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MINERAL TRANSFORMATIONS AND GEOCHEMICAL MASS BALANCE OF A DISTURBED FORESTED WATERSHED

By

Allan Beowulf Taylor

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

MINERAL TRANSFORMATIONS AND GEOCHEMICAL MASS BALANCE OF A DISTURBED FORESTED WATERSHED

By

Allan Beowulf Taylor

A geochemical mass balance model developed for use on undisturbed forested watersheds is modified and applied to a clear-cut watershed. The results of this study indicate that although the mineral weathering <u>reactions</u> of biotite, garnet and plagioclase (as determined by petrographic microscope, SEM, and XRD) appear to be equivalent between the clear-cut and undisturbed watersheds of equivalent rock type, mineral weathering <u>rates</u> one year after clear-cutting are approximately 20% faster than pre-clearcut calculated values. Decomposition of clear-cut litter, liming, and fertilization of the clear-cut watershed were found to introduce some uncertainty into the mass balance model. Small increases in soil temperature resulting from clear-cutting are calculated to increase the weathering rate of plagioclase by amounts comparable to those calculated by the mass balance model at one year after clear-cutting.

Mineral weathering rates calculated using a well constrained botanical uptake term are significantly higher than rates calculated assuming that the effect of biomass is negligible (steady state assumption). To Deborah, mother, and father (the vicarious one).

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Chapter 1

INTRODUCTION

The purpose of this research is to adapt and modify a current formulation of a geochemical mass balance model developed for use in undisturbed forested watersheds for use on a watershed whose biomass system has been dramatically disturbed. More specifically, this research seeks to answer the following questions:

1) Are mineral weathering reactions the same on two adjacent watersheds of similar bedrock geology, if the biota of one of the watersheds has been disturbed? In particular, does the disturbance of the terrestrial ecosystem of a experimental watershed result in changes in mineral weathering reactions and/or rates as compared with those occurring in a control watershed on the same parent material but whose terrestrial ecosystem has remained undisturbed?

2) What is the significance of the botanical uptake term in the output of mass balance calculations? The extension of the mass balance technique to a disturbed watershed where the biomass aggradation is known and measured should provide valuable information and constraints on the importance of the botanical uptake term in mass balance calculations. Additionally, the extension of this technique to a disturbed watershed will allow an evaluation to be made on the usefulness of conventional mass balance models as applied to watersheds with disturbed forested ecosystems.

In order to answer these questions it will also be necessary to examine in some detail the composition and weathering of some of the rock-forming minerals which occur in the study area.

Background

Small watersheds have long been recognized as valuable natural laboratories in which weathering and erosion, nutrient cycling, ecosystem dynamics, and other biogeochemical processes can be studied in a "real world" environment (Bormann and Likens, 1967). Geochemical mass balance studies performed on hydrologically tight, small watersheds are widely recognized as the most reliable means of measuring mineral weathering rates and other geochemically significant processes in nature (Clayton, 1979).

The geochemical mass balance model which is used in this study was developed by Velbel (1985a) for undisturbed watersheds located in the Southern Appalachians at the United States Department of Agriculture (Forest Service) Coweeta Hydrologic Laboratory.

Velbel (1984a, 1985a) chose six watersheds on the basis of management history, amount of hydrogeochemical data available from the Forest Service, bedrock type, mean annual discharge, and proximity to preexisting cores and wells. Undisturbed (control) watersheds were used in order to minimize variability due to botanical factors. Emphasis was placed on deep saprolite rather than surficial soils

in order to minimize problems associated with biological processes such as bioturbation, Fe and Al chelation by organic ligands and biogeochemical cycling of nutrients (Likens et al., 1977; Velbel, 1985a).

Velbel (1985a) concluded that four processes significantly modify the dissolved mineral nutrient reservoirs of sodium, magnesium, calcium, and potassium in these six watersheds at Coweeta Hydrologic Laboratory. These processes are the mineral weathering of three rock forming minerals (plagioclase feldspar, biotite mica, and almandine garnet) and the uptake of these nutrients by forest biota. Velbel (1985a) was able to calculate the mineral weathering rates of the above mentioned minerals in moles of mineral weathered per hectare of watershed per year. The details of this model are presented in Chapter 3.

This Study

Previous mass balance models (Velbel, 1985a; Cleaves et al., 1970; Johnson et al., 1968; etc.) have attempted to minimize the influence of botanical factors by dealing almost exclusively with undisturbed watersheds with presumably stable terrestrial ecosystems or ecosystems with negligible biomass.

In contrast to previous mass balance studies which have attempted to minimize the influence of the biomass state on the dissolved mineral nutrient reservoir, this investigation concentrates on a watershed whose terrestrial ecosystem has been dramatically disturbed. The influence of this disturbed

ecosystem on the dissolved mineral nutrient reservoir is presumably non-negligible. This provides the opportunity to observe the effects of a perturbed biomass on the weathering reactions and rates in this biogeochemical system as calculated by this model, and to compare these "disturbed rates" to undisturbed or control rates as calculated by this model. A previously studied control watershed adjacent to the disturbed watershed is reexamined in order to confirm Velbel's (1984a, 1985a) previous work on undisturbed watersheds, and allow a more meaningful comparision to be made between the disturbed and undisturbed watersheds.

Velbel's (1985a) model is used with modification of the biomass uptake term to determine weathering rates of minerals in a disturbed watershed. In this study mineral weathering rates are calculated for five years after the experimental watershed (WS-7) was clearcut and cable logged. An adjacent undisturbed control watershed (WS-2) is also evaluated. Mineral weathering rates in WS-2 were previously calculated by Velbel (1985a). Mineral weathering rates in WS-7 have not been previously determined.

The Study Area

The watersheds used for this study are located in the United States Forest Service Coweeta Hydrologic Laboratory (Figure 1-1). Coweeta is located about 10 miles SW of Franklin, North Carolina, and comprises approximately the SW quarter of the U.S.G.S. Prentiss, North Carolina 7 & 1/2 minute quadrangle. Coweeta is in the Nantahala mountains,

Figure 1-1

Location and geologic setting of Coweeta Hydrologic Laboratory.



adapted from Velbel (1985a)

part of the Blue Ridge Province of the Southern Appalachians.

Coweeta has been a site of major hydrologic research since 1924. Nutrient cycling was added in 1968 (Monk, 1977). Experimental watersheds are paired with control or unmanipulated watersheds. No fires or cutting operations have been conducted in the control watersheds since the Forest Service acquired all rights to the area in 1924 (Johnson and Swank, 1977).

This study utilizes the experimental/control watershed pair, watershed-7 (WS-7) and watershed-2 (WS-2). WS-7 is the disturbed watershed used in this study. This watershed is 59 hectares in areal extent, has a south facing aspect, and ranges in elevation from 720 to 1065 meters. Slope varies from 23 to 81% (Boring et al., 1981).

WS-2 (the control watershed to be restudied) is a smaller watershed adjacent to WS 7 on the eastern side. WS-2 is 12.1 ha in areal extent, ranges in elevation from 716 to 1005 meters, has a south facing aspect, and is similar in slope to WS-7.

The land use of WS-7 has been limited prior to the current experimental manipulation. The land use history of WS-7 between 1941 and 1949 (Boring et al., 1981) is as follows: Six head of cattle were used to assess the impact of woodland grazing on forested watersheds. The short range effects of this experiment were limited primarily to soil compaction and overgrazing in the cove area adjacent to the stream. Little lasting impact from the study was apparent.

After 1949 the watershed remained undisturbed for the next 28 years.

During the winter of 1976-1977 approximately 16.4 ha of the watershed were clearcut and cable-logged. The remainder of the watershed was cleared by this method the following spring. The cutting operation consisted of removing marketable timber by cable logging and felling all other stems. Although one small area was logged by tracked skidder, the vast majority of timber removal was by cable. All logging debris was left in place with no further site preparation. Soil compaction and other structural disturbances of the forest floor and plant roots were minimized by this technique. Biomass has been in a phase of active regrowth since the cessation of the logging operation.

WS-2 is directly adjacent to WS-7 on the eastern side. WS-2 is similar in all aspects to WS-7 with the exception of having remained undisturbed (other than road building and stabilization) since the Forest Service acquired all rights to Coweeta in 1924 (Johnson and Swank, 1973).

Day (1974) has reported mean annual temperatures of 12.8°C and average annual precipitation of 181 cm.

Sampling of the study area was conducted during the summer of 1985. Twenty-two sampling locations were utilized - twenty on WS-7 (the clearcut watershed) and two on WS-2 (the control watershed). Where possible a suite of samples was taken in an attempt to accurately represent the entire exposed weathering profile on these two watersheds. This

involved sampling the exposed weathering profile from top to bottom, collecting samples of soil from just below the root zone, saprolite samples, and where possible relatively unaltered bedrock samples. The distribution of the sampling sites is shown on Figure 1-2. Sample preparation and analysis techniques are detailed in Appendix A.

Bedrock Geology

The deep soils and saprolites characteristic of this part of the Blue Ridge province dominate the landscape at Coweeta. Parent rock consisting principally of schists and gneisses has weathered to leave a deep mantle of saprolite. Saprolite is a friable, decomposed, bedrock which has retained much of its original volume although a great deal of its mass has been lost.

Velbel (1985a) has described saprolite as "residual soil developed on crystalline rock in which some or all of the primary minerals have been transformed in situ into weathering products." Thus, primary textures and fabrics of the rock are retained upon saprolitzation permitting identification of the parent material and subsequent correlation with secondary products. Additionally, the spatial distribution of the secondary products with respect to the parent materials can be determined. This allows weathering reactions can be determined with relative ease and certainty.

The soil types present at Coweeta have been described by Boring et al. (1981) as follows: At lower elevations the

dominant soil series is the Tusquitee, a member of the fine loamy, mixed, mesic family of the Humic Hapludults. The ridges and slope soils are dominated by the Chandler series, a member of the coarse loamy, micaceous, mesic family of typic Dystrochrept.

Rock outcrops generally occur on steep slopes at higher elevations, probably as a result of more efficient mass wasting in these steeper areas. Essentially two major rock units occur in the study area: the Coweeta Group and the Tallulah Falls Formation. The older and mineralogically less mature Tallulah Falls Formation has been thrust eastward over the younger and mineralogically more mature Coweeta Group. The trace of the Shope Fork Fault as mapped by Hatcher (1979b) runs several hundreds of meters south of of the outlets of the watersheds of interest in this study. No hydrothermal or other fault-related alteration was observed of the rocks in WS-2 and 7 in thin section.

WS-2 and WS-7 have developed principally on the Tallulah Falls Formation. This formation is a heterogenous package of rock consisting principally of metagraywackes, pelitic schists, and metavolcanic rocks, which were derived mainly from sedimentary protoliths of low mineralogical maturity. The mineral assembleges shown in Table 1-1 indicate amphibolite facies metamorphism, which Hatcher (1979b) has associated with the Ordovician Taconic Orogeny.

An additional unit is mapped by Hatcher (1979b) as impinging slightly on the western boundary of WS-7. The Carroll Knob mafic complex is composed of hornblende gneiss

Table 1-1

Common Lithologies of the Tallulah Falls Formation and Their Mineralogies

• •

Member	Lithology	* Mineralogy
Quartzite Schist	Quartzite Schist	Q,M,P,Mi,B,C (Mt,Z,T,E) M,B,Q,P, (Mt,T)
Graywacke-Schist	Metagraywacke Schist	Q,B,P (M,Mt,S,Z,A,T,E,G) M,B,Q,P (Mt)
Garnet-Aluminous Schist	Aluminous Schis [.] Metagraywacke Amphibolite	t M,G,Q,K (or Si) P,B (Mt) Q,B,P,M (Mt,S,Z,A,T,E,G) H,P,Q (E,Mt,G,S,A,B)
Graywacke-Schist Amphibolite	Metagraywacke Schist Amphibolite	Q,B,P (M,Mt,S,C,A,T,E,G) M,B,Q,P, (Mt) H,P,Q (E,Mt,G,S,A,B)
Q = Q $P = P$ $Mi = M$ $M = M$ $B = B$ $K = K$ $Si = S$ $S = S$	puartz Plagioclase Microcline Muscovite Motite Myanite Myanite Myanite Myanite	<pre>E = Epidote (or clinozoisite) Mt= Magnetite H = Hornblende A = Apatite T = Tourmaline Z = Zircon G = Garnet</pre>

* Minerals listed in order of decreasing abundance.

(From Hatcher, 1976)

and amphibolite which were derived from the original mafic rocks of the complex. Detailed petrographic and mineralogical work on this unit has recently been completed (Velbel, in review). This unit was not observed during fieldwork.

The heterogenous nature of the bedrock combined with the structural complexity of the area eliminates the possibility of making any estiminate of the absolute or relative abundance of rock types. For the purposes of this mass balance study it is only necessary that the minerals used in the mass balance calculation be present in excess of the amounts of the minerals calculated to be weathering by this model.

Hydrogeology

The nature of the hydrology at Coweeta has been studied fairly extensively. As the name suggests, the Coweeta Hydrologic Laboratory has been the site of much research on hydrology and nutrient cycling in the watersheds of the Southern Appalachians. Research is being actively conducted on the effect of natural and man-made disturbances on the water quality and ecosystems in this natural laboratory. The extensive background data-base and careful, well documented management history of this facility makes it an ideal candidate for mass balance study.

Base flow and storm flow at Coweeta are evidently sustained principally by water from the subsurface soils and saprolites (Velbel, 1985b; Hewlett, 1961; Hewlett and

Hibbert, 1963). These flow components are thought to contribute the bulk of the water which is present in Coweeta streams. Interflow and overland flow (or runoff) are not thought to be significant processes at Coweeta in undisturbed watersheds (Velbel, 1985a).

An initial hydrologic survey conducted in the 1930's revealed that an extensive saturated groundwater table does not exist at Coweeta (Hewlett, 1961; Velbel 1985b). Twenty-eight wells were hand-dug through the soil and saprolite to the bedrock. When these wells were pumped dry three-quarters of them failed to recover until heavy rains occurred. The remaining wells which did recover quickly were located near stream channels or were in mountain flood plains and therefore were thought to be connected to local bodies of groundwater. From this behavior it was determined that in general a saturated groundwater table did not exist except near the streams themselves.

Hewlett (1961) and Hewlett and Hibbert (1963) experimentally tested the hypothetical source of base flow to the streams at Coweeta by constructing a physical model of a hillslope. Large concrete troughs were constructed on slopes and packed with saprolite at natural bulk density. These hillslope models were then saturated with water to simulate precipitation, covered to prevent evaporation and then allowed to drain naturally through a faucet at the downslope end of the trough. The result of this simulation was that drainage continued long after (more than sixty days) the pores in the artifical soil horizon became

unsaturated. Since precipitation/recharge events are very frequent at Coweeta, the conclusion was drawn that prolonged drainage from unsaturated pores is the primary source of base flow to Coweeta streams (Velbel, 1984a; 1985a,b).

