SCOPE 51 - Biogeochemistry of Small Catchments

4 Weathering and Erosion Aspects of Small Catchment Research

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4.1 INTRODUCTION

Physical weathering processes mechanically break bedrock into rock fragments, exposing fresh mineral surfaces to the atmosphere and hydrosphere. Chemical weathering processes, through the action of water, CO_2 and other acidic components, cause the chemical breakdown of bedrock minerals into soil minerals and change the composition of the waters participating in these processes. Physical and chemical weathering, together with biological and biochemical processes, form soil from bedrock and strongly influence the chemical composition of natural waters. Erosive processes, primarily through the agents of running water and wind, remove the products of weathering from catchments.

Human activities and their impact (such as increased acidity of rain and deposition of acidifying oxides such as SO_2 and NO_x by consumption of fossil fuels, smelting of ore, and other industrial processes) may have a profound effect on weathering and erosion. Elevated acid inputs increase the rate of chemical weathering in catchments underlain by reactive rock types and cause acidification of water and soil in catchments underlain by non-reactive rock types. Practices used in agriculture, timber harvesting, mining and land development may significantly increase rates of erosion.

Small hydrological catchments are excellent systems in which to conduct research on factors influencing weathering and erosion, and the effects of anthropogenic perturbations on these processes. The integrated knowledge gained in small catchment studies will be broadly applicable to larger systems. This type of information is essential to policy-makers who formulate regulations for environment protection.

4.2 ROLE OF WEATHERING AND EROSION IN ECOSYSTEMS

Weathering and erosion play a major role in shaping the features of the land surface. Physical and chemical weathering convert bedrock into regolith and into the soil on which terrestrial vegetation grows. Erosional processes act to remove the products of weathering.

Chemical weathering also plays a major role in determining the composition of natural waters (Bricker and Garrels, 1967; Hem, 1985; Garrels, 1967). The chemical reactions that govern the conversion of bedrock minerals into soil minerals predict the release of dissolved constituents to the waters. By this mechanism, base cations, silica and other essential nutrients are made available to biological systems. The more reactive the minerals in the bedrock, the greater the concentration of dissolved substances in the water. Thus, the chemical compositions of natural waters strongly reflect the geology of the catchments in which they originate (Clarke, 1924; Hem, 1985; Bricker and Rice, 1989).
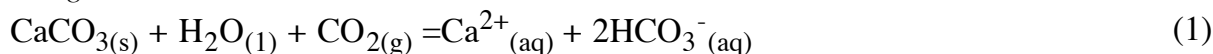
Chemical weathering may occur as a congruent or an incongruent reaction depending upon the mineral being weathered. Congruent weathering reactions dissolve bedrock minerals completely and all products of congruent reactions are dissolved species. Common examples of congruent reactions are the weathering of limestone (Table 4.1, reaction 1) and the weathering of quartzite (Table 4.1 reaction 2).

In each of these reactions, the bedrock mineral is dissolved, leaving no solid residual. There are, however, major differences in the rates and mechanisms of the reactions. Dissolution of limestone is a fast reaction dependent upon pH and temperature. Limestones and carbonaceous rocks are very effective in neutralizing acidity. Because of the high solubility of carbonates and the fast reaction rates. waters from carbonate rocks commonly contain a large amount of dissolved solids (Meybeck. 1983. 1987). Dissolution of quartzite is a very slow reaction influenced by temperature but independent of pH over the range found in most natural waters. Weathering of quartzite does not neutralize acids and. because of the low solubility of quartz and its slow reaction rate. waters from pure quartzite rocks are usually very dilute (Bricker and Rice. 1989). The difference in weathering rates of these rock types is frequently manifested in surface topographic features. In regions containing both quartzite and limestone bedrock. the quartzite usually forms ridges. or topographic highs. and the limestone forms valleys or topographic
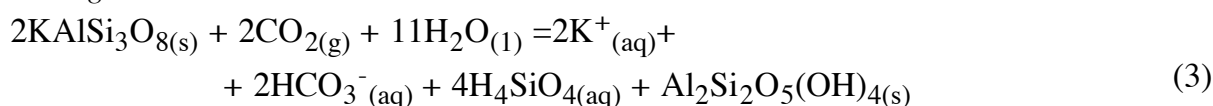
lows. due to the differential rates of weathering.

Table 4.1 Types of weathering reactions
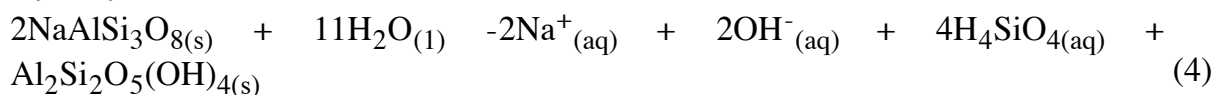
Congruent reactions

$$CaCO_{3(s)} + H_2O_{(1)} + CO_{2(g)} = Ca^{2+}_{(aq)} + 2HCO_3^-_{(aq)} \tag{1}$$

$$SiO_{2(s)} + 2H_2O_{(1)} = H_4SiO_{4(aq)} \tag{2}$$

Incongruent reactions

$$2KAlSi_3O_{8(s)} + 2CO_{2(g)} + 11H_2O_{(1)} = 2K^+_{(aq)} +$$
$$+ 2HCO_3^-_{(aq)} + 4H_4SiO_{4(aq)} + Al_2Si_2O_5(OH)_{4(s)} \tag{3}$$

Albite weathering by various agents
Hydrolysis

$$2NaAlSi_3O_{8(s)} + 11H_2O_{(1)} \quad -2Na^+_{(aq)} + 2OH^-_{(aq)} + 4H_4SiO_{4(aq)} +$$
$$Al_2Si_2O_5(OH)_{4(s)} \tag{4}$$

