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Mineral Weathering in the Lochvale Watershed,
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MINERAL WEATHERING IN THE LOCHVALE WATERSHED, ROCKY MOUNTAIN NATIONAL PARK, FRONT RANGE, COLORADO

By

Nadine Louise Romero

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ABSTRACT

MINERAL WEATHERING IN THE LOCHVALE WATERSHED, ROCKY MOUNTAIN NATIONAL PARK, FRONT RANGE, COLORADO

By

Nadine Louise Romero

The origin of high calcium water compositions draining the Precambrian crystalline rocks of the Rocky Mountains is poorly understood. Petrographic observations and x-ray diffraction results reveal mineral weathering of the Lochvale drainage in Rocky Mountain National Park, consists of four primary hydrolysis reactions: a) plagioclase-anorthite 65 weathering to kaolinite; b) plagioclase-anorthite 35 weathering to kaolinite; c) amphibole weathering to kaolinite and d) biotite weathering to vermiculite. Weathering rates of the four primary silicates were computed using a geochemical mass balance model: plagioclase (An65) weathers at a rate of 146-156 moles/ha/yr; plagioclase (An35) at a rate of 28-48 moles/ha/yr; ferrotremolite at a rate of 9-17 moles/ha/yr and biotite at a rate of 17-25 moles/ha/yr. 70 percent of the total cation releases may be due to the weathering of amphibolite--a small mafic unit composing less than 5% of drainage surface area.

Dedicated to the Memory of my brother,

Kenneth Eloy Romero

You and I we climbed
shoulder to shoulder
You decided to stay

I accept your peace
amidst these canyon walls--
our sacred land

and go you will with our Chiefs,
our grandmothers and grandfathers
across the backbone of the world.

--May 13, 1989

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TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 STATEMENT OF THE PROBLEM

The role of mineral weathering in stream water chemistry and landscape reduction of the Colorado Front Range is poorly understood. However, mineral weathering may be largely responsible for controlling the ionic character of most streams draining the Front Range and shaping the massive Precambrian crystalline terrains of the Southern Rockies. Mineral or chemical weathering is poorly understood because, in regions where severe climatic conditions prevail, mechanical weathering (e.g. glacial and periglacial processes) dominates (Birkeland, 1974; Ollier, 1984; Reynolds, 1971).

As long as the role of mineral weathering remains undefined in the Rocky Mountain Region, water quality interpretations, predictive acid rain models, denudation estimates and forest ecosystem models will remain tenuous at best.

In order to elucidate the role and implications of mineral weathering in the Rocky Mountain Region, the response of primary rock forming minerals to hydrogeochemical attack needs to be investigated. Therefore, the objective of this research is to define: 1) which minerals and rock types are weathering in present day conditions; 2) the alteration products formed as a result of mineral transformations; 3) the precise transformation-reactions of primary rock forming minerals to clays and oxides; 4) the rates of mineral weathering and 5) to provide a mineral weathering framework for additional research in landscape reduction rates for the Colorado Front Range.

1.2 DEVELOPMENT OF THE PROBLEM

1.2.1 **Globally**

Chemical weathering of primary rock-forming minerals occurs because these minerals are not at equilibrium with surface waters, temperatures and pressures (Ollier, 1984; Reiche, 1950; Birkeland, 1974). However, as the weathering environment changes (e.g., by acidification) so too do alteration products. Many approaches have been used to qualitatively and quantitatively understand chemical weathering of minerals in both laboratory and field settings. Much of the earlier work in mineral weathering was observational in approach, beginning with Goldich's (1938) "weathering series", where more mafic-related minerals appeared to weather more readily than felsic ones, paralleling Bowen's Reaction series. Other earlier work focused on bulk chemistry comparisons of altered versus unaltered rock (Wahlstrom, 1948) which produced elemental mobility indices and initiated isovolumetric techniques for the study of weathering profiles (Millot, 1970; Gardner, Kheoruenromne and Chen, 1978). Laboratory research, on the other hand, has been oriented towards understanding kinetic behaviors and ultimately those mechanisms responsible for controlling rate and morphology (Chou and Wollast, 1985; Holdren and Speyer, 1986; Busenburg and Clemency, 1976; Berner and Holdren, 1977; Velbel, 1984). Laboratory mineral weathering rates are 1 to 3 orders of magnitude greater than field weathering rates (Paces, 1983; Velbel, 1985a, 1986b; Drever, 1986). Such poor simulation of natural weathering conditions by laboratory dissolution may in part be attributed to differences in surface characteristics of naturally versus artificially weathered mineral surfaces (Velbel, 1986b). Field research on mineral weathering rates and mechanisms have been approached through: a) mass balance techniques (Cleaves, Godfrey and Bricker, 1970; Paces, 1983; Velbel, 1985a; Katz et al, 1985; Garrels and Mackenzie, 1967; Drever and Hurcomb, 1986; Clayton, 1986); b) empirical and theoretical mass-transfer techniques (Gardner, Kheoruenromne and Chen, 1978; 1981; Helgeson, Garrels and Mackenzie, 1969) and to some degree, c)statistical techniques (Reeder, Hitchon and Levinson, 1972).

One of the more reliable approaches to quantifying present-day mineral weathering rates is to utilize small scale, controlled field areas for geochemical mass balance studies (Velbel, 1985a; Plummer and Back, 1980; Drever, 1986, 1982). The mass balance approach integrates both quantitative and qualitative chemical mineral weathering information (chemical and hydrologic stream flux data, weathering reactions) into a system of simultaneous equations which are balanced and solved for elemental transfer rates. Among a handful of geochemical mass balance studies done on granitic and crystalline terrain are Cleaves _et al_. (1970), Drever and Hurcomb (1986) and Clayton (1986). These mass balance findings will be discussed in more detail in the mass balance chapter of this thesis (Chapter 5).

In R.C. Twidale's book, 'Granite Landforms' (1980), Twidale comments,

> " granites form the foundations of continents. Many are of great antiquity and have, moreover been either exposed or in the groundwater zone for a long time."(p.186).

Twidale's work profoundly elucidates the importance of granites and hydrogeochemical attack on them in the development of large, smooth erosional surfaces termed 'etchplains' or 'peneplains' exhibited worldwide. Yet globally, few studies address the chemical and mineralogical weathering of geomorphic features in terms of kinetics and weathering mechanisms responsible for their morphology and their significance to the geologic cycle.

1.2.2 **Locally**

Chemical weathering of primary rock-forming minerals may be the only major long-term process of acid rain neutralization (Drever, 1986). In light of increasing acidity found in Colorado over the past decade (Lewis and Grant, 1979 a, b; 1980; Grant and Lewis, 1982; Baron, 1983; 1984; and Kling and Grant, 1984), the sensitivity of high-elevation crystalline terrains to acid charged waters is a major research concern. There is considerable concern regarding the Rocky Mountain region due to the vast granitic bedrock, thin acidic soil veneers and sparse vegetation that may lack the ability to buffer incoming acidity (Baron, 1983). Kling and Grant (1984) suggest that toxicity and adverse effects on biota due to increased acidity on crystalline bedrock may prevail within this decade. Weekly NADP (National Atmospheric Deposition Program) measurements reveal rainwater pH levels as low as 4.16 and sulfate/nitrate concentrations as high as 150 milli-equivalents per liter. Such results indicate that sporadic polluted air masses have traveled over Rocky Mountain National Park (Baron, 1986). Consequently, as a result of anthropogenic impacts, there is a definitive need to expediently understand the effects of acid deposition on crystalline terrain. Measuring the effects of acidity can only be accomplished by identifying key water rock interactions and securing a mineralogical weathering data base.

1.3 CHEMICAL AND MINERALOGICAL WEATHERING STUDIES

1.3.1 Southern Rocky Mountains

Hembree and Rainwater (1961) performed one of the first denudation studies of the Southern Rockies. Measuring hydrologic fluxes and analyzing water quality from surface runoff of the Wind River Range, Hembree and Rainwater derived chemical denudation rates of .364 cm/1000 years and .67 cm/1000 years for western and eastern slopes, respectively. The western slope is composed of Precambrian granites, whereas the eastern slope is composed of Paleozoic and Mesozoic sandstones, shales and carbonates. Hembree and Rainwater attributed differences in the dissolved stream loads due to lithology and postulated that the rate of "chemical weathering" depended upon how fast weathered mantle could be removed. Another early study performed by Miller (1961) analyzed water quality from streams draining quartzites, granites and sandstones of the Sangre de Cristo range, New Mexico. Gaging stations were placed at various altitudes along each stream. Each stream was underlain by a single lithology. Miller calculated several chemical denudation rates, however, it is not clear precisely how these rates were derived. Although these studies provide no qualitative information on mineralogical weathering, they do address the importance of constraining the study area and allude to the complexities of ascertaining what controls stream water chemistry and rates of mineral weathering. Caine (1979) also quantifies rock weathering rates by placing crushed rhyodacite tablets in porous bags above timberline in the San Juan Mountains, Colorado. Caine derived weathering rates of .055 cm/ 1000 years and his research was essentially a laboratory experiment taken 'outdoors'--unfortunately no qualitative mineral weathering data were determined.

Detailed descriptive mineralogical weathering studies are virtually non-existent in the Southern Rockies. Isherwood and Street (1976) contend that grus formation in the Precambrian Boulder Creek granodiorite is due to the weathering and consequent expansion of biotite to vermiculite. In the Cascade Mountains, Drever and Hurcomb (1986) applied one of the first geochemical mass balance techniques to the Southern Rockies. The Cascade Mountain drainages in Drever and Hurcomb's study are underlain by diorites and migmatites. They conclude weathering of plagioclase was negligible, biotite altered to vermiculite and acid neutralization results from calcite dissolution.

The acquisition of mineral weathering data has been limited in previous studies. However, mineral transformations during weathering exert tremendous influences on soils, ecosystems and ground and surface waters. As we are inevitably charged with the task of assessing anthropogenic impacts to highly sensitive regions, it is vital that mineral weathering research be applied to the crystalline terrains of the vast Southern Rockies.

CHAPTER 2

AREA OF STUDY

2.1 Introduction

The Lochvale Watershed, latitude 40 16′, longitude, 105 41′ is located in Rocky Mountain National Park in the Colorado Front Range (Figure 1). Draining northeast from the Continental Divide, watershed elevation ranges from 2987 meters to 4009 meters in elevation in less than 5 kilometers. The catchment basin occupies 660 hectares and is composed of 3 shallow lakes: Loch (3100 m); Glass Lake (3280 m) and Sky Pond (3291 m). The surface area of the lakes total 7 hectares of the watershed; soils and vegetation, 40 hectares and bedrock comprises 613 hectares (Baron, 1987; Walthall, 1985).

To more closely study mineral transformations and kinetics by hydrogeochemical attack, it would be ideal to find a catchment that can provide as much isolation as possible from the effects of other weathering processes (e.g. biochemical and human disturbance). Although the Lochvale watershed is not 'ideal', it was chosen as the study site for the following reasons: 1) an extensive amount of chemical, hydrologic and meteoric flux data has been collected by several researchers (Baron and Bricker, 1984; 1987) providing data for kinetic/mass balance calculations; 2) the catchment is composed of over 90%

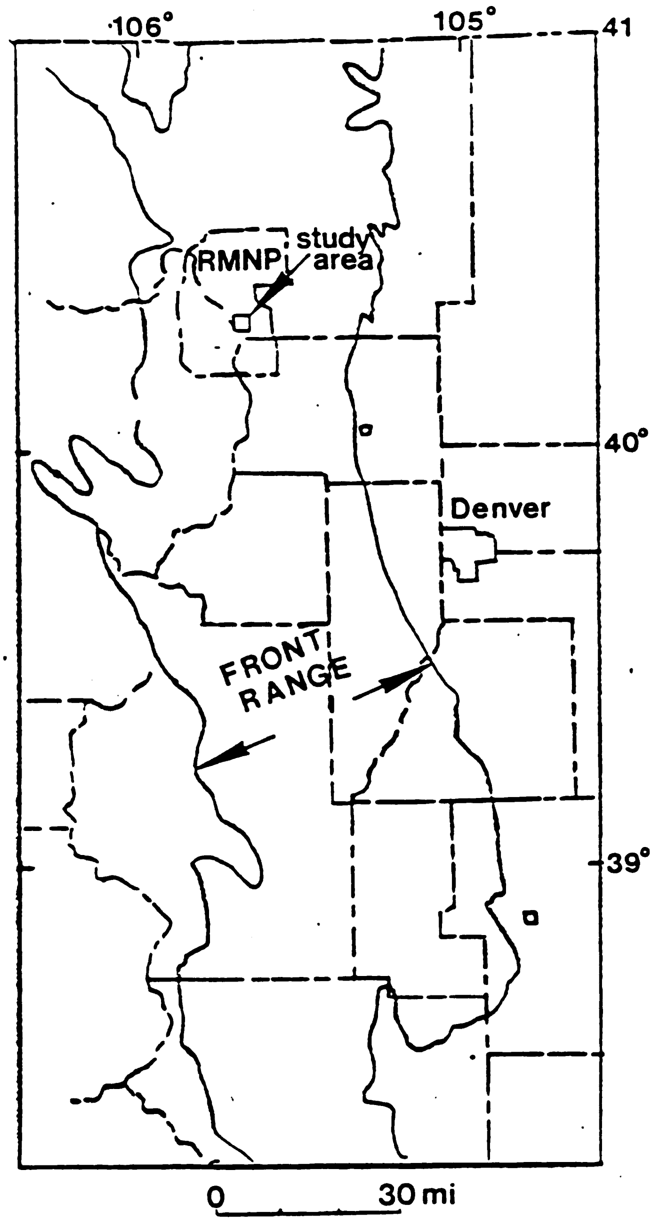


Figure 1. - Index Map of Rocky Mountain National Park, showing location of study area.

crystalline bedrock with limited vegetational cover affording a stricter focus on (inorganic) hydrogeochemical weathering; 3) the high elevation catchment is not hydraulically connected to more exotic waters as in the case of springs; 4) an extensive body of regional literature on petrology and chemical compositions of parent and weathered mineral and rock types exists which helps constrain stoichiometries of mineral weathering reactions; 5) the study area is considered environmentally sensitive with respect to 'acid-rain' effects and 6) the author's knowledge of the physical and geologic terrain of RMNP.

