Influence of Temperature and Mineral Surface Characteristics on Feldspar Weathering Rates in Natural and Artificial Systems: A First Approximation

Michael Anthony Velbel

Department of Geological Sciences, Michigan State University, East Lansing

Rates of alkali feldspar hydrolysis in the near-neutral *p*H range are up to 3 orders of magnitude slower in natural systems than in laboratory experiments. Correcting for differences in temperature between natural weathering and laboratory systems reduces the disparity by as much as a factor of 5. Any remaining disparity can be accounted for by differences in the ratio of effective surface area to total surface area; the ratio of effective-to-total surface area in natural systems is generally considerably smaller than in laboratory systems. This may be related, at least in part, to experimental preparation artifacts and to the fact that naturally weathered feldspars have lost much of their most reactive surface to the formation of etch pits. Hydrological factors such as inhomogeneous access of percolating fluids to mineral surfaces may also reduce the proportion of mineral surface area reacting in natural systems.

Introduction

Different geological substrates have widely differing abilities to "buffer" atmospherically deposited acidity; the reactivity of different geological materials determines, to a considerable degree, the sensitivity of landscapes, soils, surface waters, and groundwaters to acid precipitation [e.g., *Bricker and Rice*, 1989]. Landscapes underlain by crystalline silicate bedrock are the most sensitive to acidification, because the silicate minerals of which they are composed do not react with throughgoing solutions quickly enough to neutralize the added acidity or to release sufficient quantities of base cations to the soil exchange complex [e.g., *Johnson et al.*, 1972; *Johnson*, 1979, 1984; *Reuss et al.*, 1987]. Silicate mineral weathering reactions are therefore fundamental processes in the reaction of acid precipitation with susceptible landscapes [e.g., *Reuss et al.*, 1987] and in the contributions of continental crustal weathering to global geochemical cycles [e.g., *Berner and Berner*, 1987].

Despite the abundance of published research on the geochemical kinetics of silicate mineral-water interactions, silicate-mineral weathering rates in natural systems are poorly understood. This hampers predictive modeling of landscape and surface water sensitivity to acid deposition [e.g., *Schnoor and Nikolaidis*, 1987]. Some of the widely used models of surface water acidification (e.g., Birkenes, MAGIC, ILWAS) involve detailed quantitative descriptions of various soil and aqueous processes (e.g., ion exchange, aqueous speciation) but treat "weathering" (primary-mineral hydrolysis and replenishment of exchangeable base cations from the primary-mineral pool) as an independent parameter which is chosen and/or adjusted more or less arbitrarily during the calibration of the model output against some real data set [e.g., *Christopherson et al.*, 1982; *Cosby et al.*, 1985a, b; *Gherini et al.*, 1985]. Unfortunately, this post hoc parameterization of weathering rates bears no deterministic relationship to the abundant rate data available from laboratory experiments, preventing the use of laboratory rate data (for example, rate constants, *p*H dependence)

in models of natural systems. Others (e.g., trickledown, enhanced trickledown) combine field calibration with laboratory data on the *p*H dependence of silicate dissolution [e.g., *Schnoor and Stumm*, 1986a; *Nickolaidis et al.*, 1988]. Some forward models [e.g., *Sverdrup and Warfvinge*, 1988; *Furrer et al.*, 1989, 1990] extrapolate from laboratory rate studies; these models usually assume that reaction rate is directly proportional to mineral surface area and require ad hoc adjustment of other (e.g., hydrological) parameters before the laboratory rate data can be applied.

Because predictive modeling of landscape response to acidification is a major focus of current environmental research, there is increasing interest in rates of weathering and their relationship to environmental modeling [e.g., *Bergström and Lindström*, 1989], especially the relationship between laboratory data on the rates of silicate mineral weathering and cation budgets in natural systems [*Drever et al.*, 1989; *Drever and Swoboda-Colberg*, 1989]. Recent studies of feldspar hydrolysis rates in the laboratory consistently show that alkali-feldspar dissolution rates in laboratory systems in the near-neutral to mildly acidic *p*H range generally vary within and between laboratory investigations by slightly more than 1 order of magnitude (a factor of 30) [*Helgeson et al.*, 1984; *Velbel*, 1986a; *Knauss and Wolery*, 1986]. Rates estimated from geochemical mass balance studies in natural watersheds are up to 3 orders of magnitude slower than in the laboratory [*Pačes*, 1983; *Velbel*, 1985a, 1986a; *Schnoor and Stumm*, 1986b; *Sverdrup and Warfvinge*, 1988; *Drever and Swoboda-Colberg*, 1989]. Numerous rate-limiting factors in silicate mineral weathering might account for this laboratory-field difference. It is beyond the scope of this note to critically review them all. For reviews and recent primary literature the reader should refer to *Pačes* [1983], *Velbel* [1985a, 1986a, 1989], *Mast and Drever* [1987], *Amrhein and Suarez* [1988], *Sjöberg* [1989], *Drever and Swoboda-Colberg* [1989], and *White and Peterson* [1990].

