

3 Modeling Soil Solution, Mineral Formation and Weathering

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Simulation models are valuable tools to increase understanding of complex soil chemical processes. Initially modeling was restricted by limited computational power; thus, complex natural systems were often simulated with site-specific, regression-based models. These models (classified as functional models by Hoosbeek & Bryant, 1992) do not deal with the actual processes but were designed to simulate the response of the studied system to specific variables. Although useful for the conditions represented by the collected data set, these models are usually not suited for other environments. Often the process controlling variables or responses to these variables are different in different environments. Nonetheless, due to the complexity of natural systems, quantitative mechanistic models often do not exist.

The development of quantitative models has evolved from initial attempts to determine species distributions and ion activity, to models that attempt to represent chemical processes including soil mineral formation and prediction of soil solution composition and rates of mineral weathering. In this chapter we present an overview of the types of quantitative models suitable for describing soil chemical processes including mineral weathering. Generally following a chronological development, the models can be classified into a series of increasingly complex treatments of the natural system.

EQUILIBRIUM

Solution Speciation Models

The conceptual framework of solution speciation model was presented by Garrels and Christ (1965). One of the first chemical equilibrium models was IONPAIR developed by Thraillkill (1970). This relatively simple model required input of pH and alkalinity and computed the saturation status of a water with respect to calcite. The more extensive model WATEQ, developed by Truesdell and Jones (1974), included a complete speciation scheme for the major, naturally occurring chemical species and calculations of saturation status with respect to many important silicate minerals as well as some oxides and carbonates. This program has been updated periodically (WATEQ4F; Ball et al., 1987) and is still

one of the most utilized models for speciation and saturation status of natural waters.

These speciation models are most useful for evaluating which soil processes are thermodynamically possible. By design they are not predictive models, as it is left to the user to evaluate which of the possible processes are dominant. This is in contrast to predictive models which force equilibrium with the most thermodynamically stable solid phases. This evaluation as to which process is dominant is clearly time dependent. Reactions that may be neglected for short time intervals may be important for longer time scales. By analyzing solution composition, soil genesis and possible weathering reactions can be considered based on the minerals present in the soil. The major disadvantage of these models for long-term soil studies is that computations, and subsequent predictions, are based on solution composition at the time of analysis. No processes are included to simulate temporal changes.

Despite the limitations of speciation programs, they usually serve as the foundation for more complex predictive models. A listing of some of the speciation models is presented in Table 3-1. Popular programs are GEOCHEM (Sposito & Mattigod, 1977) and MINTEQ (Felmy et al., 1984). These programs are mostly predictive programs, but they can be used for speciation alone by excluding solid phases. The major use of speciation models has been to input soil solution data obtained from soil which was previously collected in the field and reacted in the laboratory in a soil water suspension or saturation extract. In many instances, these conditions are not representative of the soil environments. Relatively few studies have used direct soil water analyses obtained either by soil water extractors or by squeezing water from freshly collected soil cores.

Predictive Models

Predictive models generally include detailed speciation routines but are intended to calculate the distribution of chemical species in the solution and solid phases. The models include a thermodynamic data base including solid phases and calculate concentrations based on thermodynamic equilibrium. The models are extensively used to predict solution composition in contact with soil and are excellent teaching tools. However, almost no studies have been conducted to compare these predictions to actual field conditions. Despite their limitations, these models are by far the most frequently used by soil scientists.

Thermodynamic equilibria models generally give good predictions for high temperature formation of mineral assemblages and rock-solution composition ($>150^{\circ}\text{C}$). These models are less satisfactory for earth surface conditions, such as soils, where mixtures of mineral phases exist which are not in chemical equilibrium and where solution-mineral equilibrium rarely exists. Apparently reaction rates are too slow, at the relatively high water flux rates and relatively low (-10 to 40°C) temperatures to insure equilibria over short time scales (days-years). Nonetheless, the models can be used, as are the speciation models, to indicate which phases should be weathering or dissolving and which phases should be forming. This prediction of the final product is particularly useful when a speciation program calculates that a large number of phases are supersaturated. Output from the speciation program does not provide information about the relative

Table 3-1. Chemical models.

Solution speciation			Predictive		
Models	Sources	Attributes	Models	Sources	Attributes
IONPAIR	Thrailkill (1970)	Major ion activity calculations	REDEQL2 GEOCHEM	McDuff & Morel (1973) Sposito & Mattigod (1977)	All can calculate saturation status or equilibrate solution with specified minerals
SOLMNEQ	Kharaka & Barnes (1973)	Includes calculations of saturation status of soil minerals	SOLMINEQ.88	Kharaka et al. (1988)	
WATEQ	Truesdell & Jones (1974)	Includes calculations of saturation status of soil minerals	SOILCHEM	Sposito & Coves (1988)	Can calculate saturation status or equilibrate solution with specified minerals. Contains constant capacitance model for adsorption
WATEQ4F	Ball et al., 1987	Includes calculation of saturation status of soil minerals and various trace elements	MINTEQ	Felmy et al. (1984)	Can calculate saturation status or equilibrate solution with specified minerals. Contains various surface complexation models for adsorption
			HYDRAQL MICROQL FITEQL	Papelis et al., 1988 Westall, 1979 Westall, 1982	All contain constant capacitance, diffuse layer, stern and triple layer models

Table 3-1. Continued-Chemical models

Reaction models			Transport models		
Models	Sources	Attributes	Models	Sources	Attributes
PHREEQE	Parkhurst et al., 1980	Provides equilibrium	HYDROGEOCHEM	Yeh & Tripath, 1990	Multicomponent transport with triple layer model. Possible to run unsaturated water flow
NETPATH	Plummer et al., 1991	Reaction path	DYNAMIX	Liu & Narasimhan, 1989	Multicomponent transport
			FASTCHEM	Hostetler & Erikson, 1989	Saturated water flow and multi-component transport
			TRANQL	Cederberg et al., 1985	Saturated water flow and multi-component transport with constant capacitance model
			SALT-FLOW	Robbins et al., 1980	All include unsaturated water flow, multicomponent transport, ion exchange, and calcite and gypsum equilibria
			SOWACH	Dudley & Hanks, 1991	
			LEACHM	Wagenet & Hutson, 1987	
			NTRM	Schaffer & Larson, 1987	
			SOILCO2	Simunek & Suarez, 1993	Unsaturated water flow, CO ₂ production and transport
			UNSATCHEM	Suarez & Simunek, 1992	Unsaturated water flow, multi-component transport, ion exchange, calcite and dolomite kinetics, gypsum equilibrium, CO ₂ production and transport, silicate weathering kinetics

stabilities of the mineral phases or the path or evolution of the system. The predictive models are particularly useful for soil genesis problems, but do not consider intermediate unstable phases that may be transitional but nonetheless very significant. The models appear most useful for conceptually demonstrating how a solution or solid is altered at equilibrium (for example where framework silicates such as feldspars weather to clays and oxides), but are not as useful for prediction of the solution or solid composition. Use of the models for realistic simulations rather than thermodynamic calculations requires that at least some kinetic aspects be considered and the thermodynamic equilibrium criteria be relaxed. For example, if quartz is omitted from the data base, predicted silica concentrations increase and clay formation can be predicted.