2.2 Regional Geology

An extensive body of literature exists on the Precambrian geology of the Colorado Front Range (Tweto, 1980; Lovering and Goddard, 1950; Robinson, et al, 1974; Wahlstrom and Kim, 1959; Wells et al, 1964; Lovering, 1935; Sims et al, 1963; Hutchinson, 1976; Barker et al, 1975). Much of the regional literature grew out of the economic and scientific significance of early mining activity. Comprehensive public sources of literature have been USGS Professional Papers. Tweto (1980) gives an excellent summary of Colorado Precambrian geology.

Precambrian crystalline rocks constitute the core of the Colorado Front Range (Figure 2). These rocks can be

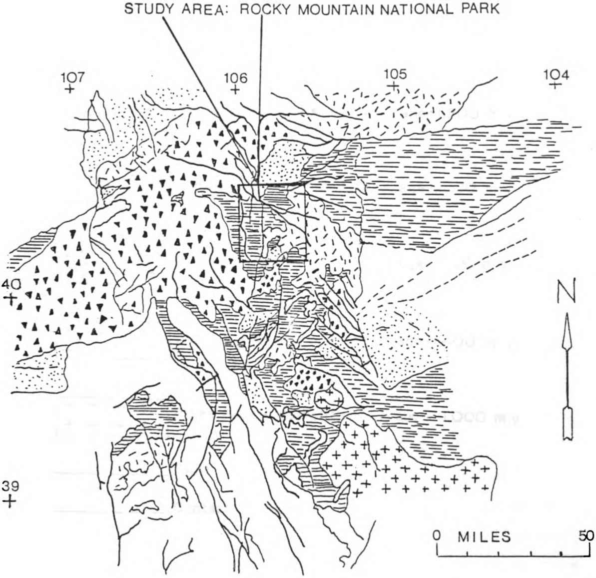


Figure 2.- A geologic map of Precambrian rocks in Northern Colorado (after Tweto, 1980). Lithologic explanation on page 13.

EXPLANATION

⁘	Metavolcanic gneisses	age ≥ 1,800 m.y.
≡	Metasedimentary gneisses	age ≥ 1,800 m.y.
▼▲	Granitic rocks	age-1,700 m.y.
⁄	Granitic rocks	age-1,400 m.y.
+	Pikes Peak - batholith	age - 1,000 m.y.
——— — — —	Fault	
———— — —	Contact	

classified into 6 major genetic classes: 1) a metamorphic complex dated 1,800 m.y. in age, consisting of biotitic gneisses an schists (known as series A) and hornblendic-felsic gneisses (Series B); 2) a group of igneous rocks about 1,700 m.y. in age; 3) a unit of moderately metamorphosed sedimentary rocks between 1,400 and 1,700 m.y. in age; 4) a group of igneous rocks 1,400 m.y. in age; 5) slightly metamorphosed sedimentary rock unit 950 to 1,400 m.y. in age and 6) igneous rocks 1,000 m.y. in age. These units also compose the entire buried basement of Colorado. Of these rock types, the complex and highly deformed metasedimentary units serve as a host for the igneous bodies.

The most areally extensive metamorphic rock types to the Rocky Mountain National Park vicinity are metasedimentary gneisses and schists, principally biotite-silliminite gneiss and schist (Nesse, 1977; Cole, 1977). Major mineral composition is plagioclase, quartz and biotite with minor sillimanite, microcline or muscovite. The metasediments are migmatized throughout the region. It is believed that the parent materials were graywackes and shales (Tweto, 1980). Interlayered lenses of calc-silicate rocks, uniform textured microcline gneisses and amphibolites (metavolcanic gneisses) are believed to be metamorphosed rhyodacitc tuffs and basalts (Hutchinson, 1976; Tweto, 1980). These rock types are not as interlayered as in other areas of the state but exist as large discrete bodies. The igneous rock types of the RMNP vicinity are primarily the result of two major intrusions: Boulder Creek Orogeny (1,700 m.y.) and the Silver Plume Disturbance Thermal Event (1,400 m.y.) which includes the Sherman Quartz Monzonite (Hutchinson, 1976).

2.3 Regional Geomorphology

The Colorado Front Range possesses numerous and striking erosional and depositional features (Figure 3) from Holocene through Recent glaciation (e.g. cirques, valleys, moraines etc.). Much of the geomorphic literature is dominated by glacial studies. However, equally as striking are massive flat to gently sloping surfaces, giving a truncated appearance to the mountains of the Front Range. These surfaces, which are beautifully exhibited in Rocky Mountain National Park, were first described by Lee (1920) as 'peneplains'. However, the term peneplain was first coined by W.M. Davis in 1899 after reading the writings of John Wesley Powell (Gerrard, 1981). Several more recent discussions on these peneplains summarize evidence for a late Eocene erosional surface. This surface is exhibited in the Front Range and Rampart Range of Colorado and extends to the Laramie Range of Wyoming (Epis and Chapin, 1975; Eggler _et al_, 1969).

Figure 3.- Topographic Map of Study Area (40 16'lat; 105 41' long).

The geomorphology of this erosional surface area, consisting of more than 10,400 km^2, was characterized by low relief and development of shallow, broad stream valleys as seen below volcanic tuff deposits (Epis and Chapin, 1975). The erosional surface truncated Middle Eocene and older rocks and deeply etched the Precambrian crystalline rocks. Development of the peneplain began with the start of the Laramide Orogeny, where erosion kept pace with uplift and kept surrounding mountain elevations no higher than the actual weathering front (Epis and Chapin, 1975). The climate of the time was warm, temperate to subtropical.

2.4 Soil Types

Walthall (1985) characterized the Lochvale soils as dominantly coarse textured, high in coarse fragments and relatively young, with poorly developed horizons. Soil temperatures were charactized as cryic with a mean annual soil temperature between 0 degrees and 8 degrees Celsius and a mean temperature difference of 5 degrees Celsius between summer and winter soil readings. The soil environment makes up aproximately 7 percent of the Lochvale Watershed (Baron, 1987; Walthall, 1985). Walthall (1985) characterized spruce and fir forest floor soils as cryoboralfs and immature soils at the base of talus slopes and alpine ridges were characterized as cryochrepts, cryumbrepts and cryorthents. Walthall's studies conclude that given increases in acidic deposition, the Cryoboralfs will promote surface water acidification. Cation exchange capacities ranged from 4 to 76 cmol+/kg).

2.5 Climate

The present climate of the Loch Vale Watershed and surrounding RMNP vicinity is temperate. The average annual precipitation is 75 to 100 cm/year and the mean annual temperature is 7 degrees Celsius. The drainage is subalpine to alpine consisting of a spruce-fir forest at the Loch elevation and alpine tundra above 3000 meters.

2.6 Hydrology

Annual hydrologic and chemical budgets of the Lochvale watershed for 1984 and 1985 have been developed by Jill Baron and others for the National Park Service (Baron and Bricker, 1987). Results of Baron's studies show that 60 - 70% of the annual water input into Lochvale is snow. The duration of snowmelt is 2 months and controls the flow of solutes out of the Lochvale system. For example, 70% of the sulphate output occurs during snow melting. Winter is also a time of increased concentrations of ions in lake water. There is negligible storage of water in the subsurface of mountain slopes due to near vertical to steep elevation gradients. Hydrologic Balance inputs and outputs are given in Appendix C.

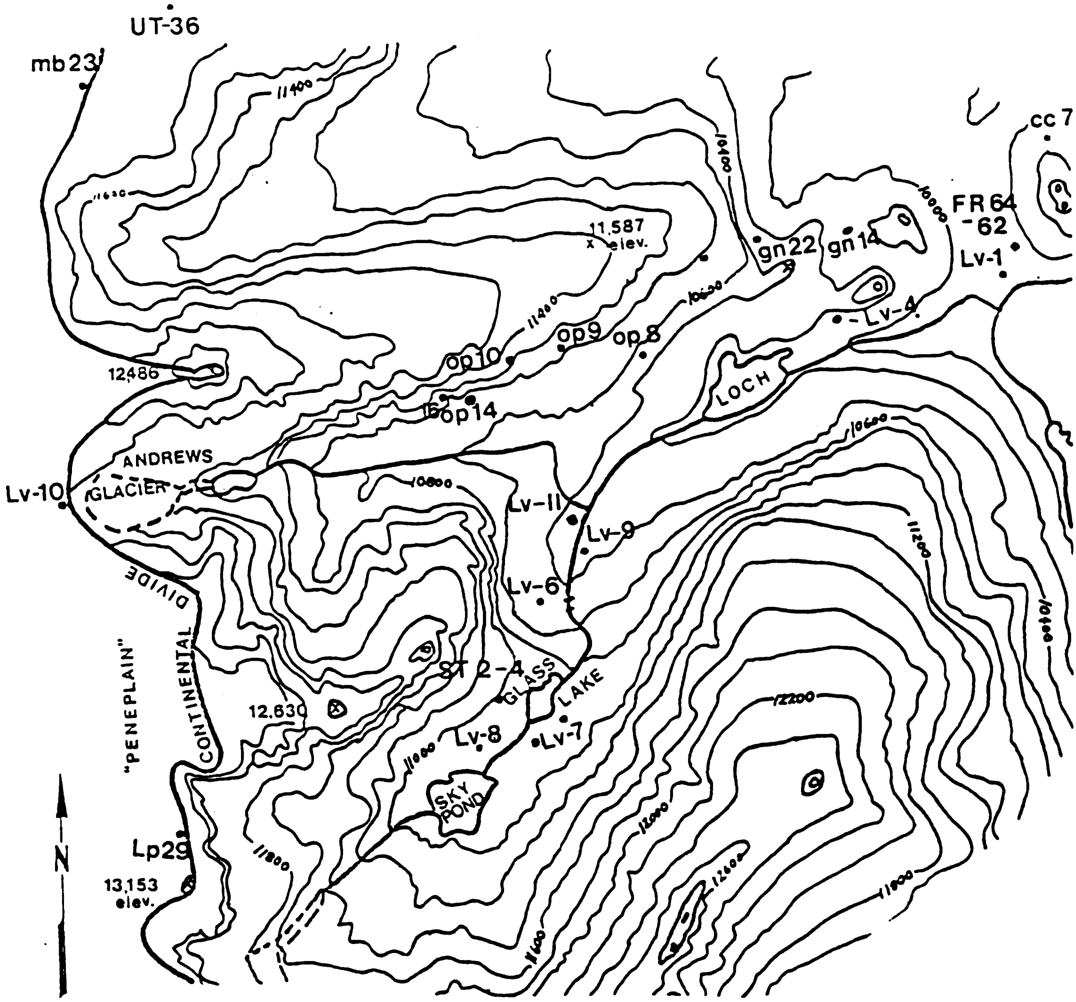
Chapter 3

METHODS

3.1 Sample Collection and Thin Sections

Thirty-four thin-sections were prepared from all rock types found in the Lochvale Drainage. Ninety percent of the total outcrop area in Lochvale is a massive granitic gneiss formed by the intrusion and cataclasis of Silver Plume granite into metasedimentary rocks (Cole, 1977; Robinson _et al_, 1974). The remaining ten percent of the total outcrop consists of discrete layers of schist (5-8%) and small discrete lenses of amphibolite (3-5%). Outcrop percentages were estimated visually during sample collection. Fresh rock, weathered rock and soils were taken wherever available in the drainage. However, due to abundant near- vertical slopes most soils were restricted to the valley bottom and in isolated pockets at the base of seeps. Thus, most soil samples for this study were taken in the vicinity of Glass Lake and Sky Pond, and in cracks of wall rocks. Thoroughly weathered rock samples were found in seeps and as rinds on granitic gneisses. See Figure 4 for a sample location map. "Classic" thick saprolite was not encountered in Lochvale; however the peneplain region of the Continental Divide did exhibit friable and decomposed rock similar to saprolite.