The purpose of this paper is to evaluate the possible role of temperature differences and differences in mineral surface characteristics in explaining the disparity in feldspar dissolution rates between laboratory and natural systems. The absolute magnitude of the temperature effect is calculated as

it applies to two specific natural systems for which "field" rates have been previously calculated by geochemical mass balance: the Trnavka catchment of Czechslovakia, studied by *Paces* [1983], and watershed 27 of the Coweeta Hydrologic Laboratory in the southeastern United States, studied by *Velbel* [1985a].

TEMPERATURE EFFECTS ON REACTION RATES IN NATURAL AND LABORATORY SYSTEMS

The importance of temperature in reaction rates is widely recognized (e.g., *Arrhenius* [1889], cited by *Glasstone et al.* [1941], *Wood and Walther* [1983], *Lasaga* [1984], and *Walther and Wood* 1984, 1986]). It is often suggested that much of the discrepancy between laboratory rates and natural rates might be due to the fact that most natural earth surface environments are cooler than the 22°C or 25°C temperature at which most laboratory experiments are performed.

Far from equilibrium, in the near-neutral to mildly acidic pH range over which the feldspar dissolution rate is independent of pH ($3 \leq pH \leq 8$) [*Helgeson et al.*, 1984], the change in mass of a solute (*i*) with time as a result of dissolution can be described by the following equation [*Knauss and Wolery*, 1986]:

$$dM_i/dt = fsk(T)n \tag{1}$$

where

M_i mass of dissolved solute *i*;

t time;

$k(T)$ rate constant for the dissolution reaction (a function of temperature);

s surface area of the reactant;

f ratio of "effective" to total surface area of the reactant [*Knauss and Wolery*, 1986] or reactive to physical surface area [*White and Peterson*, 1990];

n stoichiometric coefficient of component *i* released by the dissolution of one mole of reactant.

One way to estimate the magnitude of the temperature effect is to calculate the ratio of the rate constant at field temperatures to the rate constant at standard laboratory conditions

$$k(T_f)/k(T_l) \tag{2}$$

where $k(T)$ is the rate constant for a given reaction at temperature T, T_f is the temperature of the natural (field) system, and T_l is the temperature of the laboratory system.

Using the Arrhenius equation

$$k(T) = A \exp (-E_a/RT) \tag{3}$$

where A is the "frequency factor" or preexponential term, E_a is the activation energy (values discussed below), and R is the gas constant, and assuming that the preexponential term and activation energy are invariant over the range of temperatures being examined, the ratio of field-to-laboratory rate constants is given by

$$\frac{k(T_f)}{k(T_l)} = \exp \left(\frac{E_a[T_f - T_l]}{R[T_lT_f]} \right) \tag{4}$$

In general, use of the mean annual temperature is not strictly correct as an approximation of the actual tempera-

ture distribution in a natural weathering system. For example, consider comparing laboratory rates at 20°C with two different natural systems with a mean annual temperature of 10°C. One has a constant temperature of 10°C, the other spends 6 months at 0°C and six months at 20°C. Because of the exponential character of the Arrhenius equation, the dependence of reaction rate on temperature is highly nonlinear. Consequently, although the mean annual temperatures of the two natural systems are the same, the system that spends half its time at 20°C will have a reaction rate at least 50% that of the laboratory rate, regardless of the activation energy. Furthermore, if that natural weathering system spent any significant time above the laboratory temperature, the field rate could be higher than the laboratory rate even though the mean annual temperature was lower in the field. The natural system experiencing thermal excursions will be more similar to the laboratory system than is the natural system with constant temperature, despite the similarity of mean annual temperature between the two natural systems. In general, the temperature effects should be integrated over annual temperatures; even variations in daily extremes might play a significant role. These considerations apply especially to thin, shallow weathering profiles, where most weathering occurs in the upper (near-surface) soil horizons.