Apparently storm flow at Coweeta is also dominated by flow in the unsaturated zone. Hewlett and Hibbert (1966) as reported by Velbel (1985b) attribute the "flashy" response of Coweeta streams to subsurface translatory flow. Evidently the water stored in the unsaturated zone is pushed through the watershed system by the incident infiltrating precipitation. Hewlett and Hibbert (1966) cite experimental evidence in which a slug of tritium-labeled water is added to the top of an unlabeled water column to support this interpretation. In this study over 90% of the unlabeled water appeared in the outflow before any of the tritiumlabeled water appeared. The main point to be noted is that even during storm events overland flow or runoff is apparently not a major component of the stream waters at Coweeta. Flashy behavior can be explained in terms of rapid translatory flow. However, this may not be the case in the clearcut watershed. This problem will be further addressed in Chapter 3.

The lack of overland flow in these steep mountain watersheds is due at least in part to the highly porous and permeable nature of the saprolites which comprise the bulk of the unsaturated zone at Coweeta. Examination of saprolite samples in hand specimen and thin section indicate that much of the original mass of the rock has been removed

but that the volume of the rock has changed very little. Essentially this saprolite is like a large "sponge" overlying the landscape in this part of the Southern Blue Ridge. Observations of core materials (Velbel, 1984a and personal communication) and observations in the field indicate that porous and permeable soils and saprolites overlie a dense incipently weathered base of essentially hydrologically tight bedrock. Apparently, even on steep slopes, precipitation incident on these highly porous materials infiltrates almost immediately and continues to move downward in the weathering profile until reaching the "tight" bedrock base. At this point the water is quickly shunted laterally toward the stream (Velbel, 1985b).

Chapter 2

WEATHERING OF ROCK FORMING MINERALS

Introduction

In previous work on the mineralogy and weathering of undisturbed watersheds at Coweeta, Velbel (1985a) determined that the weathering of three minerals (biotite mica, almandine garnet, and plagioclase feldspar) could account for the bulk of the geological input of sodium, potassium, magnesium, and calcium into the dissolved nutrient budgets of undisturbed forested watersheds at Coweeta. In order to utilize Velbel's (1985a) mass balance model to calculate mineral weathering rates for WS-7 the following must be determined:

Are the mineral weathering reactions described by
 Velbel (1985a) for an undisturbed watershed (WS-2) the
 same as those occurring on a disturbed watershed
 (WS-7)? Or put another way, are the same minerals
 present and weathering in WS-7 as in the those
 watersheds previously studied by Velbel (1985a)?

2) Are there any other weathering reactions which are significant enough to be included in the mass balance model which were not previously described by Velbel (1985a)?

3) Is there any discernible difference in the way the minerals are weathering in the disturbed watershed (WS-7) as compared to the control watershed (WS-2)?

In order to answer these questions, rock, saprolite and soil samples were examined in thin section, with a binocular microscope, and with a scanning electron microscope. Additionally, the clay fractions from each sample were analyzed by x-ray diffraction analysis. These data are used in the following sections to verify and constrain previous work on the mineralogy and weathering reactions occurring on WS-2 and WS-7 at Coweeta Hydrologic Laboratory.

Biotite

The weathering of biotite has been studied extensively by soil scientists and to a lesser degree by geologists. Mica weathering in general and biotite weathering in particular are of interest to soil scientists because micas are the dominant natural mineral sources of potassium - a mineral nutrient which is extremely important to plants (Sparks and Huang, 1985).

Biotite has been shown to be readily altered to vermiculite when supplied as the only source of potassium to wheat plants (Mortland et al., 1956). Mortland et al. (1956) suggested that since biotite was so easily altered to vermiculite by plant growth that "biotite should not exist to any great extent in the clay fractions of soils subjected to extensive biologic influence".

Biotite's apparent reactivity to botanical factors makes this mineral a good "measuring stick" for use in comparing watersheds with disturbed terrestrial ecosystems with those possessing undisturbed ecosystems. Hypothetically, by closely examining the weathering of biotite in undisturbed watersheds and then comparing these data to the weathering of biotite in WS-7 (with its disturbed ecosystem), some conclusions may be drawn as to the effect of a disturbed terrestrial ecosystem on the weathering processes and products of biotite weathering.

Biotite at Coweeta

Biotite was examined by petrographic microscope in all thin sections prepared for this study. In addition individual grains of biotite were hand picked from rock, saprolite, and soil samples and examined with SEM and X-ray diffraction.

The petrographic characteristics of biotite in the fresh rock and saprolites of WS-7 and WS-2 are similar to those described by Velbel (1984c) at Coweeta and by other workers in different locations (Gilkes et al., 1979; Meunier and Velde, 1979b).

In thin section, fresh unweathered biotite is green to brown pleochroic in plain light. Incipient alteration of biotite is characterized by orange-brown staining of cleavage traces, a decrease in the pleochroism of these grains, and a decrease of birefringence. Cleavage traces become more prominent due to the staining, which is usually heaviest in grain fractures and at the edges of the grains. As degree of alteration increases, pleochroism continues to decrease, with heavily altered grains losing their pleochroic character altogether, becoming yellowish in plain

light. Alteration appears to invade the interior of the grain from the edges. Under crossed nicols Velbel (1984a,c) noted "wedges of a greenish phyllosilicate of lower birefringence" which give rise to interdigitated lamellae of high and low birefringence. These alteration features are present in the weathered biotites of both WS-7 and WS-2.

The degree of biotite alteration can vary significantly on the scale of a thin section. The more strongly altered biotites are usually proximal to microfractures. Biotites in differing states of decomposition found in the same slide suggest that the extent of biotite alteration is very sensitive to changes in the microenvironment at the scale of the biotite grains. Biotites, along with garnets, are the first minerals to show signs of alteration in incipiently altered samples.

SEM observation of fresh biotite grains reveals sharp, clean cleavage surfaces and crystal faces (Figure 2-1). Biotite grains from saprolite samples exhibit frayed and curled surfaces (Figure 2-2), apparently as a result of individual folia detaching incompletely from the main body of the grain. This gives the grain a "flaky" appearance. Surfaces of these grains can be covered with clays and/or oxides.

Biotite is essentially completely transformed to a weathering product in the soil zone. Biotite derivatives observed in soils impregnated with epoxy are nearly unrecognizable under the microscope. The edges of these grains are frayed and curled (Figure 2-3). Surfaces are

Figure 2-1

Scanning electron micrograph of fresh, unweathered biotite.





Scanning electron micrograph of weathered biotite form saprolite.



Epoxy impregnated thin section of biotite from the soil zone of WS-7. Uncrossed nicols, 30 X magnification. Note warping and curling of biotite grains at edges and interior suggesting a volume change.



generally obscured with clays or oxides. Morphologically these curled grains are distinct from those grains observed in saprolite samples and similar to the vermiculite weathering products of biotite described by Fanning and Keramidas (1977).

Petrographic comparision of biotite weathering in WS-7 to biotite weathering in WS-2 revealed no differences. The weathering of biotite in the control watershed appears to be analogous to biotite weathering in the experimental watershed. The nature of the biotite weathering was found to be essentially the same as that described by Velbel (1984c, 1985a) for control watersheds developed on the Tallulah Falls Formation. Velbel (1985a) did not examine biotite petrographically in the soil zone. However, comparison of biotites from the soil zones of WS-7 and WS-2 revealed no differences or discrepancies in the way biotite weathers in the soils of the control watershed as compared to soils in the disturbed watershed.
X-ray Characterization of Biotite and its Weathering Products

Rock and saprolite samples from WS-2 and WS-7 were dissaggregated with mortar and pestle and individual biotite grains were separated using forceps and a binocular microscope. Several suites of samples were examined in order to observe various degrees of biotite alteration in saprolitized schists and gneisses. Individual grains were crushed and mounted on petrographic glass slides with double sided "Scotch" brand tape. These mounts were then analyzed by X-ray diffraction. Since individual grains were being examined it was not possible to obtain enough of a discrete sample to employ the filter membrane peel technique utilized in the examination of bulk clay samples (as detailed in appendix A). The tape utilized for these mounts is very thin (about 1 mil) and was found not to cause significant displacement of XRD peaks as compared to mounts created using the membrane peel technique described in Appendix A.

The weathering products of biotite in soil samples were determined by bulk clay X-ray diffraction analysis due to difficulties in recognizing and separating the weathering products of biotite from the soil matrix. The procedure used for X-ray diffraction analysis of clay mounts is detailed in Appendix A. Selected diffractograms of hand picked biotite grains and their weathering products are shown in Figures 2-4 and 2-5.



Figure 2-4



Degrees 2 theta



Diffractograms of biotite from saprolite (2-2a) and from soil (2-2b) from sampling station 1. Note the enhancement of the 1.4 nm peak in the soil sample.



Fresh biotite from essentially unaltered rock samples exhibits prominent (001) and (003) reflections at .99 and .335 nm respectively. A weaker (002) peak at .497 nm may also be present. Samples exhibiting a relatively strong (002) peak were interpreted to be the result of the contamination of the biotite mount with muscovite, which is strongly interdigitated with the biotite in these schists and gneisses.

Diffractograms of biotite separated from saprolite and rock, and bulk clay sample analysis of saprolite and soil samples, indicate several biotite weathering products. Each of these products is a simple transformation weathering product, meaning that the original 2:1 clay mineral structure is preserved intact with the principle changes occurring in the interlayer cation sites and in the composition of the octahedral sheet. These simple transformation weathering products of biotite include a regularly interstratified biotite/fixed -hydroxy-interlayered vermiculite, a fixedhydroxy-interlayered vermiculite (sometimes called pedogenic chlorite) and discrete vermiculite. An expandable clay was also noted in one bulk clay separate from a rock sample but there was no direct evidence to indicate that this is a biotite weathering product. Velbel (1984a) also noted that the weathering product of biotite below the rock-saprolite interface is a randomly interstratified vermiculite-smectite. This weathering product, however, was

not detected in this study, probably as a result of the paucity of samples from below the rock-saprolite interface.

In this study, the dominant weathering product of biotite in saprolite and incipently weathered bedrock above the rock-saprolite interface appears to be the regularly interstratified-biotite/fixed hydroxy-interlayered vermiculite. This mineral weathering product was previously described by Velbel (1984a) as a "fixed hydroxy-interlayered hydrobiotite," representing a regular interstratification of a biotite layer with a basal spacing of 1.0 nm and a fixed hydroxy-interlayered vermiculite structure of 1.4 nm. However, to avoid the nomenclatural problems incurred when one invokes the name hydrobiotite (Sawhney, 1977), this author prefers to use the descriptive phrase "regularlyinterstratified-biotite/fixed hydroxy-interlayered vermiculite" which for the remainder of this chapter will be abbreviated as "RIBFHIV."

In hand-picked biotite separates the weathering product RIBFHIV is characterized by a basal spacing of around 2.4 nm and integral orders at 1.18 nm, .82 nm, and .34 nm interpreted to be respectively the (001), (002), (003) and (007) spacings of this regularly interstratified weathering product. (See Figure 2-4b for details.) In bulk clay separates RIBFHIV was generally identified by the (002) and the (007) peaks although the (003) peak is occasionally present. Solvation of magnesium saturated samples with ethylene glycol or glycerol did not result in any peak movement, indicating that smectite is not a significant

component of this weathering product. Potassium saturation at room temperature generally did not result in the collapse of the 1.4 nm component of this weathering product. When potassium saturated samples are heated to 300% and 600% C the characteristic peaks of this mineral are lost and a broad peak between 1.0 and 1.1 nm appears, indicating the almost complete collapse of the 1.4 nm component of this mineral.

The 1.4 nm biotite weathering product described by Velbel (1984a) as "pedogenic chlorite" is abundant in WS-7 and WS-2. This mineral, with a basal spacing of around 1.42 nm exhibits similar behavior on potassium saturation at room temperature in bulk clay fractions to the mineral described This weathering product seems to be more abundant in above. soils and in more heavily altered samples taken from the soils and shallow saprolites which were collected from directly below the rooting zones of WS-7 and WS-2. Less commonly, this mineral also occurs in the deeper saprolites with RIBFHIV. This spatial distribution suggests that the RIBFHIV and the 1.4 nm "pedogenic chlorite" may be genetically related to each other. The fixed 1.4 nm clay may be the product of a physical or chemical degradation the 2.4 nm structure of RIBFHIV. 1.4 nm components could form from either the physical seperation of the 1.4 nm components from the 1.0 nm biotite layers due to disarticulation or dimunition of grain size. Alternatively, further weathering or vermiculitization of the remaining 1.0 nm layers would result in the loss of the 2.4 nm stucture and the production

of more of the 1.4 nm mineral. Either process is feasible in this weathering environment and would enhance the abundance of the 1.4 nm mineral. Figure 2-5 shows diffractograms of hand picked biotite samples taken from a saprolite (1c) and from a soil/saprolite directly above this sample (1b). RIBFHIV is appears to be more abundant in the saprolite sample while the 1.4 nm mineral is more abundant in the more decomposed soil/saprolite.

Figure 2-6 illustrates the behavior of this fixed hydroxy-interlayered vermiculite or pedogenic chlorite when saturated with potassium at room temperature and when heated to 300° and 600° C. As in the case of RIBFHIV, potassium saturation at room temperature does not result in the collapse of the 1.4 nm peak. Heating to 300° C results in almost complete collapse of this peak and enhancement to the 1.0 nm mica peak thus distinguishing this mineral from discrete chlorite. At 600° C nothing remains of the 1.4 nm peak. Note also in this figure that no apparent expansion has resulted from glycerol solvation of the Mg saturated clay, indicating again that smectite is not a significant component of this weathering product.

These observations are consistent with behavior Barnhisel (1977) has reported for hydroxy-interlayered clays. Barnhisel (1977) reports that in most cases X-ray patterns obtained at room temperatures for potassium saturated, hydroxy-interlayered expanded mica structures are similar to those obtained for chlorite (i.e., no collapse of the 1.4 nm basal spacing). Although the process is not





Degrees 2 theta

completely understood, the incomplete collapse of the 1.4 nm component is apparently due to the progressive filling of the interlayer cation sites with hydroxy-aluminum (or iron?) polymers. A six-member ring structure has been proposed by Hsu (1977) as the hydroxy-interlayer material in these clays. Barnhisel (1977) refers to this structure as arguably the smallest polymer which may exist in clays which is not exchangable (i.e., fixed, and therefore not exchangable with other cations).

Barnhisel (1977) notes that the response of K-saturated samples to heat treatment is the most useful criterion in recognizing hydroxy-interlayered forms. However, as the interlayer cation sites becomes more completely filled with the aluminum-hydroxy polymers it becomes increasingly difficult to differentiate this mineral from chlorite. These fixed hydroxy-interlayered vermiculites are often referred to as "pedogenic chlorites" (as Velbel, 1984a,c did) due to the inability to distinguish them from true chlorites in the absence of heat treatments. Conversely, when only a few polymers have infilled the interlayer sites the mineral becomes difficult to distinguish from vermiculite.

Therefore, the 1.4 nm component is most probably a fixed hydroxy-interlayered vermiculite. Variations of this mineral's response to heat treatments can be explained as variations in the degree of infilling of the interlayer cation sites with hydroxy-aluminum interlayers. Based on heat treatment analyses the conclusion can be drawn that

Velbel's (1984a,c) speculations on the nature of the 1.4 nm component of biotite weathering products are most probably correct.