Caution was given to this sampling area as the peneplain



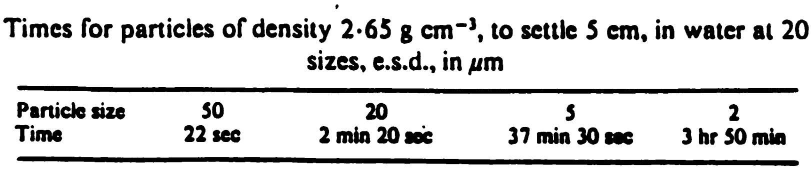
Aproximate Scale: 1" = 2500 feet

Figure 4. - Sample Location Map.

region may not be indicative of recent weathering, but of Eocene weathering associated with the peneplain. Most samples as shown in Figure 5 were taken 1000 to 2000 feet below the peneplain or Eocene weathering front.

3.2 X-Ray Diffraction and Clay Preparation Techniques

Rock samples were crushed and ground with a mortar and pestle. Aproximately 5 grams of sample was placed in a 500 ml beaker where 500 ml of deionized water was added. The beaker was then placed in an ultrasonic bath where it was agitated for a few minutes to help dissaggregate clay clumps. The beaker was removed and stirred for several seconds and then allowed to settle under gravity at 20 degrees celsius for approximately 3 hours and 50 minutes using the Stokes equation for clay particle gravity settling. Brindley and Brown (1980; p.306) show an example of some of the settling times for various particle sizes settling 5 cm:



Times for particles of density 2·65 g cm^{-3}, to settle 5 cm, in water at 20°C. Particle sizes, e.s.d., in μm

Particle size	50	20	5	2
Time	22 sec	2 min 20 sec	37 min 30 sec	3 hr 50 min

In cases where good dispersion was not possible due to flocculation of clays and organic matter, hydrogen peroxide

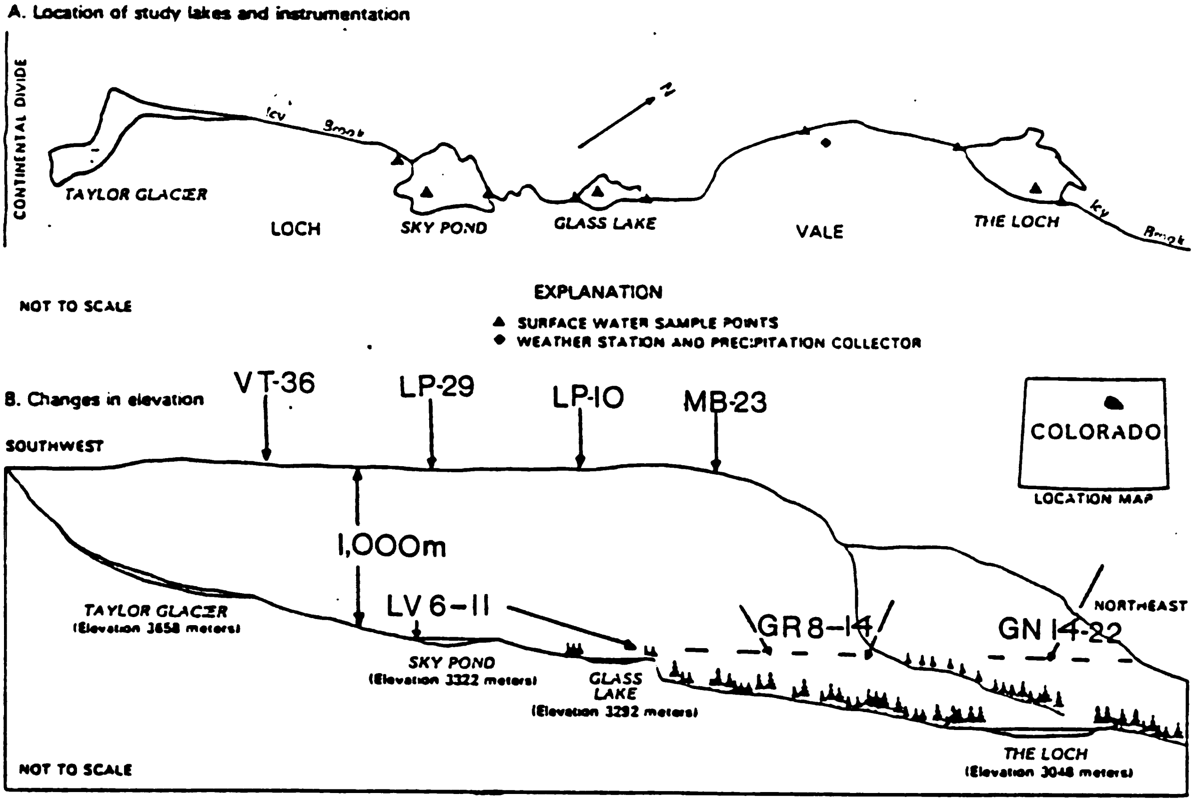


Figure 5.- Vertical Distribution of Sampling Points (after Baron and Bricker, 1987).

was added to induce oxidation and removal of organics. After the 3 hour settling period, a pipette was used to withdraw the upper 5 cm of the beaker which consisted of the less than 2 micron clay fraction. This fraction was then agitated in the ultrasonic bath for several seconds.

An oriented specimen mount was then made by placing clay dispersion in a clean cylinder attached by clamp to a porous ceramic filter overlain by a cellulose ester <.45 micron filter. A vacuum pump was used to pull an oriented film of clay on to the cellulose filter. The clay specimen was then removed by rolling a glass rod over the filter on to a glass slide. An untreated, a 1N potassium and 1N magnesium treated sample were prepared as well as a 1N Mg-glycerol and glycol solvated samples. Heat treatments were done on potassium saturated samples at 300 and 600 degrees celsius for 1 hour each. The x-ray diffraction radiation used was CuK-alpha, run at 36kV and 25 mA. Scanning speeds were 1 degree-2 theta, run at 2K (cps). The divergence slit used was .3 degrees (2-theta); the receiving slit, .6 degrees (2-theta) and the antiscatter slit was 1 degree (2-theta). The chart speed was 10 millimeters per minute and the time constant used was 1 second.

A sample of Wyoming bentonite was treated and run on XRD (see Appendix A) to test and ensure that treatment methods used could differentiate smectite clays.

Chapter 4

MINERALOGY

4.1 Schist Mineral Assemblages and Alteration Features

The dominant schist-type of the Lochvale Drainage is a coarse biotite-sillimanite schist, present in one-inch-to-two-foot thick layers within the granitic gneisses, on the faces of Otis Peak and Sharkstooth Mountain. Such schist units are often seeps and conduits for water. Preferential weathering of schist units appears to form ledges, cracks and undercuts within the canyon walls. Most of the schist layers are friable in hand sample and appear clay-rich. In thin-section, schist samples are primarily composed of coarse biotites, feldspars and sillimanite with very minor amounts of chlorite. The texture of the biotite-sillimanite schist is primarily grano-lepidoblastic (recrystallized, uniform grain size, aligned). Some samples exhibit cataclastic texture with angular clasts. Robinson _et al_ (1974) state the Silver Plume intrusion was contemporaneous with cataclastic deformation. Amphiboles are not present in any of the biotite-sillimanite schists. Blue-green pleochroic chlorite does not exhibit any alteration texture and appears only as an accessory primary mineral. Biotites of weathered schists display 'bird's eye mottling', weaker pleochroism (clear to brown) and lower birefringence than fresh biotite. Sillimanite occurs as 'bundles' (fibrolite) and as single slender, well-formed euhedral crystals. Some metamorphic alteration of sillimanite is seen in both fresh-rock interiors and surface exposures of schists and gneisses. Such altered sillimanite is cloudy (under plane light) with lower relief and grades into muscovite under cross-polars (Figure 6). Silliminite is a very common accessory mineral in the majority of the gneisses and schists of the Colorado Front Range, indicating moderate to high grade metamorphism (Nesse, 1977).

X-Ray Diffraction of Biotite-Silliminite Schist Weathering Products.

X-ray diffraction data of the < 2 micron fraction of the biotite-sillimanite schists (ST-4; Appendix A) reveal sharp and intense mica/illite peaks (10.0, 4.988 angstroms) with less intense kaolinite (7.18 angstrom) peaks and minor chlorite (14.2 angstroms). Vermiculite is not present in any of the schist rock samples (Table 1). One phenomenon noted in the biotite-sillimanite schist is a very slight collapse of the 14.24 angstrom peak at 600 celsius (Appendix A). This may be attributed to some dehydroxylation of an iron-chlorite structure. Dorothy Carroll (1964) notes that Fe-chlorite peaks become less intense and may broaden above 500 degrees Celsius versus Mg-chlorite whose peaks intensify at 650 degrees Celsius. The chlorite group itself shows gradual weight loss without structural change from 600-800 degrees Celsius. It is also possible oven temperatures may have slightly exceeded 600

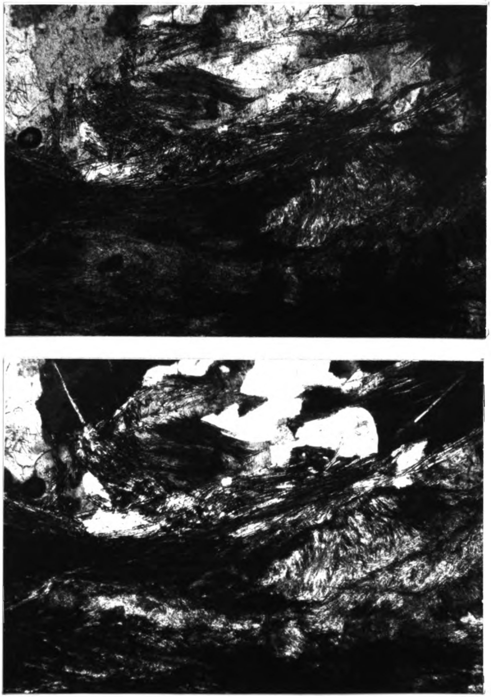


Figure 6.- Photomicrographs of altered sillimanitic schists (sample taken from seeps in Lochvale). Top: plane polarized light; high relief sillimanitic fibrolites and biotites in dark cloudy matrix; 80X. Bottom: biotite altered to a clay mineral; 80X.

Table 1

CLAY MINERALOGY SUMMARY

	SAMPLE #	Smectite	Kaolinite	Vermiculite	Chlorite	Mica/ Illite	Hydroxy Interlayer	
							Vm	Sm
	LV-1		X	X	X	X	HIV or HIS	
	LV-9		X	X			HIV	
SOILS	LV-6		X	X		X	HIV or HIS	
	LV-7		X	X		X	HIV or HIS	
	LV-11		X	X	X	X	HIV or HIS	
	LV-8		X	X				
	LV-4		X	X	X	X		
GNEISS/	OP-10		X			X		
SCHIST	OP-14		X			X		
	ST-2		X		X	X		
	ST-16		X		X	X		
	GN-22		X			X		
	OP-8		X			X		
	OP-9		X					
saprolitic	LV-10	TR	X	X			HIV or HIS	
	MB-23		X			X		
	LP-29		X			X		
	ST-4		X		X	X		
AMPHIBOLITE	GN-14		X	X	(10.5 A) amphibole pk	X	GT *	
GRANITE	D-57			X		X	HIV or HIS	
	D-61			X		X	HIV or HIS	
	FR-62		X			X		
	FR-64			X	(10.5) X amphibole pk	X	HIV or HIS	
	CC-71		X	X		X		
	HP-M		X	X		X	RIC	
	4-HP-M		X			X		
	UT-36		X	X		X	HIV or HIS	
	AP-CF		X			X		

GT* = goethite peak around 4.18 angstroms
RIC = randomly interstratified clay

degrees Celsius.

Summary of Schist Weathering

Petrography of the biotite-sillimanite schist shows the only primary mineral component presently weathering is biotite.

X-ray diffraction reveals kaolinite as the dominant clay-type, followed by minor amounts of chlorite (which was determined petrographically to be a primary accessory mineral component). No relationship was inferred from these findings that biotite was weathering directly to kaolinite.

Because most schist samples were also from seeps, it may be possible kaolinite was transported by waters from other bulk rock sources such as the granite-gneisses.

4.2 Granitic Gneiss Mineral Assemblages and Alteration

Silver Plume-related granitic gneisses are the most dominant rock type of the Lochvale drainage. The gneisses are massive and well indurated (a hammer will rebound very easily upon striking the canyon-wall rocks). Sillimanite is also distinctly present throughout the gneisses. Several thin-sections show some of the gneisses have abundant microcline and plagioclase. Unweathered specimens of gneiss exhibit foliation and idiomorphic or grano-lepidoblastic texture. Several specimens show migmatitic textures with biotite aligned in microfolds or 'fish bone' patterns.