Carbonic acid

$$2NaAlSi_3O8(s) + 2CO2(g) + 11H_2O_{(1)} = 2Na^+(aq)$$
$$+ 2HCO_3^-_{(aq)} + 4H_4SiO_{4(aq)} + Al_2Si_2O_5(OH)_{4(s)} \tag{5}$$

Organic acid

$$2NaAlSi_3O_{8(s)} + H_2C_2O_{4(aq)} + 9H_2O_{(1)} = 2Na^+_{(aq)}$$
$$+ C_2O_4^{2-}_{(aq)} + 4\,H_4SiO_{4(aq)} + Al_2Si_2O_5(OH)_{4(S)} \tag{6}$$
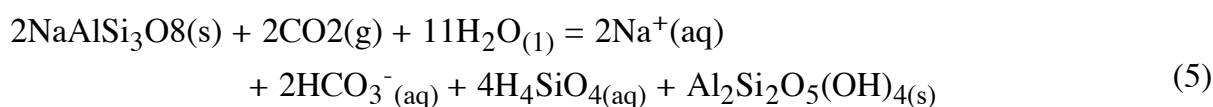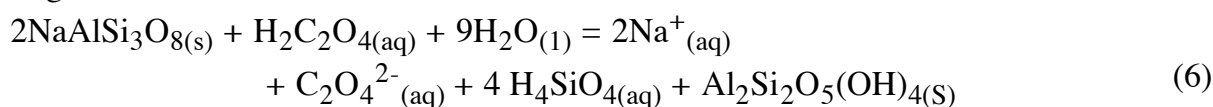
Oxalate is converted to CO_2 by microbial action:

$$C_2O_4^{2-}_{(aq)}\text{-------------------}>2CO_{2(g)} + 2e^-_{(aq)}$$
$$\text{Microorganisms} \tag{6a}$$

Strong acid

$$2NaAlSi_3O_{8(s)} + H_2SO_{4(aq)} + 9H_2O_{(1)} = 2Na^+_{(aq)}$$

$$+ \ SO_4{}^{2-}{}_{(aq)} + 4 \ H_4SiO_{4(aq)} + Al_2Si_2O_5(OH)_{4(s)} \qquad\qquad (7)$$
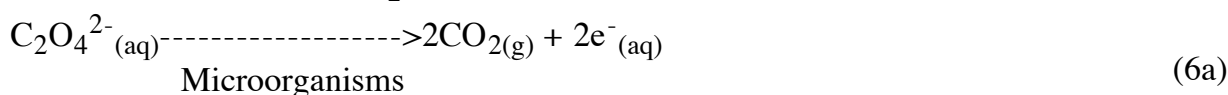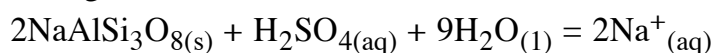
Incongruent weathering reactions produce dissolved species and new solids that are more stable in the weathering environment than the original bedrock minerals. These new residual solids are the minerals that constitute saprolite and soil (Garrels and Mackenzie. 1967). An example of an incongruent reaction is the weathering of orthoclase feldspar to kaolinite (Table 4.1. reaction 3). In this reaction $K^+{}_{(aq)}$. $HCO_3{}^-{}_{(aq)}$ and $H_4SiO_{4(aq)}$ are released as dissolved species and a new solid. kaolinite. is formed. In natural systems this reaction proceeds through many complicated steps which involve thermodynamically unstable solids such as amorphous alumina cryptocrystalline imogilite and halloysite.

Weathering occurs through the action of water on minerals. The rate of weathering is enhanced if the water contains aggressive components such as CO_2. mineral acids (e.g. H_2SO_4. HNO_3. HCl). or organic acids (e.g. oxalic. formic and malic acids). The major agent of weathering under natural conditions is CO_2. Rain in equilibrium with the CO_2 of the atmosphere contains a small amount of H_2CO_3 and has a pH value of about 5.7. Soil waters commonly contain substantially higher concentrations of H_2CO_3 than rainwater as they are formed in the environment which contains high CO_2 evelsin consequence of CO_2 production by microbial degradation of organic material (Rightmire. 1978). The major anion produced by carbonic acid weathering is $HCO_3{}^-$ (Table 4.1. reactions 1 and 3). Organic acids are ubiquitous in soils and may enhance weathering reactions (Drever. 1988; Mast and Drever. 1987). The organic anions are rapidly degraded to CO_2 by microbial activity (Table 4.1. reaction 6a) and usually are a very minor component in streamwater or groundwater. In local areas impacted by acid mine drainage or industrialized regions with serious acidic atmospheric deposition problems. H_2SO_4 may overwhelm the carbonic acid system. In these cases. sulphate becomes the dominant anion in weathering solutions. Examples of albite weathering in the presence of various agents are presented in Table 4.1. Note that weathering by strong acids produces no alkalinity.

Chemical weathering is the primary mechanism for neutralizing acidity in natural systems. Under pristine conditions. emissions of CO_2 and oxides of sulphur and nitrogen from natural sources cause rain and snow to be slightly acidic. The SO_2 and NO_x are oxidized to the strong acids H_2SO_4 and HNO_3. Enhanced emissions of these substances from burning of fossil fuels and industrial processes have greatly increased the acidity of atmospheric deposition in every major industrialized nation. Weathering reactions are able to neutralize this increased acidity in catchments developed on reactive rock types. However, the weathering reactions cannot match the increased acidity in catchments on slightly reactive rock types. Waters in these catchments then become acidic.

Several models have been developed to predict watershed response (e.g. changes in surface waters and groundwater chemistry) to acid deposition (see Section 4.3.2 below). Mineral weathering, particularly of the silicate minerals, exerts a major control on natural water composition. Understanding the reaction mechanisms and reaction rates of silicate minerals is central to modelling catchment response (see Section 4.4.1).