Discrete vermiculite was seen in several incipently altered bedrock samples. This vermiculite was also associated with an expandable component which was apparent on solvation of Mg saturated samples with ethylene glycol. These clays are only present in rock samples taken from directly below the saprolite-bedrock interface and are probably analogous to observations made by Velbel (1984a) of an expandable clay found below the saprolite interface in core samples. As these observations are few (2) and confined to samples occuring below the rock-saprolite interface they will not be considered significant in the mass balance model. This is considered a safe approximation because flow below the rock-saprolite interface (essentially flow through small fractures) is very small compared to the rapid flushing which occurs in the highly porous and permeable soils and saprolites. The overall flux of elements released from below the rock-saprolite interface would be very small in comparision to what is being released from weathering reactions occurring in the soils and saprolites.

The mineral composition of fresh biotite, the stoichiometry of the weathering reaction, and the composition of the weathering product at Coweeta as determined by Velbel (1985a) are presented in Table 2-1. As can be seen from the examination of Table 2-1, the

transformation of biotite to the fixed hydroxy-interlayered vermiculite weathering product releases potassium and magnesium into solution and fixes small amounts of sodium and calcium in the weathering product. Additionally the formation of hydroxy-interlayers acts as a sink for aluminum in the fixed- hydroxy-interlayered weathering product of biotite. For the purposes of this mass balance study it is important to note that potassium and magnesium are released into solution and that small amounts of calcium and sodium are removed from the dissolved mineral nutrient reservoir by this mineral transformation.

No differences were observed in the way in which biotite is weathering in WS-7 as compared to the control watershed (WS-2).

Biotite Weathering by Simple Transformation

As stated before all of the biotite weathering products observed in this study are "simple transformation" weathering products. In a simple transformation reaction a considerable portion of the primary mica structure (the 2:1 layer) is retained intact as a transformation product (Velbel, 1984c; Fanning and Keramidas, 1977). This transformation process is understood mainly as the loss of interlayer potassium which is compensated for by replacement with hydrated exchangable cations. In the cases of fixed hydroxy-interlayered minerals the loss of the interlayer potassium is presumably compensated for with both hydrated exchangable cations and the non-exchangable hydroxy-aluminum

interlayers. When the original potassium is exchanged with a hydrated cation such as magnesium or calcium (and hydroxy-aluminum) expandable 2:1 clay minerals such as vermiculite and smectite are formed (as are their fixed hydroxy-interlayered relatives).

This simple transformation can take place in two ways: 1) by edge weathering (Mortland, 1958; Scott and Smith, 1967) and 2) by layer weathering or weathering along preferential planes in the mica structure (Fanning and Keramidas, 1977).

Edge weathering results when the biotite (or any potassium bearing mica) grains are initally opened along cleavage traces and fractures. The expanded interlayers are not continuous throughout the grain but terminate in wedges toward the interior of the crystal. The core of the grain is initially unaffected. When potassium is released from many layers simultaneously, the result is often a particle with frayed, curled, and expanded edges surrounding a unaltered mica core. It is by this process that intergrades of biotite and expandable 2:1 phyllosilicates such as biotite-vermiculite and biotite-smectite are thought to form (Fanning and Keramidas, 1977; Sparks and Huang, 1985).

In layer weathering, the interlayers are opened or expanded throughout the crystal. If all of the interlayers are not expanded, then various types of mixed layer or interstratified minerals are formed (e.g. biotitevermiculite, RIBFHIV in the case of this study, biotite-smectite, etc.--Bidsom et al., 1982). If all the

interlayers are expanded then the biotite is completely transformed into a expandable 2:1 clay mineral. If the layer charge of the transformed mineral is greater than 1.2 per 20 oxygen unit then the secondary mineral is a vermiculite; if less than 1.2 the weathering product is a smectite (Bisdom et al., 1982).

Fanning and Keramidas (1977) cite three main factors which influence the rate and extent of transformation of the 2:1 mica structure to expanded lattice weathering products: 1) mineral factors such as chemical composition and crystal structure; 2) particle size; and 3) environmental factors.

Since the mineral composition and crystal structure of biotite is considered relatively constant at Coweeta, further consideration will only be given to particle size and environmental factors in the evaluation of biotite weathering at Coweeta.

Potassium release from the interlayer cation sites has been found to be partially dependent on the size of the weathering grains (Mortland, 1958; Sparks and Huang, 1985). Small biotite particles have been found to release potassium at a faster rate than coarser particles. However, the smaller particles, after a period of initial weathering, retain a significant portion of their potassium in essentially nonextractable form. All the interlayer potassium may be extracted from the coarser particles. Fanning and Keramidas (1977) suggest that this difference is due to a large amount of edge weathering occurring on the

smaller particles while layer weathering dominates on the coarser particles.

This apparent relationship between size and weathering process appears to be somewhat consistent with observations of biotite weathering at Coweeta. Fixed hdyroxy-interlayered vermiculite is the principal weathering product of biotite in the soil and shallow saproites in WS-7 and WS-2. Qualitatively, grain sizes are seen to diminish in the soil zone (as compared to the saprolite) due principally to physical degradation. Curled and frayed edges are observed in biotite grains present in the soil zone, and are absent in saprolite or rock samples. The lack of interlayered weathering products combined with the observed morphology and the diminished size of biotite grains in the soil zone suggests that "edge weathering" may be the primary mechanism of biotite weathering in the soil zone.

Biotite grains in saprolite and rock samples have not been subjected to physical degradation and therefore have not been diminished in grain size. The principle weathering product of biotite in saprolite and rock samples is RIBFHIV, a "layer weathering" product using the criteria of Fanning and Keramidas (1977).

One possible explanation of the observed differences in biotite weathering in the soil zone as compared to biotite weathering in saprolite is that biotites initially undergoing "layer weathering" in the saprolites are diminished in size when they become part of the soil zone,

and thus become more susceptable to "edge weathering." This edge weathering may transform the unaltered biotite layers in RIBFHIV into fixed hydroxy-interlayered vermiculite, accounting for its relative abundance in the soil zone as compared to the saprolite. Further quantitative study is needed to determine if there is a actual size-dependent change in weathering mechanisms in the soil zone as compared to weathering of biotite in saprolite.

Environmental factors which may affect the simple transformation of potassium micas include the concentration of potassium and potassium-like ions in the weathering solution, and the effect of plants which require nutrients from the weathering zone. A low concentration of potassium-like ions in the weathering solution would cause biotite to weather faster due to a large chemical gradient. Conversely, a high concentration of potassium-like ions in the weathering solution would cause the weathering products to fix potassium. Further, a low concentration of potassium in solution may make it necessary for plant life to exploit biotite as a direct source of potassium. These effects may be very significant in WS-7 and will be discussed further in Chapter 3.

For completeness it should be noted that, in the presence of organic acids; chelators for iron, magnesium, and aluminum; and under generally acidic conditions, the 2:1 mica structure may dissolve as rapidly as interlayer cations are exchanged (Fanning and Keramidas, 1977). The dissolved constituents may precipitate a variety of oxides and/or clay

minerals depending on the original composition of the mica and the conditions of dissolution. No dissolution features were noted in thin section or SEM observation of saprolite samples. Biotite simple-transformation weathering products were present in most soil samples examined by XRD, suggesting that dissolution may not be important in biotite weathering at Coweeta on the time frame of the mass balance model. Dissolution of the primary phyllosilicate structure, however, has the potential to be an important factor in the soil zones in these watershed and should at some point be the basis of further mineralogical work. Plagioclase

The composition of unweathered plagioclase feldspar in the Tallulah Falls Formation at Coweeta has been identified by Velbel (1984a, 1985a) as andesine-oligioclase. The chemical composition of this feldspar was determined by EPMA and is reported in Table 2.1. This composition was confirmed for mass balance use on WS-7 and WS-2 in this study by use of the Michel-Levy optical method (Moorhouse 1959).

Plagioclase is a principal constituent in the gneisses and to a lesser degree in the schists of WS-2 and WS-7 (Hatcher, 1976). Fresh plagioclase in thin section is generally anhedral in form, twinned according to the albite law, and may contain small oriented inclusions of mica.

Weathered plagioclase grains are characterized by a "clouded" appearance in thin section as a result of numerous small etch pits or vacuoles. Velbel (1983, 1984a) identified three types of dissolution voids in plagioclase grains at Coweeta: 1) prismatic etch pits; 2) vacuolization; and 3) wormy irregular dissolution voids. Each of these dissolution features was noted in plagioclase weathering in the study watersheds.

Dissolution features in the feldspar grains are most pronounced near fractures and previously exposed surfaces of the saprolite samples. This indicates that this feldspar alteration is a weathering process rather than being metamorphic or hydrothermal in origin. As with biotite and

garnet, the alteration of these grains tends to begin at grain and fracture boundaries, and then proceeds toward the interior of the grains. Dissolution features are conspicuously more concentrated in one of the sets of albite twin lamellae, often being totally confined to this evidently more reactive set of twins. These preferentially attacked twin lamellae appear to act as pathways into the interior of the grains. The origin and characterization of this differential attack of albite twin lamellae at Coweta has been well documented by Velbel (1983).

In early stages of weathering (i.e., in incipently weathered bedrock) these vacuoles or etch pits are not generally filled with weathering products, suggesting that the weathering products have been removed from the dissolution site. With increased degree of alteration, clays are seen to be present in dissolution voids and locally in intra- and intergrain fractures. In advanced stages of weathering these clays can form complete pseudomorphs of individual twin lamellae and in some cases entire feldspar grains. Velbel (1984a) identified these pseudomorphs as consisting of kaolinite and gibbsite by XRD of hand picked separates and EDS of plagioclase pseudomorphs. XRD work in this study of plagioclase grains seperated from saprolite and soil samples confirms kaolinite and gibbsite as the principal weathering products of feldspar in WS-2 and WS-7 at Coweeta.

Plagioclase grains examined in thin section of soils display spectacularly developed prismatic etch pits, again concentrated along the more reactive set of feldspar twins.

Velbel (1983) deduced that the clay mineral weathering products of plagioclase form by an intermediate dissolved stage. The plagioclase dissolves stoichiometrically (as inferred from empty dissolution cavities in incipently altered plagioclase), releasing all of the mineral's sodium, calcium, silica and alumina to solution. Much of the silica and alumina are then reprecipitated, according to the ambient hydrogeochemical conditions, as gibbsite or kaolinite. The spatial distribution of these clay mineral weathering products of plagioclase will be further dicussed later in this chapter in the Clay Mineralogy section.

For the purposes of the mass balance study it is important to note that all of the sodium and calcium in the weathered feldspar is released to solution to become part of the dissolved mineral nutrient reservoir. Neither gibbsite nor kaolinite act as a sink for any of cations of interest in the mass balance study. In conclusion, no differences were detected in the way in which plagioclase is weathering in WS-7 as compared to WS-2. The primary mineral compositions and weathering reactions as described by Velbel (1985a) will therefore be used in the mass balance model.

Garnet

Velbel (1984a) identified the garnet in this study area as almandine. The composition of the fresh parent mineral was determined by EPMA. The composition of the weathering products was determined by X-ray diffraction analysis. The chemical composition of this almandine garnet and the mineral weathering reaction determined by Velbel (1985a) are presented in Table 2-1.

Garnets present in the schists of WS-7 and WS-2 were examined in hand specimen, in thin section, and by SEM. To determine weathering products, garnets were hand picked from saprolite and soils and analyzed using XRD and SEM. No discernable difference was noted in the way in which garnet was observed to be weathering in WS-7 as compared to WS-2 or to that described by Velbel (1984b).

Fresh garnet in hand specimen and thin section is reddish brown in color, euhedral to subhedral in form, and contains inclusions of quartz and other materials. Individual grains are generally traversed by micro fractures.

The weathering of garnet in WS-2 and WS-7 appears to be completely analogous to that described by Velbel (1984 a, b) for garnets in control watersheds developed on the Tallulah Falls Formation. Weathered garnets in WS-2 and WS-7 possess dark red, opaque, slightly birefringent coatings of weathering products. These coating surround unaltered portions of garnet grains and penetrate the grains along intragranular fractures, mimicking the grain boundaries and

fractures present in the originally unaltered mineral. The coating of weathering products on any particular grain tends to be constant in thickness. The boundary between the unaltered garnet and the weathering products is sharp, distinct, and smooth. No pitting or vacuolization of the grains are evident in samples taken from the saprolite.

In relatively unaltered rock samples, incipient alteration of garnet is characterized by a brownish stain apparent along grain boundaries and intragranular fractures. Under crossed nicols this staining is dully birefringent. With increased weathering this stained garnet rim is transformed to the distinctive reddish brown weathering product. In advanced stages of weathering the original garnet can be completely transformed to a boxwork structure of the reddish brown weathering product surrounding void, and mimicking the original shape and form of the original unweathered grain.

Weathering products in the reddish brown crust were determined to be a mixture of gibbsite and goethite (limonite) by X-ray diffraction analysis of hand picked garnet separates. This is completely consistent with the determinations of Velbel (1984a,b). The remaining iron and alumina and all of the magnesium, calcium and silica are released into solution to become part of the dissolved mineral nutrient reservoir (see table 2-1 for weathering reaction). Manganese released from the garnet is locally deposited as an oxide.

Garnets observed in the soil zone (in epoxy impregnated thin sections) tend to have much thinner coatings of weathering products. Velbel (1984b) has suggested that biochemically mediated processes such as iron and aluminum chelation by organic acids prevent the formation of limonite coatings and removes the preexisting limonite coatings which were formed in the saprolite. Clay mineral weathering products are precipitated at some distance away from the point of dissolution. This leaves the mineral open to dissolution controlled by site selective attack (surface control) rather than being controlled by the rate at which reactants and products can move through the protective surface layer of "limonite." A surface controlled dissolution reaction in the soil zone is indicated by the presence of etch-pitted garnet grains in soils, whereas garnets from saprolites exhibit only smooth rounded surfaces when their clay coating are removed, indicating that access to the surface of the grain is controlled by the diffusion of reactants and products through the protective limonite surface layer.

For the purposes of the mass balance model it is important to note that the weathering of garnet causes the release of all of its calcium and magnesium into solution and that the weathering products of garnet do not act as a sink for any cations other than iron and aluminum, which are not considered in the mass balance equation.

Table 2-1

Mineral Compositions and Weathering Reactions in the Tallulah Falls Formation Velbel (1985a)

BIOTITE: II VI IV **K Na (Mg Fe Al) (Al Si) O (OH)** + .30 .85 .02 1.1 1.2 .4 1.3 2.7 10 2 2 2 2+ + .4C0 + .6 H O + .016Ca + .04 Na + .4Al (OH) + 2(aq) 2 + + .4Fe(OH) -----2(aq)

 III VI
 IV

 Ca
 Na
 K
 (Mg
 Fe
 (Al
 Si
 O
 (OH)
 * .8Al(OH)

 .016
 .06
 .25
 1.0
 1.6
 1.3
 2.7
 10
 2
 3

 3 + 2+ + .6K + .1 Mg + .4HCOGARNET: II II Ca Mg Mn Fe Al Si O + .625 O + 2.5CO + 5H O .2 .5 .2 2.1 2 3 12 2 2 2 ----> 2FeOOH + .1Fe(OH) 2(ag) + 2+ 2+ Al(OH) + Al(OH) + 3SiO + .5Mg + .2Ca + 3(gibb.) 2(aq) 2(aq) .2MnO + 2.5HCO 2(s) 3 PLAGIOCLASE: **Ca Na Al Si O + 2.64H O + 2.64CO ----->** .32 .68 1.32 2.68 8 2 2 2+ 2+ + + -.32Ca + .68Na + 2.68SiO + .68Al(OH) +2.64HCO 2(aq) 2(aq) 3

Other Minerals

The minerals mentioned below are present in WS-2 and WS-7 but either display no evidence of chemical weathering, or are present only in trace quantities, or do not contain any calcium, sodium, magnesium or potassium, the cations of concern in this mass balance model. All of the minerals present in the soils and saprolites of WS-2 and WS-7 are certainly undergoing some type of chemical weathering but not on a time scale or in abundances which would be significant to this mass balance model, where rates of chemical weathering are calculated in moles of mineral weathered per hectare per year.