As expected, the models differ in their input requirements, reactions considered, and ease of use. The model GEOCHEM (Sposito & Mattigod, 1977) and SOILCHEM (Sposito & Coves, 1988) require input of total inorganic C and pH or CO₂ partial pressure. This information is not usually available from soil water analysis but can be estimated by iteration by the user if only alkalinity (and pH or pCO₂) is available. Conservation of total inorganic C is not a useful model for soil reactions (field) since soils are open to the atmosphere and biological production and transport of CO₂ are important aspects of the soil C cycle. These models consider a large number of solid phases including trace metal minerals that may not exist in soils due to kinetic constraints.

Among other commonly used predictive programs is MINTEQ (Felmy et al., 1984), initially based on the speciation program WATEQ (Truesdell & Jones, 1974). The model MINTEQ accepts either total soluble inorganic C or alkalinity in the input file. Most water analyses report alkalinity, but dissolved inorganic C is rarely available. A listing of several widely used thermodynamic equilibrium programs that consider solid phases is presented in Table 3-1.

Recent chemical models have related reaction rates to concentrations of adsorbed species rather than concentrations in the bulk solution. The following sections examine adsorption modeling, which is required for modeling most mineral weathering rates, as well as for ion adsorption.

ADSORPTION MODELS

Adsorption is the net accumulation of a substance at the interface between a solid phase and an aqueous solution phase (Sposito, 1989). Numerous models exist to describe adsorption reactions. Empirical models have been utilized most often to provide descriptions of adsorption data but are limited by their lack of a theoretical basis. These models are special cases of the generalized empirical adsorption isotherm equation

$$x = \frac{bKc^\beta}{1 + Kc^\beta} \quad [1]$$

where x is the amount adsorbed per unit mass, c is the equilibrium solution concentration, and b , K , and β are empirical parameters (Goldberg & Sposito, 1984).

The Langmuir adsorption isotherm equation was developed to describe the adsorption of gases on clean surfaces, but nevertheless has been used often to describe ion adsorption by soils and soil minerals. The Langmuir equation is a special case of Eq. [1] where $\beta = 1$ (Goldberg & Sposito, 1984)

$$x = \frac{bKc}{1 + Kc} \quad [2]$$

For many studies the Langmuir equation can describe ion adsorption only under conditions of low solution concentration. The Langmuir equation implies uniform surface sites and absence of lateral interactions.

The Freundlich adsorption isotherm equation is strictly valid only for adsorption at low concentrations (Sposito, 1984) but has often been used to describe ion adsorption by soils and soil constituents over the entire concentration range studied. The Freundlich equation is a special case of Eq. [1] where $b = 1$, $0 < \beta < 1$, $Kc^\beta \ll 1$ (Goldberg & Sposito, 1984)

$$x = Kc^\beta \quad [3]$$

The Freundlich equation implies heterogeneity of surface sites. The Freundlich equation is often used empirically in situations where $Kc^\beta > 1$.

Although the Langmuir and Freundlich equations are often excellent at describing ion adsorption, they are numerical relationships used to curve-fit data (Harter & Smith, 1981). Independent experimental evidence for adsorption must be present before any chemical meaning can be assigned to Langmuir and Freundlich equation parameters. Since the use of the Langmuir and Freundlich equations is essentially a curve-fitting procedure, the parameters are valid only for the conditions under which the experiment was conducted. The models do not consider changes in adsorption as a function of pH or other chemical or physical factors.

Unlike empirical models, surface complexation models are chemical models that provide a general molecular description of adsorption phenomena using an equilibrium approach. The surface complexation models are designed to calculate values of thermodynamic properties such as activity coefficients and equilibrium constants mathematically. The most significant advancement in these models is that they consider the charge on both the adsorbing ion and the adsorbent surface. Five common surface complexation models are: the constant capacitance model (Stumm et al., 1980) the triple layer model (Davis et al., 1978) the Stern variable-charge, variable-surface potential model (Bowden et al., 1980) the generalized two-layer model (Dzombak & Morel, 1990), and the one-pK model (van Riemsdijk et al., 1986). A detailed discussion of these models is presented elsewhere. (Goldberg, 1992). All models contain the following adjustable parameters: K_s , the surface complexation constants; C, the capacitance density for the i^{th} surface plane; and [SOH]_t, the total number of reactive surface hydroxyl groups. A summary of the more frequently used constant capacitance model and triple layer model will be provided here.

The constant capacitance model was developed by Schindler, Stumm, and their coworkers (Schindler & Gamsjager, 1972; Hohl & Stumm, 1976; Schindler et al., 1976; Stumm et al., 1976, 1980). The model is based on the following assumptions: ion adsorption is based on a ligand exchange mechanism; all surface complexes are inner-sphere complexes; no surface complexes are formed with ions from the background electrolyte; the relationship between surface charge and surface potential is

$$\sigma = \frac{CSa}{F}\psi \tag{4}$$

where C is the capacitance ($F\ m^{-2}$), S is the surface area ($m^2\ g^{-1}$), a is the suspension density ($g\ L^{-1}$), F is the Faraday constant ($C\ mol^{-1}$), and σ has units mole charge per liter. A diagram of the surface-solution interface for the constant capacitance model is provided in Fig. 3-1. Applications to natural systems are complicated by the requirement of constant ionic strength.