The depth of regolith (i.e. weathered zone in a catchment) is the product of a balance between the rate of production by weathering processes and the rate at which products of weathering are removed by erosion. Erosional processes also affect water quality. Streams draining catchments in which erosion is rapid usually contain a heavy load of suspended sediment and are turbid. Removal of weathering products at a rate greater than production reduces the soil thickness. Decrease in soil thickness leads to

decreases in water retention capacity and consequently to an increase in runoff from the catchment. Stream response to storm events is more rapid in catchments with thin soils. The opportunity for water to contact and react with bedrock minerals is greater in catchments with thin soils than in those with a thick cover of weathering products, consequently, water chemistry reflects the bedrock mineralogy more closely in these catchments.

In a study of the Amazon basin, Stallard and Edmond (1983) recognized two types of denudation regimes, weathering-limited and transport-limited. Under a weathering-limited regime, the rate of removal of weathering products by erosion is greater than the rate of production. Fresh bedrock material is continually being exposed to weathering solutions and the more reactive minerals are weathered while the less reactive minerals and residuals are removed by erosion. Solute concentrations in streams tend to be relatively high due to reactions between precipitation and fresh bedrock. Under a transport-limited regime, the rate of weathering is greater than the rate of erosion. Products of weathering accumulate and impede contact of weathering solutions with fresh bedrock. Weathering reactions decrease until the rate of production of material by weathering equals the rate of removal by erosion. Under this regime, weathering solutions primarily contact the residuals of weathering and solute concentrations in the streams tend to be low.

4.3 WEATHERING AND EROSION PROCESSES

Weathering and erosion are irreversible processes because they take place in a non-equilibrium, open system in which matter and energy are exchanged between several compartments while entropy increases. The major compartments are bedrock, regolith (including soil), water, atmosphere and biomass. Matter and energy are often exchanged in cycles, such as the biological and hydrological cycles. Sometimes the flow of matter and energy is unidirectional (e.g. in mechanical and chemical erosion). The flow in one direction is often influenced by feedback. An example of such an anthropogenic feedback is a control of erosion by agricultural protective measures.

During this complex set of irreversible processes, some partial thermodynamic chemical equilibria are maintained. Equilibrium is reached by fast geochemical reactions such as ion exchange between cations in soil solution and adsorbed cations on organic and clay particles of soil or precipitation of amorphous and cryptocrystalline alumosilicates from groundwater.

Weathering and erosion may reach a steady state, where the mass of regolith and its properties become constant with time. This steady state is being disrupted by modem man on large regional scales. Humans have increased the rate of erosion is such a way that. weathering. is not sufficiently rapid to replenish regolith and soil being removed In many regions.

A master chart of weathering and erosion processes is shown in Figure 4.1. The compartments are represented by rectangles, processes by ovals and arrows indicate fluxes of matter. The chart represents fluxes of a chemical element or component i. The compartments can be characterized by their total volume or mass and the concentrations of their chemical components.

If matter is neither accumulating nor being depleted in the regolith, a steady state is maintained. The regolith consists of residual solids and secondary solids. Residual solids are rock-forming minerals which have been subjected to mechanical decomposition, but have survived chemical weathering. Secondary solids are newly formed particles such as amorphous precipitated aluminosilicates, clay minerals and organic particles. The organic particles are the product of the decay of dead organisms. Thus, microorganisms, plants and animals are very important agents of weathering. They are especially active in formation of humic and fulvic substances in soils. Soil organic matter is a reservoir of chemical components which are recycled through the processes of biological fixation (BF_i and biological decay

(BD$_i$. Only a part of this matter is removed by harvesting of crops or lumbering of timber. This represents a biological output B$_i$.

The overall mass balance for a chemical component or element *i* during weathering and erosion is given by the following mass balance equation (see Figure 4.1.):

$$W_i + p_i + D_i + G_i + A_i - R_i - M_i - B_i = \text{Net accumulation or depletion} \tag{4.1}$$

The depletion or accumulation of a component takes place through processes such as *S$_i$, EX$_i$, BF$_i$* and *BD$_i$*.

Exact measurements of individual fluxes involved in the weathering processes are difficult and in some cases direct measurements are not possible.

The concept of a hydrological catchment which can be used to determine individual fluxes is illustrated in Figure 1.1. This field approach enables us to use different mass balance models and calculate those fluxes which cannot be measured directly in field or laboratory experiments (Giovanoli *et al*., 1989; Paces, 1983, 1985, 1986a,b; Siegel and Pfannkuch, 1984; Velbel, 1985a, 1986a,b). Catchment-based estimates of weathering rates are typically made by solving Equation 4.1 for W$_i$ and making a number of simplifying assumptions. The most common assumption made is that there is no accumulation/depletion in the regolith, e.g. steady state occurs.

4.3.1 MECHANISMS AND KINETICS

One should not be misled by the simple stoichiometric equations representing the weathering reactions. The mechanism of weathering is a complex, interlocked set of mechanical, chemical and biochemical processes. We will concentrate on geochemical processes, namely water-rock interactions.

The scheme of the irreversible interaction is shown in Figure 4.2. The interaction includes congruent dissolution of rock-forming minerals, precipitation of amorphous hydroxides and oxides, ageing and crystallization of secondary metastable minerals and, finally, production of thermodynamically stable secondary minerals. During this process, reversible adsorption, de sorption and ion exchange take place at the solution/solid interface. Each of the reactive steps progresses at a different rate. The slowest step determines the overall rate of weathering.

