still reflect these geochemical processes. A mass balance going from rainwater to portal effluent will delineate the key minerals that dissolve and precipitate along the flow path. Steeff and Van Cappellen (1998) correctly state that inverse modeling cannot be applied to contaminant plumes or reaction fronts unless the spatial delineation of the reaction front is clearly defined. “Reaction inversion,” such as the dissolution of a particular mineral changing to

precipitation between two points along a flow path such that no overall reaction appears to have taken place, is an interesting problem. Without additional information it would not be possible to distinguish between no reaction and reaction inversion. In such instances, it makes no difference to the modeling or the conclusions, because the net result is the same. It is as if the element of concern was conserved in the solid phase during that increment of fluid flow, a safe assumption for silica in quartz but not for silica in weathering feldspars. It might only matter if these small-scale processes affect other processes such as the unidirectional release or attenuation of trace elements (released upon mineral dissolution but not co-precipitated or adsorbed upon mineral precipitation or vice versa) or similar irreversible processes involving nutrients. Further discussion of inverse modeling is found in [Sections 5.02.7.1](#) and [5.02.8.3](#).

5.02.3 SOLVING THE CHEMICAL EQUILIBRIUM PROBLEM

Although both kinetic and equilibrium expressions can be used in geochemical modeling computations, the “equilibrium problem” is the foundation of most calculations of this type. Simply stated, the chemical equilibrium problem is the determination of the most stable state of a system for a given set of pressure (P), temperature (T), and compositional constraints (X_i). These variables, P , T , and X_i , need not be fixed, but they must be defined for the given system. The chemical state of a system is given by the total Gibbs free energy, G , and its differential change with the progress variable, ξ , denotes the state of the system in mathematical terms. For a system at equilibrium

$$\left(\frac{\partial G}{\partial \xi} \right)_{P,T} = 0 \quad (4)$$

and any perturbation from equilibrium will cause this differential to be other than 0. The progress variable is a singular quantity that expresses the extent to which a reaction has taken place. It is equal to the change in the number of moles, n_i , of a reactant (or product) normalized to the stoichiometric coefficient, ν_i , for that component, element, or species. In differential form,

$$\partial \xi = \frac{\partial n_i}{\nu_i} \quad (5)$$

Solving the equilibrium problem means finding the minimum in the free energy curve for the defined system. Two general approaches have been used: the equilibrium constant approach and the free-energy minimization approach. As the names suggest they primarily use equilibrium

constants to solve the problem or they use free energies. Of course, the approaches are considered the same because they are related by $\Delta_r G^\circ = RT \ln K$, where R is the universal gas constant, T is the absolute temperature in kelvin, and K is the equilibrium constant, but the logarithmic conversion leads to different numerical techniques. Both approaches have to employ mass-balance and mass-action equations. Upon substitution of mass-action into mass-balance expressions (or vice versa), a set of nonlinear equations is derived that are readily solved by a numerical method coded for a computer. The mathematical formulation of the chemical equilibrium problem is explained in [Zeleznik and Gordon \(1968\)](#), [Van Zeggeren and Storey \(1970\)](#), [Wolery \(1979\)](#), and [Smith and Missen \(1982\)](#). [Harvie and Weare \(1980\)](#) and [Harvie et al. \(1987\)](#) have improved the free-energy minimization algorithm for solving the general chemical equilibrium problem and applied it to finding parameters for the Pitzer method. [Rubin \(1983, 1990\)](#) provides more formalism for dealing with reactive transport and nonequilibrium conditions. Further discussion of the numerical techniques can be found in the books by [Smith and Missen \(1982\)](#), [Nordstrom and Munoz \(1994\)](#), and many other textbooks and papers. A simple problem involving speciation of an aqueous solution at equilibrium with gypsum is solved by both the Newton–Raphson method and the “continued fraction” method in [Nordstrom and Munoz \(1994\)](#).

5.02.4 HISTORICAL BACKGROUND TO GEOCHEMICAL MODELING

The founders of geochemistry, F. W. Clarke, G. M. Goldschmidt, V. I. Vernadsky, and A. E. Fersman, clearly made major contributions to our “models” of geochemical processes. Today, however, we think of geochemical models in terms of high-speed quantitative computations of water–rock interactions made possible with fast processors and disks with large memories. This direction of research began with the principles of physical chemistry adapted for solving aqueous low-temperature geochemical problems by [Hem \(1959\)](#), [Garrels \(1960\)](#), [Sillén \(1961\)](#), [Garrels and Christ \(1965\)](#), and [Krauskopf \(1967\)](#). The scholarly structures that these authors built would not have been possible without the foundations laid by those who came before and developed the science of physical chemistry: Wilhelm Ostwald, Jacobius Henricus van’t Hoff, and Svante Arrhenius ([Servos, 1990](#)). These chemists, along with numerous others they influenced, established the principles upon which aqueous low-temperature geochemistry and geochemical modeling is based. Van’t Hoff himself was an early developer of geochemical models in his efforts to apply

physical chemistry to the interpretation of the equilibrium factors determining the stability of gypsum and anhydrite (van't Hoff *et al.*, 1903) and the equilibrium interpretation of the Permian Zechstein evaporite deposits (van't Hoff (1905, 1909), 1912; Eugster, 1971).

Probably the earliest paper to apply a speciation calculation to natural water was Goldberg's (1954) estimate of the ionic species form of copper in seawater based on Niels Bjerrum's theory of ion-pair formation and Jannik Bjerrum's data (see Bjerrum, 1950). He found that 65% was in the free ion (Cu^{2+}) form and another 33% was present as either a cation or neutral species form (copper-chloride complexes). This calculation, however, did not take into account simultaneous competitive complexing from all the other ions in seawater. Speciation was central to Krauskopf's (1951) study on gold solubility, his discussion of trace-metal enrichment in sedimentary deposits (Krauskopf, 1955), and his examination of the factors controlling trace-metal concentrations in seawater (Krauskopf, 1956). In the US Geological Survey (USGS), Hem and Cropper (1959) and Hem (1961) were estimating distribution of ionic species and activities of ions at chemical equilibrium in natural waters. Sillén's (1961) first paper on seawater considered hydrolysis and complex formation. At this time he and his colleagues were pioneering the application of computers to solve complex aqueous solution equilibria (Sillén, 1962; Ingri and Sillén, 1962; Ingri *et al.*, 1967; Dyrssen *et al.*, 1968). The next paper to apply aqueous speciation to natural water was that of Garrels and Thompson (1962) in their "Chemical Model of Seawater," which contained unique features such as the mean-salt method for estimating activity coefficients.

The adaptation of water-rock geochemical modeling to computers was pioneered by Helgeson and his colleagues, who focused on ore deposits and high-temperature, high-pressure reactions (Helgeson, 1964, 1967, 1969) but also considered low-temperature processes (Helgeson *et al.*, 1969, 1970). Helgeson's (1971) research continued with the application of computers to the calculation of geochemical kinetics. Theoretical approaches were developed for geochemical kinetics (Aagard and Helgeson, 1982; Helgeson and Murphy, 1983) and computations compared to measured reaction rates (Helgeson *et al.*, 1984; Murphy and Helgeson, 1987) and coupled with diffusion (Murphy *et al.*, 1989). These approaches provide insight to the mechanisms of controlled laboratory studies on mineral dissolution rates, but difficulties are encountered when applications are made to the complex conditions of the natural environment. Experimental and theoretical approaches to mineral dissolution fail to predict

the actual dissolution rates in catchments, because experiments do not reproduce the composition and structure of natural mineral surfaces, they do not account for adsorbed inhibitors, they do not consider the effect of variable climate and hydrologic flow rates, and they do not account for biological activity. These factors may have taken anywhere from decades to millenia to develop and they can change over short periods of time. Computer codes that incorporate reaction kinetics into groundwater or catchment codes usually do so with some type of generalized first-order rate law.

Beginning in the 1960s and expanding considerably during the 1970s, a series of computer codes were developed that could perform a wide variety of aqueous geochemical calculations (Bassett and Melchior, 1990; Mangold and Tsang, 1991) and these evolved considerably during the 1980s and 1990s to include simulation of more processes, coupling of processes (especially reaction with transport), and the availability of more options (Alpers and Nordstrom, 1999). The advances in geochemical modeling are apparent in the evolution of Barnes' "*Geochemistry of Hydrothermal Ore Deposits*" from first edition (Barnes, 1967) to third edition (Barnes, 1997), in the American Chemical Society (ACS) books *Chemical Modeling in Aqueous Systems* that have shown significant advances from the first (Jenne, 1979) to the second (Melchior and Bassett, 1990), and in the plethora of papers on this subject since the 1980s. Nevertheless, advanced sophistication for geochemical codes does not imply a parallel advance in our understanding of geochemical processes. The sophistication of software has outdistanced our capacity to evaluate the software over a range of conditions and it has outdistanced our ability to obtain the field data to constrain and test the software.

5.02.5 THE PROBLEM OF ACTIVITY COEFFICIENTS

5.02.5.1 Activity Coefficients

Aqueous electrolytes and the equilibrium constants that define various reactions in low-temperature geochemistry are inexorably linked with the problem of activity coefficients, or the problem of nonideality for aqueous electrolyte solutions. Thermodynamic equilibrium constants, defined by an extrapolation to infinite dilution for the standard state condition (not the only standard state), require the use of activity coefficients. Unfortunately, there is neither a simple nor universal nonideality method that works for all electrolytes under all conditions. This section provides a brief overview of a major subject still undergoing research and development but for

which several satisfactory approaches are available.

If the activity of a solute or ion were ideal, it could be taken as equivalent to the molal concentration, m_i , of the i ion or solute. However, interactions with other ions and with the solvent water are strong enough to cause nonideal behavior and the characteristic property relating concentration to chemical potential is the activity coefficient, γ_i :

$$a_i = \gamma_i m_i \quad (6)$$

With the accumulation of activity coefficient measurements and the search for a theoretical expression ensued, it was discovered that in dilute solutions the logarithm of the activity coefficient was an approximate function of the square root of the molality:

$$\log \gamma_i = \alpha_i m_i^{1/2} \quad (7)$$

where α_i was simply a constant. Brønsted (1922) introduced a linear term to Equation (7) in which the coefficient, β , is a “specific-ion interaction parameter,”

$$\log \gamma_i = \alpha_i m_i^{1/2} + \beta m_i \quad (8)$$

Later modifications of this general approach became known as the specific-ion interaction theory (SIT) because of the explicit dependence on the solute or ions being considered.

An important concept that aided in the development of electrolyte theory was the ionic strength, I , introduced by Lewis and Randall (1921):

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (9)$$

where z_i is the ionic charge. Thereafter, the ionic strength was used as a parameter in activity coefficient equations. Debye and Hückel (1923) derived an equation from electrostatic theory which, in the limit of infinite dilution (hence, the Debye–Hückel limiting law), becomes

$$\log \gamma_i = -A z_i^2 I^{1/2} \quad (10)$$

where A is a Debye–Hückel solvent parameter (dependent on the properties of the solvent).

The extended Debye–Hückel equation is

$$\log \gamma_i = -\frac{A z_i^2 I^{1/2}}{1 + B a_i I^{1/2}} \quad (11)$$

where B is another Debye–Hückel solvent parameter and a_i is an ion-size diameter derived by empirical fit but approximates the hydrated ion diameter.

The use of the extended Debye–Hückel equation with the appropriate equilibrium constants for mass action expressions to solve a complex chemical equilibrium problem is known as the ion-association (IA) method.

Several modifications of these equations were tried over the next several decades. Contributions by Guggenheim (1935) and Scatchard (1936) and the KTH or Swedish group (Grenthe *et al.*, 1992, 1997) became the Brønsted–Guggenheim–Scatchard or SIT method:

$$\log \gamma_i = -\frac{A z_i^2 I^{1/2}}{1 + 1.5 I^{1/2}} + \sum_k \varepsilon(i, k, I) m_k \quad (12)$$

in which the linear term is a function of molality summed for all the other ions in solutions, k , and $\varepsilon(i, k)$ tends to be constant at higher molalities but solute or ion specific. The last term in Equation (12) represents the deviation of the experimentally measured activity coefficient from the prediction of the Debye–Hückel equation. Other groups, such as Truesdell and Jones (1974), kept the ionic strength dependence throughout the equation, and the coefficient, b , became the difference factor but still a constant for a given solute or ion:

$$\log \gamma_i = -\frac{A z_i^2 I^{1/2}}{1 + B a_i I^{1/2}} + b_i I \quad (13)$$

The IA method using Equation (13) for major ions in natural water compares well with other more precise methods (see below) up to an ionic strength of seawater (0.7) but not much higher.

The next better approximation is to allow the linear coefficient to be a function of the ionic strength (Pitzer and Brewer, 1961) and was utilized by Helgeson and Kirkham (1974a,b, 1976), Helgeson *et al.* (1981), and Tanger and Helgeson (1988) in the development of the Helgeson–Kirkham–Flowers (HKF) equations, which include consideration of the Born function and ion hydration.