The equations for the inner-sphere surface complexation reactions are (Hohl et al., 1980)

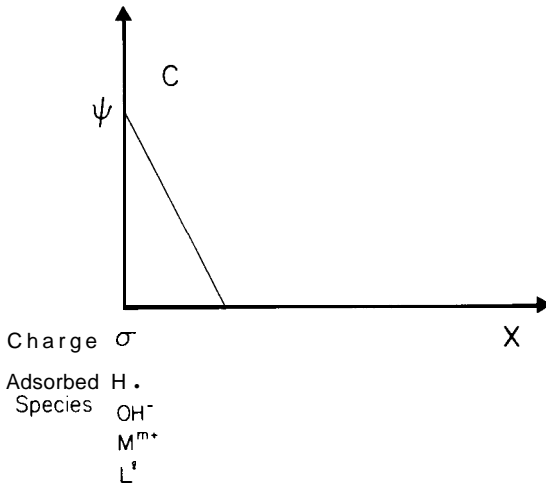
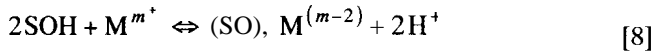
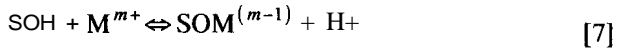
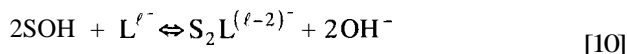
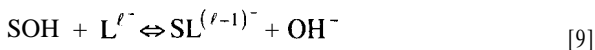


Fig. 31. Placement of ions, potential, charge, and capacitance for the constant capacitance model (after Westall, 1986).



where *SOH* represents the surface functional group, *M* is a metal ion, *m+* is the charge on the metal ion, *L* is a ligand, and *ℓ*⁻ is the charge on the ligand.

The intrinsic conditional equilibrium constants describing the above reactions are (Hohl et al., 1980)

$$K_+ (\text{int}) = \frac{[\text{SOH}_2^+]}{[\text{SOH}][\text{H}^+]} \exp[F\psi / RT] \quad [11]$$

$$K_- (\text{int}) = \frac{[\text{SO}^-][\text{H}^+]}{[\text{SOH}]} \exp[-F\psi / RT] \quad [12]$$

$$K_M^1 (\text{int}) = \frac{[\text{SOM}^{(m-1)}][\text{H}^+]}{[\text{SOH}][\text{M}^{m+}]} \exp[(m-1)F\psi / RT] \quad [13]$$

$$K_M^2 (\text{int}) = \frac{[(\text{SO}), \text{M}^{(m-2)}][\text{H}^+]^2}{[\text{SOH}]^2[\text{M}^{m+}]} \exp[(m-2)F\psi / RT] \quad [14]$$

$$K_L^1 (\text{int}) = \frac{[\text{SL}^{(\ell-1)-}][\text{OH}^-]}{[\text{SOH}][\text{L}^{\ell-}]} \exp[-(\ell-1)F\psi / RT] \quad [15]$$

$$K_L^2 (\text{int}) = \frac{[\text{S}_2\text{L}^{(\ell-2)-}][\text{OH}^-]^2}{[\text{SOH}]^2[\text{L}^{\ell-}]} \exp[-(\ell-2)F\psi / RT] \quad [16]$$

where *R* is the molar gas constant (J mol⁻¹K⁻¹), *T* is the absolute temperature (K), and square brackets represent concentrations (mol L⁻¹). Values of the intrinsic conditional equilibrium constants can be obtained by extrapolating the conditional equilibrium constants to zero net surface charge (Stumm et al., 1980). A detailed explanation of the procedure is provided in Stumm et al. (1980). An example of the ability of the constant capacitance model to describe adsorption data is indicated in Fig. 3-2 for silicate adsorption on an amorphous aluminum oxide.

The original triple layer model was developed by Davis and coworkers (Davis et al., 1978; Davis & Leckie, 1978, 1980) as an extension of the site binding model (Yates et al., 1974). The model is based on the following assumptions: only protons and hydroxyl ions form inner-sphere complexes; all ion adsorption reactions form outer-sphere complexes; three planes of charge represent the surface; the relationships between surface charges and surface potentials are

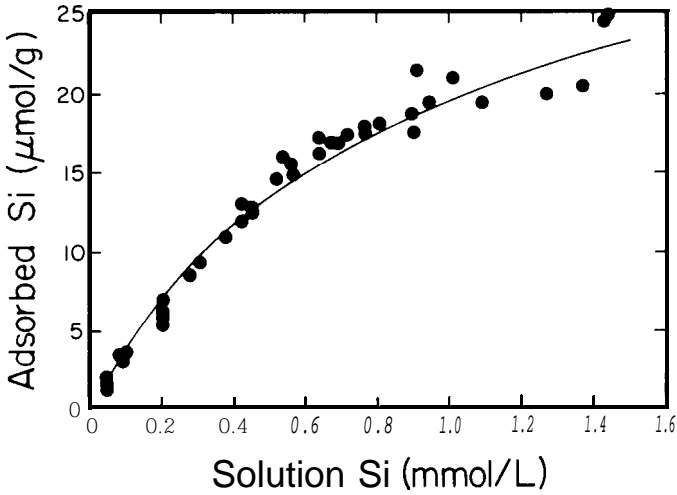


Fig. 3-2. Silicate adsorption on amorphous aluminum oxide at pH 9.2 with experimental data (circles) from Hingston and Raupach (1967). The solid line represents model results: $\log K_{s_1}^1(\text{int}) = 3.29$, $\log K_{s_1}^2(\text{int}) = -7.93$.

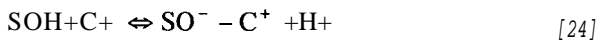
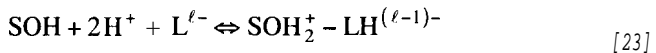
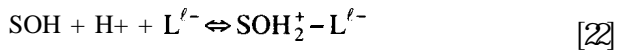
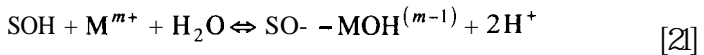
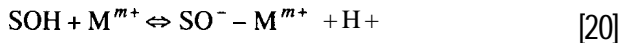
$$\psi_0 - \psi_\beta = \sigma_0 / C_1 \tag{17}$$

$$\psi_\beta - \psi_d = -\sigma_d / C_2 \tag{18}$$

$$\sigma_d = -(8RTc\varepsilon_0 D)^{1/2} \sinh(F\psi_d / 2RT) \tag{19}$$

where ε_0 is the permittivity of a vacuum, D is the dielectric constant of water, c is the concentration of a 1:1 background electrolyte, and σ has units of C per meters squared. The triple layer model has been modified to include ion adsorption as inner-sphere surface complexes (Blesa et al., 1984; Hayes & Leckie, 1986). A diagram of the surface-solution interface for the triple layer model is provided in Fig. 3-3.