Two basic models describing the dissolution step are diffusive-controlled and surface-reaction-controlled processes. Both models are consistent with experimental observations that the dissolution of aluminosilicates is initially parabolic and later linear with time (Busenberg and Clemency, 1976; Chou and Wollast, 1985; Grandstaff, 1977; Luce *et al*., 1972; Paces, 1973). The master variable of both processes is the wetted reactive surface area of dissolving minerals. The reaction rate depends not only on the extent of the surface and the chemical composition of the l solution, but also on the history of the water/mineral interface, the properties of the mineral surface and the velocity with which water flows along the surface.
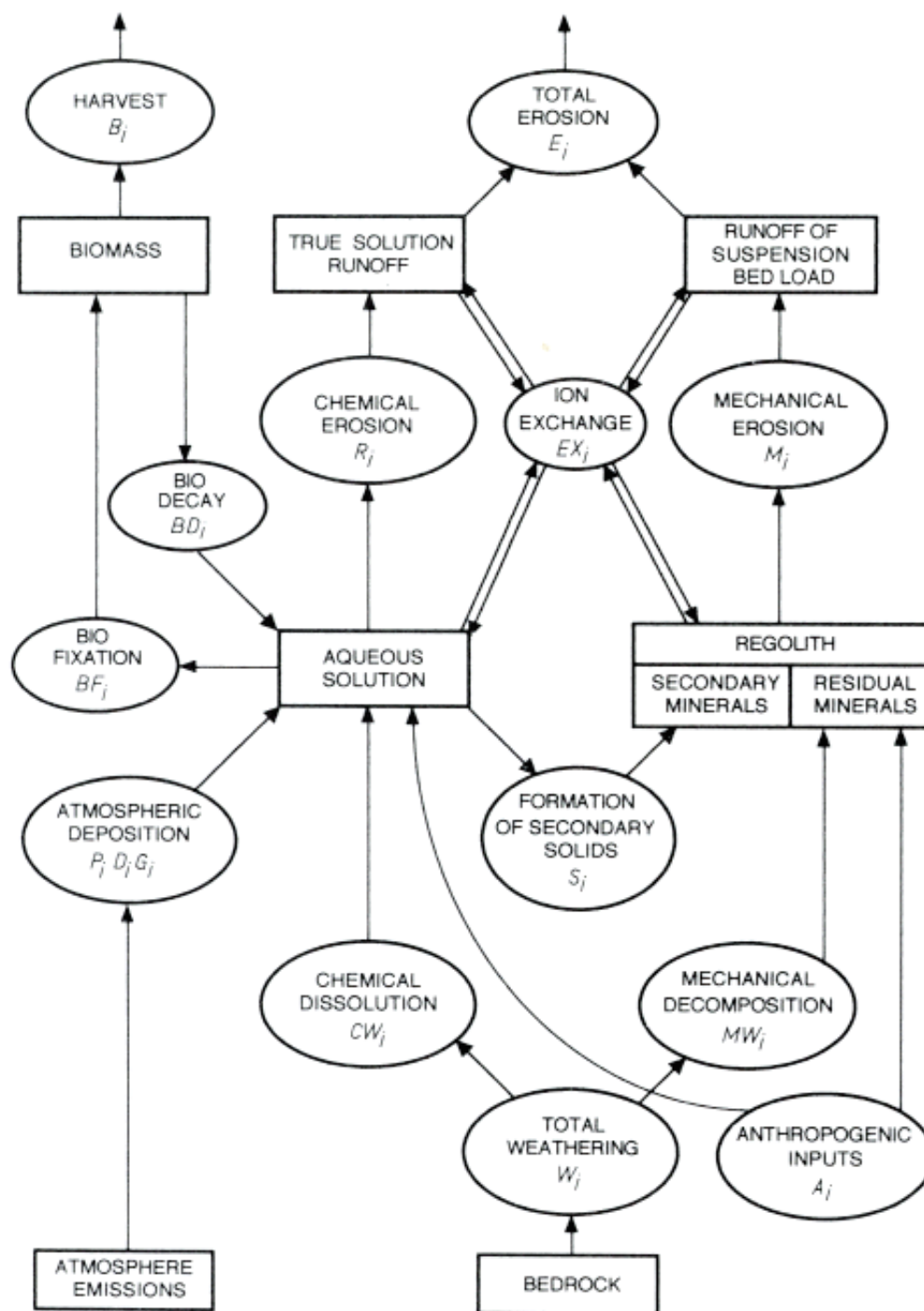
Figure 4.1 Diagram of weathering; rectangles represent compartments (reservoirs) of the systems; ovals represent fluxes of element i between the compartments and between the system and its surroundings; arrows indicate direction of fluxes (Paces, 1985; reproduced by permission of Coordinating Committee for Hydrology in Norden). The rate of flow has dimensions of mass length^{-2} time^{-1}. Common units are mol m^{-2} S^{-1} and, kg ha^{-1} year^{-1}.

The major fluxes are: W_i, release by total weathering of bedrock; CW_i, release by chemical weathering/dissolution; MW_i, release by mechanical weathering/mechanical decomposition; E_i, depletion of total erosion; R_i, depletion by chemical erosion (removal of dissolved components by runoff); M_i, depletion by mechanical erosion (removal of the components in solid particles); P_i, input of matter by

wet precipitation; D_i, input by deposition of dry particles; G_i, input of dry gases; A_i, anthropogenic input (eg. application of fertilizers); B_i, output of matter through harvesting and lumbering of timber.

Internal fluxes include: S_i, formation of secondary solids from soil solution; EX_i, ion exchange between water and soil particles; BF;, biological fixation; BV_i, biological decay.
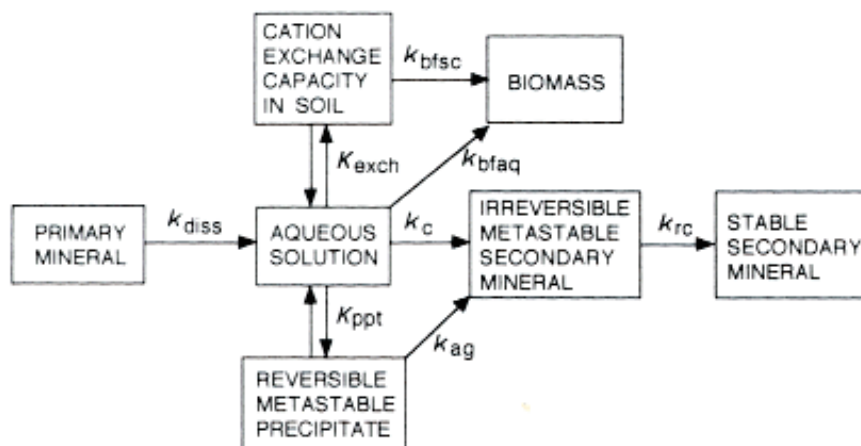