Thin-sections of weathered samples reveal clay-rich and altered plagioclases and biotites. Alteration features include pseudomorph textures of plagioclase where clay material has replaced and mimicked parent plagioclase textures such as twinning, cleavage and grain morphology. Pseudomorph textures are seen at the weathering surfaces of gneiss samples (Figure 7)-- interiors of rock samples appear 'fresh' and non-weathered (Figure 8). The biotites of the weathered gneisses also show alteration products and textures (Figure 9). Many of the weathered biotites show a mottled texture with interdigitations of fresh and weathered lamellae. Such weathered biotite interdigitations remain dull low order browns under both crossed and uncrossed nicols when the stage is turned a full 360 degrees. Some specimens show a high birefringence clay appending to scalloped edges of the biotites. Minor amounts (<5%) of blue-green pleochroic chlorite was also seen and did not appear altered, but as a euhedral primary mineral. Although fresh microcline is prominent in many of the gneisses it also did not appear altered in any of the weathered specimens, unlike plagioclase (Figure 8).

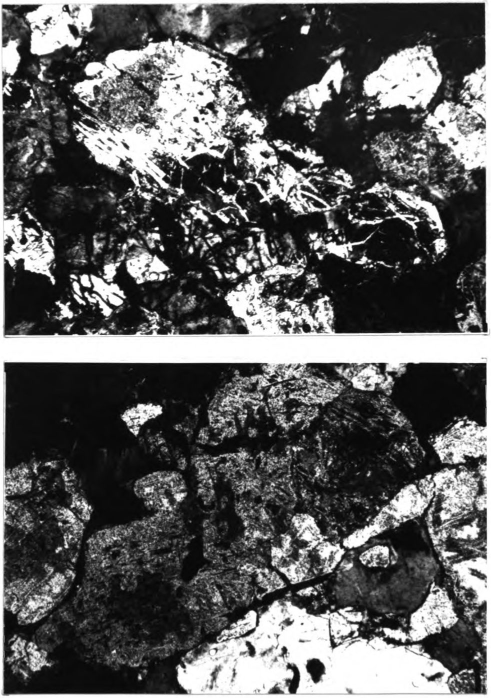


Figure 7.- Photomicrographs of plagioclase replacement textures in granitic gneiss; 80X.

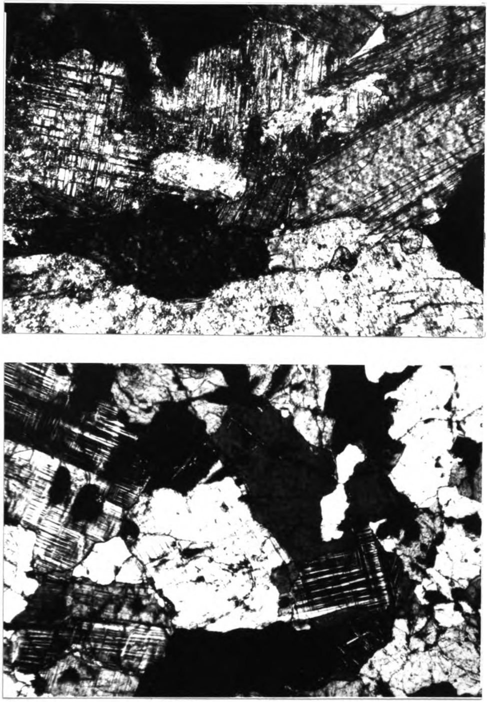


Figure 8.- Photomicrographs of altered and fresh plagioclase. Top: incipient plagioclase alteration to clay mineral taken from surface of granite gneiss; 80X. Bottom: fresh interior; clean feldspars; 80X.

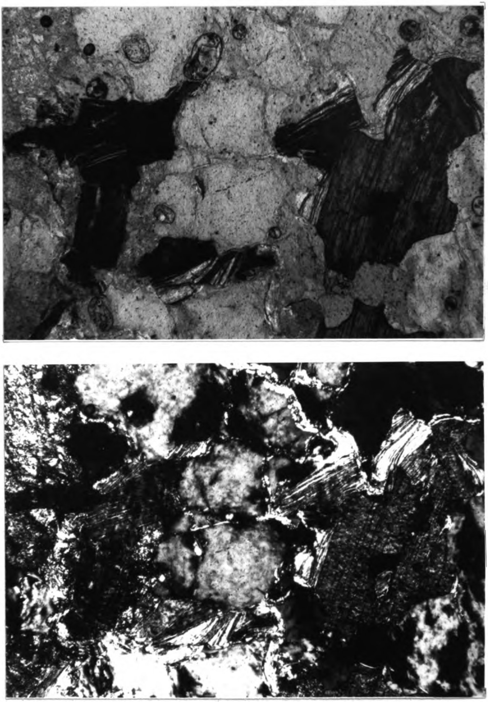


Figure 9.- Photomicrographs of altered biotites from granite-gneiss. Top: plane light; 80X. Bottom: polarized light; low order interference colors and mottled texture on biotites; alteration to a high birefringence clay mineral; 80X.

X-Ray Diffraction of Gneiss Weathering Products

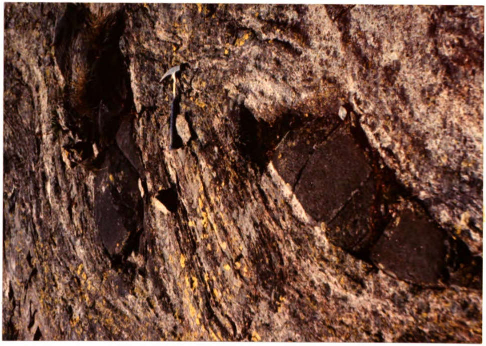
Much like the < 2 micron fraction of the biotite-silliminite schist, the < 2 micron fraction of the granitic gneisses contained kaolinite, illite and minor amounts of chlorite (Table 1; ST-2). One gneiss sample taken on the Continental Divide or peneplain surface contained hydroxy-interlayered clays which can be interpreted as either a vermiculite or smectite (LV-10; Appendix A). Unfortunately, as discussed by R. Barnhisel (1977; p. 535) there is no definitive means to identify hydroxy interlayered clays as either vermiculites or smectites, as their mineralogic properties overlap. The peneplain sample was similar to the XRD patterns of the Lochvale soils, which are discussed later in this chapter. Hand picked feldspars from weathered gneiss samples contained a dominant kaolinite peak (HP-4 of Table 1; ST-2 of Appendix A).

Summary of Granitic Gneiss Weathering

The bulk of the granite gneiss samples show plagioclase and biotite as the main weathering minerals. Textural evidence shows that plagioclase feldspars are replaced by a clay, preserving parent cleavage and twin planes along with original grain shape. Such pseudomorph textures were found only in the outer, surface exposed layer of the gneisses. The interior of the gneisses were unaltered. X-ray diffraction shows a prominence of kaolinite and a mica/illite peak shown petrographically to be dominantly biotite. X-ray diffraction of hand picked feldspars shown a dominant kaolinite peak. Chlorite, as also found in two of the samples in minor amounts, appears petrographcally to be a primary accessory mineral. One sample taken on the peneplain also has an unknown hydroxy-layered mineral and vermiculite. In summary it can be inferred from all petrographic and x-ray diffraction work of the granite-gneisses that plagioclase is weathering to kaolinite. The peneplain gneiss sample (which may be indicative of more prolonged weathering) shows plagioclase weathers to kaolinite and biotite weathers to vermiculite. In addition, the possibility exists that vermiculite may eventually weather to a hydroxy interlayered clay.

4.3 Amphibolite Mineral Assemblages and Alteration Features

Lenses of amphibolite are widely scattered in isolated pockets throughout the gneisses of the Lochvale drainage and the entire Front Range (Cole, 1977; Nesse, 1977; Robinson _et al_, 1974; Wahlstrom and Kim, 1969; Wells _et al_, 1964; Lovering, 1935; Simms, Drake and Tooker, 1963; Tooker, 1963). Dramatic hollows and depressions are left where the amphibolite appears to have preferentially weathered out with respect to the enclosing gneiss (Figure 10). The preferential weathering of these amphibolites is seen throughout the Front Range and has been described in many studies as a rock-type with such a "tendency to weather more heavily, that it is seldom seen in outcrop", (Cole, 1977; p. 41). In the Lochvale drainage, the amphibolite comprises an estimated 5% of all rock types found in the drainage. Hand samples of amphibolite show that it is a dark green to black, almost 'mafic' appearing rock, which contrasts sharply with the surrounding gray-pink granitic gneisses (Figure 10). Thin-sections (Figure 10) show abundant blue-green pleochroic amphibole and some brown to dark brown pleochroic biotite, with varied amounts of iron-staining along cracks throughout samples, suggesting iron-enriched amphiboles or biotites may be weathering. Thin-section evidence for amphibole and biotite weathering was not conclusive (Figure 11) as there was great difficulty in obtaining a weathered specimen such as weathering rind. Unlike the granites and gneisses, the finely crystalline (.2mm) amphibolites appeared to have just dissolved and disappeared, leaving no soil traces or other solid residues, but rather fresh to slightly iron stained, smooth round surfaces and weathered out hollows. One reason for the observed 'dissappearance' of the amphibolite is the small amounts of resistant quartz (less than 20%) composing the amphibolite rock matrix. The quartz may serve as a skeletal framework retaining weathered minerals and clays in other quartz rich rock types. SEM work was done on amphibolites to discern any other textural evidence for weathering such as etch-pits, dissolution voids and fractures and/or the characteristic



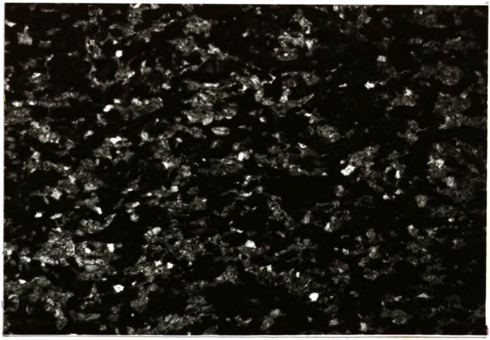


Figure 10.- Photograph of weathered amphibolite. Bottom: photomicrograph of amphibolite; polarized light; 80X.

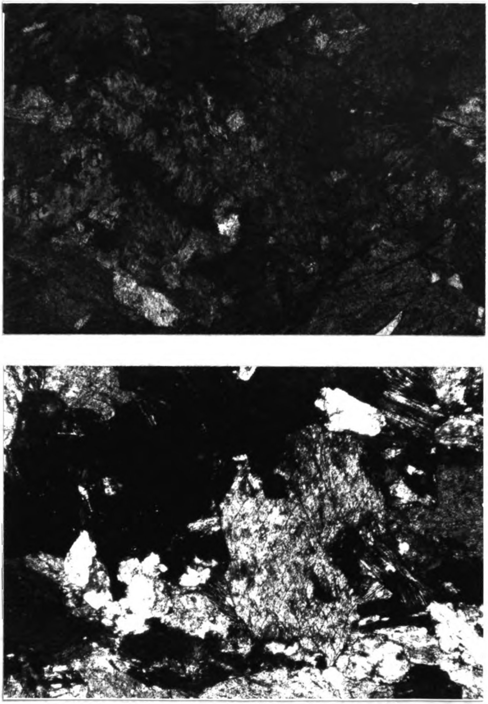


Figure 11.- Photomicrographs of altered amphibolite. Top: incipient alteration of hornblende to clay mineral; plane light; dark Fe-Mg staining; 200X. Bottom: polarized light; 200X.

'sawtooth' or denticulated terminations associated with amphibole weathering (Berner et al, 1980; Velbel, 1984). Figure 12 shows an extensively weathered amphibole with similar 'saw tooth-like' terminations from a Lochvale amphibolite. Likewise the microcrystalline feldspars, mostly plagioclase, did not have conclusive thin-section evidence for weathering. SEM micrographs show feldspar etch pits.

X-Ray Diffraction of Amphibolite Weathering

X-ray diffraction of the < 2 micron fraction of the amphibolite (GN-14; Appendix A) reveals an intense 8.41 angstrom peak which correlates to the amphibole (001). Kaolinite, mica/biotite, a mixed layered clay of 7 and 10 angstroms, goethite and a hydroxy interlayered vermiculite or smectite are also present in lesser amounts.

Summary of Amphibolite Weathering

Textural evidence based on SEM was found for the weathering of plagioclase and amphibole in the amphibolites.
X-ray diffraction data of the amphibolite shows kaolinite, a hydroxy interlayered vermiculite or smectite and a mixed layer clay.