Pitzer (1973) re-examined the statistical mechanics of aqueous electrolytes in water and derived a different but semi-empirical method for activity coefficients, commonly termed the Pitzer specific-ion-interaction model. He fitted a slightly different function for behavior at low concentrations and used a virial coefficient formulation for high concentrations. The results have proved extremely fruitful for modeling activity coefficients over a very large range of molality. The general equation is

$$\ln \gamma_{\pm} = -\frac{A}{3} |z_+ z_-| f(I) + \frac{2v_+ v_-}{v} B(I) m + \frac{2(v_+ v_-)^{3/2}}{v} C m^2 \quad (14)$$

where

$$f(I) = \frac{I^{1/2}}{1 + 1.2 I^{1/2}} + 1.67 \ln (1 + 1.2 I^{1/2})$$

and

$$B(I) = 2\beta^\circ + \frac{2\beta'}{\alpha^2 I} \left[1 - \left(1 + \alpha I^{1/2} - \frac{1}{2} \alpha^2 I \right) e^{-\alpha I^{1/2}} \right]$$

and where β° and β' are specific-ion parameters, α is a constant for a similarly charged class of electrolytes and C is a specific-ion parameter independent of ionic strength. The B and C parameters are second and third virial coefficients. The parameter $\nu = \nu_+ + \nu_-$, is the sum of the stoichiometric coefficients for the cation, ν_+ , and the anion, ν_- , of the solute. The Pitzer parameters have been fitted for a wide range of solutes and have been used for mixed electrolyte solutions to model the mineral solubility behavior in brines (Harvie and Weare, 1980; Harvie *et al.*, 1980). Grenthe *et al.* (1997) have compared the SIT method and the Pitzer method in detail and came to the following conclusions: (i) the more extensively parametrized Pitzer model allows the most precise modeling of activity coefficients and equilibrium constants provided that all the interaction coefficients are known; (ii) when Pitzer parameters are missing (not available from experimental data), they must be estimated and the precision and accuracy of the activity coefficients can be significantly compromised; (iii) the parameters in the SIT model can be related to those in the Pitzer model and provide another means of estimating Pitzer parameters; (iv) the SIT model is in good agreement with the Pitzer model for the range $m = 0.1\text{--}4\text{ mol kg}^{-1}$; and (v) the Pitzer model is the preferred formalism for solutions or brines of high ionic strength. An extensive discussion of the development of the Pitzer model and several hybrid approaches can be found in Pitzer (1991a) and Millero (2001). It appears that hybrid approaches provide the best promise in the future, because they combine the extensive data available on equilibrium constants with a better formulation of activity coefficients.

The difference between the extended Debye–Hückel equation and the Pitzer equations has to do with how much of the nonideality of electrostatic interactions is incorporated into mass action expressions and how much into the activity coefficient expression. It is important to remember that the expression for activity coefficients is inexorably bound up with equilibrium constants and they must be consistent with each other in a chemical model. Ion-pair interactions can be quantified in two ways, explicitly through stability constants (IA method) or implicitly through empirical fits with activity coefficient parameters (Pitzer method). Both approaches can be successful with enough effort to achieve consistency. At the present, the Pitzer method works much better for brines, and the IA method works better for

dilute waters because of the greater number of components and species for which basic data exist. When the effort is made to compare both approaches for the same set of high-quality data, they appear to be comparable (Felmy *et al.*, 1990). The primary challenge for the future will be to insure that consistency is maintained between the thermodynamic data, the expressions for non-ideality, and the mass-action expressions in geochemical modeling codes and to incorporate trace elements and redox species within the same formulation.

5.02.5.2 Saturation Indices

After speciation and activities have been calculated for all the free ions, ion pairs, triplets, etc., a mineral saturation index can be computed. The saturation index, SI, is defined as the logarithm of the ratio of the ion-activity product, IAP, to the solubility product constant, K_{sp} ,

$$SI = \log \left[\frac{IAP}{K_{sp}} \right] \quad (15)$$

If the solution is at equilibrium, the $IAP = K_{sp}$ and the $SI = 0$. If the $SI > 0$, then the solution is supersaturated and the mineral would tend to precipitate; if the $SI < 0$, the solution is undersaturated and the mineral would tend to dissolve, if present. Because the SI is affected by the stoichiometry of the mineral formula, it is best to normalize the SI to the total mineral stoichiometry as pointed out by Zhang and Nancollas (1990):

$$SI = \log \left[\frac{IAP}{K_{sp}} \right]^{1/\nu} \quad (16)$$

where $\nu = \nu^+ + \nu^-$, the sum of the stoichiometries of the positive and negative components in the mineral formula.

These computations describe the “tendency” of a water sample to be saturated, but they do not necessarily demonstrate whether mineral dissolution or precipitation is taking place. For dissolution to take place, the mineral must be present and it must dissolve at a rate that is fast enough relative to the flow rate of the water to affect the water chemistry (Berner, 1978). Likewise for a mineral to precipitate it must do so at a fast enough rate. The kinetics of precipitation and dissolution reactions must be applied to get a realistic interpretation of water–rock interactions.

5.02.6 GEOCHEMICAL DATABASES

Input for aqueous geochemical codes consists of field data (geology, petrology, mineralogy, and

water analyses), thermodynamic and aqueous electrolyte data, and possibly kinetic and sorption data. Thermodynamic data are fundamental to most geochemical computations and several major compilations are available. Although the guidelines and necessary relations for thermodynamic consistency are well established (Rossini *et al.*, 1952; Helgeson, 1968, 1969; Haas and Fisher, 1976; Nordstrom *et al.*, 1990; Nordstrom and Munoz, 1994), it has been difficult to employ them in the development of databases. Two general approaches have been recognized, serial networks and simultaneous regression. With serial networks, an evaluator begins with a single starting point, such as the standard state properties for an element (or all elements) and gradually builds in compound properties through the appropriate reaction combinations. Serial networks, such as the National Bureau of Standards (NBS) database (Wagman *et al.*, 1982), achieve continuity for a large data set but lose thermodynamic constraints, whereas simultaneous regression, which preserves thermodynamic relationships, can only be done on a limited subset of data, and the weighting of the regression fit depends on the judgment of the evaluator (Archer and Nordstrom, 2003). Computer codes have been developed for the purpose of correlating and evaluating a diversity of thermodynamic data (Haas, 1974; Ball *et al.*, 1988), but they have not been widely used. Serious discrepancies in thermodynamic properties do appear among these compilations and some of these discrepancies have been incorporated into the databases of geochemical codes. Many users of these codes are not familiar with these databases and the possible uncertainties propagated through the computations from thermodynamic errors. Such error propagation may or may not be important, depending on the specific objectives of the geochemical problem being addressed.

5.02.6.1 Thermodynamic Databases

Since the early compilations of thermodynamic data (e.g., Lewis and Randall, 1923), numerous measurements were made during the twentieth century leading to the well-known compilations of Latimer (1952) and Rossini *et al.* (1952). Measurements and compilations continued to expand through the latter part of the twentieth century, and comprehensive inventories such as Sillén and Martell (1964), Martell and Smith (1974–1976), Wagman *et al.* (1982), Chase (1998), Robie and Hemingway (1995), and Gurvich *et al.* (1993) summarized and organized a considerable amount of data. Unfortunately, the methods used to evaluate the data are not always transparent and occasionally the source references are not known.

Notable exceptions were the publication of the CODATA tables (Garvin *et al.*, 1987; Cox *et al.*, 1989), the Organization Economic Co-Operation and Development/Nuclear Energy Agency Thermochemical Data Base (OECD/NEA TDB) publications (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Rard *et al.*, 1999; Lemire, 2001), and the International Union of Pure and Applied Chemistry (IUPAC) compilations (e.g., Lambert and Clever, 1992; Scharlin, 1996). The OECD/NEA TDB, although focusing on radionuclides of most concern to safe disposal of high-level radioactive wastes and military wastes, contains a considerable amount of auxiliary data on other common aqueous and solid species that had to be evaluated along with the actinides. For aqueous geochemical modeling the equilibrium constant tables of Nordstrom *et al.* (1990) have proven useful and are found in USGS and US Environmental Protection Agency (USEPA) codes described below and in popular water-chemistry/aqueous-geochemistry textbooks (Appelo and Postma, 1993; Stumm and Morgan, 1996; Langmuir, 1997; Drever, 1997a). These tables have been recompiled, expanded, and tabulated in terms of thermodynamic properties (G , H , S , C_p , and $\log K$ for reaction and individual species (Nordstrom and Munoz, 1994)). The tabulation of Nordstrom and Munoz (1994) was organized in such a way that individual species can be compared with reactions measured independently. Consequently, it is easy to check thermodynamic relations to see if the properties for individual species are consistent with tabulated reaction equilibria. Only values that agreed within a close range of the stated uncertainties were included in the tables.

These tabulations represent a portion of the data needed for geochemical model computations and there have been some obvious inconsistencies. By the mid-1990s critical evaluations of thermodynamic data were tapering off and many errors and inconsistencies had not been resolved. As recently as 1994, serious inconsistencies still existed between calorimetrically derived and solubility-derived properties for such common minerals as celestine and barite, and a less common but important phase such as radium sulfate (Nordstrom and Munoz, 1994). This set of discrepancies has been resolved for celestine and barite by new measurements using high-temperature oxide-melt and differential-scanning calorimetry (Majzlan *et al.*, 2002). Listing of sources of thermodynamic data compilations can be found in Nordstrom and Munoz (1994) and in Grenthe and Puigdomenech (1997).

5.02.6.2 Electrolyte Databases

The classic books by Harned and Owen (1958) and Robinson and Stokes (1959) put electrolyte

theory on a firm basis and provided important tabulations of electrolyte data for calculations of activity coefficients and related properties. Advances in electrolyte theory, especially the use of the Pitzer method (Pitzer, 1973, 1979), led to alternate methods of calculating activities and speciation. The books edited first by Pytkowicz (1979) and later by Pitzer (1991b) provided a general overview of the different approaches and hybrid approaches to these computations. The more recent reference providing a thorough overview of the subject with tables of molal properties, activity coefficients and parameters, and dissociation/association constants is Millero (2001). These references explain the general use of the IA method with extended forms of Debye–Hückel equations, the Pitzer specific-ion interaction method, and hybrid approaches that take advantage of the best aspects of both approaches.

5.02.7 GEOCHEMICAL CODES

This listing and description of geochemical codes is not meant to be either exhaustive or complete. It is meant to be a brief overview of several codes in current and common use. Reviews by Yeh and Tripathi (1989a), Mangold and Tsang (1991), Parkhurst and Plummer (1993), and Alpers and Nordstrom (1999) provide information on more codes, their evolution, and references to earlier reviews on codes and geochemical modeling. Loeppert *et al.* (1995) also contains useful information on geochemical codes and modeling, especially for soil interactions. It is important to remember that most codes in active use often undergo enhancements, database updates, and other improvements. The descriptions given in this section may not apply to some of these same codes five years from now.

5.02.7.1 USGS Codes

The USGS has developed several codes that are useful for the interpretation of water chemistry data and for simulating water–rock interactions. Two similar aqueous speciation codes were developed in parallel, WATEQ (Truesdell and Jones, 1974) and SOLMNEQ (Kharaka and Barnes, 1973). The primary aim of these programs was to aid in the interpretation of water quality data. SOLMNEQ, however, had a different subroutine for calculating temperature and pressure dependence and could calculate reaction equilibria above 100 °C. WATEQ was intended for temperatures of 0–100 °C. Both of these programs have been updated. WATEQ4F v. 2 (Ball and Nordstrom, 1991, with database updates to 2002) uses the IA method with an expanded

form of the extended Debye–Hückel equation for major ions (the Truesdell–Jones formulation or hybrid activity coefficient; Truesdell and Jones (1974) and Nordstrom and Munoz (1994)), includes independent redox speciation computations that assume redox disequilibrium, and has database updates for uranium (Grenthe *et al.*, 1992), chromium (Ball and Nordstrom, 1998), and arsenic redox species (Archer and Nordstrom, 2003; Nordstrom and Archer, 2003). SOLMINEQ.88 (Kharaka *et al.*, 1988; Perkins *et al.*, 1990) covers the temperature range of 0–350 °C and 1–1,000 bar pressure, includes both the IA method and the Pitzer method, and has mass-transfer options such as boiling, fluid mixing, gas partitioning, mineral precipitation, mineral dissolution, ion exchange, and sorption. It has been found to be particularly applicable to deep sedimentary basins, especially those containing oil and gas deposits. The latest version, SOLMINEQ.GW is explained in an introductory text on groundwater geochemistry (Hitchon *et al.*, 1996).

Parkhurst *et al.* (1980) developed the PHREEQE code to compute, in addition to aqueous speciation, mass transfer, and reaction paths. A separate but similar code, PHRQPITZ, uses the Pitzer method for brine calculations (Plummer *et al.*, 1988; Plummer and Parkhurst, 1990). The PHREEQE code has been regularly enhanced and the recent version, PHREEQC v. 2, includes ion exchange, evaporation, fluid mixing, sorption, solid-solution equilibria, kinetics, one-dimensional transport (advection, dispersion, and diffusion into stagnant zones or dual porosity), and inverse modeling (Parkhurst and Appelo, 1999). An interface (PHREEQCI) was developed for interactive modification of the input files by Charlton *et al.* (1997). The latest development (β -test version) is PHAST, which includes three-dimensional transport. The program PHAST uses the solute-transport simulator HST3D (Kipp, 1987, 1998) and iterates at every time step with PHREEQC. Thorstenson and Parkhurst (2002) have developed the theory needed to calculate individual isotope equilibrium constants for use in geochemical models and utilized them in PHREEQC to calculate carbon-isotope compositions in unsaturated zone with seasonally varying CO₂ production (Parkhurst *et al.*, 2001).