The equations for the inner-sphere surface complexation reactions in the triple layer model are Eq. [5] through [10] as written for the constant capacitance model. The equations for the outer-sphere surface complexation reactions are (Davis et al., 1978; Davis & Leckie, 1978, 1980):



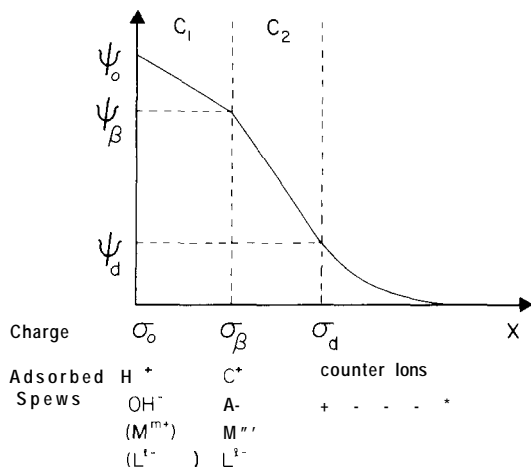
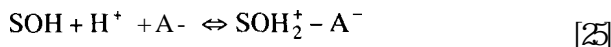


Fig. 3-3. Placement of ions, potentials, charges, and capacitances for the triple layer model. Parentheses represent ion placement allowed only in the modified triple layer model (after Westall, 1980).



where C^+ is the cation and A^- is the anion of the background electrolyte.

The intrinsic conditional equilibrium constants for the triple layer model are Equations [11] through [16] as written for the constant capacitance model for inner-sphere surface complexes. For outer-sphere surface complexes the intrinsic conditional equilibrium constants are given in Davis et al., 1978; Davis & Leckie, 1978, 1980. As for the constant capacitance model, values for the intrinsic conditional equilibrium constants can be obtained by extrapolation. A detailed explanation of various types of extrapolation procedures used for the triple layer model is provided in Goldberg (1992). The model has the potential to be used under conditions of varying ionic strength as it considers changes in surface potential with changing electrolyte concentration. Figure 3-4 provides an example of the ability of the triple layer model to describe adsorption data for Cu adsorption on amorphous iron oxide.

Adsorption models have been incorporated into various chemical speciation models. The computer program MINTEQA (Felmy et al., 1984) combines the thermodynamic data base of WATEQ3 (Ball et al., 1981) into the mathematical framework of the computer program MINEQL (Westall et al., 1976) and contains surface complexation models. The program MINTEQA1 (Brown & Allison, 1987) contains the Langmuir and Freundlich equations, the constant capacitance model and the triple layer model. The model MINTEQA2 (Allison et al., 1990) has also added the diffuse layer model. The chemical speciation program SOILCHEM (Sposito & Coves, 1988) contains the constant capacitance model. The computer programs HYDRAQL (Papelis et al., 1988), MICROQL (Westall, 1979), and FITEQL (Westall, 1982) all contain the constant capacitance model, the diffuse layer model, the Stern model, and the triple layer model.

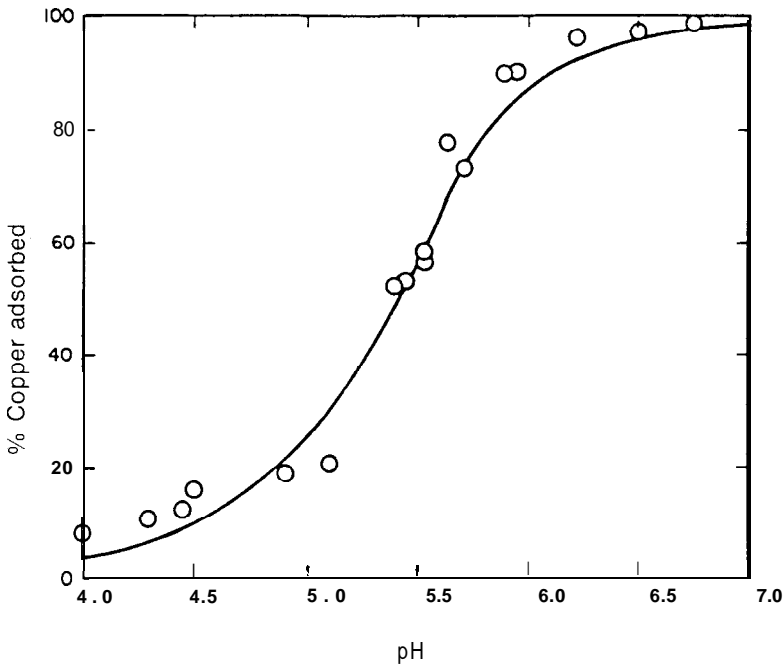


Fig. 3-4. Copper adsorption on amorphous iron oxide. Experimental data-circles. Solid line represents model results: $\log K_{Cu}^1(int) = -4.1$, $\log K_{Cu}^2(int) = -9.0$, (from Davis & Leckie, 1978).

EFFECTS OF SURFACE COMPLEXATION REACTIONS ON THE KINETICS OF DISSOLUTION

The dissolution kinetics of most silicates and oxides appears to be controlled by chemical surface processes (Furrer & Stumm, 1986, Stumm & Wollast, 1990), rather than transport through a surface layer. As a result it is necessary that the concentration of surface species rather than solution concentrations be considered for expressing reaction rates. The reaction steps are: attachment of the reactants at surface sites; rate-limiting detachment of the surface metal species, transport of the metal complex into the bulk solution, and regeneration of the active site by protonation. Under acid conditions the dissolution is promoted by protons that bind to the surface oxide ions (Furrer & Stumm, 1986). Calculation of surface species concentrations requires that activities rather than concentrations be used for the relevant species in solution. Figure 3-5 is a schematic of the proton-promoted dissolution of a trivalent oxide. The proton-promoted dissolution rate is (Stumm & Wollast, 1990)

$$R_H = k_H [SOH_2^+]^n = k_H (C_H^S)^n \quad [26]$$

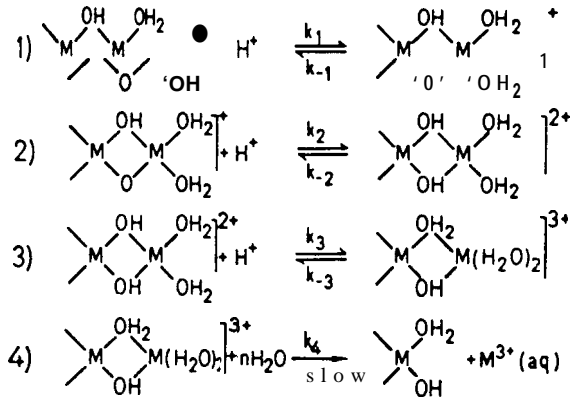


Fig. 3-5. Proton-promoted dissolution of a trivalent oxide M_2O_3 (from Furrer & Stumm, 1986).