Staurolite occurs in relative abundance in WS-2 and WS-7. Primarily an aluminum- iron silicate, staurolite has the potential to contribute a small amount of magnesium to the dissolved mineral nutrient reservoir. Fresh staurolite is occurs as large (5 mm) prismatic crystals which are euhedral to subhedral in form, and are pleochroic from yellow to brownish-orange. Iron staining is often present around mineral edges and in grain fractures. Staining is never present in the interiors of unfractured grains. It is unclear if the origin of the stain is the staurolite grain itself or if it has been mobilized from some other mineral (e.g., garnet or biotite) along grain boundaries. No further degrees of alteration were detected. Fragments showing this similar degree of staining are present in soils indicating that staurolite remains stable in the upper parts of the weathering profile.

SEM observation of grains hand-picked from rock, saprolite, and soils show no definite signs of alteration. This evidence suggests that except for a possible slight oxidation of some structural iron (to account for the staining) the staurolite is a very stable mineral in the soils and saprolites of Coweeta.

Muscovite has been previously examined by Velbel (1984a) and eliminated as a principle contributor of potassium to the dissolved mineral nutrient reservoir at Coweeta. Petrographic and SEM observation of muscovite in rock, saprolite and soil samples show no evidence of mineral weathering. Muscovite is strongly interdigitated with biotite in the schists in WS-7 and WS-2. Fresh muscovite often appeared as a contaminant in XRD patterns of hand picked biotite separates from heavily altered saprolites. Lacking evidence to the contrary, muscovite will not be considered as a significant source of potassium to the dissolved mineral nutrient budget in WS-2 and WS-7.

Chlorite was present in small quantities in some of the schist saprolite samples and in some soil thin-sections. Some chlorite exhibited slight iron staining. Chlorite was also seen in relatively unaltered form in some of the soil samples. Because chlorite is present in only trace quantities and shows only minor evidence of alteration, chlorite will not be considered to be a significant factor in the mass balance model.

Hatcher (1979b) reports the presence of K-feldspar in the mineralogy of the Tallulah Falls formation. However,

only traces of untwinned K-feldspar were detected in thin sections of gneisses by etching with hydrofluoric acid and staining with cobaltinitrate (Moorhouse, 1959). This K-feldspar was only observed in very small quantities as perthitic intergrowths in a few plagioclase grains and is probably too limited in abundance to significantly affect the mass balance model.

Apatite is present WS-2 and WS-7. Petrographically it was rarely observed in saprolite schists and gneisses and never in the soils. This mineral has the potential to be very soluble but evidence of weathering of this mineral was never observed. This mineral should be further examined in fresh rock samples.

Clay Mineralogy

An examination of Figures 2-7 and 2-8 (selected bulk clay diffractograms from soil and saprolite samples) and Tables 2-2 and 2-3 (Clay mineralogy of WS-7 and WS-2 respectively) indicates that each individual sample can be described as some combination of biotite and its respective simple transformation weathering products (RIBFHIV, fixed-hydroxy-interlayered vermiculite and vermiculite), plagioclase and its weathering products (kaolinite and gibbsite) and garnet and its weathering products (gibbsite and goethite). Other minerals which were found to be present in the .45 to 2 um. size fraction were a small amount of true chlorite (distinguished from "pedogenic chlorite" by its persistance on heat treatments to 600% C),

Figure 2-7

Diffractograms of selected bulk soils. All samples magnesium saturated, organic solvated. The weathering products of biotite are indicated by peaks at 1.42 nm, the 001 of pedogenic chlorite; and 1.18 and .342 nm, respectively the 002 and 007 peaks of RIBFHIV. Gibbsite (as both a weathering product of plagioclase and garnet) is indicated by peaks at .484 and .437 nm. Kaolinite is indicated by peaks at .714 and .355 nm. Goethite by a peak at .415 nm.



BULK CLAYS: SOILS

Mg saturated, organic solvated



DEGREES 29

.



Diffractograms of selected bulk saprolites. All samples magnesium saturated, organic solvated. See text and Figure 2-7 for peak identification.



clay sized plagioclase, and rarely clay sized quartz. It is important to note that all the clay minerals which occur in any significant quantities in the bulk clay fractions of WS-2 and WS-7 have been identified as weathering products of garnet, plagioclase, and biotite. This is strong evidence that Velbel's (1985a) mass balance model has correctly identified all of the major mineral weathering reactions occurring in watersheds developed on the Tallulah Falls formation.

The simple transformation weathering products of biotite have been examined previously in this chapter. One further point to note is that the magnesium saturated, organic solvated bulk clay samples from saprolites and soils in WS-2 and WS-7 (Figures 2-7 and 2-8) show no evidence of expansion indicating that smectite is not a common component of these weathering products.

The clay mineral weathering products of garnet in the Tallulah Falls formation are gibbsite and goethite (as identified by Velbel (1984b, 1985a, and confirmed earlier in this chapter). Gibbsite is generally identified by a distinctive sharp peak at .484 nm and a secondary peak at .437 nm. Goethite is identified by a peak occuring at .415 nm (Jackson, 1979).

The mechanism of deposition of the clay mineral weathering products of plagioclase differ from those of biotite and garnet in that after initial stoichiometric dissolution of the parent grain the dissolved alumina and silica may move some distance away from the loci of

dissolution before precipitating out as either gibbsite or kaolinite. The clay mineral which precipitates out of solution is dependent on the local hydrogeochemical conditions, principally the concentration of silica in the ambient solution. Velbel (1984a) noted that precipitation of the dissolved constituents may occur very close to the site of original dissolution, forming clay pseudomorphs after the dissolved grains; or after movement some distance away from the point of dissolution to form clay mineral fracture linings.

Conclusions

No significant differences in mineral composition, weathering reactions, or products were determined in comparision of the mineralogy of WS-7 with WS-2 and with the other watersheds developed on the Tallulah Falls formation previously examined by Velbel (1984a; 1985a). The mineral weathering reactions of plagioclase feldspar, biotite mica, and almandine garnet appear to be adequate to describe the majority of the geologic input in the mass balance model for WS-7.

Table 2-2

Clay Mineralogy of WS-7

SAMPLE #	TYPE	CLAY MINERALS PRESENT
1 A	SOIL	K,Gi,Go,M
1B	SAP	K,Gi,Go,M,R,PC
1C	SAP	K.Gi.Go.M.R
1D	SAP	K.Gi.GO.M.R.C
	0.12	x,02,00,11,x,0
2A	SOIL	K,Gi,M,PC
2B	SAP	K,GI,M,PC,C
2C	SAP	K,Gi,M,PC
3 A	SAP	K,Gi,Go,M
4A	SOIL	K.Gi.Go.M
4B	SAP	K.Gi.M
. 2	U	.,
5A	SAP	K,Gi,Go,M,R,PC
5B	SAP/SOIL	K,Gi,PC
64	SOTI	K Gi GO M PC
6B	SAD	K Gi GO M P
60	SAD	K,GI,GO,M,K K Gi Co M PC
00	JAF	K,GI,GO,M,PC
7A	SOIL	K,Gi,Go
7B	SAP	K,Gi,Go,M
97	COTI	r ci r do
OA OD	SOLL	K,GI,M,PC
80	SAP	K,GI,GO,M,PC
9A	SAP	K,Gi,M,R,PC
9B	SAP	K,Gi,M,PC
10A	SAP	K,GI,M,R,E?,P
10B	SOIL	K,Gi,M,R
112	ROCK	KGIMVPO
	ROCK	R,GI,M,V,I,Q
13A	ROCK	K,M,R,E?,P
13B	ROCK	K,M,R,E?,P
14A	SOIL	K,Gi,M,PC
14B	SAP	Gi,PC
14C	SAP	K,Gi,M,PC
153	CAD	KO GI K DO KO
TOA	JAP	K:,GI,M,PC,V:
16A	SAP	K,Gi,PC,E?
16B	SAP	K,GI,GO,PC

<u>SAMPLE</u> <u>#</u>	TYPE	CLAY MINERALS PRESENT
17A	SOIL	K,Gi,M
17B	SAP	K,Gi,R
17C	SAP	K, M, R, O*
18A	ROCK	K,M,V,E
18B	SAP	K,Gi,M,PC
18C	ROCK	K,GO,M,V,E
19A	SAP	Gi.R.PC
19B	SAP	Gi,R,PC
20A	ROCK	K,M,R

Clay Mineralogy of WS-7 con't

Table 2-3

Clay Mineralogy of WS-2

21 A	SOIL	K,Gi,M,R,PC
21B	SAP	K?,Gi,M,R,PC,E
21C	SAP	Gi,M,V,E?
21D	SOIL	K,Gi,M,R,PC,E?
22A	SOIL	K,Gi,M,R,PC
22B	SAP	K,GI,M,R,PC

KEY

SAP- saprolite

- K Kaolin minerals (kaolinite or hallosite)
- Gi- Gibbsite
- Go- Goethite
- M- Mica
- R- RIBFHIV (regularly interstratified biotite/ fixed-hydroxy-interlayered vermiculite)
- PC- Pedogenic Chlorite
 (fixed-hydroxy-interlayered vermiculite)
 V- Vermiculite
- E- Expandable
- C- Chlorite
- P- Plagioclase
- Q- Quartz
- 0*- Unknown present
- ? Mineral may be present
Chapter 3

GEOCHEMICAL MASS BALANCE

The purpose of this chapter is to use a modified version of Velbel's (1985a) mass balance model developed for use on undisturbed forested ecosystems to calculate the mineral weathering rates of plagioclase feldspar, almandine garnet, and biotite mica in a disturbed forested watershed (WS-7) at Coweeta. The goals of this chapter are the following:

1) To review the mass balance concept.

2) To examine the nature and significance of biomass uptake terms in mass balance models.

3) To define the mass balance model used in this study.

4) To calculate mineral weathering rates of biotite, garnet and plagioclase in a disturbed forested ecosystem.

5) To compare these calculated rates to baseline rates calculated for mineral weathering in WS-7 when this watershed was in an essentially undisturbed condition.

Background

As stated earlier (Chapter 1) mass balance studies of watershed geochemical processes are considered the most reliable means for making quantitative determinations of mineral weathering rates in the natural laboratory of the earth's surface environment (Clayton, 1979).

Mass balance studies of watershed geochemical processes were largely pioneered and implemented by Garrels (1967),

Garrels and Mackenzie (1967), and Cleaves et al. (1970) in the late 1960's and the early 1970's. More recent mass balance studies include Owen and Watson (1979), Paces (1983), Drever (1971), Drever and Hurcomb (1986), Katz and others (1985), and Velbel (1985a). A review of each individual study is beyond the scope of this work. However, some of the main points of these studies will be examined as the evolution of the mass balance concept is a direct consequence of these previous works.

Watershed mass balance models involve determining and quantifying fluxes of certain elements or materials into and out of a system and determining the major processes releasing, fixing, acting on, and altering these materials as they come into contact with the system. In this study and the studies noted above the systems are watersheds and the materials being "balanced" are chemical elements or species. These chemical elements or species are augmented or depleted from the groundwater/soil solutions by mineral weathering reactions and other processes which must be included either implicitly or explicitly in the model. Since it is often impossible to represent all the processes operating in the system it may be necessary in the mass balance model to approximate and/or ignore the effect of some processes. The purpose of the mass balance model is to represent as accurately as possible the processes which augment or deplete the chemical constituents of interest in the water and to quantify the fluxes of the elements involved in these processes. The goal of the mass balance

models in these studies is to calculate mineral weathering rates.

Velbel (1984a, 1985a) has extended and improved on earlier mass balance models in the several ways. The chemical compositions of the primary minerals and their weathering products are determined directly, using petrography, electron microscopy, X-ray diffraction, and microprobe analysis. This contrasts with earlier mass balance studies in which mineral compositions have been estimated (from geological occurrence and standard mineralogy texts) or back calculated from drainage water chemistry (e. g., Cleaves et al., 1970). In Velbel's (1985a) model, analytically determined mineral compositions are combined with micromorphological (petrographic) and textural data in order to arrive at more accurate and realistic mineral weathering reactions and stoichiometries. This is important because small differences in mineral stoichiometries can make significant difference in the weathering rates calculated by mass balance models. The classic mass balance study done by Garrels and Mackenzie (1967) for Sierra Nevada ephemeral springs provides a good example. The amount of source plagioclase mineral alteration is calculated by conversion of kaolinite back into plagioclase using spring water chemistry. Simply changing the composition of the plagioclase from An 38 as reported by Garrels and Mackenzie to An 30 decreases the amount of plagioclase calculated altering in moles/liter by more than 10%.

Secondly, and very important from the point of view of this study, is that botanical uptake of the mineral nutrients of interest in the model (sodium, potassium, magnesium, and calcium in this study) is explicitly included in the mass balance calculation. This permits biomass uptake of nutrients to be determined directly rather than by difference as has been done in previous mass balance studies (e.g., Cleaves et al, 1970). Velbel (1985a), however, sought to minimize the effect of biomass by using watersheds in which the biomass is stable and has remained undisturbed since the 1930's.

The Nature and Importance of Botanical Uptake

The nature of biomass terms in mass balance calculations of mineral weathering rates is poorly understood. A better understanding of the interplay between biological and geological processes can be achieved by identifing and quantifying the importance of botanical uptake terms in watershed mass balance models.

Many investigators (Cleaves et al., 1970; Paces, 1983; Likens et al., 1977; Velbel, 1985a) have recognized the potential importance of the botanical component in mass balance models of watershed geochemical processes. However, relatively few attempts have been made to quantify this effect. In general mass balance studies of watershed geochemical processes are performed on watersheds where biomass is negligible (biomass absent or limited) or with

the constraint that the biomass system is at "steady state."

In some high mountain watersheds there may be no appreciable terrestrial biota (for example, Drever and Hurcomb, 1986). Any botanical components can therefore be removed from consideration in mass balance models with this special constraint.

A terrestrial ecosystem which is at steady state is one in which the rate of nutrient uptake by the biomass system is not changing appreciably over the period of data acquisition (Velbel, 1985a; 1986). An example of a system at steady state is a mature hardwood forest which is no longer actively aggrading (e.g., the mature undisturbed control watersheds at Coweeta). Any yearly growth or "annual net primary production" is principally to replace biomass which has died or has been naturally removed from the system. Overall biomass aggradation has been completed and the system is currently in a state of "equilibrium." The accumulation of new nutrients (i.e., those released by the weathering of primary minerals) in a terrestrial hardwood ecosystem at steady state is often considered small and therefore negligible in comparision to other fluxes of nutrients out of the system (Johnson et al., 1968; Cleaves et al., 1970).