Geochemical modeling of reactants in flowing mountainous stream systems can be done with the USGS codes OTIS (Runkel, 1998) and OTEQ (Runkel *et al.*, 1996, 1999) that model solute transport and reactive transport, respectively. OTIS, or one-dimensional transport with inflow and storage, is based on the earlier work of Bencala (1983) and Bencala and Walters (1983). The OTEQ code combines the OTIS code with MINTEQA2 for chemical reaction at each

incremental step of transport. These codes are calibrated with constant-flow tracer injection studies and testable assumptions regarding the solubility product constant of the precipitating phases (Kimball *et al.*, 2003). They have been tested in numerous settings, primarily with the objective of quantifying and predicting the sources, transport, and fate of acid drainage from mined environments in the western US.

Codes for inverse modeling began with the program BALANCE (Parkhurst *et al.*, 1982) from which the interactive code NETPATH (Plummer *et al.*, 1991) evolved. NETPATH, in addition to mass balances, does database management for a suite of wells and can compute speciation and saturation indices with WATEQ. NETPATH has now been incorporated into PHREEQC along with uncertainty propagation (Parkhurst, 1997). Bowser and Jones (1990, 2002) have incorporated the mass-balance approach into a spreadsheet format that allows graphical output and a quick reconnaissance of ranges of mineral compositions that are permissible models for silicate solid-solution series (see Chapter 5.04).

USGS codes and manuals can be downloaded free of charge at <http://water.usgs.gov/nrp/gwsoftware/>. The more current version and additional bibliographic and information files for PHREEQC are available at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/. Updates on revised thermodynamic data and WATEQ4F can be found at http://wwwbrr.cr.usgs.gov/projects/GWC_chemtherm/ with links to software and thermodynamic property evaluation. The OTIS code can be accessed at <http://co.water.usgs.gov/otis> (see Chapter 5.04).

5.02.7.2 LLNL Codes

A set of computer codes known as EQ3/6 was originally developed by Wolery (1979) to model rock–water interactions in hydrothermal systems for the temperature range of 0–300 °C. Software development was later sponsored by the US Department of Energy at Lawrence Livermore National Laboratories (LLNL) to model geochemical processes anticipated in high-level nuclear waste repositories. This geochemical code has become one of the most sophisticated and most applicable for a wide range of conditions and processes. In addition to speciation and mass transfer computations, it allows for equilibrium and nonequilibrium reactions, solid-solution reactions, kinetics, IA and Pitzer methods, and both inorganic and organic species. The program has been used for several municipal and industrial waste situations and has been used to assess natural and engineered remediation processes. It has five supporting thermodynamic data files

and the thermodynamic data are evaluated and updated with the SUPCRT92 software (Johnson *et al.*, 1992), based on Helgeson's formulation for activity coefficients and aqueous thermodynamic properties over a wide range of temperature and pressure (Helgeson and Kirkham, 1974a,b, 1976; Helgeson *et al.*, 1981) and solid-phase thermodynamic properties (Helgeson *et al.*, 1978). Thermodynamic data are updated with the availability of published research (e.g., Shock and Helgeson, 1988, 1990; Shock *et al.*, 1989). Several manuals for operation and general information are available at <http://geosciences.llnl.gov/esd/geochem/eq36.html> (last accessed February 17, 2003).

5.02.7.3 Miami Codes

It would be difficult to find more comprehensive or more detailed studies on the physical chemistry of seawater than those done at the University of Miami (Millero, 2001). Several programs were developed for calculation of activity coefficients and speciation of both major ions and trace elements in seawater. The activity coefficient models have been influenced strongly by the Pitzer method but are best described as hybrid because of the need to use ion-pair formation constants (Millero and Schreiber, 1982). The current model is based on Quick Basic; computes activity coefficients for 12 major cations and anions, 7 neutral solutes, and more than 36 minor or trace ions. At 25 °C the ionic strength range is 0–6 m. For major components, the temperature range has been extended to 0–50 °C, and in many cases the temperature dependence is reasonably estimated to 75 °C. Details of the model and the parameters and their sources can be found in Millero and Roy (1997) and Millero and Pierrot (1998). Comparison of some individual-ion activity coefficients and some speciation for seawater computed with the Miami model is shown in Section 5.02.8.6 on model reliability.

5.02.7.4 The Geochemist's Workbench™

A set of five programs known as The Geochemist's Workbench™ or GWB was developed by Bethke (1994) with a wide range of capabilities similar to EQ3/6 and PHREEQC v. 2. GWB performs speciation, mass transfer, reaction-path calculations, isotopic calculations, temperature dependence for 0–300 °C, independent redox calculations, and sorption calculations. Several electrolyte databases are available including ion association with Debye–Hückel activity coefficients, the Pitzer formulation, the Harvie–Møller–Weare formulation, and a

PHRQPITZ-compatible formulation. The program X2t allows the coupling of two-dimensional transport with geochemical reaction. Basin3 is a basin-modeling program that can be linked to GWB. Another advantageous feature is the plotting capability that can produce $p\epsilon$ –pH or activity–activity or fugacity–fugacity diagrams from GWB output. Bethke (1996) has published a textbook on *Geochemical Reaction Modeling* that guides the reader through a variety of geochemical computations using GWB and provides the basis for a course in modeling. The GWB is a registered code and must be obtained from Dr. Bethke and the University of Illinois.

5.02.7.5 REDEQL-MINTEQ Codes

One of the first speciation programs that included mass transfer reactions at equilibrium was REDEQL (Morel and Morgan, 1972). The primary aim of this set of codes was to compute the equilibrium chemistry of dilute aqueous solutions in the laboratory and was among the first to include sorption. It also has been widely used to interpret water quality in environmental systems. This FORTRAN code has evolved through several versions, parallel with advances in computer hardware and software. Incorporation of the WATEQ3 database (Ball *et al.*, 1981) with the MINEQL program (Westall *et al.*, 1976) produced MINTEQ (Felmy *et al.*, 1984) which became the USEPA-supported code, MINTEQA2 (Allison *et al.*, 1991). The more recent upgrade is MINTEQA2/PRODEFA2 v. 4 (USEPA, 1998, 1999 (revised)), and contains code revisions, updates in thermodynamic data, and modifications to minimize nonconvergence problems, to improve titration modeling, to minimize phase rule violations, to enhance execution speed, and to allow output of selected results to spreadsheets. PRODEFA2 is an ancillary program that produces MINTEQA2 input files using an interactive preprocessor. Thermodynamic data and computational abilities for Be, Co(II/III), Mo(IV), and Sn (II, IV) species have been added to the program. Unfortunately, the numerous inconsistencies, lack of regular upgrades, and tendency for numerous independent researchers to make their own modifications to the program have led to several versions that differ in reliability. Examples of test cases to demonstrate the input setup, capabilities of the code, and comparisons of standard test cases have not been included in the documentation as has been done for other programs. The more recent upgrade information can be obtained at <http://epa.gov/ceampubl/mmedia/minteq/supplei.pdf> (last accessed February 17, 2003).

Perhaps the most noteworthy aspect of the upgraded MINTEQA2 code is the Gaussian model

for interactions of dissolved organic matter with cations. The model formulation is based on the statistical treatment of proton binding (Posner, 1964) that was developed by Perdue and Lytle (1983), Perdue *et al.* (1984), and Dobbs *et al.* (1989). This approach uses a continuous distribution of sites as opposed to discrete site binding. It is equivalent to a collection of monoprotic ligands, each able to bind protons and metal cations, with the variations in $\log K$ described by a single Gaussian distribution for each class of sites. Another code, MODELm (Huber *et al.*, 2002), uses a linear differential equilibrium function to account for trace-metal complexation with natural organic matter. Computations were compared to those done by MINTEQA2. MODELm predicted greater amounts of metal-organic complexing than MINTEQA2, but no conclusions were drawn as to the cause of this difference. MODELm can be used in MINTEQA2 instead of the Gaussian distribution model. Although cation-organic binding in natural waters is a highly complex and challenging subject to quantify for modeling purposes, advances since the early 1990s are leading us much closer to practical approaches that can be incorporated into computerized equilibrium and nonequilibrium chemical codes. Geochemistry will benefit from continued research in this area because organic matter exerts such a strong control on the behavior of trace elements in most aquatic systems. More testing and evaluation of a range of natural waters with different trace-element concentration and organic matter types is needed in the future. This can be accomplished by comparing analytical speciation with computed speciation.

A Windows version of MINTEQA2 v. 4.0, known as Visual MINTEQ, is available at no cost from <http://www.lwr.kth.se/English/OurSoftware/vminteq/> at The Royal Institute of Technology, Sweden (last accessed February 17, 2003). It is supported by two Swedish research councils, VR and MISTRA. The code includes the National Institute of Standards and Technology (NIST) database, adsorption with five surface complexation models, ion-exchange, and metal-humate complexation with either the Gaussian DOM Model or the Stockholm Humic Model. Input data are accepted from Excel spreadsheets and output is exported to Excel. A major update was completed in January 2003. The Royal Institute of Technology also has produced HYDRA and MEDUSA for creating a database for a given system and creating activity–activity and $p\epsilon$ –pH diagrams. Links to other similar programs can be found online.

A Windows version of MINTEQA2, known as MINEQL + v. 4.5, has several enhancements that make it an attractive alternative to other versions.

The user interface with a relational database technique for scanning thermodynamic data, a utility for creating a personal database, a relational spreadsheet editor for modifying chemical species, a multi-run manager, special reports for convenient data extraction or additional calculations, and a tutorial with several examples provide a much more flexible and practical code for modelers. It also provides graphic output for log *C*–pH plots, ion-fraction diagrams, solubility plots, titration curves, and sensitivity plots. It is limited in temperature to 0–50 °C and ionic strength <0.5 M. The program is available through Environmental Research Software, <http://www.mineql.com/> (last accessed February 21, 2003).

5.02.7.6 Waterloo Codes

A considerable history of hydrogeochemical modeling and its application has evolved at the University of Waterloo, Ontario, Canada, and a series of reactive-transport codes have evolved with it. These codes have been primarily applied to mine tailings piles. A finite element transport module, PLUME2D, was utilized with the MINTEQA2 module in an efficient two-step sequential solution algorithm to produce MINTRAN (Walter *et al.*, 1994). Leachates from heterogeneous mine overburden spoil piles that made a contaminant front were modeled with MINTRAN and other codes at open-pit lignite mines in Germany (Gerke *et al.*, 1998). When a numerical model that coupled oxygen diffusion and sulfide-mineral oxidation, PYROX, was added to MINTRAN, it became MINTOX (Wunderly *et al.*, 1996). MINTOX proved to be capable of simulating 35 yr of contaminant transport at the Nickel Rim mine tailings impoundment (Bain *et al.*, 2000). The more recent version is MIN3P (Mayer *et al.*, 1999), which is a general reactive transport code for variably saturated media. It has been applied to the Nickel Rim impoundment and to the contaminated groundwater downgradient of the Königstein uranium mine in Saxony, Germany (Bain *et al.*, 2001). At Königstein, reactions involving iron, uranium, sulfate, cadmium, chromium, nickel, lead, and zinc were all modeled. A short review of similar codes and an update on those codes can be found in Mayer *et al.*, (2003).

5.02.7.7 Harvie–Møller–Weare Code

With the arrival of the Pitzer method for calculating activity coefficients at high ionic strengths (≥ 1 m), research by Harvie and Weare (1980) led to computations of equilibrium mineral solubilities for brines. They could calculate

solubility data from gypsum ($I < 0.06$ m) to bischofite saturation (>20 m). This capability made it possible to more accurately calculate the mineral sequences during seawater evaporation and quantitatively solve a problem that had puzzled van't Hoff (Harvie *et al.*, 1980). The original model included the components Na, K, Mg, Ca, Cl, SO₄, and H₂O and was applied to the simpler salt systems and to mineral equilibria in seawater (Eugster *et al.*, 1980). With further revision of the parameters the model was expanded to include more complex electrolyte mixtures and their salts for seawater evaporation (Harvie *et al.*, 1982). Later the number of components was expanded to include H, OH, HCO₃, CO₃, and CO₂ (Harvie *et al.*, 1984). Incorporating the temperature dependence to allow calculations from 25–250 °C was achieved by Møller (1988) and for lower temperatures (0–250 °C) by Greenberg and Møller (1989) and Spencer *et al.* (1990). Marion and Farren (1999) extended the model of Spencer *et al.* (1990) for more sulfate minerals during evaporation and freezing of seawater down to temperatures of –37 °C. Pressure dependence for aqueous solutes and minerals in the Na–Ca–Cl–SO₄–H₂O system to 200 °C and 1 kbar were obtained by Monnin (1990) and applied to deep Red Sea brines and sediment pore waters (Monnin and Ramboz, 1996). Møller *et al.* (1998) developed the TEQUIL code for geothermal brines. Ptacek and Blowes (2000) have reviewed the status of the Pitzer method applications for sulfate mineral solubilities and demonstrated the applicability of a modified Harvie–Møller–Weare (HMW) to mineral solubilities in mine tailings piles.