As supported by previous textural evidence, plagioclase is

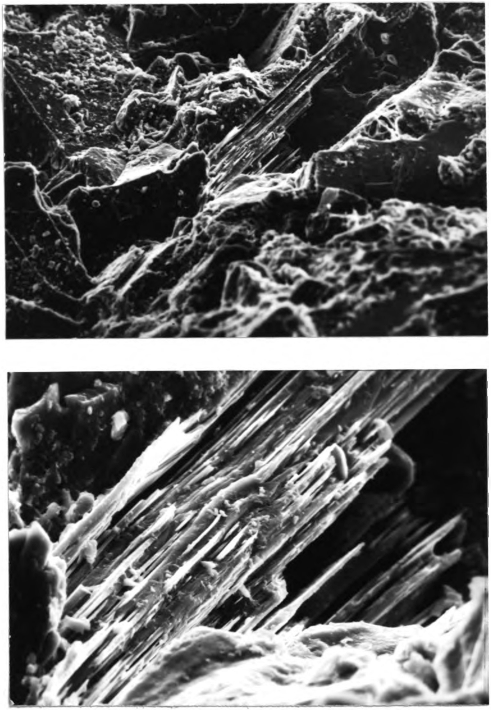


Figure 12.- SEM micrographs of weathered amphibole with characteristic 'sawtooth' terminations from a Lochvale amphibolite; 200X; 1000X.

weathering to kaolinite; amphibole is weathering to kaolinite and biotite is weathering to vermiculite.

4.4 Granite Mineral Assemblages and Alteration

Discrete non-foliated granites are not as areally extensive as the granitic gneisses of the Lochvale drainage and are harder to discern from weakly foliated gneiss. Near the junction of Icy Brook and Andrews Creek, a large noteable outcrop of gray-pink, medium-grained Silver Plume granite can be seen. Thin sections of the Silver Plume granite show typical granular igneous textures with random subjunctions (idiomorphic) to annealing textures, with some triple junctions. Granites contain abundant microcline, quartz and biotites and minor amounts of plagioclase. Weathered biotites exhibit brown to dull, low order birefringence, with mottled texture. Some weathered biotites have altered rims and clay-appendages on terminations. No other weathering or alteration features were observed.

X-Ray Diffraction of Granite and Weathering Products

The <2 micron fraction of the granite (FR-64) consists of vermiculite, mica/illite (biotite), hydroxy-interlayered vermiculite or smectite and minor amounts of kaolinite. On several diffraction patterns, hydroxy-interlayered clays show a characteristic peak at 14.1 angstroms 'bridged' to a 10.0 angstrom mica/illite peak. After potassium treatment, part of this peak collapses towards 10.0 angstroms; the peak shifts even further towards the 10.0 angstrom peak upon heat treatment to 300 degrees Celsius. The peak then almost entirely collapses to 10.0 A at 600 degrees Celsius. Such patterns may indicate a hydroxy-interlayered vermiculite or smectite, where pillared smectite or vermiculite is propped open by an aluminum or magnesium hydroxide (gibbsite or brucite) sheet (R. Barnhisel, 1977; p. 535). Successive heat treatments can dehydroxylate these interlayer materials. Similarily, the soils also exhibit the same hydroxy-interlayered patterns. Unlike the gneisses or schists, kaolinite is not consistently found in the granites. X-ray diffraction of hand-picked micas was also done for the granites (HP-M; Appendix A). Vermiculite and some kaolinite was found, however it was difficult to remove micas without disturbing other minerals such as feldspars and clays. Therefore, the kaolinite peak on the biotite sample pattern may not be from the weathering of biotite, but may be a product of the feldspar. Sample HP-M also contained a broad 8.0 angstrom peak which may represent a randomly interstratified clay of vermiculite/kaolinite; smectite/kaolinite ; chlorite vermiculite or other (Sawhney, 1977; p. 413-431). One XRD pattern (FR-64) also contained a moderate amphibole peak at 8.41 angstroms.

Summary of Granite Weathering

Based on petrographic and x-ray diffraction work it appears biotite weathers to vermiculite and possibly a hydroxy-interlayered vermiculite or smectite. This weathering scheme has also been well documented in the Front Range literature by other researchers (Isherwood and Street, 1976; Blair, 1976). Minor amounts of plagioclase also appear to be weathering to kaolinite, where present in the granites. The sporadic and minor amounts of kaolinite in the granites may indicate biotites are not weathering to kaolinite but are transformed directly to vermiculite.

4.5 Soil Mineral Assemblages and Alteration Products

Soils of the Lochvale drainage were mostly taken from below the massive gneiss wall rocks near Sky Pond, Glass Lake and above the Loch. Such soils were not very thick (approximately 6 inches to 1 foot) and were sampled below an aproximately 1 inch thick black organic surface layer. Several soil samples were also taken from granites at the entrance of the Lochvale drainage (Figure 4). Like the granites, the soils also show a variety of clay mineral assemblages. X-ray diffraction of the <2 micron soil fraction reveals large quantities of kaolinite, vermiculite, and some chlorite (LV-7; Appendix A). In addition, virtually all samples show the same hydroxy-interlayered clay patterns as observed in the granite diffraction patterns.

Summary of Soil Weathering

The Lochvale soil environment occupies less than 6% of the total watershed surface area. Even though the soil areal extent is small in contrast to the exposed bedrock surfaces, it is not precluded from supplying, exchanging or storing significant sources of cations or anions from the Lochvale drainage. Lochvale soils may represent ongoing, dynamic weathering unit, composed of older and possibly more advanced stages of weathering. The predominance of hydroxy-intelayered clays and vermiculites may suggest additional soil-biotite weathering to vermiculite and pedogenic chlorite, vermiculite weathering to a hydroxy-intelayered clay and lithic fragments of plagioclase weathering to kaolinite. The Lochvale soil samples collected for this thesis, however, revealed no additional clay types outside those weathering products observed for the various lithologies. Walthall (1985) did find smectite in his soil samples from Lochvale, however, many of his soil samples were taken in poorly drained areas, such as the forest floor. Furthermore, most of his soils had generally low CEC capacities indicating a predominance of relatively non-exchangeable clay types such as kaolinite and vermiculite.

4.6 Summary of Mineralogical Findings

A summary chart of X-ray diffraction data is given for Lochvale gneisses, schists, amphibolites, granites and soils in Table 1. The most prominent clay mineral is kaolinite, occuring in all rock types and soils of the Lochvale drainage, with the exception of some granite samples. All samples have biotite with the exception of 1 soil sample, which was composed entirely of kaolinite, vermiculite and a hydroxy-interlayered clay. Virtually all of the soils, (as well as the granites) have a hydroxy-interlayered vermiculite or smectite clay present.

X-ray diffraction of hand-picked plagioclase and biotite reveal strong evidence that plagioclase weathers to kaolinite and biotite weathers to vermiculite.

The amphibolites contained large amounts of relict primary amphibole, followed by biotite, kaolinite and minor vermiculite and goethite.
Granite rock samples contained hydroxy-interlayered clays, vermiculite, mica/biotite, amphibole and several granite samples lacked kaolinite.

In order to validate mineral transformation reactions, it is necessary to link petrographic evidence with the clay mineralogy findings summarized above.

Textural evidence from thin-sections and SEM show only plagioclase, biotite, and amphibole as primary minerals presently weathering. Plagioclases were observed to weather into pseudomorphs on surface rinds of granite gneisses and were observed to contain etch-pits in amphibolites. Weathered biotites displayed mottled, dull birefringent colors with interdigitations of more highly birefringent (fresh) biotite. Amphibolites consisting predominantly of amphibole were observed to extensively weather only on a field scale forming holes and vugs once occupied by amphibolite. SEM work done on amphiboles also showed characteristic 'sawtooth-like' or denticulated terminations on amphiboles, indicating pronounced weathering.

In summary, the following key mineral transformations are defined for the Lochvale drainage:

Plagioclase -------->Kaolinite
Biotite -------->Vermiculite
Amphibole -------->Kaolinite + Goethite

Based on the petrographic and x-ray diffraction findings, the weathering of the amphibolites, gneisses, granites and schists are considered as the key reactions controlling the cation budgets of the watershed. Complete stoichiometric weathering reactions are based on literature-derived mineral compositions for the various Lochvale lithologies.

4.7 Literature Derived Mineral Compositions

A thorough search of the literature on the granitic, gneissic and amphibolite lithologies of the Colorado Front Range was done: a) to establish the rock types of the Lochvale drainage; and b) to secure mineralogical data, especially mineral compositions, for use in mineral weathering reactions. Several local dissertations were studied (Nesse, 1977 and Cole, 1977) as well as an extensive body of literature describing the rocks of the Front Range (Robinson et al, 1974; Wahlstrom and Kim, 1969; Wells et al, 1964; Lovering, 1935; Simms, Drake and Tooker, 1963; Tooker, 1963).

In addition, several local 'weathering' papers and dissertations (Isherwood and Street, 1976; Blair, 1976; Nesse, 1977) supplied microprobe analyses for biotite, vermiculite/hydrobiotite and plagioclase of the Silver Plume and Boulder Creek granites which were calculated into full cell mineral formulas (hand calculations in Appendix B; formulas on Table 2). Granite and gneiss plagioclase compositions ranged from anorthite 15 to 35.

A thorough search of the literature was also done on the Front Range amphibolites, however, chemical compositions for amphiboles were virtually non-existent. Front Range amphibolites have not been considered as an important or significant rock type because of their 'non-mappable' or small areal extent (Cole, 1977; Robinson _et al_, 1974). It is theorized that the amphibolites are metamorphosed basalts (Tweto, 1980; Cole, 1977). Barker _et al_ (1975) studied the chemical composition and origin of the Pikes Peak batholith and its relationship to the older Boulder Creek (calc-alkalic magma source), the Silver Plume (peraluminous magma source) and the once overlying 15,000 meters of basaltic volcanics. They concluded that the formation of the Pikes Peak batholith was due to reaction melting of overlying and surrounding rocks and a parent basaltic magma.

Although Barker _et al_ (1975) microprobed only quartz syenite amphiboles, their model suggests amphibolite-amphiboles are extremely calcic and iron-enriched: ferrotremolites (actinolite) solid solution series. Other literature also suggests tremolite and a generic hornblende based solely on optical properties (Robinson _et al_, 1974; Wells _et al_, 1964).

The dominant plagioclase of the amphibolite is labradorite --Anorthite 60-65, determined through microprobe analysis done by Nesse (1977) and Cole (1977). Other researchers prior to Nesse (1977) and Cole (1977) optically determined the plagioclase composition of the amphibolite to be less calcic--Anorthite 35-45 (Robinson et al, 1974), but still more calcic than the plagioclase of the granites or gneisses.

Table 2 summarizes literature derived compositions and respective references.

4.8 Stoichiometric Weathering Reactions Summary

Based on the X-ray diffraction data, the literature derived mineral compositions and the textural and mineralogical evidence, the following mineral transformations (Table 3) are proposed as the key weathering reactions supplying the vast majority of base cations out of the Lochvale watershed.

Table 2

Front Range Literature-Plagioclase Compositions

Biotite Gneisses and Schists	An 20-35	(Robinson *et al*, 1974)
Granitic Gneisses and Schists (Migmatites)	An 15-35	(Robinson *et al*, 1974)
Sillimanite Gneisses and Schists (calc-silicate rocks)	An 20-35	(Robinson *et al*, 1974)
Amphibolites	An 60-65	(Cole,1977; Nesse,1977)
Silver Plume Granites and Monzonites	An 15-25 An 20-25 An 24-30	(Robinson, et al, 1977) (Nesse, 1977) (Nesse, 1977)

Front Range Biotite Compositions

Fresh Biotite (Isherwood and Street, 1976)

$K^{+}_{1.994}(Fe^{3+}_{.448}Fe^{2+}_{1.772}Mg^{2+}_{3.118}Ti^{4+}_{.242})(Al_{.012}Si_{5.988})$
$O_{20}(OH)_{4}$

Weathered Biotite (Isherwood and Street, 1976)

$K^{+}_{1.094}\ Ca^{2+}_{.226}(Fe^{3+}_{1.988}\ Fe^{2+}_{.178}\ Mg^{2+}_{2.250}\ Ti^{4+}_{.208}$
$Al^{3+}_{.220})(Al^{3+}_{1.854}Si^{4+}_{6.146})O_{20}(OH)_{4}$

Amphibole Compositions

Ferrotremolite-Actinolite Intermediate (Barker et al, 1975; Deer et al, 1980)

$$Ca_2(Mg_1Fe^{2+}_4)[Al_1Si_6]O_{22}(OH)_2$$

Table 3

Balanced Mineral Weathering Reactions

Anorthite $_{65}$$^{(\text{Nesse, 1977})}$ -------------->Kaolinite

$Na_{.35}\ Ca_{.65}\ Al_{1.65}\ Si_{2.35}\ O_8 + 3.885\ H_2O + 1.65CO_2$ --------------> $.82\ Al_2Si_2O_5(OH)_4 + .35Na^+ + .65Ca^{++} + 1.65HCO_3^- + .71\ H_4SiO_4$

Anorthite$_{35}$$^{(\text{Robinson et al, 1974})}$-------->Kaolinite

$Na_{.65}\ Ca_{.35}\ Al_{1.35}\ Si_{2.65}\ O_8 + 4.625\ H_2O + 1.35CO_2$ ---------------->$.675\ Al_2Si_2O_5(OH)_4 + .65Na^+ + .35Ca^{++} + 1.35\ HCO_3^- + 1.30\ H_4SiO_4$

Biotite$^{(\text{Isherwood et al.,1976})}$ ------>
Vermiculite$^{(\text{Isherwood et al.,1976})}$