However, there are some natural hydrogeochemical systems for which the mean annual temperature is likely a satisfactory approximation. Base flow and storm flow at Coweeta are sustained principally by water from deep portions of soils and saprolites [*Velbel*, 1985b]. Interflow and overland flow (runoff) are not significant processes at Coweeta; precipitation on WS27 infiltrates almost immediately, even on steep slopes. This water continues to move downward through the weathering profile until it reaches the hydrologically impervious unaltered bedrock. At this point the water is shunted laterally toward the stream [*Velbel*, 1985b]. Stream water samples therefore represent water which has participated in weathering reactions throughout the entire thickness of the weathering profile (average thickness of saprolite at Coweeta is 6–7 m) [*Velbel*, 1985b].

Stream water temperatures in such groundwater-dominated systems tend to reflect the moderating influence of groundwater temperature [*Shanley and Peters*, 1988]. This was recognized by the Cherokee Indians who inhabited the southern Blue Ridge and who incorporated the relevant observations into their origin myths: "There is another world under this, and it is like ours in everything—animals, plants, and people—save that the seasons are different. The streams that come down from the mountains are the trails by which we reach this underworld, and the springs at their heads are the doorways by which we enter it, but to do this one must fast and go to water and have one of the underground people for a guide. We know that the seasons in the underworld are different from ours, because the water in the springs is always warmer in winter and cooler in summer than the outer air." [*Mooney*, 1900, p. 240]. Diurnal and seasonal thermal excursions are largely damped out [*Freeze and Cherry*, 1979; *Shanley and Peters*, 1988] at the depths at which most of the mineral weathering takes place in deeply weathered regoliths like those at Coweeta. Mean annual temperatures are therefore used in these calculations.

The mean annual temperature in *Velbel*'s [1985a] field area is 12.8°C at 685 m elevation (Coweeta Climate Station 1)

TABLE 1. Temperature and Activation Energy Effects on Feldspar Weathering Rates in Forested Watersheds, Relative to Laboratory Rates

E_a, kcal/mol	Field-To-Laboratory Ratio	
	Velbel	Pačes
7.1	0.51	0.46
9.0	0.42	0.37
13.5	0.28	0.22

The ratio of field-to-laboratory rate constants is given in (4). T_l = 25°C. Mean annual temperature (T_f) is 9.1°C in Velbel's [1985a] study area and 6.5°C in Pačes' [1983] study area.

[Swift et al., 1988, Table 3.1]; using the mean atmospheric thermal lapse rate of 6.5°C/km, the mean annual temperature at the mean elevation (1260 m) of Coweeta watershed 27 is 9.1°C. Laboratory temperature is taken to be 25°C and constant.

The activation energy for feldspar dissolution is not well constrained. Pačes [1983] used a value of approximately 7.1 kcal/mol. Helgeson et al. [1984], Lasaga [1984, Table 3], and Walther and Wood [1986] suggest activation energies around 9.0 kcal/mol. Wood and Walther [1983] suggest an activation energy of 13.27 kcal/mol; Lasaga [1984] suggests using an estimate of 60 kJ mol^{-1} (14.3 kcal/mol). Recent experimental work of Knauss and Wolery [1986] suggests activation energies for albite in the pH-independent range of around 13.48 kcal/mol or higher. Taken as a body, this recent work suggests activation energies for albite in the pH-independent range of approximately 13.5 kcal/mol. To the extent that the actual value may be somewhat lower than this, the calculations here represent the maximum possible effect of temperature.

Table 1 summarizes calculations of temperature effects for the field areas of Velbel [1985a] and Pačes [1983], assuming a variety of activation energies. For the most extreme case (using 13.5 kcal/mol) the rate-reducing effect of natural temperatures becomes

$$k(9.1)/k(25) = 0.28$$

for Velbel's [1985a] study area. The mean annual temperature in the field study area of Pačes [1983] is 6.5°C; therefore

$$k(6.5)/k(25) = 0.22$$

The lower natural temperatures clearly result in deceleration of feldspar dissolution, by as much as a factor of 5 below the room temperature rates determined in the laboratory. Consequently, provided that activation energies for the appropriate minerals and mechanisms are available or can be estimated [e.g., Wood and Walther, 1983; Lasaga, 1984; Walther and Wood, 1984, 1986; Knauss and Wolery, 1986], temperature differences should be included in any attempt to compare natural and experimental rates, or to extrapolate laboratory rate data to natural systems.