5.02.7.8 WHAM Models

Tipping (1994) has proposed an alternative and practical model for humic acid–metal binding embodied in the speciation code Windemere Humic Aqueous Model (WHAM) that has two versions, one for water and one for soils (Tipping, 1998). This aqueous metal-organic model is based on the concept of electrostatic interactions at discrete sites. Hence, it is readily amenable to use with inorganic chemical speciation programs for aqueous solutions and includes ionic strength and temperature effects. Tipping *et al.* (2002) provide a thorough evaluation of humic substance binding with aluminum and iron in freshwaters. They demonstrate that 60–70% of the dissolved organic carbon (DOC) in their samples was humic substances involved in metal complexation: after accounting for organic complexing, the inorganic speciation is consistent with control of dissolved aluminum and iron concentration by their hydrous oxides. A full explanation of the developments

that led up to the WHAM model and descriptions of many other models (multiple versus single discrete models, continuous models, competitive versus noncompetitive models, empirical models, site heterogeneity/polyelectrolyte models, and Gaussian distribution models) can be found in [Tipping \(2002\)](#). The latest WHAM code, version 6, is available at http://www.ife.ac.uk/aquatic_processes/wham/WHAMtitlebar.htm (last accessed February 16, 2003). An example of a continuous distribution for binding sites can be found in the development of the Natural Organic Anion Equilibrium Model, or NOAEM ([Gryzb, 1995](#)) which also can be used in conjunction with ionic components and electrostatic theory.

5.02.7.9 Additional Codes

The coupled code developed by [Steefel and Lasaga \(1994\)](#) for multicomponent reactive transport with kinetics of precipitation and dissolution of minerals has been developed further into the OS3D/GIMRT code ([Steefel and Yabusaki, 1996](#)). This model has been applied to reaction fronts in fracture-dominated flow systems ([Steefel and Lichtner, 1998](#)). Further developments for nonuniform velocity fields by [Yabusaki et al. \(1998\)](#) required the use of massively parallel processing computers, although “... the accuracy of the numerical formulation coupling the nonlinear processes becomes difficult to verify.”

The model BIOKEMOD has been developed to simulate geochemical and microbiological reactions in batch aqueous solutions ([Salvage and Yeh, 1998](#)). It has been tested and found to simulate a range of processes that include complexation, adsorption, ion-exchange, precipitation/dissolution, biomass growth, degradation of chemicals by metabolism of substrates, metabolism of nutrients, and redox. The code has been coupled to HYDROGEOCHEM ([Yeh and Tripathi, 1989b](#)) for simulation of reactive transport modeling with biogeochemical transformation of pollutants in groundwaters. FEREACT was developed for two-dimensional steady-state flow with equilibrium and kinetically controlled reactions ([Tebes-Stevens et al., 1998](#)). Another code, that was developed for biogeochemical transport and interactions of oxidative decay of organics with oxygen, iron, manganese, and sulfur redox species, has been introduced by [Hunter et al. \(1998\)](#).

[Lichtner \(2001\)](#) developed the computer code FLOTRAN, with coupled thermal–hydrologic–chemical (THC) processes in variably saturated, nonisothermal, porous media in 1, 2, or 3 spatial dimensions. Chemical reactions included in FLOTRAN consist of homogeneous gaseous reactions, mineral precipitation/dissolution, ion exchange, and adsorption. Kinetic rate laws and redox

disequilibrium are allowed with this code. Debye–Hückel and Pitzer options are both available for computing activity coefficients, and thermodynamic data are based on the EQ3/6 database or user defined databases.

Several options are available in FLOTRAN for representing fractured media. The equivalent continuum model (ECM) formulation represents fracture and matrix continua as an equivalent single continuum. Two distinct forms of dual continuum models also are available, defined in terms of connectivity of the matrix. These models are the dual continuum connected matrix (DCCM) and the dual continuum disconnected matrix (DCDM) options. A parallel version of the code, PFLOTRAN, has been developed based on the PETSC parallel library at Argonne National Laboratory.

[Park and Ortoleva \(2003\)](#) have developed WRIS.TEQ, a comprehensive reaction-transport-mechanical simulator that includes kinetic and thermodynamic properties with mass transport (advection and diffusion). A unique property of this code is a dynamic compositional and textural model specifically designed for sediment alteration during diagenesis.

Further research on reactive transport theory, modeling, and codes can be found in the *Reviews in Mineralogy* volume edited by [Lichtner et al. \(1996\)](#) and the special issue of *Journal of Hydrology*, vol. 209 (1998).

5.02.8 WATER–ROCK INTERACTIONS

About a dozen or so major hydrogeochemical processes dominate the compositions of most surface and groundwaters. These processes include calcite dissolution and precipitation, gypsum dissolution and precipitation, pyrite oxidation and formation of hydrous ferric oxide, silicate mineral dissolution (feldspars, micas, chlorites, amphiboles, olivines, and pyroxenes) and clay mineral formation (kaolinitization, lateritization, and illitization), dolomite dissolution and calcite precipitation (dedolomitization), dolomite formation (dolomitization), sulfate reduction and pyrite formation, silica precipitation, evaporation, and cation exchange. They are explained in several available textbooks (e.g., [Appelo and Postma, 1993](#); [Langmuir, 1997](#); [Drever, 1997a](#)), and only a few examples are given here to demonstrate how complex geochemistry can be easily computed with available codes. Aqueous speciation is discussed first, because it is required for more complex computations. For geochemical modeling, aqueous speciation occurs so quickly that it can safely be assumed to be at equilibrium. This assumption is valid for the vast majority of aqueous reactions but not for redox reactions.

5.02.8.1 Aqueous Speciation

Some brief examples of aqueous speciation are given here to demonstrate the large decreases in free ion concentration or activity that occur as a result of ion-pair formation or complexing. Polyvalent ions have a greater tendency to associate with other ions of opposite charge and among polyvalent cations that are found commonly in waters, iron and aluminum are prime examples. [Alpers and Nordstrom \(1999\)](#) tabulate analyses of four acid mine waters with pH in the range 4.9–0.48 and show the effects of speciation for copper, sulfate, aluminum, and iron using the WATEQ4F code. [Table 1](#) shows the total dissolved concentrations and the main species for aluminum and sulfate. Several conclusions are readily apparent. First, to approximate the free ion concentrations by the total dissolved concentrations is fair, as for sulfate in AMD-A (83%), to poor, as for aluminum in AMD-D (4.1%). Furthermore, for a wide range of total dissolved sulfate concentration, the AlSO_4^+ ion pair is always important (50–70% of the dissolved aluminum) but with increasing sulfate concentration and decreasing pH, the $\text{Al}(\text{SO}_4)_2^-$ ion triplet becomes increasingly important. This ion triplet has an association constant that is not well established and some codes might not include it in their database.

Another example of aqueous speciation that includes redox can be shown with the arsenic pE – pH diagram shown in [Figure 1](#). Arsenic can exist in several oxidation states including As(–III) as in arsine gas (AsH_3), As(0) as in elemental arsenic, As(II) as in realgar (AsS), As(III) as in orpiment (As_2S_3) and dissolved arsenite, and As(V) as in dissolved arsenate. [Figure 1](#) shows the dominant dissolved species, arsenate and arsenite, and their hydrolysis products as a function of redox potential and pH based on the thermodynamic evaluation of [Nordstrom and Archer \(2003\)](#). These results show the dominance of hydrolysis for arsenate species, but it is of minor consequence for the arsenite species.

Hydrolysis is of major importance in understanding mineral reactions, kinetics of reactions, and sorption behavior. At neutral to high pH, the adsorption of arsenate onto hydrous ferric oxides is weak to nonexistent, and the high anionic charge on the dissolved arsenate developed through hydrolysis combined with negatively charged surfaces helps to account for this lack of adsorption. The lack of significant arsenite hydrolysis helps explain the more competitive adsorption of arsenate relative to arsenite.

5.02.8.2 Modeling Sorption Reactions

Although sorption modeling should be included in our discussion, this extensively researched area warrants an entirely separate chapter. Several books cover the subject well, including [Dzombak and Morel \(1990\)](#), [Davis and Hayes \(1986\)](#), [Stumm \(1987\)](#), and [Hochella and White \(1990\)](#).

5.02.8.3 Model Simulations of Mineral Reactions

One of the most ubiquitous geochemical processes is the dissolution of calcite. Dissolution of calcite in the environment can be the dominant source of dissolved calcium in many waters, but dissolved inorganic carbon (DIC) can have at least two sources: calcite and CO_2 produced from organic decay. Calcite dissolution has been modeled with PHREEQCI for a range of carbon dioxide partial pressure, P_{CO_2} . [Figure 2\(a\)](#) is a plot of calcite dissolution in terms of calcium and DIC concentrations at P_{CO_2} values ranging from atmospheric ($10^{-3.5}$) to 10^{-1} . Computationally, increments of calcite were dissolved in water at fixed partial pressure until solubility equilibrium was reached. The solid line represents the equilibrium solubility of calcite for this range of carbon dioxide partial pressure and the

Table 1 Example of aqueous aluminum and sulfate speciation for acid mine waters covering a range of pH and composition.

| Sample | AMD-A | AMD-B | AMD-C | AMD-D |
|---|-------|-------|--------|---------|
| Temperature (°C) | 16.0 | 19.5 | 24.0 | 34.8 |
| pH | 4.9 | 3.25 | 1.10 | 0.48 |
| Total dissolved Al (mg L ⁻¹) | 5.06 | 19.8 | 1,410 | 2,210 |
| % as Al^{3+} | 29 | 26 | 10 | 4.1 |
| % as AlSO_4^+ | 51 | 66 | 57 | 61 |
| % as $\text{Al}(\text{SO}_4)_2^-$ | 2 | 4.5 | 32 | 32 |
| Total dissolved SO_4 (mg L ⁻¹) | 206 | 483 | 50,000 | 118,000 |
| % as SO_4^{2-} | 83 | 71 | 18 | 8 |
| % as HSO_4^- | 0 | 2 | 32 | 53 |
| % as AlSO_4^+ and $\text{Al}(\text{SO}_4)_2^-$ | 4.5 | 11 | 12 | 8 |
| % as Fe(II/III)– SO_4 ions | 0 | 2 | 29 | 26 |

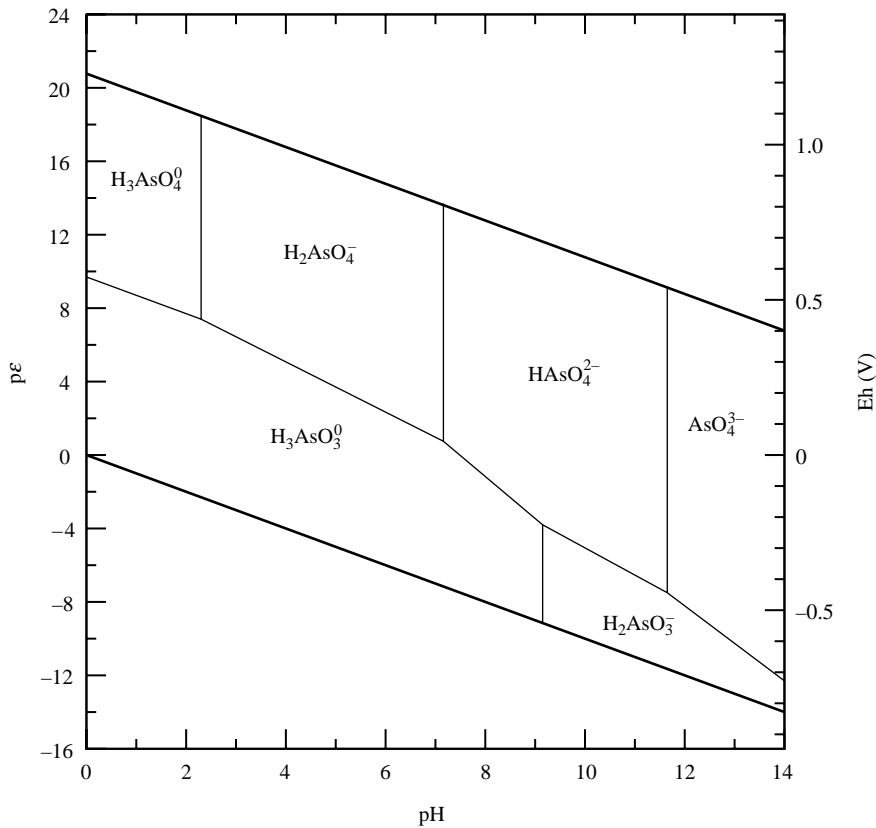


Figure 1 Species predominance diagram for dissolved arsenic at 25 °C and 1 bar (source [Nordstrom and Archer, 2003](#)).

equilibrium pH values at each P_{CO_2} from 8.3 to 6.7 are shown in parentheses.

Many shallow groundwaters reflect calcite dissolution as the dominant control on water quality. Groundwaters incorporate higher P_{CO_2} than that of the atmosphere because of carbon dioxide production in the soil zone and organic matter decomposition in the groundwater. A range of P_{CO_2} from 10^{-2} to 10^{-1} and pH values from 7 to 8 are common for most groundwaters. Water analyses in a carbonate terrain of Pennsylvania ([Langmuir, 1971](#)) are compared in [Figure 2\(b\)](#) to the predictions in [Figure 2\(a\)](#). Although this plot simplifies the water chemistry and does not take into account dissolution of other minerals, it does show the dominant control by a relatively simple reaction. The P_{CO_2} fall within the expected range and calcite solubility equilibrium provides an upper boundary. The saturation index plot in [Figure 3](#) for the same samples takes into account temperature and ionic strength effects on the activities and also shows that saturation with respect to calcite is reached and provides an upper limit to calcium and DIC concentrations. As the pH increases, there is a greater proportion of carbonate ions relative to bicarbonate that increases the saturation with respect to calcite.