Figure 4.2 Diagram of chemical weathering of primary (rock-forming) minerals such as feldspar and formation of secondary solids and minerals such as amorphous aluminosilicate allophane halloysite and kaolinite (Paces. 1978; reproduced by permission of Pergamon Press). k_{diss}. rate constant of dissolution; k_c. rate constant of crystallization of metastable mineral; k_{ag}. rate constant of ageing of amorphous precipitate and crystallization of a secondary mineral; k_{rc}. rate constant of recrystallization of a metastable mineral into stable secondary mineral; k_{bfsc}. rate constant of biological fixation of a chemical component such as Ca^{2+} from sorption complex of soil; k_{bfaq}. rate constant of biological fixation of a chemical component such as Ca^{2+} from solution; K_{ppt}. equilibrium constant (solubility product) of amorphous precipitate; K_{exch}. equilibrium constant of ion exchange between solution and sorption complex of soil.

Surface etch pits. kinks and crystal defects affect both the mechanism and the rate of dissolution as shown by observations with the scanning electron microscope and measurements by energy dispersive X-ray spectroscopy (Bemer and Holdren, 1977, 1978). The same minerals under different conditions apparently dissolve with different mechanisms. The rate of dissolution is affected by the pH of the solution and the concentration of dissolved organic matter. although uncertainty remains regarding the strengths of the relationships (Sverdrup and Warfvinge, 1988).

Theoretical considerations of Aagaard and Helgeson (1982) and Helgeson *et al*. (1984) strongly suggest that aluminosilicates dissolve predominantly by surface-controlled reactions. The order of the kinetic laws of such reactions is fractional with respect to H^+ activity in solution. Kinetics of chemical weathering can be explained by surface coordination chemistry where the detachment of an activated surface complex is the rate-determining step of dissolution (Furrer and Stumm, 1986; Wieland *et al*., 1988).

Discrepancies still exist between the dissolution rates determined by laboratory experiments with crushed minerals and the dissolution rates derived from field measurements of elemental mass balance in small hydrological catchments. The relationship between these two methods of rate determination is expressed by the equation relating the rate constant of mineral dissolution to the measurements of flux of dissolved

elements from a hydrological catchment (Paces, 1983):

$$k_{Na} = \frac{W_{Na}}{n \times s \times H \times P} \qquad\qquad 4.2$$

where k_{Na} is the dissolution rate of sodium feldspar expressed as release of Na^+ in mol m^{-2} $year^{-1}$, based on mineral surface area. The rate is related to the reacting wetted surface of feldspar. W_{Na} is the dissolution of sodium from bedrock in the catchment derived from the steady-state (S = 0) mass balance equation $W_{Na} = R_{Na} + M_{Na} + B_{Na} -P_{Na} -A_{Na}$. All fluxes are in mol m^{-2} $year^{-1}$ related to the Earth's surface, n is the dimensionless fraction of rock surface occupied by reacting feldspar, s is the specific wetted surface area of rock (in m^{-2} m^{-3} related to the volume of percolating water), H is the mean thickness of the permeable layer in the catchment and p is the dimensionless porosity of water-saturated rock.

The rate constant k determined from the field data has the same dimension as the rate constant determined by laboratory dissolution experiments, hence these two rate constants derived from independent measurements should be comparable.

Table 4.2 indicates that comparative studies performed by many researchers show repeatedly that the apparent dissolution rate of feldspar derived from field measurements of mass balance is one to two orders of magnitude slower than the rate determined by laboratory experiments. The discrepancy is attributed to our insufficient knowledge of the properties and extent of the reactive surface areas of weathered minerals in the field and of inadequate data on hydrological control of the reactions due to macropore and micropore flow through soil and subsoil in the unsaturated zone.

4.3.2 MODELLING

Modelling is an important component of small catchment studies because models link information obtained from laboratory and field observation with theory (Chen *et al*., 1983; Furrer *et al*., 1989; Velbel, 1986a). The importance of modelling is especially evident when considering the weathering processes. Generally, estimates of weathering rates in small catchments are obtained from the chemical analyses of soil, soil water and surface water. However, a great number of reactions and edaphic factors combine to regulate soil and water chemistry. Carefully constructed element balances can be used to estimate the amount of an element released in weathering reactions, but some sort of model is required to estimate the rates at which individual reactions proceed.

A second important role of modelling is the development of hypotheses. Combining information gained from field studies with a biogeochemical model allows a researcher to expand the scope of a study beyond a specific site. This process involves three steps: (1) calibration of the model for conditions at the site; (2) validation of the model; and (3) gaming with the model. During the gaming phase, the model can be used to simulate systems slightly different from the study. For example, the depths of soil horizons could be varied to estimate changes in weathering rates based on soil morphology. Potential changes in weathering rates due to climate change can be estimated by introducing small changes in soil temperature and moisture regime.