Even in a mature forested ecosystem at steady state, however, a finite increment of mineral nutrients may need to be extracted from the mineral nutrient reservoir to replace those mineral nutrients which have been lost from the

boundaries of the watershed. Mineral nutrients can be lost by particulate export; animals and insects foraging and then migrating outside the boundaries of the watershed; etc. (Velbel, 1984a). Further, if the overall ecosystem is growing larger from year to year, and if the inputs of mineral nutrients from sources such as precipitation and dustfall are insufficent to meet the needs of this growing system, then the dissolved mineral nutrient bank may become the principle source of these nutrients.

The importance of biomass in the mass balance calculation of rock weathering rates was convincingly demonstrated by Likens et al. (1977). Johnson et al. (1968) used calcium as an index ion and the assumption that biomass accumulation was sufficently low to assume a steady state to calculate rock weathering rates of 1267 eq/ha/yr at Hubbard Brook Experimental Forest. Likens et al. (1977) recalculated these rock weathering rates taking into account the yearly accumulation of cations into the biomass. This quantity was estimated to be about 722 eq/ha/yr, increasing the calculated weathering rate to about 2000 eg/ha/yr. The inclusion of biomass uptake into this apparently non-steady-state system caused the calculated denudation rate to increase by over one third (37%). Velbel (1985a) utilized data on the composition of annual

net primary production data in his mass balance calculation of mineral weathering rates in unidisturbed Southern Applachian watersheds. These watersheds probably are much closer to steady state that those studied at the Hubbard

Brook Experimental Forest. Velbel found that significant quantities of potassium, calcium, and magnesium were taken up by the "steady state" biomass system at Coweeta Hydrologic Laboratory.

Velbel (1984a) suggested that the bulk of this new growth probably resulted from recycled nutrients and nutrients which came into the watershed in precipitation. Strontium isotope studies by Graustein (1983) and Graustein and Armstrong (1981) indicate that strontium in plants is largely botanically-cycled atmospherically derived strontium (Velbel,1984a). No imprint of atmospherically derived strontium was noted in the stream waters of Graustein's study area, suggesting that all of atmospherically derived strontium had been utilized by the biota. If the botanical cycling of calcium and other nutrient elements is as "tight" as that of strontium then most of the atmospherically derived nutrients may well be utilized directly by the biota as a principal source of mineral nutrients.

The potential importance of atmospherically derived nutrients at Coweeta was demonstrated by Velbel (1984a) who calculated the rates of calcium, magnesium and potassium uptake by biomass in WS-18 (a control watershed with measured biomass growth rates) for calcium, magnesium, and potassium. These values were then compared with the measured atmospheric input of these cations. The results indicate that the rate of nutrient uptake of calcium and magnesium by biota almost exactly equaled by the rate of atmospheric input of these cations. Only in the case of

potassium does the rate of nutrient uptake by biota significantly exceed the potassium which is available via atmospheric input. Velbel (1984a) realized that the actual nutrients which came directly from the dissolved mineral nutrient reservoir probably only represent a small portion of new growth; the remaining nutrients in new growth are recycled from previous year's litter. The drain on the mineral nutrient reservoir representated by actual mineral weathering may be only that necessary to replace those nutrients which were lost from the boundaries of the watershed (such as loss of particulate organic matter in streams, etc.).

Ecosystems can be very efficent at conserving and recycling their mineral nutrients. Recycling and conservation of mineral nutrients has been demonstrated to account for up to 90% of the mineral nutrient budgets of sodium, potassium, calcium, and magnesium in undisturbed northern hardwood hardwood forests (Likens et al., 1977). Apparently, as a terrestrial ecosystem moves closer to "steady-state" it becomes more efficient at nutrient conservation and recycling; therefore a smaller demand is made on the mineral nutrient bank. Conversely it can be postulated that terrestrial ecosystems far away from steady state or equilibrium may require mineral nutrients in excess of those supplied by recycling and external sources. In these cases the nutrients supplied by mineral weathering of the mineral nutrient bank have the potential to become an important source of plant nutrients. The ultimate source of

most inorganic plant nutrients is the mineral nutrient reservoir of the earth's crust. Most of the 16 elements known to be essential to the higher plants, are originally supplied by rock weathering (Clayton, 1979).

Mortland et al. (1956) designed an experiment to observe the weathering of biotite when supplied as the only source of potassium to wheat plants. Sucessive crops of wheat were grown and then removed from a soil in which the only source of potassium was biotite. After one year and three crops of wheat, much of the biotite had weathered to vermiculite by the removal of interlayer potassium. Obviously the potassium in the biotite was accessable to the wheat on the time frame of a year.

Experiments like the one described above along with field studies like that of Likens et al. (1977) and Velbel (1985a) suggest that in non-steady state systems biomass has the potential to a become very important factor in the mass balance calculation of mineral weathering rates.

This study examines a watershed which was originally in essentially a steady state condition but which has been moved out of steady state by clearcutting and logging. This transition of the ecosystem from "steady state" to a system which is now rapidly aggrading dramatically affects the nature of the botanical uptake term on the dissolved mineral nutrient reservoir and therefore the mass balance calculation of mineral weathering rates.

The Mass Balance Model

The model developed by Velbel (1985a) to determine mineral weathering rates in undisturbed forested ecosystems is used here with some modification to calculate mineral weathering rates of plagioclase feldspar, biotite mica, and almandine garnet in a disturbed forested ecosystem (WS-7) at Coweeta.

Figure 3-1 (Velbel, 1985a) depicts the mass balance model. Six sources and sinks for the cations potassium, calcium, magnesium, and sodium in the dissolved mineral nutrient reservoir are recognized.

The mineral nutrient reservoir is augmented by input from atmospheric deposition (precipitation), and by the weathering of primary minerals. The addition of K+, Na+, Ca++, and Mg++ by the mineral weathering of biotite, garnet, and plagioclase is given by the stoichiometries of these weathering reactions as shown in Chapter 2 (Table 2-1) and Velbel (1985a). Other minerals either do not weather to contribute these cations to the mineral nutrient reservoir, or are not weathering at a rate fast enough to make a detectable contribution to the dissolved mineral nutrient reservoir.

Depletion of cations from the mineral nutrient reservoir occurs by removal via the streams, uptake in the formation of clay mineral weathering products, and uptake into the biomass of the terrestrial ecosystem. Additionally a net accumulation of soil moisture/groundwater and/or subsurface leakage out of the watershed (e.g., water which

Figure 3-1

Diagramatic representation of mass balance model.

(adapted from Velbel, 1985a)



is not accounted for at the weir) would represent additional outputs of elements from the dissolved mineral nutrient bank.

Input of sodium, potassium, calcium and magnesium in precipitation and stream export of these cations are known from the data of Swank and Douglass (1977) for WS-7 for several years prior to the clearcutting. These data are supplemented by Swank (1988) for each of the 5 years after clearcutting. Removal of cations by the formation of clay minerals as weathering products is known from the stoichiometries of the weathering reactions presented in Chapter 2.

The uptake of potassium, calcium and magnesium by the biomass on WS-7 after 1 year of regrowth is known from the data of Boring et al. (1981). Control or baseline values are calculated using annual net primary production data measured on a control watershed (WS-18) at Coweeta. This control biomass data is the same as Velbel (1985a) used in his original mass balance calculations on undisturbed watersheds. No data on sodium uptake by biomass is available for the control or the disturbed watersheds. However, since sodium is utilized by biomass to a much smaller extent than potassium, calcium or magnesium in these watersheds (see data by Day and Monk, 1977) this is not considered a major problem.

A net accumulation of groundwater in the watershed or the subsurface leakage of water out of the watershed are considered to be negligibly small due to the hydrology and

relief of the watersheds. Additionally, Velbel (1985a) found chloride (a inorganic ion not thought to be produced by weathering reactions at Coweeta) to be approximately in balance for previously studied control watersheds. In the absence of evidence to the contrary, groundwater accumulation and subsurface leakage will be considered insignificant in this study.

Since input and output fluxes are known and groundwater storage/leakage problems are considered negligible, only four source or sink terms are thought to affect sodium, potassium, magnesium and calcium in the dissolved mineral nutrient reservoir. These terms are the mineral weathering of plagioclase, biotite, and garnet and the uptake of the nutrient cations of interest by the terrestrial ecosystem.

Velbel (1985a, 1986a) mathematically represented this model using the formalism of Plummer and Back (1980). The mass balance relationships can be summarized as follows:

Equation 3-1:
$$\left. \begin{array}{c} \phi \\ \sum_{j=l}^{j} \alpha_{j} \beta_{c,j} = \Delta m_{c} \\ c = l, n \end{array} \right|_{c=l, n}$$

Am c is the net flux of element c in moles/ha/yr from the watershed. The net flux represents the stream output minus any atmospheric input. This value is positive for net efflux from the system. As stated before this data comes from Swank and Douglass (1977) for baseline and control data and from Swank (1988) for post-disturbance data and is detailed in Appendix B.

 $\beta_{c,j}$ is the stoichiometric coefficent of element c in reaction j. Units are moles of c per mole of weathering reaction j. Biomass units are moles of c per kilogram of annual new growth. Bc,j is positive for products and negative for reactants in these reactions.

^aj is the rate of mineral weathering (the object of the calculation) or of biomass growth expressed as the number of moles of weathering reaction j or kilograms of biomass growth per hectare per year. is positive when when the mineral weathering reactions of plagioclase, biotite, and garnet proceed forward as written, and when biomass is produced.

The stoichiometric coefficients for the mineral weathering reactions are known from Velbel (1985a) and Chapter 2 of this work. Baseline (control) uptake of calcium, magnesium, and potassium by biomass is determined from the data of Boring et al. (1981) as is the total uptake of these mineral nutrients by biomass at one year post-clearcut. These coefficents along with the corresponding m values are detailed in Appendix B.

The above equations now represent a system of four equations in four unknowns. When these equations are solved simultaneously, mineral weathering rates for pre- and postdisturbance WS-7 are determined.

Calculated Results

The mineral weathering rates as calculated by the above model are presented in Table 3-1 and graphically illustrated in Figures 3-2, 3-3 and 3-4 for plagioclase, biotite and garnet in WS-7. The percent increase in weathering rates over calculated baseline values is also shown in Table 3-1.

Mineral weathering rates in clearcut WS-7 as calculated by this model are faster as compared to pre-clearcut (baseline) values. The weathering rates of each of these minerals increase to peak values during the third year after clear-cutting. The weathering rates of each of these minerals return to near baseline values by the fifth year after clear-cutting. In general, garnet weathering rates varied the least (weathering up to 29% faster in year 3) and biotite weathering rates increased the most (weathering up to 39% faster in year 3).

However, due to botanical constraints and other factors which will be discussed later (in the next chapter) the most accurate weathering rate calculated by this model is considered to be plagioclase at one year post clear-cutting. The weathering rate of plagioclase at one year post clearcut is 17% higher than its calculated undisturbed biomass baseline weathering rate.

Table 3-1

WS-7 Calculated Mineral Weathering Rates in moles/ha/yr

<u>Time after Clearcut</u>	<u>Plagioclase</u>	<u>Biotite</u>	<u>Garnet</u>
4 months	560	358	332
1 year	621	353	364
2 years	678	404	389
3 years	708	416	406
4 years	600	329	337
5 years	538	288	311
Baseline (pre-clearcut)	530	300	314



WS-7 plagioclase weathering rates.



Figure 3-3

WS-7 biotite weathering rates.



Figure 3-4

WS-7 garnet weathering rates.



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Chapter 4

ANALYSIS OF RESULTS

The purpose of this chapter is to examine the output of the mass balance model presented in Chapter 3. Specifically the goals of this chapter are the following:

1) To determine how representative the mineral weathering rates calculated for this disturbed forested watershed are.

2) To examine the calculated increases in the mineral weathering rates of biotite, garnet, and plagioclase in WS-7 for the five year period after clearcutting.

3) To examine these calculated increases in mineral weathering rates in terms of the management history of WS-7.

4) To analyze differences in pre- and post-disturbance weathering rates in terms of what is currently known about mineral weathering rates in order to evaluate the significance of these differences.

5) To determine the nature and significance of botanical uptake terms in the output of mass balance models of forested watersheds.

Introduction

In order to evaluate the representativeness of the rates which have been calculated for this disturbed watershed system, the following questions must be answered: 1) How well does this model actually describe a disturbed

forested ecosystem?; and 2) What changes produced by the clearcutting of WS-7 can account for the calculated increases in mineral weathering rates? Put another way, it must be determined if these calculated changes in rates of mineral weathering are reasonable in light of what we know about the physics and chemistry of mineral weathering.

Disturbance of the terrestrial ecosystem of WS-7 has resulted in calculated increases in rates of mineral weathering as compared to rates of mineral weathering calculated for undisturbed ecosystems. Assuming that these results actually reflect what is happening to the minerals in WS-7, it can be postulated that these effects are probably most pronounced in the soils and shallow saprolites of the watershed. These are the areas which are under the direct influence of the biomass. Enhanced nutrient uptake would only affect that part of the weathering profile which can be reached by the roots of the plants. Any changes in microclimate will probably be most pronounced in the upper parts of the weathering profile. Effects of the increased production of organic acids and chelators of metal ions due to increased biomass decomposition will most pronounced in the soil zone.

Indirectly disturbance of the the biomass has the potential to effect weathering rates in the deeper saprolites through changes in the temperature and pH of the weathering solutions and through changes in the flushing rate of the weathering solution.

Validity of Model

Fertilization Problems

A potential problem which must be addressed in this study is an additional manipulation of WS-7 which occurred during the clearcutting. Parts of WS-7 were fertilized during the clearcutting operation. This author was unaware of this additional factor until this study was being "written up." The fertilization was evidently necessary to help stabilize roads constructed for the access of the cable logging equipment. The fertilizer applied consisted of lime (CaO) containing calcium and a commercial fertilizer (10-10-10) which contains potassium. Both of these materials have the potential to be highly soluble. To compound the problem, the amount of the fertilizer added to the watershed is unknown, making it difficult to deal with this factor quantitativly in the mass balance model.

A possible solution to this problem is to deal with the fertilizer as a mineral in the mass balance model. Unfortunately, this is not a realistic solution. The mass balance model is limited to four equations and therefore four unknowns. This means that it would be necessary to substitute the calculation of the fertilizer "weathering rate" for the calculation of a mineral weathering rate or the biomass accumulation. Since only a limited amount of fertilizer was added to the system, the best alternative is probably to leave the model "as is."

The significance of this problem in terms of the mass balance model can be dealt with semi-quantitatively by

calculating of the amount of fertilizer which would be required to account for the all the observed increases in the flux of cations out of the system. Simple calculations (as detailed in Appendix C) indicate that the addition of approximately 3500 lbs. of lime (as calcium carbonate) could account for the observed increase in export of calcium from WS-7 during the five years following clearcutting. This is a large amount of lime, but by no means so unrealistically large that the fertilization of this watershed can be discounted. Therefore liming of the watershed must still be considered as a major factor in evaluation of the mineral weathering rate results.

Further, the amount of 10-10-10 needed to account for the all of the observed increases in the potassium budget would be similar in magnitude to that of lime (assuming that the form of the potassium is potassium oxide). As this is not an unreasonable amount of fertilizer for a 59 ha watershed, this fertilization must be considered as potentially significant in effecting the output of the mass balance weathering rates of biotite.