At pH values below ~ 7 , waters are nearly always undersaturated with respect to calcite (and most other carbonate minerals).

Pyrite oxidation is a complex hydrobiogeochemical processes that accounts for 11% of the sulfate found in river drainages ([E. K. Berner and R. A. Berner, 1996](#)). Mining activities have increased the rate of pyrite oxidation and caused severe contamination of many waterways with acid and metals. When pyrite oxidizes, the sulfur rapidly converts to sulfate but the oxidation of the iron proceeds more slowly, depending on pH. Simulating the oxidation of pyrite is instructive in summarizing the chemistry of this complex process ([Nordstrom, 2000](#)). In [Figure 4](#), PHREEQCI was used to simulate pyrite oxidation by adding increments of oxygen to pyrite in water. The reaction also could be simulated by adding increments of pyrite to an excess of oxygen. The results vary with the amount of oxidation allowed and are represented in the figure by a solution pH as a function of the amount of pyrite oxidized. First, pyrite oxidation to an acid ferrous sulfate solution only, is shown by the solid line. Second, the same reaction occurs but the ferrous iron is allowed to oxidize without forming a precipitate, shown by the dashed line with a crossover

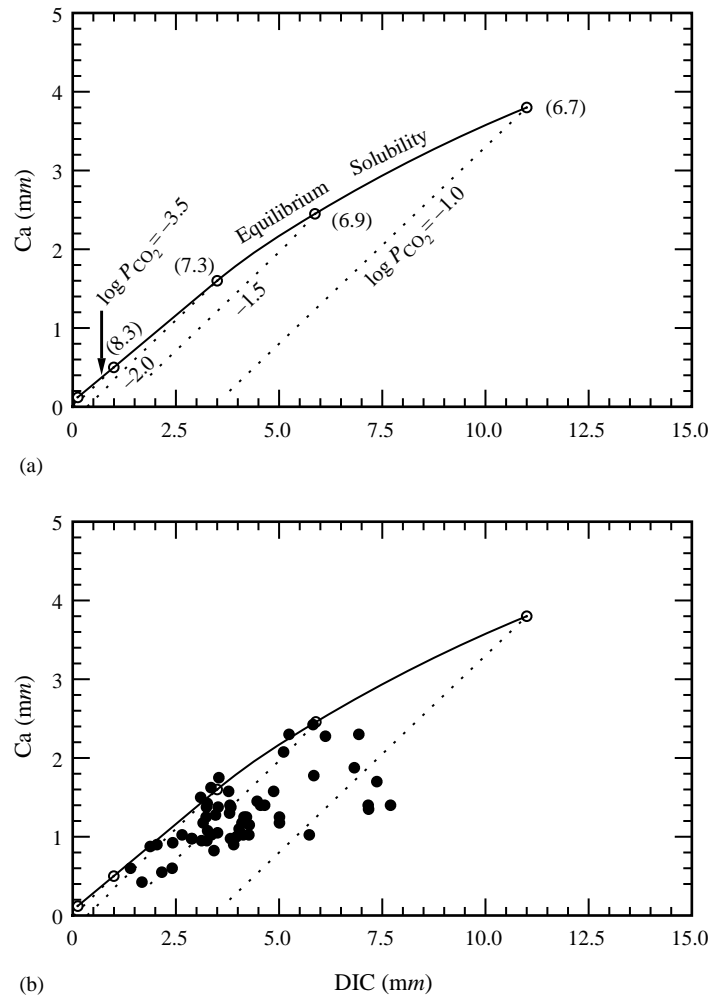


Figure 2 (a) Calcium and DIC concentrations plotted for calcite dissolution at $\log P_{CO_2} = -3.5, -2, -1.5$, and -1 (dotted lines) up to equilibrium calcite solubility (solid line). The pH values for each equilibrium solubility at the specified $\log P_{CO_2}$ are shown in parentheses. Plot was computed with PHREEQCI for 25 °C and 1 bar. (b) Calcium and DIC concentrations plotted for groundwaters taken from a limestone aquifer in Pennsylvania. Dotted and dashed lines are the same as those in (a).

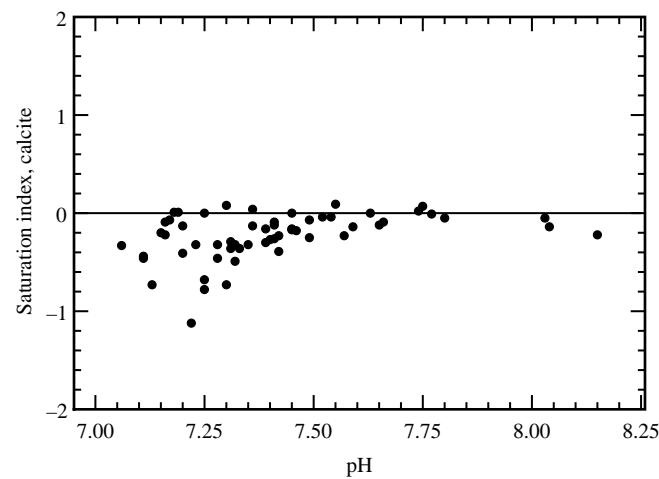


Figure 3 Saturation indices for calcite from the same groundwaters as in Figure 2, plotted as a function of pH.

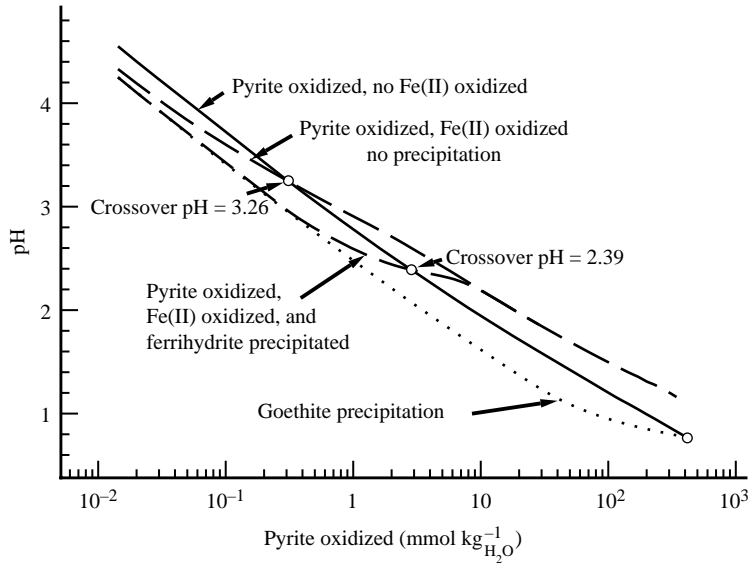
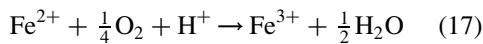
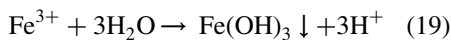


Figure 4 Change in pH as a function of the amount of pyrite oxidized under four scenarios: (i) pyrite oxidizes to an acid ferrous sulfate solution without any further oxidation (solid line); (ii) pyrite oxidizes and the resultant ferrous sulfate solution is allowed to oxidize, but no precipitation is allowed (upper dashed line); (iii) pyrite oxidizes, the ferrous sulfate solution oxidizes and precipitates ferrihydrite ($pK_{sp} = 4.89$, lower dashed line); and (iv) pyrite oxidizes, ferrous sulfate solution oxidizes, and goethite precipitates (dotted line). Computed with PHREEQCI at 25 °C and 1 bar, thermodynamic data from Nordstrom *et al.* (1990).

pH of 3.26. Third, a precipitate such as ferrihydrite is allowed to form, which lowers the crossover pH to 2.39. If the K_{sp} of the precipitating phase is lower, such as that for crystalline goethite, the crossover pH is much lower as shown by the dotted line. However, crystalline goethite is not stable at pH values below 2 and jarosite would precipitate instead. The reason for showing the goethite curve is to demonstrate the effect of lowering the K_{sp} for a precipitating phase of the same stoichiometry. The dashed lines cross over the original line, because the oxidation of ferrous iron involves both proton-consuming and proton-producing reactions. The oxidation of Fe^{2+} to Fe^{3+} consumes protons:



which happens at all pH values. The hydrolysis and precipitation of a ferric hydroxide phase produces protons:



which only happens if the pH has reached the point of hydrolysis, i.e., near or above a $pH = pK_1 = 2.2$ for Fe^{3+} hydrolysis. Consequently, at lower pH values there is no hydrolysis and the pH can only increase on oxidation. The crossover pH reflects the balance between the proton-consuming and the proton-producing

reactions, a small buffering process represented by the small plateau in the curves. This diagram, although explaining some of the complexities of the chemistry of acid rock drainage, does not include the consequences of acid dissolution involving calcite and aluminosilicate minerals. Nevertheless, some water analyses are available from mine sites that are predominantly affected by pyrite oxidation and little else. These samples, collected from the Leviathan mine area, California, and Iron Mountain, California (Ball and Nordstrom, 1989; Nordstrom, 1977), include a pH measured *in situ* and a pH measured some weeks later after the ferrous iron had oxidized and precipitated. Figure 5 reproduces Figure 4 with only the two lines shown for pyrite oxidation but no ferrous iron oxidation (solid line) and pyrite oxidation with precipitation of ferrihydrite (or the most soluble hydrous ferric oxide, as a dashed line). Because there are low concentrations of cations in these samples, the initial pH values (open circles) can be assumed to be caused by pyrite oxidation. The final pH after oxidation and precipitation is shown by the closed circles. The final pH can be seen to closely approximate the dashed line in agreement with the simulation. In this comparison of a simulation with actual field data, two aspects are noteworthy. First is the good agreement but since this simulation is sensitive to the chosen K_{sp} of the precipitating phase, the agreement indicates that the solubility product constant for freshly

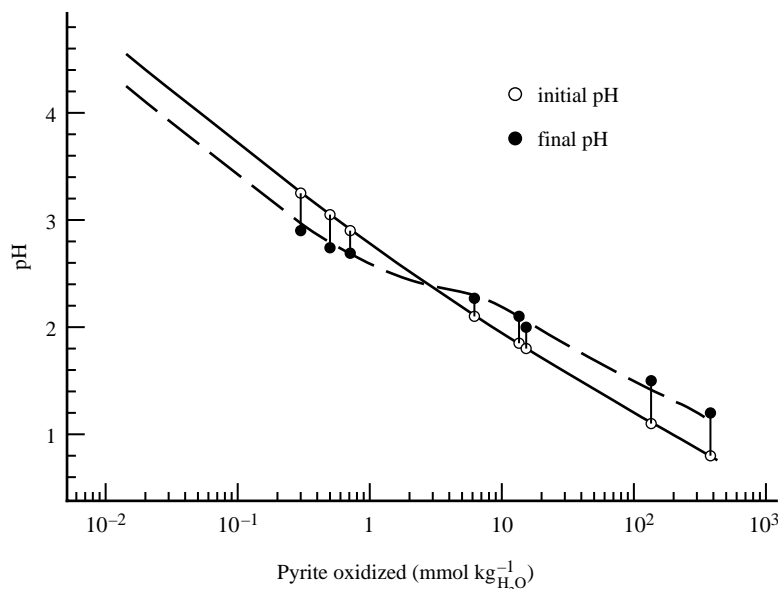


Figure 5 Change in pH as a function of the amount of pyrite oxidized under scenarios (i) and (iii) from Figure 4. Points are actual values measured from acid mine waters. Initial pH is based on field measurements taken on site and the amount of pyrite oxidized is derived from stoichiometry assuming that all the dissolved sulfate is from pyrite oxidation. Final pH was measured after the sample had been allowed to oxidize for at least two weeks in an unfiltered, unpreserved bottle.

precipitating hydrous ferric oxide is a reasonable model choice.

Waters not only undergo geochemical reactions but they commonly mix. One of the classic examples of mixing is seawater intrusion into coastal aquifers, often enhanced because of groundwater withdrawal. When seawater and fresh groundwater mix, both at saturation with respect to calcite, the result can lead to undersaturation with respect to calcite, i.e. calcite dissolution. The possibility of this scenario and other combinations (some leading to mineral precipitation from the mixing of waters that are both initially undersaturated) was outlined by Runnells (1969). Computations made by Plummer (1975) showed the proportion of mixing over which the undersaturation effect, and consequent dissolution of coastal limestone, was operative. Figures 6(a)–(d) are examples from Plummer (1975) and demonstrate that for a large range of seawater in the mixture, calcite undersaturation can occur, depending on carbon dioxide partial pressure and temperature. These calculations were done over a range of temperatures, partial pressures, and pH values. They also were conducted with actual carbonate groundwater compositions and coastal seawater for several locations along the Florida coast.