DISCUSSION

Temperature differences between natural weathering profiles and laboratory systems result in deceleration of field weathering rates relative to laboratory rates. However, temperature compensation of estimated field rate constants to laboratory temperatures does not by itself explain more than a factor of 5 difference between laboratory and field rates. The differences between individual laboratory rates and field rates range from less than an order of magnitude to 3 orders of magnitude [Velbel, 1985a, 1986a]. Temperature corrections can bring the slowest laboratory rates into perfect accord with the field rates. However, for the laboratory rates which differ by 3 orders of magnitude before temperature correction a 200-fold discrepancy remains to be accounted for even after adjusting the rates for temperature differences.

In most experimental rate determinations the stoichiometry and surface area of the reactant are known and are combined with the measured mass flux to calculate an apparent rate constant k_a, which is actually the product $k(T)f$ (equation (1)). The temperature-dependent variation in the rate constant, $k(T)$, is shown here to be significantly smaller than the previously reported variation in k_a [Helgeson et al., 1984; Velbel, 1986a]. Therefore variation in f, the fraction of total or physical surface area which actually participates in weathering reactions, must account for observed variations in weathering rates.

Field rates are estimated from geochemical mass balance (input-output budgets) by using one or more elemental fluxes to determine the number of moles of a specific weathering reaction that is taking place in a natural system per unit time. The resultant number is then divided by the estimated mineral surface area within the system [e.g., Velbel, 1986b]. The surface area is estimated using parent material abundances and simple geometric models of grains and/or fractures [e.g., Velbel, 1986b]. Fracturing and etching during weathering (e.g., olivine) [Grandstaff, 1978] will tend to make real surface areas larger than the geometric estimates for spheres or simple polyhedra which are used in normalizing the bulk field rates. Even in laboratory studies, actual (bulk) surface areas as measured by BET methods are generally 3.5–7 times larger than values estimated from particle size and geometry [Nickel, 1973; Knauss and Wolery, 1986; Sverdrup and Warfvinge, 1988; White and Peterson, 1990]. Field rates estimated using geometric surface areas are orders of magnitude slower than laboratory rates [Pačes, 1983; Velbel, 1985a, 1986a]; increasing the surface area to correct for nongeometric surface area effects would result in even slower field rates per unit mineral surface area, because the same amount of weathering (as determined by mass balance) would be apportioned over a larger surface area. Consequently, errors in estimating bulk surface area in the natural systems are not likely to be responsible for the laboratory/field rate disparity [Velbel, 1985a, 1986a; Drever and Swoboda-Colberg, 1989].

One way to increase the estimates of field weathering rates based on mass balance (and bring them into better accord with laboratory rates) would be to reduce the mineral surface area in natural systems. The mass-balanced rate would then be divided by a smaller surface area, thereby increasing the surface area normalized rate. The problem therefore becomes one of reducing the proportion of the mineral surface which is available to react in natural systems (f in equation (1)); natural systems may have lower ratios of effective-to-total surface area (f in equation 1)) available for reaction with fluids than do laboratory systems.

There are numerous possible mechanisms of reducing the effective-to-total surface area ratio in natural systems rela-

tive to their laboratory counterparts. Hydrologic factors, such as inhomogenous fluid migration through pore or fracture networks, may limit the amount of water coming into contact with mineral surfaces, so that the amount of mineral surface participating in fluid-rock interactions is some fraction of the total available surface area of that mineral [e.g., *Walther and Wood*, 1986; *Velbel*, 1986a; *Sverdrup and Warfvinge*, 1988; *Drever and Swoboda-Colberg*, 1989]. Simple mechanical occlusion of portions of the mineral surfaces would also achieve this if the coatings prevent transport of reactants or products. Some organic compounds or other trace constituents present in nature, but absent in the laboratory, may be acting as inhibitors by forming stable, insoluble surface complexes, "poisoning" active sites (e.g., dislocation outcrops) [*Berner and Holdren*, 1977, 1979], and reducing the number of available active sites per unit area of natural mineral surfaces [*Berner*, 1978; *Schnoor and Stumm*, 1986a]. Alternatively, the extensive etching widely observed on naturally weathered feldspar grains may indicate that many of the active sites have been consumed. The surface area that remains is larger (see discussion of etching and surface roughness, above), but much less reactive, because a much smaller proportion of this surface area consists of dislocation outcrops or other active sites. Substantial differences in the number of active sites per unit surface area have been invoked to explain variability between different experimental studies and between different size fractions within individual experimental studies [*Holdren and Speyer*, 1985, 1987; *Helgeson et al.*, 1984; *White and Peterson*, 1990].