where k_H is the rate constant, C_H^s is the surface proton concentration in moles per meter squared, and n is the number of protonation steps in the dissolution mechanism. The concentration of protonated surface hydroxyl groups, $[\text{SOH}_2^+]$ can be obtained using the constant capacitance model or determined from titration data. In the presence of complex-forming ligands the dissolution is promoted by ligands that form surface complexes by ligand exchange (Furrer & Stumm, 1986). Figure 3-6 shows the ligand-promoted dissolution of a trivalent oxide. The ligand-promoted dissolution rate is (Stumm & Wollast, 1990)

$$R_L = k_L [SL] = k_L C_L^S \quad [27]$$

where k_L is the rate constant and C_L^s is the concentration of adsorbed ligand in moles per meter squared. The concentration of surface sites occupied by ligand, $[SL]$ is obtained by adsorption studies and can be modeled using the constant capacitance model. The proton-promoted and the ligand-promoted dissolution are considered independent and the total rate is additive (Furrer & Stumm, 1986)

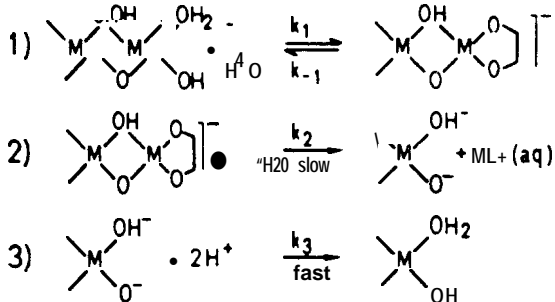


Fig. 3-6. Ligand-promoted dissolution of a trivalent oxide M_2O_3 (from Furrer & Stumm, 1986).

$$R_{\text{tot}} = R_{\text{H}} + R_{\text{L}} \quad [28]$$

Figure 3-7 is a schematic of the ligand- and proton-promoted dissolution of a trivalent oxide. The dependence of the rate of the proton-promoted dissolution of $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ on the surface concentration of protons is indicated in Figure 3-8. The slopes are close to three indicating that n is equal to three for $\delta\text{-Al}_2\text{O}_3$ and $\alpha\text{-FeOOH}$. Furrer and Stumm (1986) suggested that the reaction order n may correspond to the oxidation number of the metal ion in the oxide. Figure 3-9 indicates the dependence of the rate of the ligand-promoted dissolution of $\delta\text{-Al}_2\text{O}_3$ on the surface concentration of organic ligands.

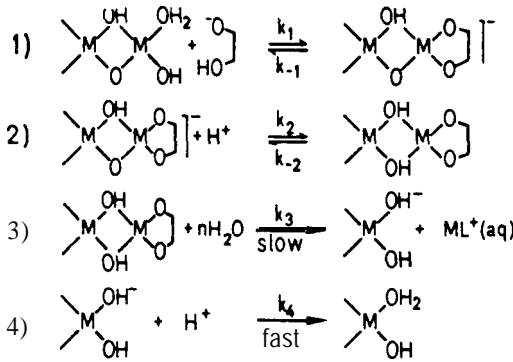


Fig. 3-7. Ligand/proton-promoted dissolution of a trivalent oxide M_2O_3 (from Furrer & Stumm, 1986).

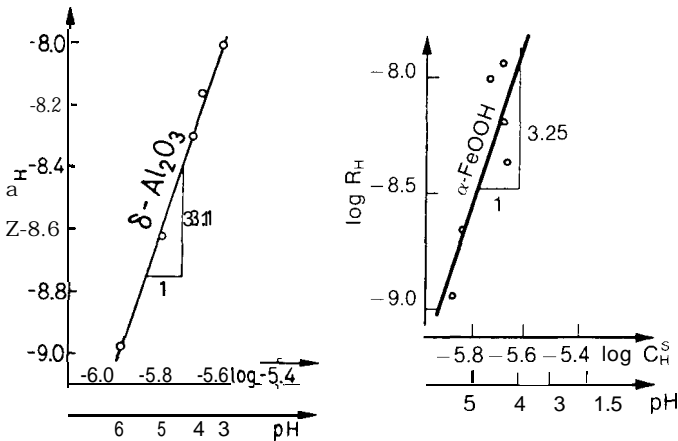


Fig. 3-8. Dependence of the rate of the proton-promoted dissolution of $\delta\text{-Al}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ (from Stumm & Wollast, 1990, based on data from Furrer & Stumm, 1986, for $\delta\text{-Al}_2\text{O}_3$ and Zinder et al., 1986 for $\alpha\text{-FeOOH}$).

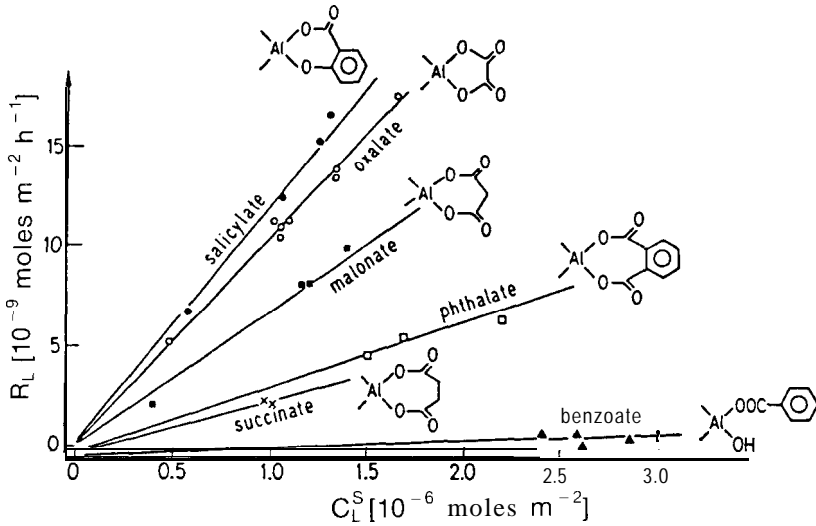


Fig. 3-9. Dependence of the rate of the ligand-promoted dissolution of $\delta\text{-Al}_2\text{O}_3$ on the surface concentration of ligands (from Stumm et al., 1987, based on data from Furrer & Stumm, 1986).