The inverse or mass-balance modeling approach provides additional constraints on reactant and product mineral phases when the mineral mass transfers are plotted as a function of the range of solid solution compositions. Bowser and

Jones (2002) discovered this application when investigating the effect of compositional ranges of feldspars, phyllosilicates, and amphiboles on mass balances for catchments and groundwaters dominated by silicate hydrolysis. They investigated nine drainages in six areas of widely varying lithology and climatic settings in the US. One of these is shown below in Figure 7 for the Wyman Creek drainage in the Inyo Mountains, California. Mineral mass transfers for dissolution (positive values in mol kg^{-1}) and precipitation (negative values in mol kg^{-1}) are plotted as a function of the percent montmorillonite solid solution. The gray band shows the restricted range of solid solution composition (27–45%) determined by the crossover points for K-feldspar and goethite, respectively. These restrictions apply, because K-feldspar cannot precipitate in these dilute waters and goethite is a weathering product being formed, not dissolved. Similar arguments show that there are restrictions on the range of plagioclase subject to weathering. Indeed, it is surprising to find how closely tied the fluid compositions for major cations are to the Na/Ca ratios of plagioclase, the Ca/Mg ratio of ferromagnesian silicates, and to the Fe/Mg ratio of ferromagnesian silicates.

The final example in this set is from the Madison regional aquifer study by Plummer *et al.* (1990). The Madison Limestone aquifer occurs in Wyoming, Montana, and South Dakota. Plummer *et al.* (1990) utilized a combination of saturation index constraints, inverse modeling, and carbon

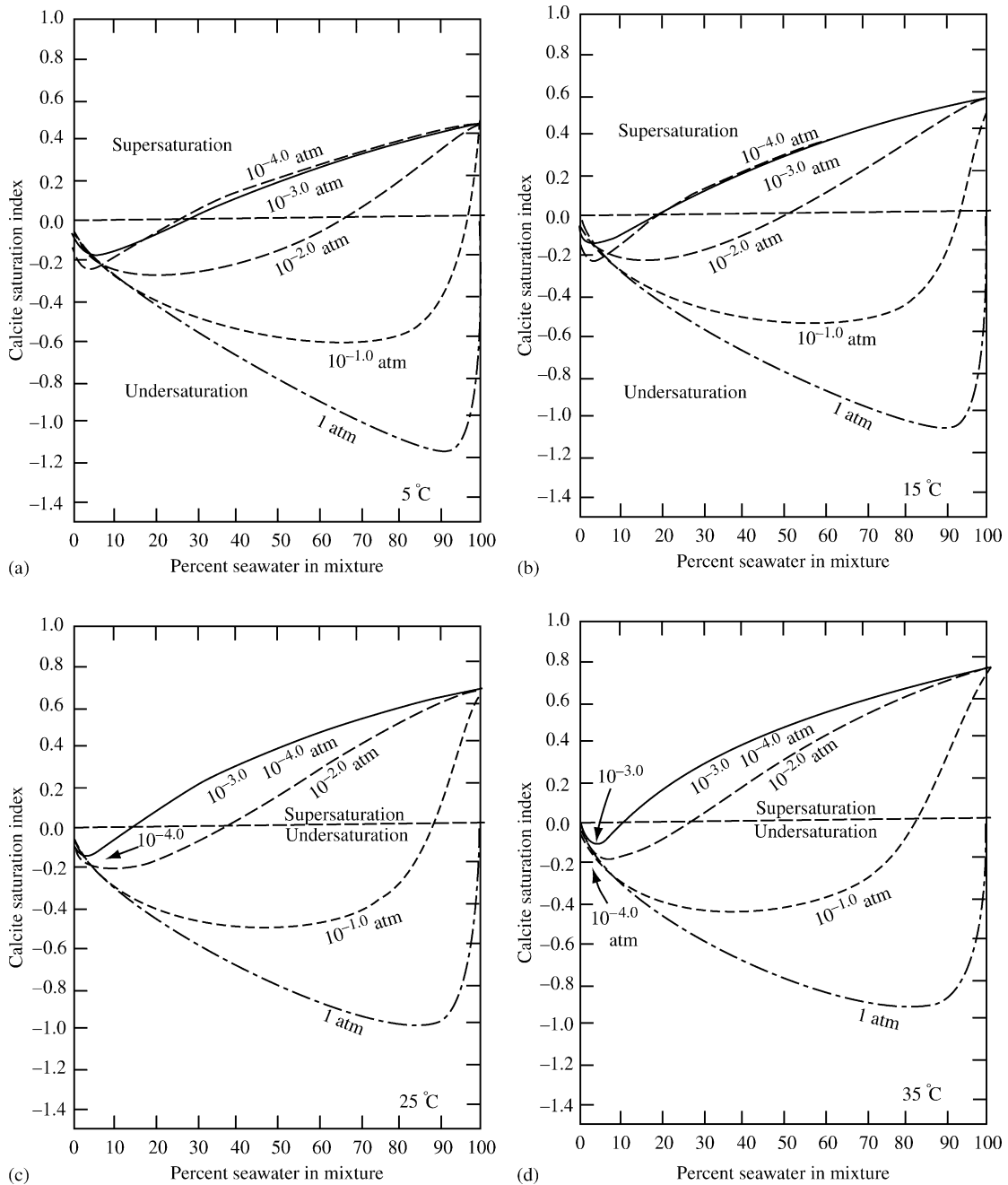


Figure 6 Calcite saturation indices plotted as a function of percent seawater mixing with a carbonate aquifer water with contours representing different levels of P_{CO_2} (source [Plummer, 1975](#)).

and sulfur isotopes to delineate geochemical reaction models for the flow paths. The models indicated that the major reaction is dedolomitization, i.e., dolomite dissolution and calcite precipitation driven by anhydrite dissolution, sulfate reduction, $[Ca^{2+} + Mg^{2+}]/Na^{+}$ cation exchange, with some local halite dissolution. Sulfur isotopes were treated as an isotope dilution problem and carbon isotopes were treated as Rayleigh distillations (see [Chapter 5.11](#)). Corroboration of

the isotopic modeling was achieved by predicting the isotopic compositions of the dolomite and the anhydrite. Actual $\delta^{34}S$ values for anhydrite fit the values assumed in the model calculations. Further consistency was found when the adjusted ^{14}C ages combined with Darcy's law resulted in groundwater flow velocities that agreed within a factor of five of those calculated by a digital flow model. [Figure 8](#) portrays the saturation indices of calcite, dolomite, and gypsum (surrogate for anhydrite)

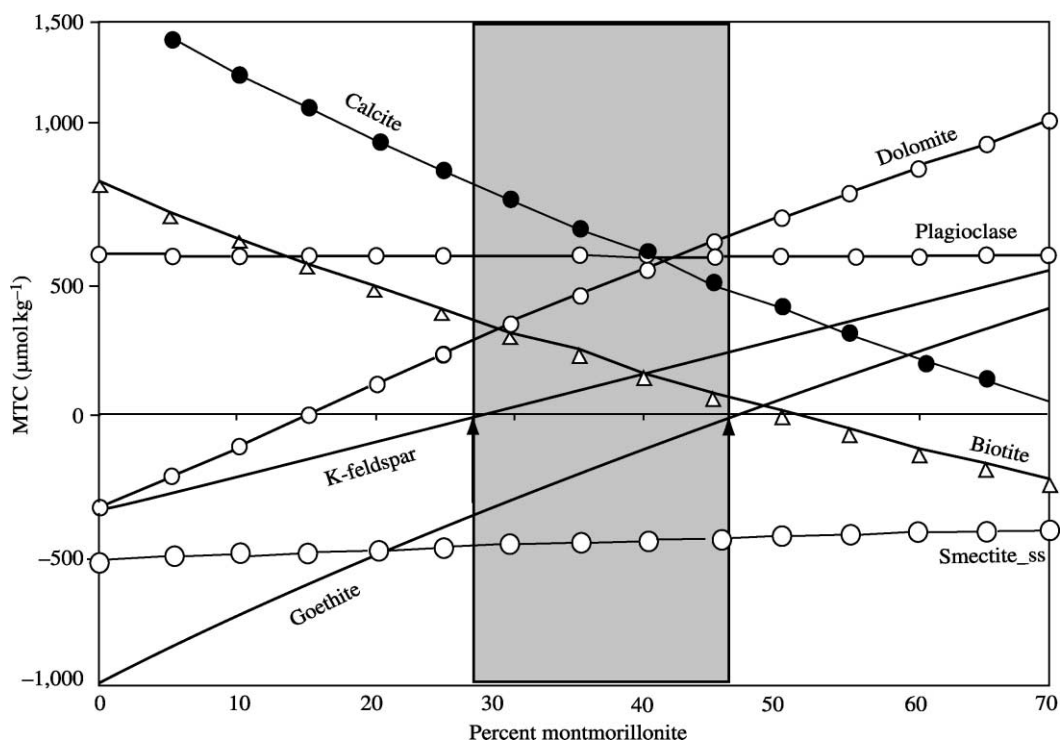


Figure 7 Mineral mass transfer coefficients versus smectite solid solution composition for Wyman Creek mass balances, Inyo Mountains (Bowser and Jones, 2002). Upper and lower bounds on possible smectite compositions are where goethite and K-feldspar mass transfers are equal to zero.

for waters from the Madison aquifer. Calcite reaches saturation quickly and tends to be supersaturated. This supersaturation may reflect the pressure effect on the ion activities and the solubility product constant (pressure corrections were not modeled), it may be caused by pH changes on pumping pressurized water to the surface, it may result from calcite that has some substituted elements displacing the SI values, it may be caused by an inhibition on calcite precipitation kinetics by magnesium, or it may be caused by gypsum dissolving faster than calcite can precipitate.

A subset of the mass-balance results for the Madison aquifer study is shown in Table 2 covering the range of parameters encountered from recharge to discharge although these selected samples are not along the same flow path. The general trend in chemistry is indicated here. Samples near recharge are low in sulfate and the amount of mass transfer is low. As the water moves down gradient and evolves chemically, it increases in sulfate from anhydrite dissolution. Increased anhydrite dissolution leads to increased dissolution of dolomite and increased calcite precipitation. With increasing age there is more organic matter (represented by CH_2O in Table 2) available for decomposition which results in greater amounts of hydrous ferric

oxides dissolving (reducing) and pyrite being formed. Cation exchange in Table 2 refers to $(\text{Ca} + \text{Mg})/\text{Na}$, i.e., exchange of calcium and magnesium for sodium. The measured sulfur isotopic compositions of the H_2S and of the anhydrite match nicely with the model simulation and the stable carbon isotopes.

Mazor *et al.* (1993) pointed out that some of the samples from the Madison aquifer had high tritium contents when the ^{14}C results indicated dates too old for tritium and suggested that significant mixing of younger and older waters may have occurred. Mixing and dilution trends can have similar chemical appearances to hydrochemical evolution, and caution must be used to distinguish evolutionary trends from mixing trends by age-dating techniques.

5.02.8.4 Reactive-Transport Modeling in Streams

Although biological reactions, mostly dissolved oxygen degradation or nutrient uptake, have been modeled in flowing streams and rivers for a long time, trace-metal reactions have not been modeled until relatively recently. Bencala (1983) considered solute transport in pool-and-riffle streams using a kinetic term for sorption; Bencala and Walters (1983) introduced transient storage into

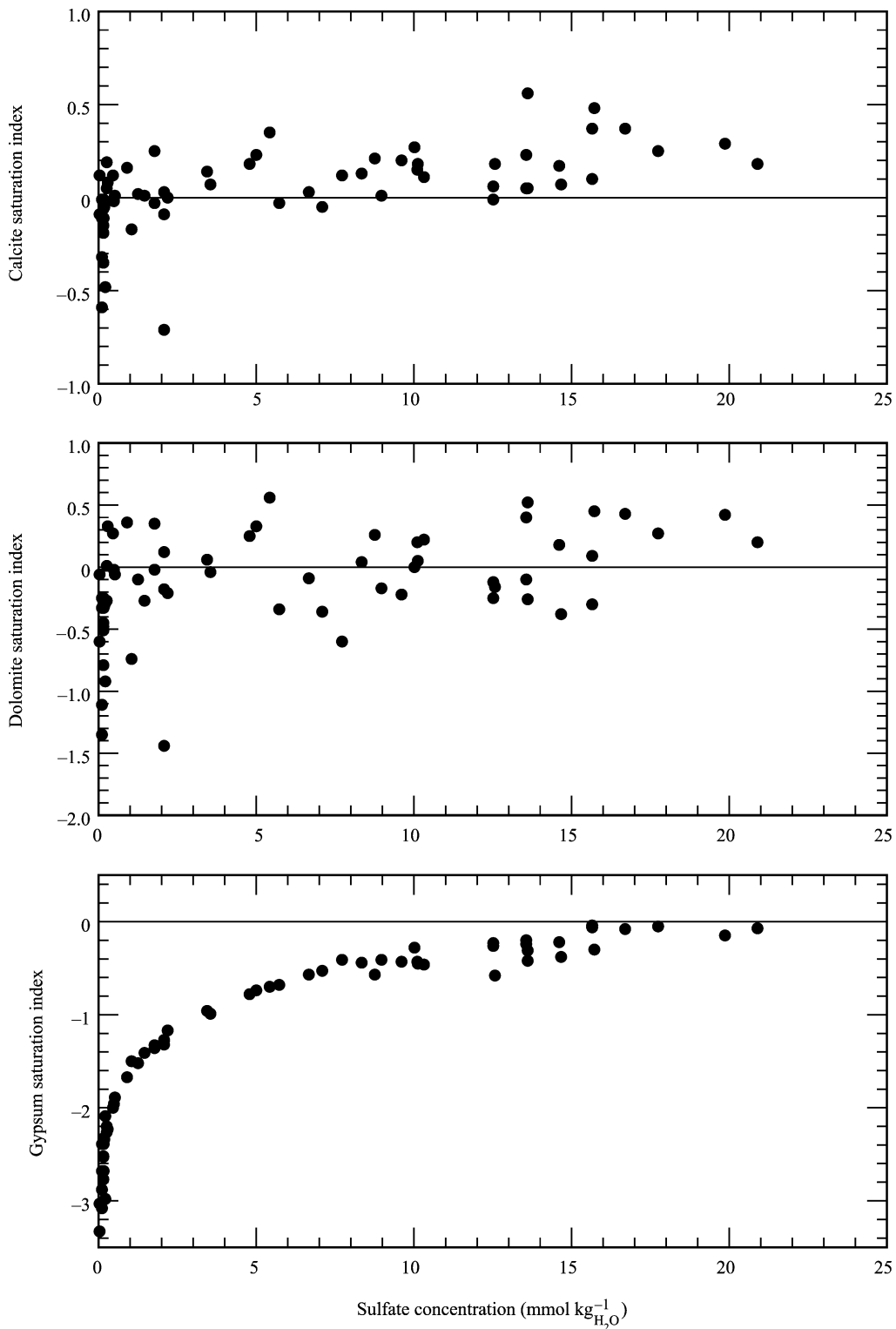


Figure 8 Saturation indices for calcite, dolomite, and gypsum for groundwaters from the Madison limestone aquifer (source [Plummer *et al.*, 1990](#)).