$K^+_{1.994}(Fe^{3+}_{.448}Fe^{2+}_{1.772}Mg^{2+}_{3.118}Ti^{4+}_{.242})(Al_{.012}Si_{5.988})\ O_{20}(OH)_4 + .226Ca^{2+} + 1.05O_{2\ (g)} + 3.20\ CO_2 + .71\ H_2O$ -----------------------> $.970\ K^+_{1.094}\ Ca^{2+}_{.226}(Fe^{3+}_{1.988}\ Fe^{2+}_{.178}\ Mg^{2+}_{2.250}\ Ti^{4+}_{.206}\ Al^{3+}_{.220})(Al^{3+}_{1.854}Si^{4+}_{6.146})O_{20}(OH)_4 + .933K^+ + .119Fe(OH)_{2(aq)} + .936Mg^{2+} + .042Ti^{4+} + 3.20HCO_3^- + .026H_4SiO_4$

Ferrotremolite(Actinolite)$^{(\text{Barker et al. 1975})}_{}$ $^{(\text{Deer et al. 1980})}$-------------> Kaolinite + Goethite

$Ca_2(Mg_1Fe^{2+}_4)[Al_1Si_6]O_{22}(OH)_2 + 12H_2O + 6CO_2 + 1.25O_{2(g)}$---> $.5Al_2Si_2O_5(OH)_4 + 2Ca^{++} + 1Mg^{++} + 18HCO_3^- + 5H_4SiO_4 + 4FeO(OH)$

CHAPTER 5

RATES OF MINERAL WEATHERING: APPLICATION OF A GEOCHEMICAL MASS BALANCE MODEL

5.1 Introduction

Watershed geochemical mass balance studies of mineral weathering rates are believed to provide the most reliable estimates of field mineral weathering rates (Cleaves, Godfrey and Bricker, 1970; Paces, 1983; Velbel, 1985a; Katz et al, 1985; Garrels and Mackenzie, 1967; Drever and Hurcomb, 1986; Clayton, 1986). For this research a watershed mass balance study of mineral weathering rates was performed using the mineralogical findings of Chapter 4 and hydrogeochemical flux data (Appendix C) for the Lochvale Drainage, Rocky Mountain National Park.

5.2 Model Assumptions

The geochemical mass balance technique assumes that all water leaving the catchment originated as precipitation that fell directly within the catchment boundaries. As discussed in Chapter 2, there are no known springs in the Lochvale drainage due to the very high basin elevation. Hydrologic budgets computed by Baron and Bricker (1987) in 1984 and 1985 did show conservative ion chloride with a 35% discrepancy. However, it was concluded precipitation measurement errors were made due to high winter winds altering gauges and underestimating catch efficiencies and not to unlikely, exotic water sources. Input cation budgets were normalized to chloride.

Mass balance techniques also assume steady-state conditions, where net cation exports equal the sum of precipitation inputs and weathering rates, and that exhangeable base pools such as biomass and soils are negligible and static with respect to growth and time. The Lochvale drainage, as discussed in chapter 2, is predominantly an alpine-subalpine catchment, where only 6 percent of the drainage surface area is covered by soil and vegetation and 94 percent is exposed bedrock. Severe climatic conditions of the alpine form little or no soil, readily removing regolith and weaker friable material. Consequently, fresh bedrock surface areas are continually renewed, promoting a greater potential for primary mineral hydrolysis. A small biomass and soil areal extent may influence cation export budgets, but primary mineral hydrolysis may outrank exchangeable base pool processes in alpine-subalpine scenarios. Baron and Bricker (1987) state that the hydrology of the Lochvale watershed exerts the most influence on the water chemistry, as sulfate budgets suggest solutes have little opportunity to interract with the ecosystem before they are flushed out during snowmelt. They further contend net exports of major cations 2.5 to 4.0 greater than inputs is the direct result of mineralogical weathering.

5.3 Thermodynamic Stability Relations of Lochvale Waters

Figure 14 shows that the waters draining the Lochvale watershed (average, high and low concentrations plotted) are in equilibrium with the kaolinite.

5.4 Matrix Setup

The geochemical mass balance used for this study is illustrated as a box model which quantitatively maps inputs and ouputs of base cations (Figure 15).

In many watershed field settings, as many as 6 major sources and sinks are responsible for net cation imports and exports. In the Lochvale box model, uptake into forest or other biomass, and storage in ground water, are considered negligible as discussed earlier. The most significant cation inputs are mineral weathering and precipitation. Plummer and Back (1980) summarize the following mass balance relationship with the following equations :

$$\sum_{j=1}^{\phi} \alpha_j \beta_{c,j} = \Delta m_c$$

The delta m_c term is the net flux of element c, determined by subtracting precipitation input from stream output fluxes, and is expressed in moles/ha/yr (Table 4). The

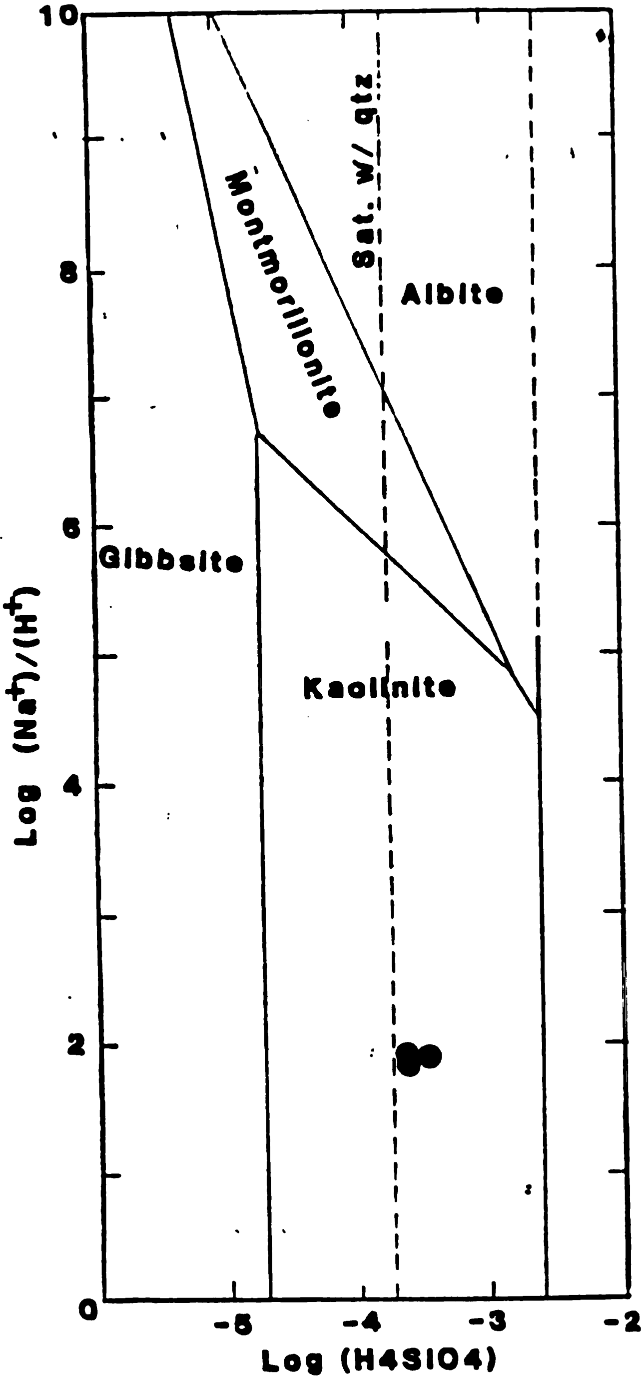


Figure 14.-Stability diagram for the Na-Al-Si-H20 system at equilibrium for 25 Celsius and 1 bar pressure --circles represent Lochvale water analyses (from Feth *et al.*, 1984).

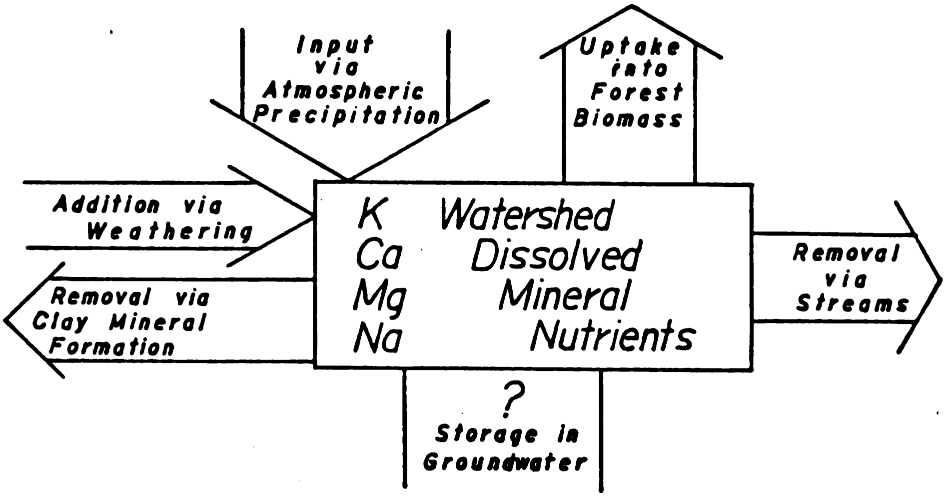


Figure 15.-Box Model (from Velbel, 1985a)

beta term (β_c) is the stoichiometric coefficient of element c in reaction j which is expressed in moles of c per mole of weathering reaction j. The alpha term is the number of moles of weathering reaction j and is expressed in moles/ha/yr. If alpha is a negative value then the reaction is not forward as written, but reverse. In order to solve the Plummer and Back mass balance equations, the stoichiometric coefficients of the mineral weathering reactions are found from the clay mineralogy and petrographic studies. As shown in Chapter 4, the primary mineral transformations observed consist of 4 different weathering reactions and the stoichiometric coefficients listed in Table 5.

Thus, the Lochvale model consists of four mass balance equations ($n=4$) for calcium, sodium, potassium and magnesium and four unknown alpha values (ϑ =4) or four different mineral weathering rates in terms of moles/ha/yr. These components comprise a 4 by 4 linear algebraic matrix which is solved by computer and checked with hand calculations (Table 5 and Appendix B).

5.5 Matrix Solution: Results and Discussion

The most significant weathering processes in the Lochvale drainage are the transformation of plagioclase composition-An_{65} (amphibolite) and An_{35} (granitic gneisses) to kaolinite. Releasing 3.3 to 3.8 metric tons of dissolved

Table 4

Elemental Flux Numbers
(Lochvale Watershed)

	Inputs minus Outputs/Molecular Wt. g/ha / g/mol / yr		Moles per hectare per year 1984	 1985
Ca	4950/40.08	=	123.50	82.64
Mg	800/24.31	=	32.90	16.11
Na	1690/22.99	=	73.51	33.73
K	940/39.10	=	24.04	143.46

Table 5

Mass Balance Equation Matrix

Element Removed		Moles ha^{-1} yr^{-1} 1984	 1985		Coefficient Matrix (in X moles of mineral weathered per hectare per year) Biotite		 Anorthite 65		 Anorthite 35		 Actinolite
Na	=	73.51	82.64	=	0	+	.35	+	.65	+	0
K	=	24.04	16.11	=	0.933	+	0	+	0	+	0
Mg	=	32.9	33.73	=	0.936	+	0	+	0	+	1
Ca	=	123.5	143.46	=	-.226	+	.65	+	.35	+	2

Table 6

Solution to Mass Balance Matrix
(Moles per hectare per year)

	Biotite	Anorthite 65	Anorthite 35	Ferrotremolite-Actinolite
1984	25.7663	156.38	28.8876	8.7827
1985	17.2669	146.743	48.1231	17.5682

calcium per year and 1.1 to 1.25 metric tons of dissolved sodium, the weathering of An $_{65}$ occurs at a rate of 146.7 to 156.4 moles/ha/year and An $_{35}$ at a rate of 28.9 to 48.12 moles/ha/year. Weathering of the ferrotremolite-actinolite amphibole and biotite have lesser effects on solute budgets in the Lochvale drainage. Producing a half-metric ton of both magnesium and potassium per year, the transformation of biotite to vermiculite occurs at a rate of 17-25 moles/ha/year and ferrotremolite to kaolinite at a rate of 8.7 to 17.6 moles/ha year (Table 6).

One way to check whether the mineral weathering reactions and rates accurately describe the system being modelled, is to compare measured silica outputs to the silica release rates predicted by the stoichiometric mass balance equations. As shown in Table 7, the predicted silica releases described by the four stoichiometric weathering reactions from Chapter 4 was within 2% of the actual silica measurement for 1984 and within 37% for 1985.