Recent laboratory experiments show that natural, already-weathered soil mineral grains experimentally dissolve at the same rate as artificially prepared minerals [*Drever and Swoboda-Colberg*, 1989]. These results suggest that intrinsic differences in mineral surface properties are not significantly different in artificially and naturally weathered minerals and that external (e.g., hydrologic) controls determine mineral behavior in natural systems [*Drever and Swoboda-Colberg*, 1989]. This single pairwise comparison does not, however, address the considerable (factor of 30) variability among laboratory rates [*Helgeson et al.*, 1984; *Velbel*, 1986a], which cannot be due to hydrological factors, so it is premature to dismiss intrinsic mineral surface properties as a potential factor in the laboratory/field rate discrepancy.

Intrinsic (factor of 30) variability among laboratory rates [*Velbel*, 1986a] implies considerable variability in the critical mineral surface properties, casting doubt upon the results of forward models, because the forward models involve choosing a "best estimate" rate and making hydrologic corrections to it without acknowledging the large variability among laboratory rates. The intrinsic surface characteristics (e.g., ratio of effective-to-total surface area) of natural materials appear to be significantly different from those used in laboratory experiments [*Velbel*, 1986a]. Unfortunately, there is no convenient a priori way of determining the magnitude of the surface effect difference between nature and the field. Furthermore, it is not clear at present whether intrinsic surface effects can be distinguished from hydrological factors such as inhomogeneous fluid flow in natural systems; both intrinsic and extrinsic factors could result in similar reduction of effective or reactive surface area.

CONCLUSIONS

Surface-specific rates of alkali feldspar hydrolysis in the near-neutral pH range vary within and between most laboratory investigations by slightly more than 1 order of magnitude. Rates estimated from geochemical mass balance studies in natural watersheds are up to 3 orders of magnitude slower than the laboratory. Correcting for differences in temperature between natural weathering and laboratory systems reduces the disparity by as much as a factor of 5; future attempts to relate field and laboratory silicate rate data should correct for the effects of temperature. However, the temperature effect alone is not sufficient to account for order of magnitude discrepancies. Any remaining disparity can be accounted for by differences in the ratio of effective surface area to total surface area; the ratio of effective-to-total surface area in natural systems is generally considerably smaller than in laboratory systems. This may be related, at least in part, to experimental preparation artifacts and to the fact that naturally weathered feldspars have lost much of their most reactive surface to the formation of etch pits. Hydrological factors such as inhomogeneous access of percolating fluids to mineral surfaces may also reduce the proportion of mineral surface area reacting in natural systems. Unfortunately, it is not presently possible to distinguish the relative influences of intrinsic (e.g., mineralogical) versus extrinsic (e.g., hydrological) factors on mineral surface characteristics in natural systems.

REFERENCES

Amrhein, C., and D. L. Suarez, The use of a surface complexation model to describe the kinetics of ligand-promoted dissolution of anorthite, *Geochim. Cosmochim. Acta, 52*, 2785–2793, 1988.

Bergström, S., and G. Lindström, Models for analysis of groundwater and surface water acidification: A review, *Rep. 3601*, 37 pp., Natl. Swedish Environ. Prot. Board, Solna, 1989.

Berner, E. K., and R. A. Berner, *The Global Water Cycle: Geochemistry and Environment*, 397 p., Prentice-Hall, Englewood Cliffs, N. J., 1987.

Berner, R. A., Rate control of mineral dissolution under earth surface conditions, *Am. J. Sci., 278*, 1235–1252, 1978.

Berner, R. A., and G. R. Holdren, Mechanism of feldspar weathering: Some observational evidence, *Geology, 5*, 369–372, 1977.

Berner, R. A., and G. R. Holdren, Mechanism of feldspar weathering, II, Observations of feldspars from soils, *Geochim. Cosmochim. Acta, 43*, 1173–1186, 1979.

Bricker, O. P., and K. C. Rice, Acidic deposition to streams, *Environ. Sci. Technol., 23*, 379–385, 1989.