their modeling of trace-metal transport. One of the most obvious inputs of trace metals to surface waters is from mining and mineral-processing wastes. Techniques for modeling these acid mine

water reactions continued to develop during the 1990s from empirical rate constants and partition coefficients to mechanistic sorption models such as surface complexation and equilibrium

Table 2 Selected mass transfer results from [Plummer *et al.* \(1990\)](#) for the Madison Limestone aquifer, units in millimoles per kilogram water.

| Well no. | F6-19 | F6-17 | F6-13 | F7-10 | F8-25 | F8-21 | F3-20 |
|--------------------------------------|--------|--------|--------|-------|--------|--------|--------|
| SO ₄ | 0.18 | 0.52 | 2.19 | 5.73 | 8.97 | 13.56 | 19.86 |
| Dolomite | 0.14 | 0.14 | 0.60 | 0.74 | 1.87 | 2.90 | 3.54 |
| Calcite | -0.18 | -0.41 | -1.62 | -2.64 | -4.70 | -7.15 | -5.33 |
| Anhydrite | 0.15 | 0.51 | 2.27 | 5.93 | 9.19 | 13.56 | 20.15 |
| CH ₂ O | 0.01 | 0.02 | 0.20 | 0.44 | 0.71 | 0.30 | 0.87 |
| FeOOH | 0.00 | 0.01 | 0.05 | 0.12 | 0.21 | 0.11 | 0.09 |
| Pyrite | -0.00 | -0.01 | -0.05 | -0.12 | -0.19 | -0.06 | -0.09 |
| Ion exch. | 0.01 | 0.03 | 0.04 | 0.44 | 0.19 | 0.14 | 8.28 |
| NaCl | -0.01 | -0.02 | 0.03 | 2.83 | 1.38 | 0.97 | 15.31 |
| KCl | 0.01 | 0.02 | 0.02 | 0.27 | 0.28 | 0.33 | 2.52 |
| CO ₂ | -0.07 | 0.17 | -0.21 | -0.42 | -1.18 | -0.40 | -0.04 |
| $\delta^{13}\text{C}$ (‰) calculated | -8.86 | -9.33 | -7.79 | -9.67 | -5.52 | -3.59 | -2.21 |
| $\delta^{13}\text{C}$ (‰) measured | -7.82 | -10.0 | -6.80 | -9.70 | -5.50 | -3.50 | -2.34 |
| Apparent age (yr) | Modern | Modern | Modern | 2,386 | 14,461 | 13,310 | 22,588 |

Positive values signify dissolution, negative values precipitation. Samples, although not along the same flow path, are in the general direction of recharge to discharge from left to right.

precipitation of mineral phases ([Brown and Hosseinipour, 1991](#); [Kimball *et al.*, 1994, 1995](#); [Runkel *et al.*, 1996, 1999](#)). Reaction-transport models such as these require more accurate stream discharge measurements than can be obtained from current-meter measurements. These are obtained from constant-flow tracer injection studies along with synoptic sampling, including all possible inflows, so that the transport model can be reliably calibrated. Not only has this approach been used to define sources and sinks of trace metals in mountainous streams but it also has been helpful in predicting remediation scenarios for mine sites ([Runkel and Kimball, 2002](#)).

An example of modeling reactive transport of acid mine waters with OTEQ is shown in [Figure 9](#) ([Ball *et al.*, 2003](#)) for the drainage released from the Summitville mine in the San Juan Mountains of southwestern Colorado into the Alamosa River. The model was calibrated with tracer injection and synoptic sampling techniques including measurements of Fe(II/III) that helped constrain precipitation of hydrous ferric oxides in the model. Sodium chloride was used as the tracer. [Figure 9\(a\)](#) shows measured pH and simulated pH with reaction. The main in-stream reactive chemistry in this system is the oxidation of iron, the precipitation of hydrous ferric oxides, the precipitation of hydrous aluminum oxides, the adsorption of trace metals, and pH changes (controlled by the oxidation, hydrolysis, and precipitation reactions and by the neutralization of inflows). Simulated and measured dissolved and total aluminum and iron concentrations are shown in [Figures 9\(b\) and \(c\)](#), respectively. Iron and aluminum concentrations decrease rapidly because of precipitation during downstream transport. [Figure 9\(d\)](#) shows the copper concentrations; when adsorption is invoked in the model the agreement between

measured and simulated copper concentrations is within analytical error.

5.02.8.5 Geochemical Modeling of Catchments

Attempts to model chemical weathering of catchments have used a variety of approaches and were originally designed to understand acidification processes. The BIRKENES code ([Christophersen *et al.*, 1982](#)) was one of the first developed to model catchment stream chemistry. It used cation-anion charge balance, a gibbsite equilibrium solubility control for aluminum concentrations, a Gapon ion exchange for metals sorption, and rates for sulfate adsorption/desorption in a two-reservoir model. The model was calibrated by input mass fluxes and output mass fluxes for the Birkenes catchment in Norway to provide the water flux information and to fit empirical parameters.

The ILWAS code (Integrated Lake-Watershed Acidification Study; [Chen *et al.*, 1983](#); [Gherini *et al.*, 1985](#)) also contains a semi-empirical model but is much more detailed than the BIRKENES code with respect to its hydrologic and geochemical compartments. Alkalinity was one of the key chemical components in the model. Because the code was originally calibrated on three watersheds receiving acid rain in upstate New York, it was programmed with mineral rate dissolution data, gibbsite solubility equilibrium, and other parameters pertinent to those environments. The considerable quantity of detailed data needed to calibrate the ILWAS code limits its general usefulness.

The MAGIC code (Model of Acidification of Groundwater In Catchments; [Cosby *et al.*, 1985a,b](#)) is similar in many respects to the BIRKENES code, but parameters for soil-water

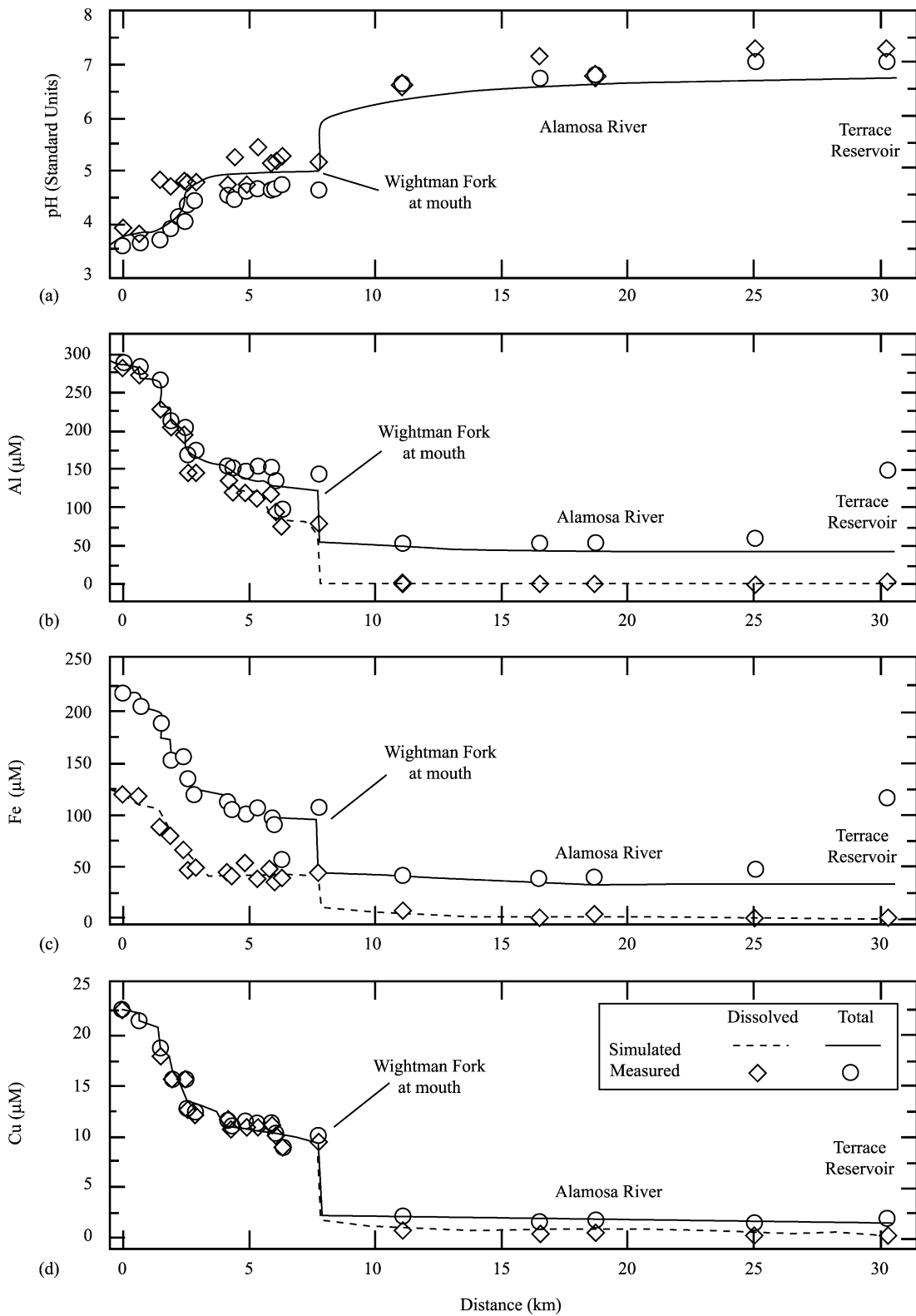


Figure 9 Downstream profiles in the Wightman Fork/Alamosa River system of: (a) pH measured and simulated; (b) dissolved aluminum concentrations measured and simulated; (c) dissolved iron concentrations measured and simulated; and (d) copper concentrations measured and simulated. Simulations were obtained with the OTEQ code after calibration on tracer-injection data and Fe(II/III) determinations.

and stream-water chemistry are “lumped” or averaged over the spatial scale that can include many heterogeneities. MAGIC was designed to simulate long-term (annual) averages, whereas BIRKENES was designed to simulate short-term (hours to days) responses. Equilibrium reactions include soil cation-exchange reactions, solubility control by gibbsite, $\text{CO}_2\text{--H}_2\text{O}$ hydrolysis reactions, aqueous speciation of aluminum among sulfate and fluoride complexes, water dissociation, ion balance, and temperature dependence. Activity coefficients appear not to have been used and the sensitivity of the model to this factor has not been addressed. Wright and Cosby (1987) found good agreement between simulated and measured alkalinities for two manipulated catchments in Norway using the MAGIC code. Organic acids have been included with the code and the simulations of the Norway catchments revisited with improved results (Cosby *et al.*, 1995). An alternative to ILWAS and MAGIC is the code Enhanced Trickle Down (ETD; Nikolaidis *et al.*, 1989, 1991). Geochemical processes include cation exchange, chemical weathering, sulfate adsorption, and sulfate reduction. Comparisons of the three codes, ILWAS, MAGIC, and ETD, were made by Rose *et al.* (1991a,b). The codes were found to provide similar forecasts on a relative scale but substantial differences with respect to specific concentrations (absolute scale). Codes that contain more detailed consideration of chemistry, especially reaction kinetics, include PROFILE (Sverdrup, 1990; Warfvinge and Sverdrup, 1992) and UNSATCHEM (for the unsaturated zone, Suarez and Simunek (1996)).

The main problem with any of these models is that they are calibrated with data that are too short-term for the long-term processes they are trying to predict on the catchment scale (Drever, 1997b; Hornberger, 2002).