The Furrer and Stumm (1986) dissolution model requires modification to represent silicate dissolution rates. Helgeson et al. (1984) did not express their data in terms of adsorbed proton concentrations but reported that feldspar dissolution rates were independent of pH in the range of pH 2.9 to 8.0. Anorthite dissolution rates shown in Fig. 3-10 (Amrhein & Suarez, 1988) indicate that feldspar dissolution cannot be represented directly with the oxide model. Amrhein and Suarez (1988) modified the Furrer and Stumm model by adding a

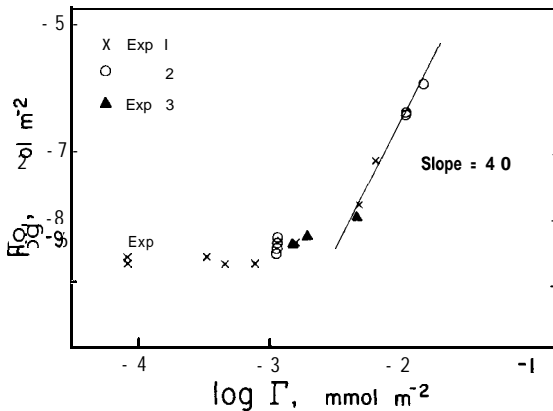


Fig. 3-10. The log of the proton-promoted rate vs. the log of the net concentration of adsorbed protons and hydroxide ions (Amrhein & Suarez, 1988).

rate term proportional to the quantity of uncharged silanol sites (SOH). In addition, the dissolution rate at high pH was represented by the adsorbed hydroxyl concentration, whose reaction rate was equal to the proton promoted rate. Thus the term C_H^s was replaced by the term Γ , which then represented the sum of the adsorbed proton and hydroxyl concentrations. Although there is evidence that the order of the proton and hydroxyl promoted rates are similar (Furrer & Stumm, 1986) this result does not mean that the reaction rate constant must be the same. Schott (1990) determined that for the dissolution of a basalt glass, the reaction order was 3.8 for protons and 3.7 for hydroxyls, but the reaction rate for hydroxyls was about seven times greater than for protons.

The anorthite reaction rate in the presence of organic ligands was related to the adsorbed ligand concentration, as in the Furrer and Stumm model for oxides. Figure 3-11 shows the ligand-promoted dissolution rate for anorthite (Amrhein & Suarez, 1988). Combining these terms produces an overall rate expression for anorthite (Amrhein & Suarez, 1988)

$$R_T = 37.0(\Gamma)^{4.0} + 2.09 \times 10^{-8} (\text{SOH}) + 4.73 \times 10^{-6} (S - L). \quad [29]$$

Differences in reaction dependence on ligand concentration are also related to the Al content and likely to the Fe content. The rate term k_L for the plagioclase feldspar series is proportional to the Al content, as shown in Fig. 3-12 (Amrhein & Suarez, 1988). This concept can likely be generalized to most minerals, as Bales and Morgan (1986), and Bennett et al., (1988) indicated no effect of ligands on chrysotile and quartz dissolution, respectively. These organic ligands do not form important complexes with silica. It appears likely that the ligand promoted rate is dominant under the pH and ligand concentration range of natural systems.

Application of these reaction models to predict reaction rates in natural systems is not yet possible. Dissolution rates are related to the concentration of active sites, which are related indirectly to the measurable entity, surface area.

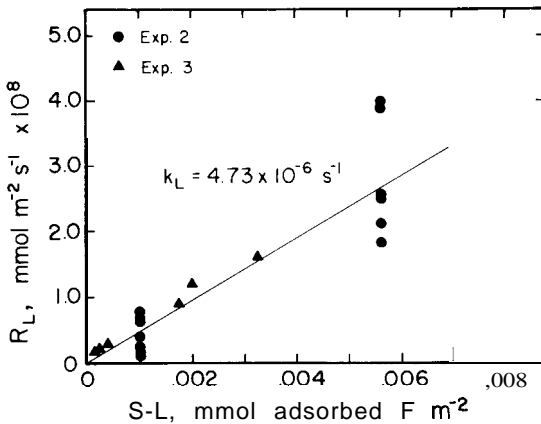


Fig. 3-11. Ligand-promoted dissolution rate of anorthite vs. the concentration of adsorbed F⁻ (Amrhein & Suarez, 1988).

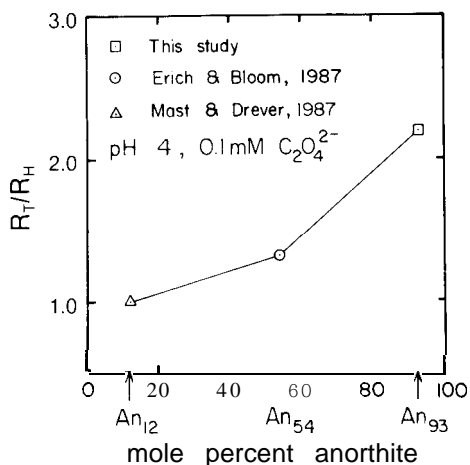


Fig. 3-12. Effect of oxalate on the anorthite dissolution rate vs. the mole percent Ca in the plagioclase. A ratio of 1.0 represents no effect of oxalate on the rate of dissolution (Amrhein & Suarez, 1988).