Table 4.2 Comparison of laboratory and field weathering rates (after Schnoor, 1990)

Mineral	Laboratory weathering rate (mol Si m^{-2} S^{-1})	Field-estimate weathering rate (mol Si m^{-2} S^{-1})	Field-measured cation export (eq ha^{-1} year^{-1})	Cation(s)	Notes	Reference
Plagioclase (oligoclase)	5 x 10^{-12a}	3 x 10^{-14}	210	Na$^+$	Tmavka River Basin, (CR)	Paces (1983)
Plagioclase (oligoclase)	5 x 10^{-12a}	8.9 x 10^{-13}	350	Na$^+$, Ca^{2+}	Coweeta Watershed, NC (USA)	Velbel (1985a)
Almandine		3.8 x 10^{-12}	300	Mg^2, Ca^{2+}		
Biotite		1.2 x 10^{-13}	150	K$^+$, Mg^{2+}		
Plagioclase (bytownite)	5 x 10^{-12a}	5 x 10^{-15}	330	Ca^{2+}, Na$^+$	Filson Creek, MN (USA)	Siegel and Pfannkuch (1984)
Olivine	7 x 10^{-12b}	1 x 10^{-13}	310	Mg^{2+}		
Plagioclase, epidote, biotite		6 x 10^{-14}	200	Ca^{2+}, Na$^+$, K$^+$	Cristallina, Switzerland	Giovanoli *et al.* (1989)
Plagioclase, biotite	6 x 10^{-12}	9 x 10^{-15}	960	Ca^{2+},Na$^+$	Bear Brooks Watershed Maine (USA) Assumption: 50 cm saturated regolith, 0.5 m^2 g^{-1} surface area of mineral grains measured, 40% of mineral grains active in weathering	Schnoor, 1990

[a] Rate detennined in the laboratory by Busenburg and Clemency (1976) and Mast and Drever (1987) at pH 4.

[b] Rate determined in the laboratory on beach sand by Grandstaff (1986) at pH 4.5.

The development of weathering models applicable to catchment research has suffered from differences of perspective between Earth and ecosystems scientists. Earth scientists have a long tradition of studying weathering and denudation as a control on water chemistry (Reade, 1876; Clarke, 1910). Recent models developed from this perspective tend to be complex and require information which is difficult, if not impossible, to measure in a catchment (e.g. specific surface area of a mineral phase). On the other hand, recent interest in the acidification of surface waters and soils has resulted in the development of general-purpose biogeochemical models in which weathering is one of several element "inputs". Models developed from this perspective tend to oversimplify the weathering process. The gap between these two perspectives is gradually narrowing and the development of models suitable for estimating weathering rates in the field is currently one of the most active areas of research in weathering (Velbel, 1985a; Santore and Driscoll, 1991; Sverdrup and Warfvinge, 1988).

4.3.2.1 Weathering in biogeochemical models

Computer models developed to simulate watershed biogeochemical processes have modelled weathering with varying degrees of complexity. Models of this type are either lumped parameter models or process-oriented models. Eary *et al*. (1989) compared the overall structure and performance of three well-known watershed biogeochemistry models (MAGIC II, ETD and ILWAS-see below). The weathering formulations for several prominent biogeochemical models, including those reviewed by Eary *et al*. (1989), are given in Table 4.3. In general, the rate of weathering, or mineral dissolution is expressed in these models as a function of hydrogen ion (H^+):

$$\text{Rate} = dM_i[dt] = k_i[H^+]^n \tag{4.3}$$

Where M_i is the mass of mineral i, k_i is the rate constant for the weathering reaction associated with mineral, $[H^+]$ is the concentration of hydrogenion, and n is the fractional order of the weathering reaction with respect to hydrogen ion.

Lumped weathering rates (MAGIC, ETD)

The latest version of the Model of Acidification of Groundwater in Catchments (MAGIC II; Cosby *et al*., 1985a,b) and Enhanced Trickle Down models (ETD;

Table 4.3 Formulation of weathering terms in several catchment-based biogeochemistry models (after Eary *et al*., 1989)

Model	Model type	Weathering formulation	
		Input	Output
Reuss-Johnson	Lumped parameter, steady-state	None	None

MAGIC II	Lumped parameter, steady-state	$[H^+]$	$d[X]/dt$
ETD	Lumped parameter, steady-state	$[H^+]$, A_s, Q_w	$dANC/dt$
ILWAS	Process-oriented, dynamic	$[H^+]$, M_i	dM_i/dt
STEADYQL	Process-oriented, steady-state	$[H^+]$, Q_w	Q_x
MANE	Process-oriented, dynamic	$[H^+]$, M_i, Q_w	dM_i/dt, Q_x
PROFILE	Process-oriented, steady-state (weathering only)	$[H^+]$, q, As	dM_i/dt, Q_i

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X-any element X
A_s-surface area of weathering mineral(s).
Q_w-water flux in soil.
ANC-acid-neutralizing capacity.
M_i-mass on mineral i.
Q_x,-flux of element x from weathering reactions.
q -soil moisture content.

Schnoor *et al*., 1986; Nikolaidis, 1987) are lumped-parameter models which view weathering as a source of base cations (MAGIC) or, in the case of ETD, acid-neutralizing capacity (ANC). Site-specific data are used to estimate weathering rates (release of base cations or ANC) and the order of the generalized weathering reaction with respect to H^+. Neither model is capable of estimating rates of dissolution of individual minerals. However, MAGIC II can estimate weathering fluxes of individual base cations, whereas ETD can only estimate an ANC flux associated r with weathering.

Individual mineral weathering (STEADYQL, ILWAS, MANE)

Process-oriented biogeochemistry models are generally more sophisticated in their treatment of chemical weathering. The Integrated Lake Watershed Acidification Study (ILWAS; Chen *et al*., 1983; Goldstein *et al*., 1985; Gherini *et al*., 1985) and STEADYQL (Furrer *et al*., 1989, 1990) models are biogeochemical models which can consider individual mineral equilibria, formation of secondary minerals and reaction thermodynamics. The ILWAS model is a dynamic (i.e. non-steady-state) model capable of estimating weathering rates for as many as five minerals. During calibration of the model, values of the rate constants for the weathering reactions are adjusted to explain observed base cation and silica concentrations in streamwater. These adjustments can result in awkward estimates of weathering rates during simulations.

The STEADYQL model is a steady-state equilibrium model which builds a system of linear equations based on inputs and outputs of acidity to the soil or soil solution. Thus, any watershed process (e.g. biomass uptake or mineral weathering) can be written as a reaction involving production or consumption of hydrogen ion (H^+) and other cations and anions. The rate constants and fractional dependencies of the reactions with respect to H^+ must be specified and are not adjusted by the model.