In 1984 the mineral weathering reactions and mass balance derived mineral weathering rates clearly account for the observed water chemistry, however, in 1985 the accuracy drops. Few studies successfully match predicted silica release rates with measured flux rates. Clayton (1988) computes mass balance weathering rates for three forested watersheds in the Idaho batholith. His predicted silica

Table 7

Silica Release Rate Predictions vs. Actual

	1984	**1985**
Measured SiO2 (moles/ha/yr)	197.3	161.0
Predicted from stoichiometric reactions	193.2	255.3
Predicted vs. actual accuracy	98%	63%
	(+/- 2%)	(+/-37%)

release rates were also within 94% of the measured silica flux, suggesting that primary mineral hydrolysis accounts for the net loss of cations from the watersheds. Clayton (1988), Velbel (1985a), Drever and Hurcomb (1987) suggest the reason that few predictions of silica release rates are successful in watershed mass balance studies may be due to complex lithologies and incorrect characterization of weathering products and reactants. In this thesis it is not clear why a discrepancy exists between the 1984 and 1985 predicted versus the actual silica release rates. Mineral weathering rates increased in different proportions from 10 to 20 moles of mineral per hectare per year, yet there were no significant differences in pH (in fact, pH rose by .05 units; Table 8) and precipitation and measured water outflow decreased in 1985 (Table 9).

A study of Baron and Bricker (1987) cation and anion data shows an aproximate 6 to 12% increase in their measured outputs, yet an 8% decrease in the measured inputs was found (Table 8).

Another interesting trend found was sulfate had a 12% increase in output from 1984 to 1985, yet a 24% decrease in inputs. Such trends may indeed indicate a non-steady state source or sink exists within the Lochvale drainage. Baron and Bricker (1987) cite soil and biomass as the long term sink in the Lochvale watershed, producing the observed cation and anion trends. However, Baron and Bricker (1987)

Table 8 Annual Budgets for Major Cations and Anions for 1984 and 1985 in Loch Vale Watershed. Values (kg/ha) have been Normalized to the Balanced Chloride Budget. In 1984 This Caused a 35% Increase in Input Values. In 1985 This Caused a 6% Increase in Output Values.

	1984			1985		
Species	In kg/ha	Out kg/ha	Out/In	In kg/ha	Out kg/ha	Out/In
Ca^{2+}	2.61	7.55	2.90	2.46	8.21	3.34
Mg^{2+}	0.57	1.36	2.40	0.42	1.24	2.95
Na^+	1.07	2.76	2.59	0.79	2.69	3.41
K^+	0.31	1.25	4.02	0.40	1.03	2.58
NH_4^+	1.88	0.37	0.20	1.21	0.11	0.09
SO_4^{2-}	10.68	8.25	0.77	8.18	9.30	1.14
NO_3^-	10.23	7.14	0.70	8.25	6.49	0.79
Cl^-	1.39	1.39	1.00	1.21	1.21	1.00
SiO_2	-	11.84	-	-	9.68	-
pH	5.01	6.33	-	5.06	6.27	-

Table 9 Hydrologic Balance for Loch Vale Watershed for 1984 and 1985. Values are in Million Cubic Meters.

	1984		1985	
Water parameter	Value	Adjusted by Cl-balance	Value	Adjusted by Cl-balance
Deposition (D) (measured)	7.337	9.905	7.162	7.162
Evaporation (E) (calculated)	5.165	5.165	4.078	4.078
Outflow (O) (measured)	5.996	5.996	4.152	4.401
D - (E+O)	-3.824	-1.256	-1.068	-1.317
Percent deposition as snow	64%		68%	

(from Baron and Bricker, 1987)

also note (as discussed earlier) problems with the deposition and chloride imbalance--where more deposition and chloride inputs should have been measured. Their explanation for this problem was error in measurement due to wind, snow and/or the evaporation model used.

In summary, the mass balance findings suggest the cation budgets can be explained by the weathering of four primary minerals. 1985 mass balance findings suggest a possible sink as silica's release rate predictions become less accurate.

5.6 Calculation of Tardy's Re

Mineral weathering findings of this thesis are consistent with the plot of Lochvale waters in the kaolinite stability relation diagram of section 5.3. Because mass balance findings may suggest a component of non-steady state release in the Lochvale system another useful and simple semiquantitative mass balance tool was used to confirm kaolinite. Tardy's Re consists of a formula for estimating the silica to alumina ratio retained in the solid weathering products from dissolved cations and silica of stream waters (Tardy, 1971; Velbel, 1985b).

$$\mathrm{Re} = (\mathrm{Si\ O_2/Al_2O_3})_{\mathrm{residue}}$$
$$= 2\ (3\mathrm{K}^+ + 3\mathrm{Na}^+ + 2\mathrm{Ca}^{2+} - \mathrm{SiO_2}/\ \mathrm{K}^+ + \mathrm{Na}^+ + 2\mathrm{Ca}^{2+})_{\mathrm{streams}}$$

Several assumptions are built into Tardy's Re: a) quartz and muscovite are unweatherable and weatherable minerals have feldspar and biotite stoichiometries and b) all minerals dissolve stoichiometrically. When the Re=0 the predicted weathering residues are aluminous (e.g. gibbsite); when Re=2, a 1:1 atom ratio of silica to aluminum is attained which corresponds to a 1:1 clay mineral (e.g. kaolinite) and when Re=3, silica is withheld by the weathering profile to form 2:1 clays (e.g. smectite). The following Re's were calculated for the Lochvale drainage:

Table 10

Lochvale Drainage
Tardy Re Calculations

1.090
0.910
1.263

The results of the Lochvale Tardy Re's show Lochvale weathering products should be more kaolinitic to aluminous as opposed to 2:1 clay type residues. Such results support the observed kaolinite mineralogy of the Lochvale watershed but do not support the formation of a smectite dominated weathering profile. As stated previously, however, Tardy's Re is used only as a semiquantitative tool and the results are looked at more qualitatively.

5.7 Comparison of Mineral Weathering Rates to Other Research

The following Table 11 modified after Velbel (1985a) shows plagioclase weathering rates from various watershed mass balance studies which are normalized to modal abundance of plagioclase. As shown, the results of this thesis combines both plagioclases (An35 and An65) weathering rates into a combined weathering rate of 194.86 moles/ha/year. Although An65 is known to occur only in amphibolite rocks, which occupy roughly 5% of the total lithologies in Lochvale, the modal percentage (43%) was normalized to the entire drainage area, to a new modal value (2.15%). Likewise, using an average modal percent for An35 (15%), which composes granitic gneisses representing 95% to the total rock types, a surface area normalization was done to the entire drainage giving a new modal value of (14.2%).

Table 11

Plagioclase weathering rates from watershed mass balance studies

Watershed	Rate (moles/ha/yr)		Modal % Feldspar	Normalized Rt. (rate/%felds)
Coweeta 2	Velbel, 1985a	613		
18		453		
34		497		
36		732		
14		274		
27		305	8.3	36.7
32		308		
Pond Branch	Cleaves *et al*, 1970	148	10.6	14.0
Trnavka X-O	Paces, 1983	210	(19)	11.1
X-9		550	14	39.4
Filson Creek	Siegel, 1984	235		
Silver Creek	Clayton, 1988	448		
Lochvale	This study	194.86	16.35	11.9

$$\text{Ratio} \frac{\text{Rate}^{\text{max}}}{\text{Rate}_{\text{min}}} = 4.95 \qquad \text{Ratio} \frac{\text{Normalized rate}^{\text{max}}}{\text{Normalized rate}_{\text{min}}} = 3.54$$

(after Velbel, 1985b)

Adding both the new An35 and An65 modal values together gives a net surface area normalized value of 16.35%. Thus, the normalized rate of plagioclase for Lochvale becomes 11.9, within the range of other normalized values. Taking only one of plagioclases, however, and normalizing to surface area and modal abundance brings the normalized plagioclase weathering rate to less than 4, far slower than other findings.

5.8 Significance of Rock Types

As shown in the mass balance modeling, the Lochvale watershed cation chemistry may be largely controlled by four key hydrolysis reactions. Two of the minerals, An 65 plagioclase and ferrotremolite, are predominant minerals of amphibolite units arranged in lenses and pods throughout the granitic gneisses of the Front Range. The striking dark green to black amphibolites have been described to profusely weather throughout the Front Range as well as Rocky Mountain National Park forming holes and hollows in the sturdier and more massive granite-gneiss complex (Cole, 1977; Nesse, 1977; Robinson _et al_, 1974). A visually estimated 5% of the Lochvale drainage contains small 3 to 5 foot amphibolite lenses within the gneisses, larger lenses and layers (10-30 feet) are seen at the entrance of Lochvale and Mills Lake as well as the Bear Lake area.

Along the Ute trail, northwest of Lochvale, even larger lenses of dark green to black amphibolite can be seen. Amphibolite weathering in the Colorado Front Range may be a significant source of base cations, contributing a significant fraction of acid neutralization. Furthermore, a winter visit to Lochvale, reveals that the holes and vugs once or partially occupied by dark green to black amphibolite serve as hydrologic conduits and preferential pathways for water. Frozen seeps emanated from all of the amphibolite units. Thus, the reasons for preferential weathering of amphibolites can be considered two fold: 1) as observed by previous researchers (Goldich, 1938; Reiche, 1950) more mafic minerals, following Bowens Reaction series, tend to weather more rapidly-- more calcic plagioclases for example, are observed to weather more rapidly than sodic ones (Goldich, 1938) and 2) as a consequence of their rapid weathering hydraulic pathways are formed where precipitation can collect and continually keep in contact with fresh amphibolite mineral surfaces. Consequently, disproportionately high ionic contributions are made per unit mass or surface area. Thus, small amounts of highly reactive rock types can account for the bulk cation chemistry of waters. Even though amphibolites represent only 5% of the total lithologies of the Lochvale drainage, it is evident from the mass balance model, the accuracy of the silica release rate check, field evidence and previous research that preferential weathering of this unit supplies roughly 70 percent (refer to Table 6) of the total cation flux of Lochvale.

The less calcic An35 granitic gneisses are also very important suppliers of sodium and calcium. Although gneisses represent 95% of drainage rock types, their weathering appears less pronounced than the amphibolites. One reason for this is the short water-mineral surface contact time due to steep terrain and lack of hydraulic conduits. Petrographic and mass balance results do suggest granite-gneisses also help neutralize proton inputs on a long term scale due their extensive nature.

Finally, the weathering of the biotite fraction of schists soils and granitic gneisses of the Lochvale drainage to vermiculite appears to supply the potassium to the drainage.

Chapter 6

CONCLUSIONS

Mineral weathering in the Lochvale drainage consists of 4 key hydrolysis reactions: 1) plagioclase (An65) to kaolinite; 2) plagioclase (An35) to kaolinite; 3) amphibole (ferrotremolite) to kaolinite and 4) biotite to vermiculite.

Mass balance calculations using the 4 stoichiometric weathering reactions as stated above and the net cation fluxes for Lochvale shows plagioclase (An65) weathers at a rate of 146-156 moles/ha/year. Plagioclase (An35) weathers at a rate of 28-48 moles/ha/year. Ferrotremolite weathers at a rate of 9-17 moles/ha/year and biotite at a rate of 17-25 moles/ha/year.

The mass balance model accuracy was checked by comparing the model predicted silica release rates to actual measured silica fluxes. Few studies have been able to accurately predict silica release rates (Clayton, 1988). Lochvale mass balance reactions and rates accurately predict 1984 silica fluxes within 2% and 1985 silica fluxes within 36%. The decreased accuracy in 1985 and the 8% increase in cation fluxes suggests a component of non-steady state release may exist in the Lochvale watershed.
Following Goldichs weathering observations (1938) where

more mafic minerals were observed to weather more readily than felsic ones, the mafic Lochvale amphibolites were observed to weather more extensively than the more felsic granite gneisses. Volumetrically, the amphibolite represents less than 5% of all rock types found in the Lochvale drainage (in contrast to the granite gneisses which represent 95%). Yet, disproportionately large amounts (70%) of the cation releases out of Lochvale are from the weathering of this highly reactive rock type. The weathering of amphibolite units throughout the Colorado Front Range may be largely responsible for calcium dominated stream waters and neutralizing hydrogen ion inputs.

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APPENDIX A

X-ray Diffraction Patterns

Table 12

Characteristic X-Ray Diffraction Peaks

	Angstroms	CuK-alpha 2 theta	Peak
Amphibole	8.40 - 8.41	10.5	001
Kaolinite	7.15	12.35	001
Kaolinite	3.57	24.9	002
Kaolinite	2.35	38.2	003
Oriented mounts	4.48	19.8	_
Oriented mounts	4.35	20.4	110
Oriented mounts	4.17	21.3	111
*1			
Nacrite	7.18	12.3	002
(type of Kaolinite	3.58	24.8	004
Vermiculite	14.2	6.22	001
*2	4.6	19.22	003
Smectite	15	5.8	001
Chlorite	14.1-14.2	6.27-6.22	001
Mica	10	8.8	001
Muscovite	5	17.7	002
Biotite	10.1	8.77	002
Mica 2M	9.29	8.85	002
	10.4	8.8	
Calcite	3.03	29.47	104
Dolomite	2.88-2.87	30.05	104

1: Disorder in Kaolinite results in broadening of 001, 002 deflections.

2: By heating to 500 C interlayer water is expelled but quickly rehydrates on heating to 700 Cvariance will collapse to 4.3 A for the (001).