Laboratory reaction rates have been demonstrated to be orders of magnitude faster than measured field dissolution rates. This result is related both to the number of active sites per meter squared surface area, as well as to the adsorption of inhibiting ions. Reduction of reaction rates with time may be related to release of Al and possible absorption of Al onto the surface silanol polymers causing dehydration and crosslinking (Casey et al., 1988). Evidence for this mechanism is provided by the fact that above pH = 3, Al addition has been observed to decrease feldspar dissolution rates (Amrhein & Suarez, 1992). Addition of K⁺ to solution also causes a reduction in the dissolution rate (Amrhein & Suarez, 1992) apparently due to the competition of K⁺ for protons in the cavities of the siloxane surface. True back reaction effects have not been observed, probably because these aluminosilicates are far from equilibrium in these experiments as well as in almost all natural systems in earth surface environments. Long-term reaction rates (after 4.5 yr) of specimen minerals in the laboratory decreased to below 0.005 times the initial rates (Amrhein & Suarez, 1992). These long-term rates are similar to feldspar reaction rates determined in the laboratory for material separated from soils (Suarez & Wood, 1991) as well as reaction rates calculated under field conditions (Velbel, 1986).

Carbonate Kinetics

Detailed carbonate reaction models have been developed by Plummer et al. (1978) for calcite and Busenberg and Plummer (1982) for dolomite. These authors determined that the dissolution process was controlled by different rate limiting steps, dependent on pH. The overall reaction expression is

$$R = k_1(\text{H}^+) = k_2(\text{H}_2\text{CO}_3^*) + k_3(\text{H}_2\text{O}) - k_4(\text{Ca}^{2+})(\text{HCO}_3^-) \quad [30]$$

where

$$k_4 = \frac{K_2}{K_c} \left(k_1 + \frac{1}{(H_s^+)} \left[k_2 (H_2CO_3^*)_s + k_3 (H_2O)_s \right] \right) \quad [31]$$

and k_1 , k_2 and k_3 are first-order rate constants dependent on temperature; k_4 is the backward rate constant; K_2 is the second dissociation constant for carbonic acid; K_c is the solubility product of calcite, and $H_2CO_3^*$ is the sum of undissociated carbonic acid and dissolved aqueous CO_2 . The value H_s^+ represents the H activity at the calcite surface. Similarly the dolomite rate expression of Busenberg and Plummer (1982) below 45°C is

$$R = k_1 (H^+)^{0.5} = k_2 (H_2CO_3)^{0.5} + k_3 (H_2O)^{0.5} - k_4 (HCO_3^-) \quad 1321$$

where k_1 , k_2 and k_3 again are the forward rate constants and k_4 is the backward rate constant. Suarez (1983) Inskeep and Bloom (1985) and Chou et al. (1989) in detailed experiments, observed that the Plummer et al. (1978) model underestimated precipitation rates at low CO_2 . A simpler expression for precipitation is given by Inskeep and Bloom (1985) who modified the Nancollas and Reddy (1971) precipitation model to account for changes in ionic strength. The proposed precipitation model is

$$R = \gamma_2^2 k_f S \left[Ca^{2+} \right] \left[CO_3^{2-} \right] - K_c \gamma_2^{-2} \quad [33]$$

where $k_f = 118 \text{ L}^2 \text{ mol}^{-1} \text{ m}^{-2} \text{ s}^{-1} \gamma$ is the divalent ion activity coefficient and S is the calcite surface area in meters squared per liter (Inskeep & Bloom, 1985). Chou et al. (1989) examined carbonate precipitation and dissolution under low CO_2 conditions. They developed the relationship

$$R = k_1 (H^+) + k_2 (H_2CO_3^*) + k_3 (H_2O) - k_{-3} (Ca^{2+}) (CO_3^{2-}) \quad [34]$$

where $\log k_1$, $\log k_2$, $\log k_3$ equal -4.05 , -7.30 , -10.19 respectively, and $\log k_{-3}$, equals -1.73 for calcite. The back reaction value k_{-3} is very close to that determined by Inskeep and Bloom (1985).

Use of these crystal growth models provides a description of the changes in ion concentrations with time but may not be mechanistically applicable for soil systems. Inskeep and Bloom (1986) determined that dissolved organic carbon (DOC) values of $146 \mu\text{mol L}^{-1}$ resulted in complete inhibition of calcite crystal growth. Suarez et al. (1992) measured DOC values of 500 to 2000 $\mu\text{mol L}^{-1}$ in suspensions of arid land soils that were supersaturated and not precipitating calcium carbonate. From these data it seems that crystal growth is not the major process controlling calcite precipitation and that heterogeneous nucleation may be more realistic. Recently, Svensson and Dreybrodt (1992) modified the Plummer et al. (1978) model to account for reduction in precipitation rates (crystal growth) due to adsorption of inhibitors. The data show that the effect of the inhibitors is not constant, but rather increases dramatically as the solution approaches calcite equilibrium.

Transport Models

To provide a more realistic representation of natural systems, it is necessary to consider water flow and the spatial differences in chemical and mineralogical properties of the soil. The following sections describe some modeling approaches useful to soil systems.

Reaction Path

Reaction path models provide a more realistic representation of chemical reactions in soils than do the batch equilibrium models. Reaction path models have not been generally utilized in soil science but represent a substantial advance over the batch reaction models. Simulations with these models have been made in hydrochemical and geochemical studies both to evaluate evolution of groundwaters along flowpaths in aquifers, as well as, to calculate necessary water composition and quantify boundary conditions for specified rock alterations. Among the available models, PHREEQE (Parkhurst et al., 1980) and NETPATH (Plummer et al., 1991) are likely the most utilized, and are based on the WATEQ speciation model and data base. Other available models are listed in Table 3-1.

These reaction path models contain mass balance relations for both the solid and solution phases, thus they can be used to simulate soil weathering processes. Although not yet extensively used for pedogenic studies, they are well suited for this purpose.

Multicomponent Transport

Saturated and/or Steady-State Water Flow

The unnamed model of Jury et al. (1978) couples steady state water flow with a chemical equilibrium model. The model considers major ion chemistry, ion exchange, and the possibility to dissolve or precipitate calcite or gypsum to equilibrium. Water uptake is accounted for by specifying the leaching fraction and proportioning the water uptake at various depths in the root zone. The model is suited for generation of calcite and gypsum distribution profiles. Other models in this category include the model of Schulz and Reardon (1983) and the model CALDEP (Marion, et al., 1985). The model CALDEP, discussed in detail in Marion and Schlesinger (see Chapter 8; 1994) includes a "tipping bucket" flow model (water flow from one layer to another only when saturation is achieved) and a simplified chemical model to enable long-term simulations.