Another approach in adapting chemical equilibrium models to catchment studies is through the development and linkage of separate, stand-alone modules for each of the major catchment processes. For example, Santore and Driscoll (1991) have designed a Multiphase, Aqueous, Non-steady-state, Equilibrium model (MANE) for modelling chemical processes in natural, aqueous systems. The core of the MANE model is a chemical equilibrium model which can solve aqueous speciation reactions, and surface reactions such as adsorption and exchange, which are fast enough to assume that they will always be at equilibrium. For slow processes such as weathering, a kinetic formulation is used.

The kinetic formulations used in the MANE model make use of chemical information to allow reaction rates to depend on such information as pH, ligand concentration or surface complexation. As substances are released from one pool (e.g. through weathering or ion exchange), they are allowed to participate in other reactions. This interdependence between reactions in the aqueous and solid phases allows the incorporation of a wide variety of reaction mechanisms.

Ultimately, the MANE model is designed to be linked with a vegetation dynamics model (VEGIE Vegetation Effects on Geochemistry in Ecosystems; Aber *et al*., 1991) and a hill slope hydrology model (COMPHY; C. Anthony Federer, US Forest Service, Durham, New Hampshire, USA, unpublished) to form an integrated watershed biogeochemistry model. This model differs from other integrated models such as ILWAS because it incorporates three stand-alone modules, rather than linking many subroutines.

4.3.2.2 Detailed weathering models (PROFILE)

There are few models available which were developed exclusively to estimate weathering rates in catchments. Most notable is PROFILE (Sverdrup and Warfvinge, 1988; Sverdrup, 1990), a steady-state model which extrapolates reaction rate data from the laboratory setting to field conditions. The PROFILE model uses transition state theory, which assumes that the weathering rate is controlled by the formation and decomposition of an "activated complex". Thermodynamic constants are adjusted for temperature and estimates of soil moisture by depth, mineral abundance and mineral surface area are required. Estimates of the release of elements in weathering can be compared with estimates based on other methods (see Section 4.1). Sverdrup and Warfvinge (1988) compared estimates of weathering release of base cations based on PROFILE simulations and element mass balances for three catchments in southwestern Sweden. They found remarkably close agreement for the sum of base cations, although PROFILE produced lower estimates for Mg and higher estimates for K than the element balance method. A dynamic (non-steady-state) version of the PROFILE model called SAFE is currently being tested in connection with catchment measurements (Warfvinge and Sverdrup, 1991).

4.4 METHODS USED TO DETERMINE RATES OF WEATHERING AND EROSION

4.4.1 ESTIMATION OF WEATHERING RATES

Weathering rates have been estimated using a number of different techniques (Velbel, 1985a; Williams *et al*., 1986; Schnoor, 1990; Paces, 1983, 1986a; Clayton, 1986; April *et al*., 1986).

Cronan (1985) compared six different methods for estimating weathering rates on three forest soils from

the northeastern USA. In a soil column study, he calculated weathering rates by: (1) "maximum" mass balance (assuming no change in exchangeable cation pools); (2) "minimum" mass balance (assuming net depletion of exchangeable cations); (3) Na flux with congruent dissolution; and (4) Si flux with congruent dissolution. For a Becket Spodosol (a common soil type in the northeastern USA), these estimates were compared with weathering rates based on: (5) catchment mass balances for Woods Lake, NY, USA and Hubbard Brook Experimental Forest (HBEF), New Hampshire, USA; and (6) the cation depletion estimates of April *et at*. (1986). The estimates of weathering rates varied by nearly two orders of magnitude for a given soil type. The large difference between estimates of weathering using the "maximum" and "minimum" mass balances illustrates the importance of assessing changes in exchangeable cation pools when using mass balances to compute weathering rates (see also Paces, 1986a; Wright, 1988).

4.4.1.1 Discrepancy in mass balance

Field-based weathering rates are difficult to measure directly and are generally determined by differences in element mass balances (e.g. Garrels and Mackenzie, 1967; Bricker *et al.*, 1968; Reynolds and Johnson, 1972; Cleaves *et al.*, 1970, 1974; Paces, 1983). Uncertainties associated with mass balance calculations are often compounded when investigators assume that vegetation, forest floor or soil pools are at steady-state (Cronan, 1985; Paces, 1986a; Wright, 1988). If any of these assumptions is inappropriate, estimates of weathering will be in error by a corresponding amount.

4.4.1.2 Indicator elements (Na, Si)

Weathering studies based on element mass balances have often focused on elements that are presumed to have limited interaction with other ecosystem processes (e.g. Paces, 1983, 1986b; Siegel and Pfannkuch, 1984; Clayton, 1986). Paces (1985, 1986a) pointed out that dissolved Si or Na can be used because it is generally assumed that they are not accumulated in plant tissues nor retained in large quantities in the soil sorption complex.

Researchers have extended the catchment mass balance approach by determining mineral chemistry and deducing the stoichiometries of individual weathering reactions (Paces, 1985, 1986a,b; Velbel, 1985a,b, 1986a; Clayton, 1986; Williams *et al.*, 1986). The weathering rates of individual minerals can be estimated by solving a system of linear equations when the number of hypothesized weathering reactions equals the number of elements for which reliable mass balances exist (Plummer and Back, 1980).

4.4.1.3 Soil profile depletion

Newton and April (1982) and April *et al*. (1986) studied weathering in glacial tills in two forested watersheds in the Adirondack region of New York, USA, using a different type of mass balance approach. They assumed that the mineral and chemical composition of the soil immediately following deglaciation equalled that of the unweathered till present today. Thus, at any depth, the difference in base cation (Ca, Mg, K, Na) concentrations between the current soil (base-poor) and the unweathered till (base-rich) could be due to weathering. Depletion of base cations was then summed for the entire profile to estimate average weathering rates for the period since glaciation. They found that current weathering rates determined by element mass balances were considerably greater than the historical average. They attributed this difference to enhanced cation leaching due to acidic deposition. However, changes in vegetation and climate could also have contributed to these differences.