Christopherson, N., H. M. Seip, and R. F. Wright, A model for streamwater chemistry at Birkenes, Norway, *Water Resour. Res., 18*, 977–996, 1982.

Cosby, B. J., R. F. Wright, G. M. Hornberger, and J. N. Galloway, Modeling the effects of acid deposition: Estimation of long-term water quality responses in a small forested catchments, *Water Resour. Res., 21*, 1591–1601, 1985a.

Cosby, B. J., G. M. Hornberger, J. N. Galloway, and R. F. Wright, Time scales of catchment acidification, *Environ. Sci. Technol., 19*, 1144–1149, 1985b.

Drever, J. I., and N. Swoboda-Colberg, Mineral weathering rates in acid-sensitive catchments: Extrapolation of laboratory to the

field, in *Water-Rock Interaction WRI-6*, edited by D. L. Miles, pp. 211–214, A. A. Balkema, Rotterdam, 1989.

Drever, J. I., N. Swoboda-Colberg, J. L. Schnoor, and R. W. Valentine, Predicting effects of acid deposition on mineral weathering rates, paper presented at the 28th International Geological Congress, Washington, D. C., July 1989.

Freeze, R. A., and J. A. Cherry, *Groundwater*, 604 pp., Prentice-Hall, Englewood Cliffs, N. J., 1979.

Furrer, G., J. Westall, and P. Sollins, The study of soil chemistry through quasi-steady-state models, I, Mathematical definition of model, *Geochim. Cosmochim. Acta, 53*, 595–601, 1989.

Furrer, G., P. Sollins, and J. Westall, The study of soil chemistry through quasi-steady-state models, II, Acidity of soil solution, *Geochim. Cosmochim. Acta.*, in press, 1990.

Gherini, S. A., L. Mok, R. J. M. Hudson, G. F. Davis, C. W. Chen, and R. A. Goldstein, The ILWAS model: Formulation and application, *Water Air Soil Pollut., 26*, 425–459, 1985.

Glasstone, S., K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, 611 pp., McGraw-Hill, New York, 1941.

Grandstaff, D. E., Changes in surface area and morphology and the mechanism of forsterite dissolution, *Geochim. Cosmochim. Acta, 42*, 1899–1901, 1978.

Helgeson, H. C., W. M. Murphy, and P. Aagaard, Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions, II, Rate constants, effective surface area, and the hydrolysis of feldspar, *Geochim. Cosmochim. Acta, 48*, 2405–2432, 1984.

Holdren, G. R., and P. M. Speyer, Reaction-rate surface area relationships for an alkali feldspar during the early stages of weathering, *Geochim. Cosmochim. Acta, 49*, 675–681, 1985.

Holdren, G. R., and P. M. Speyer, Reaction-rate surface area relationships during the early stages of weathering, II, Data on eight additional feldspars, *Geochim. Cosmochim. Acta, 51*, 2311–2318, 1987.

Johnson, N. M., Acid rain: Neutralization within the Hubbard Brook ecosystem and regional implications, *Science, 204*, 497–799, 1979.

Johnson, N. M., Acid neutralization by geologic materials, in *Geological Aspects of Acid Deposition*, edited by O. P. Bricker, pp. 37–54, Butterworths, Stoneham, Mass., 1984.

Johnson, N. M., R. C. Reynolds, and G. E. Likens, Atmospheric sulfur: Its effect on the chemical weathering of New England, *Science, 177*, 514–516, 1972.

Knauss, K. G., and T. J. Wolery, Dependence of albite dissolution kinetics on pH and time at 25° and 70°C, *Geochim. Cosmochim. Acta, 50*, 2481–2497, 1986.

Lasaga, A. C., Chemical kinetics of water-rock interactions, *J. Geophys. Res., 89*, 4009–4025, 1984.

Mast, M. A., and J. I. Drever, The effect of oxalate on the dissolution rates of oligoclase and tremolite, *Geochim. Cosmochim. Acta, 51*, 2559–2568, 1987.

Mooney, J., Myths of the Cherokee, 19th annual report, 1897–1898, pt. 1, *Bur. Am. Ethnolog.*, Washington, D. C., 1900.

Nickel, E., Experimental dissolution of light and heavy minerals in comparison with weathering and intrastratal dissolution, *Contrib. Sedimentol., 1*, 1–68, 1973.