The unfortunate results of this liming and fertilization is that it casts considerable doubt on the increases calculated for the mineral weathering rates of biotite and garnet. The effect of a highly soluble fertilizer on the output of the mass balance model is probably to artifically boost the calculated weathering rates of these minerals.

Fortunately, however, the calculated plagioclase weathering rate can still be considered to be representative. The calculated weathering rate of plagioclase is effectively constrained by the sodium balance. Plagioclase constitutes the principal source of sodium in this mass balance model. A very small amount of sodium is involved in the biotite weathering reaction, but not enough to significantly effect the calculated weathering rate of plaqioclase in this model. This is shown in Table 4-1 where weathering rates of plagioclase are calculated using the full mass balance model (which includes biotite as a sink for sodium). These rates are compared with plagioclase weathering rates which have been calculated using only the stoichiometic coefficient of sodium in plagioclase and the sodium flux from the system (essentially one equation with one unknown). Removing the influence of biotite from the mass balance calculation decreases the weathering rate of plagioclase by less than 4% during each of the five years after clearcutting. This suggests that the weathering rates of plaqioclase are effectively constrained by the sodium balance in the mass balance calculation.

Although rates of biotite and garnet weathering are presented in Table 3-1, the author warns that these calculated rates may be considerably higher than the weathering rates of these minerals in actuality. Only the weathering rates calculated for plagioclase in WS-7 will be discussed further.

Sodium Balance in moles/ha/yr

		α;	α_{j} plag.	
	<u>∧m (moles)</u>	J plag <u>Na balance</u>	total <u>mass balance</u>	% <u>increase</u>
4 months	367	539	560	3.75
1 year	408	600	621	3.38
2 years	445	654	678	3.53
3 years	465	684	708	3.41
4 years	395	580	600	3.33
5 years	354	520	538	3.34
baseline	349	512	530	3.39

= .68 Na,plag

see text for details

There are some other major factors which must be examined when comparing a undisturbed forested ecosystem at steady state and a forested ecosystem which has been clearcut. The state of the biomass has been radically changed and this change must somehow be represented in the biomass uptake term in the mass balance model. This has been done at least partially by altering the stoichiometry of the biomass uptake term to reflect the actual measured uptake of mineral nutrients by the biomass at one year post-clearcut (Boring et al., 1981).

Clearcut Litter Decomposition

What this model may not represent is the loss of nutrients from watershed system due to decomposition of the litter from the clearcut (i.e., disrupting the "tightness" of nutrient recycling from litter, allowing nutrient elements to "leak out" of the watershed system). Release of calcium, potassium, magnesium, and sodium from this source has the potential to artifically increase the rates of mineral weathering as calculated by this model.

In order to test the significance of this potential problem we will: 1) examine the stream chemistry data for WS-7 independently of the mass balace model and 2) attempt to calculate the release of calcium, sodium, magnesium, and potassium due to the decomposition of the clearcut litter. One way to get some idea as to the relative release of nutrients from the decomposing clearcut litter is to examine the flux data for these cations independently of the mass

balance model. Sodium in the dissolved mineral nutrient budget is less affected by biomass than potassium, calcium, and magnesium in undisturbed forested ecosystems at Coweeta (as seen in net primary production data presented by Day and Monk, 1977). Therefore, the sodium budget should be relatively independent of any botanical influences--including litter decomposition. If the fluxes of potassium, magnesium, and calcium are normalized to sodium fluxes for the period prior to clearcutting and these ratios are compared to those calculated for each of the five years after clearcutting we may be able to determine some of the effects of litter decomposition on the nutrient budget of this system. These ratios are presented in Table 4-2.

One year after clearcutting, the calcium, magnesium, and potassium ratios have increased relative to pre-clearcut or baseline ratios. This means that one year after clearcutting the watershed system is losing more of these cations relative to sodium than it was before clearcutting. These ratios are highest at one year post clearcut and then decrease in the next four subsequent years. Potassium ratios seem to return to preclearcut levels by year four. Magnesium seems to be the least affected returning to preclearcut ratios by year two after clearcutting. The calcium ratio remains significantly elevated even five years after clearcutting. This increase may be in part be due to liming of the watershed as discussed in the previous section.

There are several possible explanations for this phenomenon. The first is that the increased nutrient exports of calcium, potassium, and magnesium are due to the decomposition of litter left over from the clearcutting. Alternatively, these nutrient export increases relative to sodium could represent the lack of a biomass system large enough to use, conserve, and recycle these excess elements. In other words, the clearcutting may have reduced the need and ability of this watershed system to conserve its previously acquired nutrients. Finally, as stated above these increases may be more related to the liming and fertilization of the watershed that to decomposing clearcut litter. This is supported by the relatively constant Mg/Na ratios shown in table 4-2. Neither magnesium nor sodium was added during the liming/fertilization, and this is the ratio which remains constant. Both potassium and calcium (added during fertilization) increase significantly relative to sodium in the first year, and remain elevated for several years.

The most likely solution is that the observed relative increases are probably the result of a combination all of the above effects. These interpretations are supported by the fact that the highest ratios are observed for the first year after clearcutting. The first year after clearcutting is probably the time in which leaf litter decomposition would be at its peak (Likens et al., 1970) and when the total watershed biomass (and its capacity to recycle elements) is at its lowest point during the five year study

Table 4-2

Cation/Na molar ratios.

	<u>Na</u>	<u>K</u>	<u>K/Na</u>	<u>Ca</u>	<u>Ca/Na</u>
4 months	366.7	125.8	.34	170.9	.46
1 year	408	165.5	.40	229.8	.56
2 years	445	164.7	.37	227.5	.51
3 years	465	176.2	.38	243.8	.52
4 years	395	135.3	.34	205.6	.52
5 years	354	128.1	.36	194.6	.54
baseline	348.4	114.8	.33	164.9	.47

		Mg	<u>Mg/Na</u>
4	months	173.6	.47
1	year	202.4	.49
2	years	210.2	.47
3	years	221.4	.47
4	years	181.9	.46
5	years	170.3	.48
ba	aseline	162.9	.47

Flux data from Swank (1988).

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See text for discussion.

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period. The stability of the Mg/Na ratio suggests that the liming and fertilization may be significant.

In any case, it does not appear possible to completely isolate the litter decomposition effect from the calculated weathering rates in this model.

Decomposition Calculation

The mass balance model can be used to calculate the amount of sodium, magnesium, potassium, and calcium which is lost from WS-7 as a result of decomposition of litter left on the watershed after clearcutting. Biomass is basically treated as a fouth mineral in the mass balance model, with its composition being approximated by the composition to the clear-cut litter. Since the exact elemental composition of the clearcut litter is not known it must be approximated. Two approximations are made herein: 1) that the composition of the clearcut litter is similar to the composition of the total standing stock biomass present on WS-18 (data from Day and Monk, 1977) or 2) the composition of the clear-cut litter is similar to the composition of the annual net primary production for a control watershed (data from Boring et al., 1981).

In each of the above cases the quantities of calcium, magnesium, and sodium fixed by the first year of biomass growth on WS-7 are accounted for by increasing the \triangle M terms by the appropriate amount for each cation (based on the data from Boring et al., 1981). In this way the effects of biomass growth are still accounted for in the mass balance model.

The results of these calculations are presented in Table 4-3 and compared with mineral weathering rates calculated for the first year after clearcutting. These results indicate that when a litter composition similar to that of annual net primary production (Boring et al., 1981) is used, the weathering rates of plagioclase and garnet are fairly similar to rates calculated assuming no contribution from the decomposition of the clearcut litter. When litter of "total standing stock" composition is used the mineral weathering rates differ significantly from those calculated assuming no contribution of nutrients from the clearcut litter. The amount of litter decomposition required to satisify the equations is also presented.

A more direct way of determining the potential effect of litter decomposition on the output of the mass balance model (the plagioclase weathering rate) is to calculate the total sodium which would be released if all of the biomass on the watershed decomposed or weathered. This should reveal how durable the calculated weathering rates of plagioclase are. Total standing stock and annual net primary production data from Day and Monk (1977) for WS-18 at Coweeta are utilized in making these calculations. These calculations are detailed in Appendix D.

The results of these calculations which are presented in Table 4-4 indicate that there is 35 times as much sodium in biomass of total standing stock composition at Coweeta as

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Litter Decomposition Calculations

	Plagioclase moles/ha/yr	Biotite <u>moles/ha/yr</u>	Garnet <u>moles/ha/yr</u>	Biomas's <u>Kg/ha/yr</u>
Total Standing Stock Litter Composition	556	987	470	4341
Annual NPP Litter Composition	595	524	331	3251
<pre>1 year model results (for comparison)</pre>	621	353	332	

Table 4-4

Biomass as a Potential Source of Sodium in WS-7 Streamwaters

	moles Na available <u>in biomass</u>	"Excess Na" in <u>streamwater</u>	Ratio of Na "biomass" to <u>Na "excess"</u>
Total Standing Stock Biomass Sodium	2082	59.6	35
Net Primary Production Biomass Sodium	66.5	59.6	1.1

See Appendix C for details of calculation.

is needed to account for all of the observed increases in sodium in WS-7 stream waters for the five years after clearcutting. However most of the marketable timber was removed from this watershed after clearcutting. A more realistic estimate of the litter composition is probably that of the annual net primary production (mainly leaves and twigs). Results of these calculations indicate that there is slightly more than enough sodium in this potential source to account for the observed increases of sodium in stream chemistry after clearcutting. The conclusion is that even the calculated plagioclase weathering rates may be artifically higher than the true weathering rates.

The previous sections have discussed uncertainties associated with calculated weathering rates for disturbed watersheds. There are uncertainties associated with the plagioclase weathering rates, but they appear to be minimal. Assuming, therefore, that the calculated increases in the plagioclase weathering rates are at least in part real, the remainder of this chapter will test various hypotheses to explain why the rate of plagioclase weathering would increase.

Factors Which Can Increase Rates of Mineral Weathering.

Cutting of a hardwood forested ecosystem can set into motion a variety of effects related to the removal of the living vegetation and the disruption of the forest floor. Of interest in this investigation are those factors which have the potential to affect mineral weathering rates.

Likens et al. (1977) have identified many potential factors which have the potential to effect mineral weathering rates. Three of these factors which will be examined in this study are changes in the microclimate (increases in temperature), decreases in solution pH, and increases in flow.

These factors will be related principally to the weathering of plagioclase. Plagioclase is best constrained with respect to fertilization and biomass decomposition problems and by far the best studied mineral with respect to mineral weathering.

Temperature

In any treatment of chemical reactions (including chemical weathering reactions) temperature is one of the most important variables. Rate constants can change by several orders of magnitude as temperature is varies over 100%C (Lasaga, 1981a). It is therefore important to determine any changes in the temperature of the weathering environment which resulted from the clearcutting of WS-7. Data provided by Swift (written communication, 1987) indicate that temperatures measured at the soil-litter interface increased an average of 2.3°C over a period of 4 years after clearcutting. Air temperature fluctuations are more extreme increasing by as much as 7°C during the post clearcut period (Bhowmik, 1987). Litter/soil interface temperature values are used in these calculations as they are thought to more accurately represent the temperatures in the soil mineral weathering environment. Air temperature
data for WS-2 are provided to show that the increase in soil temperature is related to a the clearcutting of WS-7 and not to a basin-wide climatological warming trend (see Table 4-5).

The dependence of reaction rate (rate constant) on temperature is described by the classic equation proposed by Arrhenius in 1889 (Lasaga, 1981a).

Arrhenius Equation: $k = A \exp -Ea/RT$

where:

k= apparent rate constant at temperature T

T= temperature in degrees Kelvin

Ea= Activation Energy (@13.5 Kcal/mol for Na feldspar (see below)

R= Gas Constant 1.987 X 10-3 Kcal/mol K

A= Pre-exponential term

Note that the rate constant calculated by the Arrhenius equation is exponentially dependent on the temperature term and the activation energy term. A problem with the Arrhenius expression is that the activation energy term is difficult to obtain, especially for minerals with non-ideal compositions. A range of activation energies have in fact been determined for sodic plagioclase feldspar. Recent work by Wood and Walther (1983), Lasaga (1984), and Knauss and Wolery (1986), suggests that a realistic estimate of the activation energy for albite is around 13.5 kcal/mol. This value will be used to calculate rate constants of

Table 4-5

Soil and Air Temperatures (degrees C) from 1975-1981

Data from Swift (1987) written communication.

	WS-7 (clearcut) measured at <u>soil/litter interface</u>	WS-2 (control) open air <u>temperature</u> <u>measurement</u>
1975	13.9	13.4
1976	13.6	12.29
1977	incomplete data	13.12
1978	15.86	12.86
1979	16.24	12.61
1980	16.12	12.77
1981	15.85	12.34
		Mean = 12.77

Mean annual temperature reported by Swift (1982) is 12.8° C. Pre-clearcut soil/litter interface temperature average is 13.75. Average increase over pre-clearcut values is 2.3° C. plagioclase dissolution in WS-7 at Coweeta. Unfortunately similar estimates biotite and garnet activation energies are not currently available.

If we use the Arrhenius expression to calculate rate constants for plagioclase using post-disturbance temperature values and an activation energy of 13.5 kcal/mol, and normalize this value to the reaction rate constants calculated at temperatures in pre-disturbance WS-7, a quantitative determination can be made of the effect of the increased temperature of the soil/litter interface.

Results indicate that an average temperature increase of only 2.3°C can increase the weathering rate of plagioclase by 20.7%. This increase of 20.7% is slightly greater than the 17% increase which is calculated by the by the mass balance model for WS-7 one year after clearcutting. Obviously, relatively small changes in temperature can affect weathering rates significantly. Significant increases in weathering rates in the soil may be attributable to increases in soil temperature due to clearcutting.

These results may also have implications for the the deeper saprolite portion of the weathering profile. Swift (1982) has reported an average increase in stream temperatures of 3.3°C for the first two summers after clearcutting. Swift (1982) attributes much of this increase in temperature to the loss of shade along the streams reach. However, since most of the streams at Coweeta are fed by interflow or deep seepage through the saprolite (Swank,

1987; Velbel 1985b) it is possible that the waters moving through the weathering profile in clearcut WS-7 are at a higher temperature than they were in the weathering profile of undisturbed WS-7. In theory, mineral weathering rates in the entire weathering profile could be increased significantly if warmer water is seeping through the entire weathering profile due to clearcutting.

A final point about the apparent temperature dependence of mineral weathering rates increases is that peak weathering rates calculated by the model occur during the second and third years post-clearcut. This coincides with peak temperature increases at the soil/ litter interface which also occur during the second to third year after clearcutting. Figure 4-1 shows the mineral weathering rate of plagioclase as calculated by the mass balance model (recall that these rates are relatively independent of biomass factors and other mineral weathering reactions due to the sodium constraint mentioned above). Figure 4-1 also shows the increases in mineral weathering rates due to temperature increases associated with the clearcutting. Each curve is similar in shape indicating peak weathering rates during the second to third years after clearcutting with weathering rates beginning to decrease after the third year post clearcut. The good correlation of these two curves (which were produced independently of each other) is consistant with the hypothesis that the apparent increase in the plagioclase weathering rate in the disturbed watershed



Plagioclase weathering rates calculated by mass balance as compared to temperature corrected rates.



may be largely due to increases in soil temperature produced by clearcutting.