4.4.1.4 Strontium isotopes

Strontium isotopes hold great promise as a means of estimating weathering rates (Jacks *et al*., 1989; Wickman and Jacks, 1991). Because of their high atomic weights, Sr isotopes are not fractionated by

biological processes (Graustein, 1989). Thus, variations in Sr isotopic ratios reflect variations in contributions from different sources. In forest ecosystems, the ultimate sources of Sr in streamwater are chemical weathering of parent materials (including rocks, till and soils) and atmospheric deposition.

^{87}Sr/^{86}Sr ratios for precipitation are generally close to seawater (0.709), ranging from 0.7088 to 0.7200 (Dasch, 1969; Gosz *et al*., 1983; Graustein and Armstrong, 1983). If parent material has an isotopic ratio distinct from precipitation, then Sr isotope ratios in streamwater can be modelled as a mixture of the two sources:

$$^{87}\text{Sr}/(^{87}\text{Sr}+^{86}\text{Sr})_{\text{PM}}x + {}^{87}\text{Sr}/(^{87}\text{Sr}+^{86}\text{Sr})_{\text{PR}}(1-x) = {}^{87}\text{Sr}/(^{87}\text{Sr}+^{86}\text{Sr})_{\text{S}} \qquad (4.4)$$

where PM refers to parent material, PR refers to precipitation and S refers to streamwater. This equation may be solved for x to determine the proportion of Sr in streamwater which was released from the weathering of parent material. The precision of the estimate of x depends on the variability of the ^{87}Sr/^{86}Sr ratios for the two sources. The rate of parent material weathering can be estimated if the streamwater efflux of Sr and the bulk Sr content of the parent material are known (Aberg *et al*., 1989; Jacks *et al*., 1989; Wickman and Jacks, 1991).

4.4.1.5 Weathering bags

Weathering rates have been estimated using small (*c*. 5 x 10 cm) porous bags containing mineral or rock fragments (Berthelin *et al*., 1990). These are buried in the soil profile and removed after several years. The contents of the bags may be reanalysed and the rate of release of elements determined. The advantage of this method is that the often substantial variability of soils and parent material is negated since the chemical composition of the contents of the bags is known. However, disturbance of the soil profile around the bags and differences in the small-scale weathering environment in the field may lead to problems interpreting the data.

4.4.1.6 Laboratory experiments

Weathering rates of minerals determined in the laboratory have been recently extrapolated to the watershed level by Sverdrup and Warfvinge (1988). Paces (1983), Velbel (1986b) and Schnoor (1990) have compared laboratory weathering rates with field measured values and have explained the existing discrepancies by: (1) the artificial treatment of mineral surfaces in the laboratory leading to more reactive fresh surface than exists in nature; (2) uncertainty in the measurement of the area of reactive mineral surfaces in the field; (3) greater wetted surface area of minerals in the laboratory than in the field; and (4) higher temperatures in laboratory experiments than occur in nature.

4.4.2 ESTIMATION OF EROSION RATES

Measurement of erosion and sediment yield from catchments rely on a wide range of field-based techniques (Hornung, 1990). These can be broadly divided into methods for estimating sediment erosion on slopes and in river channels and methods for measuring sediment yield from catchments (Gregory and Walling, 1973). Errors in measurement are usually unavoidably large because of the localized nature and unpredictability of many types of erosion. Aeolian erosion is usually not quantified in the calculation of sediment losses from catchments.

Techniques for measuring hill slope erosion processes vary from erosion frames, plots and traps to erosion pins and stakes. Specific techniques are selected according to whether the desired objective is to measure mass movement, gully erosion or surface lowering. Remote techniques involving surface or aerial photography have been used for erosion studies of small topographic features or whole catchments (Thomas *et al*., 1986; Dymond and Hicks, 1986). Isotope studies have also been used to quantify surface erosion. For example, Walling and Quine (1990) have used the distribution of ^{137}CS to study erosion and deposition rates in arable land in Britain.

Measurements of sediment yields and erosion rates in rivers are usually very different from measurements of hill slope erosion, and Walling (1983) has suggested that only 10% of the sediment eroded in a drainage basin will reach the catchment outlet. This highlights the need to measure hill slope erosion rates if meaningful comparisons are to be made with weathering rates.

4.5 SUMMARY

Weathering and erosion are major processes affecting the shape of the land surface, the development of soils and the chemical composition of natural waters. The balance between rates of weathering and rates of erosion determines the thickness of the regolith and soil mantling bedrock.

Understanding of mineral weathering rates and mechanisms has increased rapidly during the past decade, however the large discrepancies between weathering rates determined in laboratory studies and these observed in catchment investigations have not yet been adequately explained. Similarly, significant advances have been made in modelling surface water chemistry in catchments, but a major problem in model development has been the lack of data on mineral weathering rates. Active research in mineral dissolution kinetics coupled with parallel developments in catchment modelling is beginning to bridge this gap.

The processes of physical weathering and erosion remove particulate matter from catchments. This particulate matter is carried as suspended and bed load by streams and rivers. Measurement of erosion rates based on the sediment load of rivers is usually significantly less than predicted from measurements of hill slope erosion in catchments. Further research is needed to quantify the rates of hill slope erosion and reconcile these differences.

4.6 SUGGESTED READING

Recent publications dealing with weathering and erosion in relationship to small catchment research include volumes of Colman and Dethier (1986) and Drever (1985). European studies were summarized in the *Journal of Geological Society* (London), Volume 143. Scandinavian countries held a symposium on weathering studies (Rosen, 1991). A summary of field studies and their discussion is included in Sverdrup (1990). Authoritative papers dealing with topic of weathering appear regularly in *Geochimica et Cosmochimica Acta*.

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