Nikolaidis, N. P., H. Rajaram, J. L. Schnoor, and K. P. Georgakakos, A generalized soft water acidification model, *Water Resour. Res., 24*, 1983–1996, 1988.

Pačes, T., Rate constants of dissolution derived from the measurements of mass balance in hydrological catchments, *Geochim. Cosmochim. Acta, 47*, 1855–1863, 1983.

Reuss, J. O., B. J. Cosby, and R. F. Wright, Chemical processes governing water acidification, *Nature, 329*, 27–31, 1987.

Schnoor, J. L., and N. P. Nikolaidis, Field verification model of an alkalinity mass balance model for watersheds receiving acid deposition in the United States, paper presented at the International Workshop on Geochemistry and Monitoring in Representative Basins, Czech. Geol. Surv., Prague, Czech., 1987.

Schnoor, J. L., and W. Stumm, Acidification of aquatic and terrestrial systems, in *Chemical Processes in Lakes*, edited by W. Stumm, pp. 311–338, John Wiley, New York, 1986a.

Schnoor, J. L., and W. Stumm, The role of chemical weathering in the neutralization of acidic deposition, *Schweiz. Z. Hydrol., 48*, 171–195, 1986b.

Shanley, J. B., and N. E. Peters, Preliminary observations of streamwater generation during storms in a forested Piedmont watershed using temperature as a tracer, *J. Contam. Hydrol., 3*, 349–365, 1988.

Sjöberg, E. L., Kinetics and non-stoichiometry of labradorite dissolution, in *Water-Rock Interaction WRI-6*, edited by D. L. Miles, pp. 639–642, A. A. Balkema, Rotterdam, 1989.

Sverdrup, H., and P. Warfvinge, Weathering of primary silicate minerals in the nature soil environment in relation to a chemical weathering model, *Water Air Soil Pollut., 38*, 387–408, 1988.

Swift, L. W., Jr., G. B. Cunningham, and J. E. Douglass, Climatology and Hydrology, in *Forest Hydrology and Ecology at Coweeta*, edited by W. T. Swank and D. A. Crossley, Jr., pp. 35–55, Springer-Verlag, New York, 1988.

Velbel, M. A., Geochemical mass balances and weathering rates in forested watersheds of the southern Blue Ridge, *Am. J. Sci., 285*, 904–930, 1985a.

Velbel, M. A., Hydrogeochemical constraints on mass balances in forested watersheds of the southern Appalachians, in *The Chemistry of Weathering*, edited by J. I. Drever, pp. 231–247, D. Reidel, Hingham, Mass., 1985b.

Velbel, M. A., Influence of surface area, surface characteristics, and solution composition on feldspar weathering rates, in *Geochemical Processes at Mineral Surfaces, Symp. Ser.*, vol. 323, edited by J. A. Davis and K. F. Hayes, pp. 615–634, American Chemical Society, Washington, D. C., 1986a.

Velbel, M. A., The mathematical basis for determining rates of geochemical and geomorphic processes in small forested by mass balance: Examples and implications, in *Rates of Chemical Weathering of Rocks and Minerals* edited by S. M. Colman and D. P. Dethier, pp. 439–451, Academic, San Diego, Calif., 1986b.

Velbel, M. A., The effect of chemical affinity on feldspar hydrolysis rates in two natural weathering systems, *Chem. Geol., 78*, 245–253, 1989.

Walther, J. V., and B. J. Wood, Rate and mechanism in prograde metamorphism, *Contrib. Mineral. Petrol., 88*, 246–259, 1984.

Walther, J. V., and B. J. Wood, Mineral-fluid reaction rates, in *Fluid-Rock Interactions during Metamorphism, Adv. Phys. Geochem.*, vol. 5, edited by J. V. Walther and B. J. Wood, pp. 194–211, Springer-Verlag, New York, 1986.

White, A. F., and M. L. Peterson, Role of reactive-surface-area characterization in geochemical kinetic models, in *Chemical Modeling of Aqueous Systems II, Symp. Ser.* vol. 416, edited by D. C. Melchior and R. L. Bassett, pp. 461–475, American Chemical Society, Washington, D. C., 1990.

Wood, B. J., and J. V. Walther, Rates of hydrothermal reactions, *Science, 222*, 413–415, 1983.

M. A. Velbel, Department of Geological Sciences, Michigan State University, East Lansing, MI 48824.