Other more generalized multicomponent transport models include HYDRO-GEOCHEM (Yeh & Tripathi, 1989), DYNAMIX (Liu & Narasimhan, 1989) and FASTCHEM (Hostetler & Erikson, 1989). The model HYDROGEOCHEM has the added advantage that it also can be used for unsaturated water flow by running a separate water flow program and inputting the results to HYDRO-GEOCHEM. These generalized programs are very flexible in their ability to handle different chemical environments but do require the user to define chemical species, solids, and thermodynamic constants for the reactions. The models can consider reduction-oxidation dependent species, carbonates and silicates. All models require input of pH or $p\text{CO}_2$. This requirement prevents them from being

used for long-term simulations, such as long-term acidification where these variables change.

Surface complexation models have not yet been incorporated widely into transport models (Mangold & Tsang, 1991). The computer program TRANQL (Cederberg et al., 1985) and an unnamed program by Jennings et al. (1982) have incorporated the constant capacitance model into transport programs. The transport model HYDROGEOCHEM (Yeh & Tripathi, 1990) contains the triple layer model.

Unsaturated Water Flow

These models have all been developed primarily for soil environments in general and are oriented to agricultural lands. Among the fixed pH models are SALT-FLOW (Robbins et al., 1980) LEACHM I (Wagenet & Hutson, 1987) and NTRM (Schaffer & Larson, 1987) and SOWACH (Dudley & Hanks, 1991). These models are all primarily major species models that consider ion exchange and calcite and gypsum precipitation-dissolution, although some (e.g., LEACHM I and NTRM) also include N species. These models are primarily useful for intermediate-term simulations where pH is not changing over the long term and where transient changes can be neglected. The model LEACHM II (discussed in detail by Wagenet et al., 1994; see Chapter 2) considers fixed CO₂ as an input, thus allowing for changes in soil pH with time associated with changes in input water chemistry.

Chemical Kinetic Models

The model UNSATCHEM (Suarez & Simunek, 1992) combines the program SOILCO2 (Simunek & Suarez, 1993) with an unsaturated water flow-major ion chemistry program. The model differs from other soil simulation models in that the CO₂ content is calculated based on environmental factors (water inputs, temperature, soil properties), rather than used as an input. Prediction of pH is made by combining the CO₂ distributions with the chemistry routine, requiring only the input of major ion solution composition (rainfall or irrigation). The model includes a chemical speciation routine, cation exchange and mineral reactions. Use of kinetic expressions in UNSATCHEM for calcite dissolution-precipitation and dolomite dissolution allows for more realistic representations of soil conditions than simulations utilizing mineral equilibrium conditions.

Figure 3-13 presents the predicted calcite distribution with depth at various times for a 1-yr cycle of irrigation using lower Colorado River water. This simulation using the equilibrium option in the UNSATCHEM model (Suarez & Simunek, 1992) assumes a constant water application of 1 cm d⁻¹ and a water extraction of 0.09 cm d⁻¹. The simulation assumes a fixed atmospheric CO₂, upper boundary and a linearly increasing CO₂ concentration reaching a value of 2 kPa. The water content distribution stabilized after about 200 d (data not shown). Since Colorado River water is initially calcite supersaturated, large quantities of calcite are precipitated in the first node (Fig. 3-13a). Below the first node, increasing CO₂ results in calcite dissolution and then subsequent precipitation. Eventually the steady-state profile was reached after 200 d, showing a sharp precipitation front at 55 cm. The same simulation using the kinetic option in

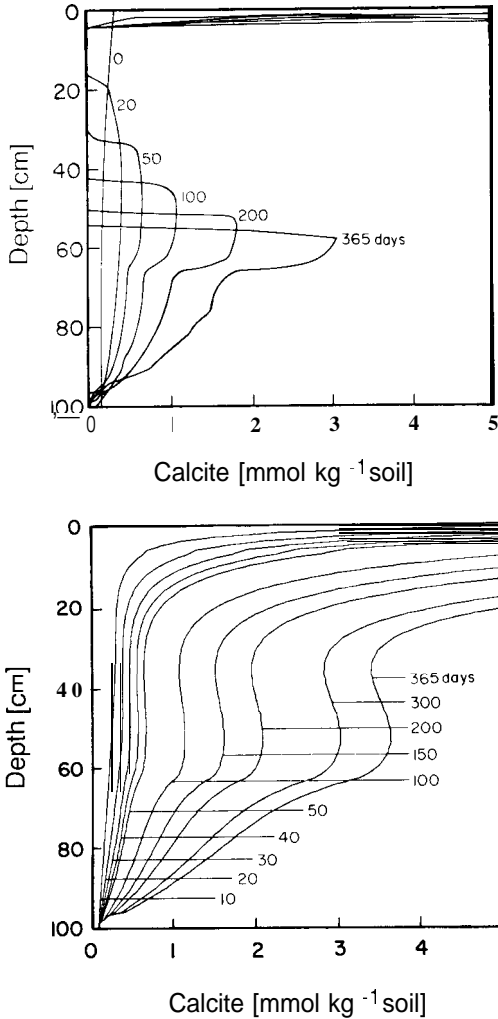


Fig. 3-13. (a) Calcite precipitation distribution with depth for a 1-yr irrigation sequence using Colorado River water and the UNSATCHEM model (Suarez & Simunek, 1992, p. 32, in preparation) with the equilibrium option; (b) Calcite precipitation distribution with depth for a 1-yr irrigation sequence using Colorado River water and the UNSATCHEM model (Suarez & Simunek, unpublished data) with the nonequilibrium option.

UNSATCHEM presents a much different calcite distribution, as shown in Fig. 3-13b. In addition to the differences in the calcite distribution, the increased concentrations of Ca in solution with the kinetic option result in gypsum precipitation at a shallower depth as compared with the results with the equilibrium option. These differences have obvious implications both for predicting soil mineral weathering and dissolution and for reconstruction of paleoclimates. Since the model includes a plant growth model that considers environmental factors such

as water, 0, and salt stress, it can simulate water consumption and recharge on a daily basis. Paleoclimate simulations could include temporal changes in rainfall distribution temperature, and subsequently plant water uptake.

Realistic representations of chemical weathering require not only knowledge of existing mineralogy and surface area but temperature, water inputs, evapotranspiration, hydraulic properties, and biological production and its influence on dissolution-enhancing ligands and soil CO₂ concentrations. To date, consideration of biological factors is minimal and probably the aspect most lacking in the existing models. In addition, predictive models will need to incorporate reaction rates rather than equilibria assumptions for most processes. This development is presently limited by the lack of kinetic information.

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