5.02.8.6 Reliability of Geochemical Model Simulations

One approach to determine the reliability of geochemical codes is to take well-defined input data and compare the output from several different codes. For comparison of speciation results, Nordstrom *et al.* (1979) compiled a seawater test case and a river-water test case, i.e., seawater and river-water analyses that were used as input to 14 different codes. The results were compared and contrasted, demonstrating that the thermodynamic databases, the number of ion pairs and complexes, the form of the activity coefficients, the assumptions made for redox species, and the assumptions made for equilibrium solubilities of mineral phases were prominent factors in the results. Additional arsenic, selenium, and uranium redox test cases were designed for testing of

the WATEQ4F code (Ball and Nordstrom, 1991). Broyd *et al.* (1985) used a groundwater test case and compared the results from 10 different codes. Such test cases could be expanded to include examples of heterogeneous reactions, mixing with reaction, sorption, temperature dependence, reactive transport, and inverse modeling. The current version of PHREEQC includes 18 examples of code testing. Some of these are true “tests” in that they can be compared with measurements or independent computations, while others are just examples of the code capability. The EQ3/6 code also shows several examples of code capability in addition to comparative tests.

In another example, five test cases were computed by PHREEQE and EQ3/6 and the same thermodynamic database was run for each program (INTERA, 1983) to test for any code differences. The five examples were speciation of seawater with major ions, speciation of seawater with complete analysis, dissolution of microcline in dilute HCl, reduction of hematite and calcite by titration with methane, and dedolomitization with gypsum dissolution and increasing temperature. The results were nearly identical for each test case. Test cases need to become standard practice when using geochemical codes so that the results will have better credibility. A comparison of code computations with experimental data on activity coefficients and mineral solubilities over a range of conditions also will improve credibility (Nordstrom, 1994).

Bruno *et al.* (2002) compared the results of blind-prediction modeling for geochemical modeling of several trace elements of concern to radioactive waste disposal for six natural analog sites. Blind-prediction modeling was an exercise developed in radioactive research on repository analog sites whereby actual water analyses for major ions were given to different groups of geochemical modelers who were asked to simulate dissolved trace-element concentrations based on assumed solubility equilibria; the results were compared with actual trace-element concentrations determined on the groundwaters but kept secret from the modelers until the modeling was completed. They found that thorium and uranium seem to be controlled by mineral solubilities, whereas strontium, zinc, and rare-earth element (REE) mobilities seem to be related to the major ions and complex formation. Other elements such as nickel suffer from insufficient thermodynamic data. Sorption reactions were not examined in sufficient detail to draw conclusions.

Another approach to determining model reliability is to perform sensitivity or uncertainty analyses. One of the first examples is the examination of equilibrium aluminum computations for surface waters using the Monte Carlo method of randomizing sources of error

in the water analysis and thermodynamic data (Schecher and Driscoll, 1987, 1988). The results showed that uncertainties in the input data did not contribute significantly to computational speciation errors. Nordstrom and Ball (1989) used two different sets of water analyses, groundwater analyses from a granite in Sweden, and surface-water analyses from a creek receiving AMD in California, to evaluate uncertainties in the water analyses and uncertainties in the thermodynamic data as possible sources of consistent supersaturation effects for calcite, fluorite, barite, ferric oxyhydroxide, and aluminum hydroxide. Instead of Monte Carlo methods, they used a brute force approach and recomputed the speciation assuming reasonable errors in the input analytical data and in the thermodynamic data. The conclusion was that supersaturation for these minerals could not be accounted for by errors in the water analyses nor in the thermodynamic data. For ferric oxyhydroxide, iron colloids were probably getting through the filter and contributing to the apparent dissolved Fe(III) concentrations and the supersaturation effect. For aluminum hydroxide, the saturation indices did not indicate supersaturation with respect to amorphous aluminum hydroxide and hence they were probably reasonable. For the remaining minerals it was concluded that the supersaturation may have been realistic, because it could not be accounted for by propagation of these errors. Other causes of supersaturation include impure mineral phases (solid substitution or defects), disordered or fine-grained nature, inhibition of precipitation rates, and possible unaccounted for pressure effects on equilibria.

Criscenti *et al.* (1996) determined overall uncertainty from geochemical computations by a combination of propagating Monte-Carlo-generated analytical and thermodynamic uncertainties through a geochemical code and applying the “generalized sensitivity analysis” (Spear and Hornberger, 1980) to the output. One of the results of this study is that the aqueous speciation scheme used in many geochemical codes is not necessarily consistent with the speciation scheme used to define standard pH buffers by the National Bureau of Standards. This conclusion raises the possibility that geochemical computations introduce an error when speciating a natural water based on a field pH measurement calibrated with one of these buffers. Cabaniss (1999) investigated methods of uncertainty propagation, comparing the derivative-based method (assumes a linear approximation) with the Monte Carlo technique for solubility equilibria computations of gibbsite, calcite, and jarosite. He found that derivative methods and the assumption of Gaussian uncertainty can misrepresent the propagated uncertainty.

Computational speciation can be compared to analytical speciation for some species. There is always the problem that analytical methods also suffer from operational definitions, interferences, limits of detection, and associated assumptions. Nevertheless, there is no better method of determining accuracy of speciation than by comparing analytical results with computational results (Nordstrom, 1996). In the few instances where this has been done, the comparison ranges from excellent to poor. Examples of studies of this type can be found in Leppard (1983), Batley (1989), and Nordstrom (1996, 2001). Sometimes comparison of two analytical methods for the same speciation can give spurious results. In Table 3, measured and calculated ionic activity coefficients for seawater at 25 °C and 35‰ salinity are compared, after adjusting to a reference value of $\gamma_{\text{Cl}} = 0.666$ (Millero, 2001). These values would indicate that for a complex saline solution such as seawater, the activity coefficients can be

Table 3 Comparison of measured and calculated ion activity coefficients in seawater at 25 °C and 35 ‰ salinity, referenced to $\gamma_{\text{Cl}} = 0.666$ (Millero, 2001).

| <i>Ion</i> | <i>Measured</i> | <i>Calculated</i> |
|---------------------------------|-----------------|-------------------|
| H ⁺ | 0.590 | 0.592 |
| Na ⁺ | 0.668 | 0.674 |
| | 0.670 | |
| | 0.678 | |
| K ⁺ | 0.625 | 0.619 |
| NH ₄ ⁺ | 0.616 | 0.624 |
| | 0.592 | |
| Mg ²⁺ | 0.242 | 0.211 |
| | 0.22 | |
| Ca ²⁺ | 0.203 | 0.205 |
| | 0.180 | |
| F [−] | 0.296 | 0.297 |
| Cl [−] | 0.666 | 0.666 |
| OH [−] | 0.242 | 0.263 |
| | 0.254 | |
| | 0.254 | |
| HS [−] | 0.681 | 0.688 |
| | 0.673 | |
| | 0.550 | |
| HCO ₃ [−] | 0.576 | 0.574 |
| | 0.592 | |
| | 0.528 | |
| B(OH) ₄ [−] | 0.419 | 0.384 |
| | 0.398 | |
| | 0.351 | |
| SO ₄ ^{2−} | 0.104 | 0.110 |
| | 0.112 | |
| | 0.121 | |
| | 0.121 | |
| CO ₃ ^{2−} | 0.040 | 0.041 |
| | 0.041 | |
| | 0.035 | |
| | 0.035 | |

calculated with a high degree of confidence. Much more effort along these lines is needed to better determine the errors and uncertainties for speciation calculations and to identify reaction equilibria and species for which thermodynamic data need to be measured.

Iron redox speciation was evaluated by comparing the Eh values computed from a speciation code that accepts Fe(II) and Fe(III) concentrations determined analytically with Eh values measured electrometrically with a platinum electrode. An example of this comparison is shown in Figure 10 (Nordstrom, 2000). For iron concentrations greater than 10^{-6} m, the comparison is generally excellent (usually to within 30 mV), indicating that the analytical data, speciation calculations, and redox measurements are all consistent with equilibrium as predicted by the Nernst equation. This comparison is one of two redox speciation computations that can be tested electrometrically. Deviations from equilibrium are apparent at low iron concentrations, because the electroactivity of iron is low enough that other electron acceptors, such as dissolved oxygen, begin to interfere. The other redox condition that permits testing with the Nernst equation is sulfide. Berner (1963) showed that the platinum electrode gives Nernstian behavior in anoxic marine sediments in response to dissolved sulfide activities. All other redox species in natural waters are not sufficiently electroactive to establish Nernstian equilibrium.

Nordstrom (2001) demonstrated that if one compares computed free-fluoride ion activities or concentrations (in this example, with WATEQ4F) with measured values obtained with a fluoride ion-selective electrode, the results are in good agreement down to $\sim 10^{-6}$ m. This agreement between measurement and calculation corroborates the fluoride speciation by the IA method.

5.02.9 FINAL COMMENTS

Numerous models and codes have been developed over the last century for interpreting and portraying low-temperature geochemical processes. They have been applied to a great variety of conditions and processes and have enhanced our ability to understand how low-temperature earth systems work. However, many of these models have a dangerous sophistication for computing almost any type of possibility without adequately constraining what is probable. Perhaps this affair is little different from many centuries ago when we had fewer scientific tools and more imagination to play with. The danger in greater model sophistication is the difficulty in testing and refuting it. If we cannot test a model, then we have no means of determining its reliability. And yet if we do not strive for greater sophistication, then the model lacks representativeness (Oreskes, 2000).

What we must remember is that modeling is a tool—a useful tool to be sure, but not something that can ever replace the experience gained from directly working on a hydrogeochemical problem for several years. Expert judgment, developed over long time periods and involving many mistakes, along with carefully acquired empirical observations in the field and in the laboratory, will ultimately guide our models from possibility to probability. “... even the most mathematically and computationally sophisticated model will not absolve us of the need for judgment, nor of the need to justify our judgment in human terms” (Oreskes, 2000). Expert judgment is particularly important in identifying the appropriateness of assumptions in applying a model and constitutes a bigger problem than that of model formulation.

Model reliability is a very important aspect of communicating computational results to

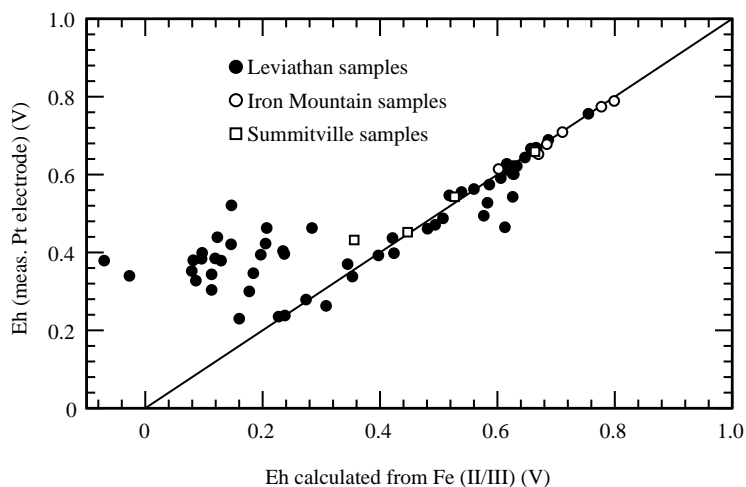


Figure 10 Eh measured with a Pt electrode on site compared to Eh calculated from Fe(II/III) determinations and speciated with WATEQ4F (source Nordstrom, 2000).

managers, risk assessors, stakeholders, politicians, and the public. Unfortunately, sophisticated model computations are not easy to interpret, model results are often nonunique, and modeling is often state-of-the-art science whose reliability has not been adequately tested. Because reliability has often been couched in terms of “verification” and “validation” for the convenience of regulatory requirements (Jenne and Krupka, 1984; Mattigod, 1995; OECD/NEA, 1994; Kirchner *et al.*, 1996; Huguet, 2001; Freedman and Ibaraki, 2003; Celia *et al.*, 1992), confusion about the limitations of models and even misunderstandings about how science works have been propagated. Words such as verification and validation might make sense in a regulatory or legal setting but are inappropriate and even incompatible with scientific research and the scientific method (Konikow and Bredehoeft, 1994; Oreskes *et al.*, 1994). Validation is a matter of legitimacy and has a different context and meaning than what is sought in science. Science progresses by testing hypotheses. Success is measured by consistency between observations and calculations (which is not proof of validity), logical structure, simplicity combined with wide applicability, and consensus through independent peer review (also not proof of validity). Oreskes (2000) quotes Richard Feynman, “Doubt is the essence of understanding.” Yet doubt is exactly what regulatory agencies are trying to minimize or eliminate. Oreskes (2000) quotes Richard Feynman, “Doubt is the essence of understanding”. Yet doubt is exactly what regulatory agencies are trying to minimize or eliminate. Oreskes (2000) offers a solution that seems obvious the earth scientists: our computational process has far exceeded our observational data on natural systems. More field data and related empirical observations are needed. Field data will provide the necessary constraints to achieve the legitimacy that is being sought by the public. Sophisticated computations, especially in the hands of the unskilled, have the possibility of achieving any pre-conceived result unless adequately constrained by empirical data.

Future efforts should be directed toward developing standardized test cases for a wide variety of processes against which code performance can be compared and tested, incorporation of reliable methods of accounting for metal-organic complexing involving humic substances, recognition of artifacts of sample collection in the determination of trace elements in natural waters, more comparisons of analytical versus computed speciation to obtain accuracy estimates of aqueous speciation, development of routine techniques for estimating uncertainties in model calculations, and more detailed studies of fine-grained mineralogy that are reactive phases in geochemical systems.

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