The Effect of pH

The dissolution rate (or weathering rate) of many minerals is pH dependent (Lasaga, 1984). Often, as the hydrogen ion activity increases, so does the weathering rate of the minerals. Clearcutting of watersheds has been shown to decrease the pH of stream waters in forested hardwood ecosystems. Likens et al (1970) found found that clearcutting significantly decreased the pH of stream waters draining a clearcut watershed at Hubbard Brook Experimental Forest. pH values in these normally slightly acidic waters decreased from a average value of 5.1 to 4.3 or put another way, the hydrogen ion content of these waters increased five-fold.

The pH of Coweeta waters is principally controlled by the dissolution of atmospheric CO2 in the water. One effect of clearcutting may be to increase litter decomposition and thereby increase the amount of CO2 which equilibrates with the water. Increasing the pCO2 of the water decreases the pH. The observed effect should be a general lowering of pH values of the waters moving through the disturbed watershed.

Velbel (1985b) reports that stream water composition at Coweeta is closly correlated to well-water compositions as almost all stream water originates as deep seepage through the saprolite. Velbel (1985b) noted that pH values of the stream waters are in general about 1.5 pH units

higher than the well water (deep seepage) pH values, apparently due to reequilibration with atmospheric gasses. In the absence of soil- or well- water pH values, this relationship will be used to estimate the pH of saprolite weathering solutions.

Waide (Coweeta Hydrologic Laboratory data, written communication) reports no change in pH values for stream waters for the period following clearcutting as compared to the control watershed (WS-2). The average pH of waters draining these watersheds for the five years after clearcutting is 6.81. However, total export of H+ as measured in eq/ha increases significantly in the period following clearcutting (Waide (Coweeta Hydrologic Laboratory, written communication). pH apparently does not increase because of increased flow (dilution effect-there is an increase in H+ export but there is also an increase in water due to decreased evapotranspiration) and perhaps due to increases in neutralizing bases released by increased amounts of mineral weathering and biomass decomposition. Initially, the pH of waters incident on the watershed may be lower, but by the time the water reaches the stream the pH has been increased to preclearcut values.

Knauss and Wolery (1986) and Helgeson et al (1984) have determined dissolution rates of albite in the near neutral pH range at 25°C in the laboratory. Knauss and Wolery (1986) suggest that the dissolution of albite at 25°C in the 4 - 8 pH range is pH independent. Put another way, if the pH value is above 4 but less than 8, then pH has no

significant effect on the dissolution rate of albite. As the estimated pH values for the weathering solutions in clearcut WS-7 are in this pH independent range (6.81 - 1.5 = 5.31) we can conclude that pH probably does not affect the dissolution (weathering) rate of plagioclase.

The Effect of Flow

Figure 4-2 illustrates the flow change in centimeters (over previously calculated baseline values) for the five year period following clearcutting (Swank, 1988). Peak flow occurred during the first two years after clearcutting, increasing an average of 25.5 cm then declining to 13 cm above baseline flow rates during the third year after clearcutting. This increase is thought to be due to the loss of evapotranspiration due to clearcutting of the terrestrial ecosystem. By the fifth year flow was only 8 cm. above the value expected if the watershed had not been cut. Swank (1988) notes that, although significant increases in nutrient export occurred during the first two years, maximum nutrient export occurred during the third year when flow increases showed a significant decline. Thus the timing of nutrient losses is not entirely related to the timing of hydrologic processes.

Weathering rates as calculated by the mass balance model are also highest during the third year after clearcutting -- reflecting peak nutrient exports during this time period-- and presumably not directly related to the timing of hydrologic processes.







Velbel (1985a) has demonstrated that weathering rates calculated at Coweeta are apparently independent of flow rates. Berner (1978) has also convincingly argued that increased renewal of water or increased flushing increases the dissolution of minerals in water saturated soils and rocks only up to a "limiting flushing rate." Beyond this rate increased flushing has virtually no effect on mineral weathering rates and dissolution is controlled mainly by mineral reactivity (interfacial reactions).

Although mineral weathering rates are apparently not directly related to flow at Coweeta, an indirect effect of increased early flow can be postulated. Bormann et al. (1974) have reported leaching of mineralized nutrients in the soil as a result of increased flow due to clearcutting. If leaching of mineralized soil nutrients occurred during the first two years of extremely high flow then it is possible that a major source of nutrients to the plants was removed. This may increase the need of the plants to utilize mineral nutrients released by weathering (e.g., Mortland, 1956) as other more available sources of nutrients have been removed from the system.

The Importance of Biomass: A Second Examination

A more direct way of determining the significance of botanical uptake terms in the mass balance calculation of mineral weathering rates is to compare rates of mineral weathering calculated with botanical uptake terms to those calculated without botanical uptake terms. This was done by

Likens et al. (1977) for the mass balance calculation of cationic denudation rates in the Hubbard Brook Experimental Forest (HBEF). As discussed in Chaper 3 of this work, Likens et al. (1977) determined that cationic denudation rates increase by over 35% when the accumulation of nutrients in living and dead biomass is taken into account. Likens et al. (1977) postulated that a net accretion of biomass represents a long term sink for nutrient cations supplied by mineral weathering. Likens recognized that HBEF was in the process of recovering from a logging operation and was currently accumulating biomass. Likens stated that until "steady state" conditions prevailed within the forest that some of the elements released by chemical weathering must continue to be taken up and stored in the aggrading ecosystem.

Likens et al. (1977) concluded the following: 1) that cations within the biomass must be included in the mass balance calculation of mineral weathering rates or cationic denudation rates; 2) that the rate of storage of cations is a function of the ecosystems current state of forest succession; and 3) the existance of the forest and its state of development must be included in estimates of mineral weathering rates.

An important implication that Likens et al. (1977) have drawn is that, after the forest has reached a condition of steady state, the primary mineral nutrients released from the mineral nutrient reservoir are of little consequence to the terrestrial ecosystem. This in fact forms the basis for

the "steady state and therefore negligible biomass influence" assumption which is commonly used in conventional mass balance studies.

The results of mass balance calculations for seven undisturbed watersheds at Coweeta are shown in Table 4-6. The mineral weathering rates of biotite and garnet are calculated using the model presented in Chapter 3 of this work and in Velbel (1985a). The 4 X 4 column (i.e. four equations with 4 unknowns) shows mineral weathering rates calculated using a biomass uptake term determined from the elemental composition of the annual net primary production for a mature "steady state" undisturbed forested watershed at Coweeta (Boring et al., 1981). These results were determined previously by Velbel (1985a). The 3 X 3 column shows mineral weathering rates calculated using the same model but without a botanical uptake term (i.e. three equations with 3 unknowns). The equations were solved using the mass balances for potassium, magnesium, and sodium. This is equivalent to conventional mass balance calculations in which the biomass is considered to be at steady state and is therefore negelected. The third column is a ratio of the 3 X 3 to the 4 X 4 values.

Neglecting the biomass term in the mass balance calculation results in the mineral weathering rates of biotite and garnet being considerably lower than those calculated using a well-constrained biomass uptake term. Calculated weathering rates of biotite, a mineral which is particularly susceptable to botanical influence (Fanning and

Table 4-6

Weathering Rates with (4 X 4) and Without (3 X 3) Biomass.

	BIOTITE			GARNET		
	<u>4 X 4</u>	<u>3 X 3</u>	<u>Ratio</u>	<u>4 X 4</u>	<u>3 X 3</u>	<u>Ratio</u>
Tallulah Fai	lls					
WS-7 (baseline)	299.5	191.4	.63	314.5	287.6	.91
WS-7 1 yr. post clearcut	353	275.8	.78	364	349.8	.96
WS-2	488	162.9	.34	288	209	.72
WS-18	355	238	.67	244	199.6	.82
WS-34	299	167.5	.56	355	317	.89
WS-36	390	176.5	.45	389	335.8	.86
Coweeta Group						
WS-27	187	104.4	.55	275	256.4	.93
WS-32	145	122.4	.84	315	310.4	.98
WS-14	185	117.6	.63	241	224.2	.93
Average = .55					Average	= .88

Rates in moles/ha/yr.

Kerimadas, 1977; Sparks and Huang, 1985), are on average a factor of two higher than weathering rates calculated assuming the influence of biomass is negligible. Weathering rates of garnet are also significantly higher in calculations where biomass terms are explicitly included in the equations.

The above calculations show that there is a major inconsistancy in the common assumption that biomass systems at "steady state" do not significantly influence mass balance models. As long as biomass is regarded as a phase reacting with solutions passing through the watershed it is must be explicitly included in the the mass balance model. This has been shown mathematically by Velbel (1986) in the derivation of the basic mass balance equation shown in Chapter 3 (equation 3-1). Stating that biomass is at steady state is an important constraint because it implies that the rate at which mineral nutrients are fluxing to and from the mineral nutrient reservoir is constant over time. This is exactly the same constraint we apply to the mineral vectors in the mass balance model. This mass balance model assumes that the rate at which nutrients are being released from a particular mineral is constant or linear, but finite, over time. This work does not seek to address problems of non-linear release of nutrients from the weathering of minerals.

Obviously biomass is an important component of the mass balance model. Ignoring biomass can lead to a serious underestimate of mineral weathering rates in the field.



This relationship underscores the need to better understand the interplay biologic and geologic forces in nature, especially in the earth's near-surface environment. Only by the intergration of geology and ecology based on the fundamental physical and chemical processes which link all sciences together will a more correct and holistic view of natural processes develop.

Conclusions

Clearcutting of WS-7 has produced increases in mineral weathering rates as calculated by this particular formulation of geochemical mass balance. The representativeness of these calculated rates is in question, however, because of several factors which at this time are beyond the control of the mass balance model. Fertilization and liming of the watershed as well as an unknown contribution of nutrient cations into the dissolved mineral nutrient reservoir from decomposing clearcut litter cast uncertainty on these results. In consideration of the above mentioned problems, the weathering rate of plagioclase at one year after clearcutting is considered to be the most representative rate calculated by this model. Plagioclase is calculcated to weather about 17% faster in the first year after clearcutting than pre-clearcut calculated values. Examination of temperature, pH, and flow changes as a result of clearcutting suggests that only temperature has the potential to increase the mineral weathering rates of plagioclase in WS-7 after clearcutting. Mineral weathering



rates were not found to vary directly as a function of the rate of flushing. No change in the pH of the streams was observed after clearcutting, and the pH of WS-7 drainages was found to be in the "pH independent" zone of plagioclase mineral weathering (Helgeson et al., 1984; Knauss and Wolery, 1986).

The soil temperature of post-clearcut WS-7 was observed to increase several degrees as a result of clearcutting. Increasing the soil temperatures by only a small amount (about $2^{\circ}C$) was sufficient to cause calculated increases in the mineral weathering rate of plagioclase by approximately This increase is comparable to the 17% increase in 20%. mineral weathering rates calculated by the mass balance model for plagioclase during the first year after clearcutting. The fact that such a small change in temperature can lead to a relatively large change in mineral weathering rates demonstrates the need to adjust for temperature differences when comparing mineral weathering rates. It is also apparent that changes in mineral weathering rates may result from changes in the overall physics and chemistry of the watershed system in addition to changes in demands by biomass on the dissolved mineral nutrient reservoir.

Although the nature of the biomass uptake term in the mass balance calculation of mineral weathering rates remains poorly understood, several major points are apparent: 1) Biomass is a dynamic and significant factor in watershed mass balance calculations of mineral weathering rates.

Exclusion of well constrained biomass uptake terms from mass balance models of forested watersheds can lead to serious underestimations of mineral weathering rates in the field. Even under "steady state" conditions the uptake and fixation of nutrient cations from the dissolved mineral nutrient reservoir can significantly influence calculated mineral weathering rates.

2) By disrupting the tightness of nutrient cycling some major uncertainties are introduced regarding the applicability of this particular mass balance model to a disturbed forested watershed. The decomposition of clearcut litter is a potentially significant additional source of nutrient cation flux out of the disturbed watershed. This may be especially true when the ability of the biomass to recycle these nutrients is limited by the quantity of biomass which is present to utilize the nutrient elements released by clearcutting.

Chapter 5

SUMMARY, IMPLICATIONS, and CONCLUSIONS

Summary

The purpose of this project has been to use a current formulation of a geochemical mass balance for undisturbed, control watersheds at Coweeta Hydrologic Laboratory to calculate mineral weathering rates in an experimental watershed with a disturbed terrestrial ecosystem.

Investigation of the mineralogy and mineral weathering reactions occurring in WS-2 and WS-7 indicate that the mineral weathering of plagioclase, garnet, and biotite mica account for the bulk of the geologic contribution of sodium, potassium, magnesium, and calcium to the dissolved mineral nutrient reservoirs of these watersheds. This observation is consistant with the determinations of Velbel (1985a). Other minerals either do not contribute these cations to the dissolved mineral nutrient reservoir, or are not weathering at rates fast enough to significantly influence the mass balance model on the time scale of this study. Further, it was determined that the chemical compositions of biotite, garnet, and plagioclase and the stoichiometries of their weathering reactions in the experimental watershed (WS-7) are equivalent to those ocurring in the control watersheds developed on the same bedrock (WS-2 and other control watersheds previously examined by Velbel (1985a).

This finding enabled the stoichiometries of the mineral weathering reactions determined by Velbel (1985a) to be used

to calculate mineral weathering rates for WS-7 (the disturbed watershed), using water chemistry data for each of the five years after clearcutting. The botanical uptake term (the beta term for biomass) in this mass balance model is derived from the elemental composition of the biomass on WS-7 at one year after clearcutting. Baseline weathering rates have been calculated using pre-clearcut water chemistry data and a botanical uptake term derived from the elemental composition of annual net primary production. The botanical uptake terms used in the baseline calculations are annalogous to those used by Velbel (1985a).

Calculated rates of mineral weathering of plagioclase, biotite and garnet increase in the clearcut watershed as compared to pre-clearcut (baseline) calculated rates. Figures 3-2, 3-3, and 3-4 indicate that the weathering rates of each of these minerals in WS-7 increased after clearcutting to peak values during the third year after clearcutting. During the fourth and fifth years after clearcutting the calculated mineral weathering rates of biotite, plagioclase and garnet decrease to near-baseline values.

Several factors which are not explicitly included in the mass balance model have been identified as having the potential to artificially increase rates of mineral weathering as calculated by this model. These are 1) the fertilization of the watershed during the clearcutting event with lime and a commercial fertlizer (10-10-10); and 2) the decomposition of forest litter produced by the clearcutting

event (i.e., the disruption of the tightness of the botanical cycling of nutrients). These factors are examined in detail in Chapter 3 and the implications of these results are summarized below.

The weathering rate of plagioclase at one year (17% above baseline) after clearcutting is considered to be the most representative weathering rate calculated by this mass balance model. This is due to the fact that the weathering rates of plagioclase calculated by this mass balance model are effectively constrained by the sodium mass balance. Sodium is utilized by biomass to a much lesser extent than potassium, calcium, or magnesium (Velbel, 1985b; Day and Monk, 1977). The only factor other than the dissolution of plagioclase which influences the sodium mass balance is the mineral transformation of biotite. A small amount of sodium is "sunk" in the formation of the weathering products of biotite. This sink is sufficiently small that ignoring it increases the calculated mineral weathering rate of plagioclase by less than 4%. No sodium was added to the watershed in the fertilization of the watershed during the clearcutting event.

The decomposition of clearcut litter, however, introduces considerable uncertainty into the mineral weathering rate calculations of plagioclase, biotite and garnet. The potential contribution of nutrient cations to the dissolved mineral nutrient budget by the decomposition of clearcut litter is significant. This problem is especially prevalent for potassium and calcium, and to a

much smaller extent in magnesium and sodium. According to Likens et al. (1977) sodium is present in very small quantities in the annual net primary production of biomass (unlike potassium, calcium, and magnesium). However, sodium is present in significant quantities in biomass having a elemental composition of total standing stock composition.

Calculation of the total amount of sodium available for release into the dissolved mineral nutrient budget from the decomposing clearcut litter (based on total standing stock compositions) suggests that there is potentially enough sodium in this source to account for thirty times the excess sodium observed in the drainage waters of WS-7 after clearcutting. However, since all marketable timber was removed from watershed during the clearcut, a more realistic estimate of the potential contribution of sodium from decomposing clearcut litter can be made by using the composition of the annual net primary production. The mass of sodium available in the annual net primary production is approximately equal to the total excess of sodium observed in the drainage waters of WS-7 after clearcutting. However, it is not known how much of this material (how many years worth) is available to decompose and release cations into the dissolved mineral nutrient budget. In theory the observed increases in sodium (and presumably calcium, magnesium, and potassium) can be accounted for in part or in total by biomass decomposition.

The calculated increases in the mineral weathering rates of plagioclase were also examined in terms of changes

in temperature, flow, and pH factors. Results indicate that only temperature has the potential to significantly increase the rate of mineral weathering of plagioclase feldspar in this watershed. A soil temperature increase of as little as 2%C was found to be sufficent to increase the mineral weathering rate of plagioclase by nearly 20% as calculated by the Arrhenius equation. This is comparable to the 17% increase in plagioclase mineral weathering rates calculated by the mass balance model for the first year after clearcutting.

Biomass was found to be a significant factor in the mass balance calculation of mineral weathering rates in both disturbed and undisturbed forested watersheds. Mineral weathering rates calculated using well constrained botanical uptake terms are significantly faster than weathering rates calculated without biomass uptake terms (the "steady state" assumption).

Implications and Conclusions

To determine the significance of botanical uptake terms on the mass balance calculation of mineral weathering rates we have attempted to determine changes in weathering rates resulting from the perturbation of a terrestrial ecosystem. Clearcutting of the mature forested ecosystem of WS-7 essentially changed the biomass system from a steady state condition to a non-steady state condition. Post clear-cut calculation of mineral weathering rates indicate a marginal increase over pre-clearcut calculated baseline values. It

is not clear, however, that these calculated increases are the direct result of a increased botanical drain on the dissolved mineral nutrient budget. These calculated increases may also reflect factors which are beyond the control of this study. Decomposition of the clearcut litter, while a natural process, is not accounted for explicitly in the mass balance model. Liming and fertilization of the watershed have been demonstrated to be capable of artifically increasing in calculated mineral weathering rates of garnet and biotite.

As a result it must be concluded that this particular formulation of geochemical mass balance is not sensitive enough to unequivocally determine any changes in mineral weathering rates as a result of disturbing the biomass. Mineral weathering rates may have increased, decreased, or remained the same relative to preclearcut baseline rates. Increases in mineral weathering rates could have occurred principally in the soil zone, the part of the weathering profile under direct botanical influence. Large increase in mineral weathering rates in a relatively small part of the weathering profile could be "damped out" in mineral weathering rates calculated for the whole weathering profile.

Based on the results of this mass balance model it is evident that the "true mineral weathering rates" in this disturbed watershed are not different enough from the undisturbed "baseline" mineral weathering rates to draw a

conclusion regarding actual changes in mineral weathering rates as function of the state of the biomass on WS-7.

One of the most significant determinations of this study is the potential importance of microclimate on mass balance calculations of mineral weathering rates. Clearcutting of the forest canopy caused significant increases in soil temperatures. These temperature increases directly affect mineral weathering reactions even if weathering rates are not increasing as a result of a increased botanical drain on the dissolved mineral nutrient reservoir.

Future Work

It is apparent that any future watershed mass balance studies which attempt to quantify the effect of biomass on mineral weathering rates will need to be more sensitive to detect the apparently small changes in mineral weathering rates associated with the disturbance of a terrestrial ecosystem. One way to do this is to use a more sophisticated mass balance model in which the dissolved mineral nutrient reservoir is divided into a soil zone and a The soil zone is the area under the direct saprolite zone. influence of the biomass and in direct contact with the biomass litter. Weathering reactions in the soil zone may be significantly different in an organically mediated environment as compared to the predominantly inorganic processed which dominant in the saprolite. Processes which could be represented in soil zone include biomass



decomposition and accumulation, soil mineral weathering reactions, and biomass recylcing factors.

Processes in the saprolite would presumably remain similar to those already accounted for in Velbel's (1985a) model. However, some method of quantifying nutrient fluxes between the "soil box" and the "saprolite box" would be needed. This would probably require a extensive period of data collection. Additional methods to improve the accuracy of the model would be to quantify the importance of dustfall into the watershed and the particulate export of organic matter out of the watershed.

Watershed mass balance studies are the most reliable means of quantifying mineral weathering rates and other biogeochemically significant processes in nature (Clayton, 1979). However, in any natural system there are many variables which are beyond the control of the researcher. While further refinements of mass balance models will certainly improve the output of these models it may be wise to heed the admonition of Aristotle (384-322 B. C.):

"The mark of an educated mind is to rest satisfied with that degree of precision which the nature of the subject admits; and not to seek exactness where only an approximation of the truth is possible."

APPENDICES

APPENDIX A

SAMPLE PREPARATION

Samples of rock, saprolite, and soil were collected from roadcuts and streambeds in WS-7 and WS-2. When possible a complete suite of samples was taken in order to completely represent the shallow weathering profile. Fist-sized samples were taken from the "rooting zone," saprolite, and bedrock in a vertical profile. The depth below ground level was noted and the sampling stations position was plotted on a topographic map. Samples were stored in labled "Ziplock" plastic bags and transported in a manner which retained the integrity of the friable samples.

Thin Section Preparation

All samples collected were prepared for observation with the petrographic microscope. The preparation technique used for each sample depended the degree of alteration of the sample. Convential thin sectioning techniques were not appropriate for most saprolite and soil samples. Non-friable samples were prepared according to standard methods on a Buehler Petrothin thinsectioning machine. Soil and saprolite samples were impregnated with "Scotchcast" (trademark) Electrical Resin in order to preserve textural relationships and avoid loss of minerals and mineral weathering products. This epoxy was preferred over standard resins due to its

superior viscosity and curing times. The impregnation procedure is described in detail below:

1) A small chunk of saprolite was carefully separated from the main sample and placed in a metal or plastic cup which was resistant to the solvent properties of the resin. The "chunk" should be large enough that when cut in half the cross sectional area is large enough to make a standard thin section. The samples and the containers should be clearly labeled.

2) The Scotchcast resin is measured out in its appropriate porportions (2 parts A to 3 parts B by WEIGHT) into heat and solvent resistant containers. These components are then heated to approximately 70 $^{\circ}$ C. When mixed these two components begin to harden slowly over a period of about 24 hours.

3) The sample(s) are then placed in a Vacuum impregnator (Buehler) along with the hot, thouroughly mixed components of the epoxy resin. Care needs to be taken to protect the bottom of the impregnator as this is a messy procedure. This worker found that paper plates placed in the bottom of the impregnator worked very well. The samples and resin are sealed into vacuum and pumped down to the limit of the equipment. The epoxy resin will boil and spill over onto the bottom of container (paper plates) for a while. In order to dry the samples thouroughly system should remain under vacuum for 15 to 20 minutes before covering the samples in resin. At this point the epoxy is poured over



the sample(s) while the whole system is under vacuum. The stage of the Impregnator rotates and it is generally possible to impregnate three samples a one time. Each individual sample needs to be completely covered by resin so that when exposed to the ambient atmosphere the air pressure will further "drive" the resin into the sample. The hotter the resin is at this point the lower the viscosity of the resin and the better the impregnation of the sample. After the sample(s) are completely covered let the system remain under vacuum for another 15-20 minutes. At this point the samples are removed and placed in an oven at 50 C until cured (about 2 days).

4) These samples are then prepared as "normal" thin sections on the Buehler Petrothin. Sections cut through the impregnated samples should be thouroughly impregnated and therefore retain spatial and textural relationships. Best results are achieved if the epoxy is allowed to thouroughly cure before gluing the sample onto a slide. Epo-qwick (trademark) epoxy was found to be adequate for this step of the operation.

5) The remainder of the thin section operation follows standard procedures.

6) If color impregnation is desired a dye can be added to the epoxy resin before impregnation.
Clay Mineral Preparation

Clay minerals were prepared for X-ray diffraction analysis by a method based on that of Drever (1973). The goal of this method is to produce oriented clay mounts by drawing a suspended clay solution onto a filter membrane with the aid of vaccuum. In this way consistant, uniform, well orientated clay mounts are produced.

The procedure used for this study is similar to that used by Velbel (1984a) with several modifications. Rock, saprolite, and soil samples were disaggregated with mortar and pestal and dispersed ultrasonically in about 500 ml of distilled water. In the case of some soil samples, organic matter was oxidized before dispersion with the aid of a small amount of hydrogen peroxide (after the method of Carroll, 1970b). Samples which did not disperse with the ultrasonic treatment were treated with several drops of "calgonite solution" (Velbel, 1984a) and then re-sonicated until sucessful dispersion occurred. At this point the sample was allowed to settle under the influence of gravity for approximately 3.5 hours which allows the greater than 2 um fraction of the clay dispersion to settle out (Jackson, 1979). At this point the top 5 cm. of the solution was decanted and placed in a capped Nalgene holding bottle.

This decanted solution containing the less than 2 um fraction of the clay suspension is then drawn onto millipore brand .45 um nominal pore aperturefilters with a vaccuum aparatus. Four separate mounts are produced from the same sample dispersion. One mount was left untreated and one

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mount treated with a potassium chloride solution and then rinsed with distilled water. Two mounts were treated with a magnesium chloride solution. One of these was then rinsed with distilled water and the other rinsed with distilled water mixed with 10% by weight glycerol. In this fashion a untreated mount, a potassium saturated mount, a magnesium saturated mount, and a magnesium saturated glycerol solvated mount were created.

After the appropiate chemical treatment and rinsing the filter (and the attached clay cake) is removed from the vaccuum aparatus and inverted onto a petrographic glass slides. Potassium saturated samples were inverted onto a Pyrex plate glass slides in preparation for heat treatments. The filter "cakes" are then gently "rolled" onto the slides with a glass rod. The used filter was then peeled of the cake and discarded.

The samples were then run on a Rigaku Gigerflex X-ray diffractor. Scans were made from 2 to 30 degees 2 theta using nickel filtered copper radiation scanning at a rate of one degree-2 theta per minute using a 1/6 degree diffraction slit. This produced untreated, potassium saturated, magnesium saturated, and magnesium saturated glyerol solvated x-ray diffractograms at room temperature. The potassium saturated mounts were then heated to 300°C for one hour and rerun. These same samples were then heated to 600°C for one hour and rerun. Heat treatments were performed in a Thermolyne (Type 1500) Furnace. If needed, the magnesium saturated mount was put into a dessicator

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containing ethelyene glycol and heated to produce magnesium saturated ethelene glycol solvated mounts. Thus six and ocassionally seven X-ray diffractograms were produced and subjected to the intrepretation techniques described in Chapter 2.

SEM Sample Preparation

Selected samples of rock, saprolite and soil were examined by scanning electron microscope. In addition, individual mineral grains were separated from samples in order to help identify individual mineral weathering reactions. In order to avoid sample preparation artifacts rock and mineral fragments were mechanically disaggegated and mounted without further preparation. Samples were carbon coated using a Denton DV-502 Vaccuum Evaporator. Sample examination was performed on the departmental Jeol T20-CSI scanning electron microscope.

APPENDIX B

MASS BALANCE COEFFICIENTS

Table A-1

Mineralogical Stoichiometric Coefficients "Beta terms"

	<u>Plagioclase</u>	<u>Biotite</u>	<u>Garnet</u> 0	
Na =	.68	04		
Mg =	0	.1	.5	
K =	0	.6	0	
Ca =	.32	016	.2	

Table A-2

Biomass Stoichiometric Coefficients "Biomass Uptake Terms"

1 year Net Primary Production Boring et al.,1981

> Na = 0 Mg = -.101 K = -.32 Ca = -.249

Control/Baseline Net Primary Production Day et al., 1977

> Na = 0 Mg = -.055 K = -.150 Ca = -.148

Appendix B con't

Flux	Values for	WS-7	in mo Na	les/ha/yr Mg	From Swar K	nk (1988) Ca
4	months	366	5.68	173.63	125.84	170.90
1	year	408	8.0	202.43	165.48	229.79
2	years	444	1.98	210.24	164.71	227.54
3	years	464	1.98	221.35	176.22	243.76
4	years	394	1.96	181.86	135.30	205.59
5	years	354	1.07	170.33	128.14	194.61
Avg. pric clear-cu Swank and 1977	or to it 1 Douglass,	348	3.41	162.93	114.84	164.92
WS-2 avg clear-cut Swank and 1977	prior to c 1 Douglass,	396	5.7	121.4	101.5	65.6

Table A-3

APPENDIX C

LIME CALCULATION

Lime necessary to account for the total increase in the WS-7 calcium budget can be calculated as follows: Total "excess" calcium from Swank (1988): 248 moles/ha X 59 ha in watershed = 16760.7 moles calcium "excess" Since there is 1 mole of calcium per mole of CaCO3; 16760.7 moles of calcium need to dissolve to account for the total observed increase in the calcium budget of WS-7. Atomic weight of CaCO3 = 100.8 grams/mole 16760.7 moles CaCO3 X 100.8 grams = 1.68 E6 grams CaCO3

1.68 E6 grams CaCO3 X $\frac{1}{454}$ grams = 3694 lbs. of "lime"

Approximately 3700 lbs. of lime would account for the total increase in the calcium budget for the first five years after clearcutting.

mole CaCO3

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APPENDIX D

SODIUM CALCULATION

The potential sodium released from decomposing clear-cut litter can be calculated as follows. There are 47.863 Kg of Na/ha in total standing stock biomass (Day et al., 1977 for WS-18). 47.863 Kg Na/ha X 1000 g/22.989 g/mole = 2082 moles Na/ha in total standing stock 1 year post clear-cut sodium flux for WS-7 is 408 moles/ha Baseline (pre clear-cut) flux is 348.41 moles/ha 408 - 348.41 = 59.59 moles Na "excess" over baseline 2082/59.59 = @ 35 i.e. there is 35 X as much Na available in the total standing stock as needed to produce the observed excess. Assuming the composition of the decomposing biomass can

be approximated by the composition of annual net primary production:

1.528 Kg/ha (Day et al., 1977) X 1000/22.989 = 66.5 moles Na/ha

66.5/59.59 = 01

This suggests that the decomposition of annual net primary production is enough to account for the observed increase in the first year. LIST OF REFERENCES

LIST OF REFERENCES

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