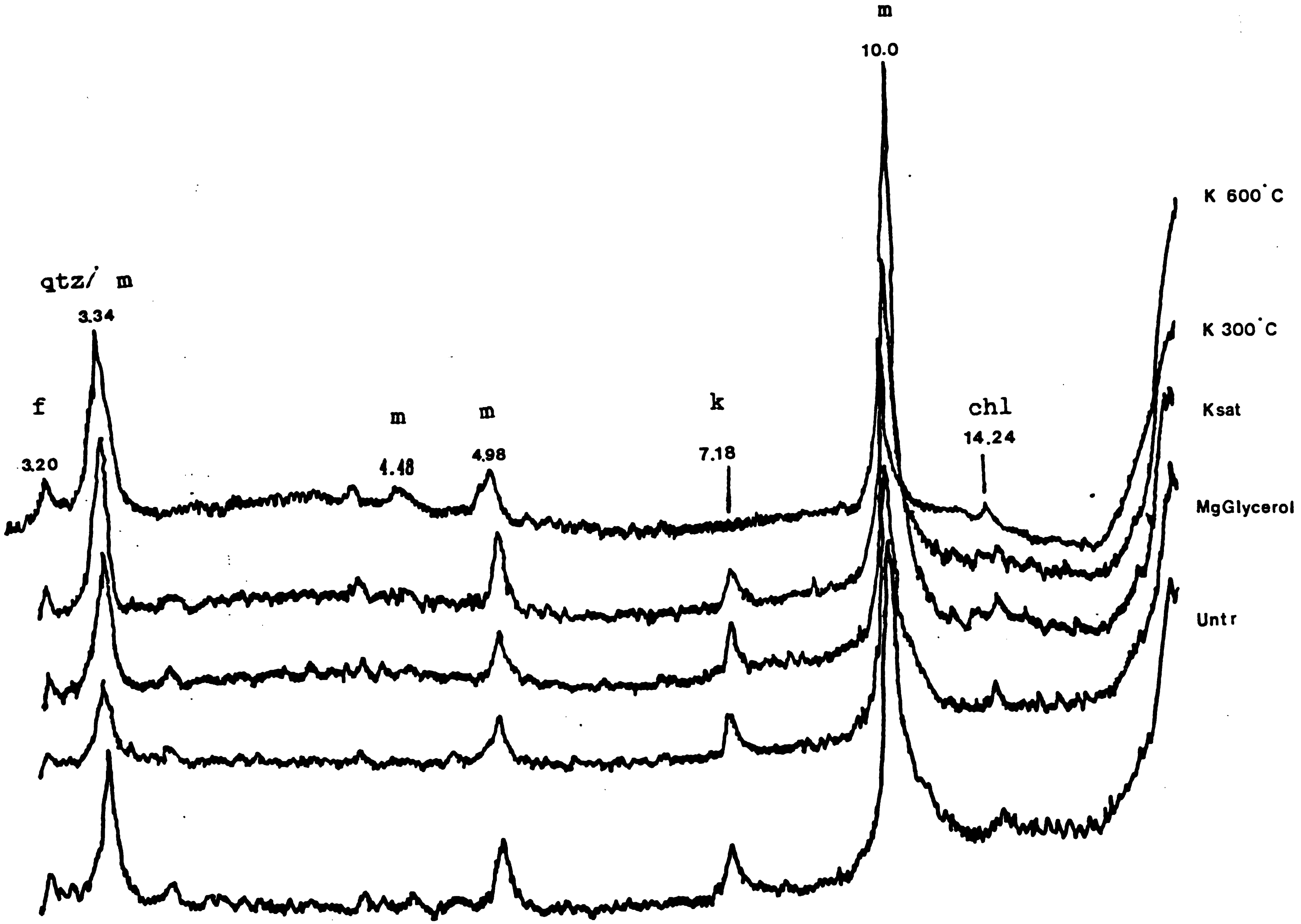


Figure 16.- Schist (ST-4)

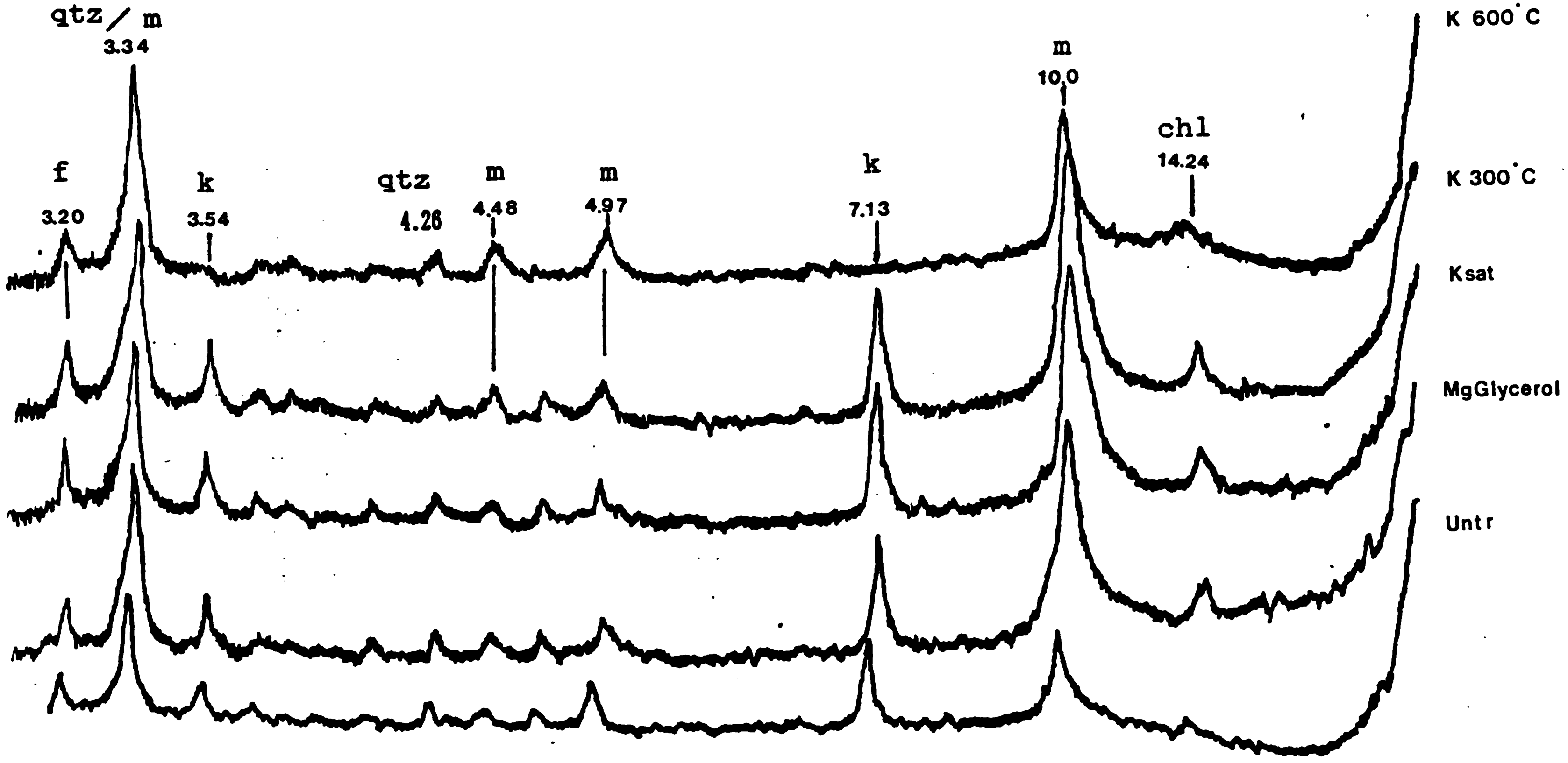


Figure 17.- Gneiss (ST-2)

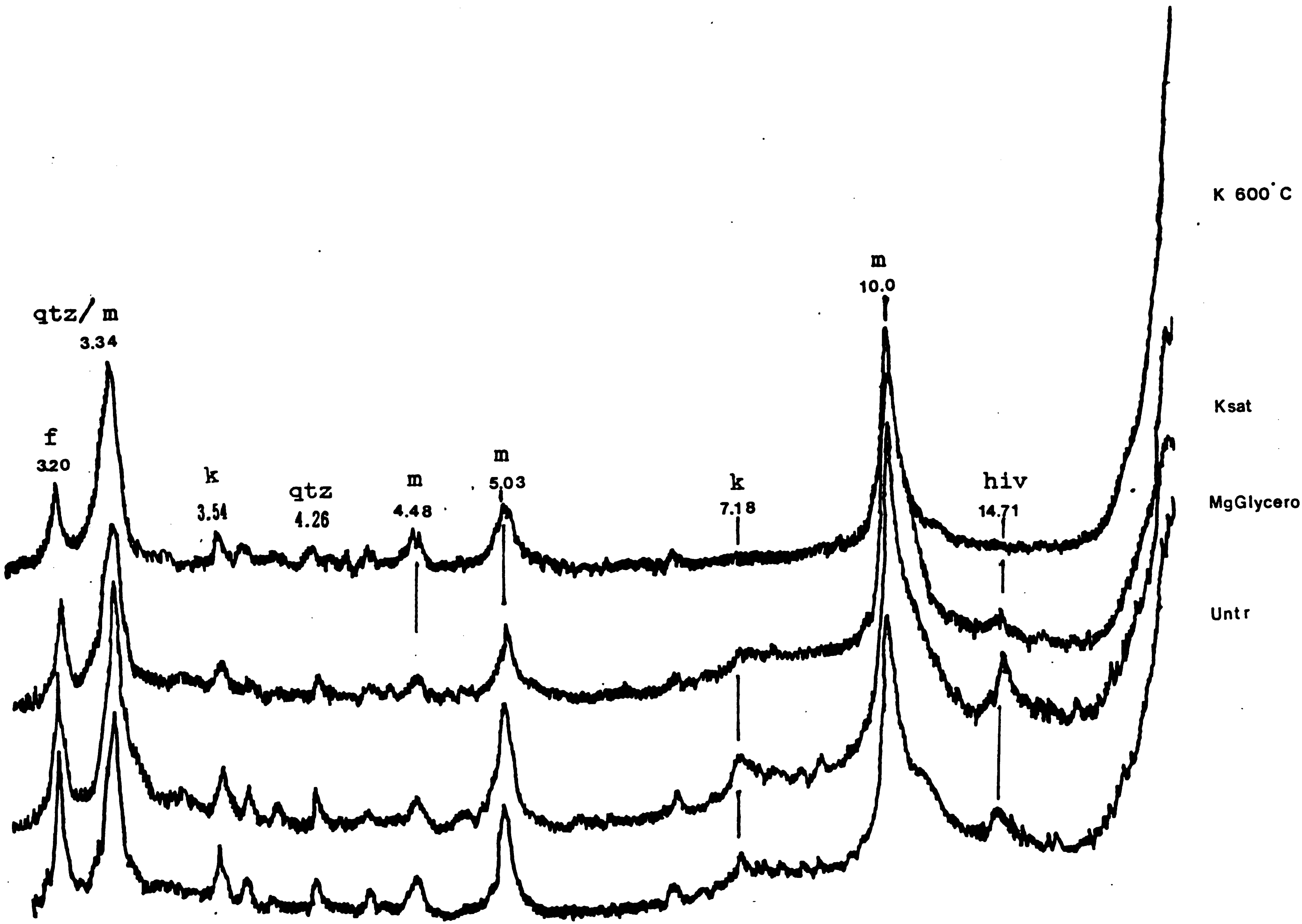


Figure 18.- Gneiss (LV-10)

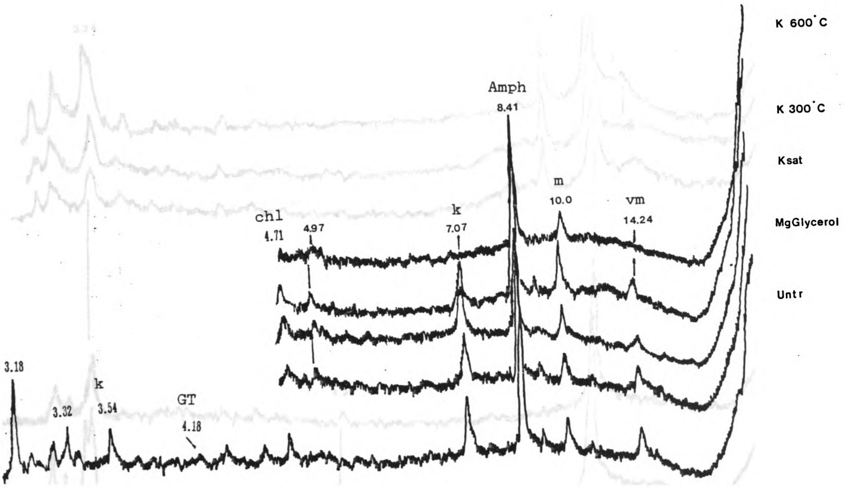


Figure 19.- Amphibolite (GN-14)

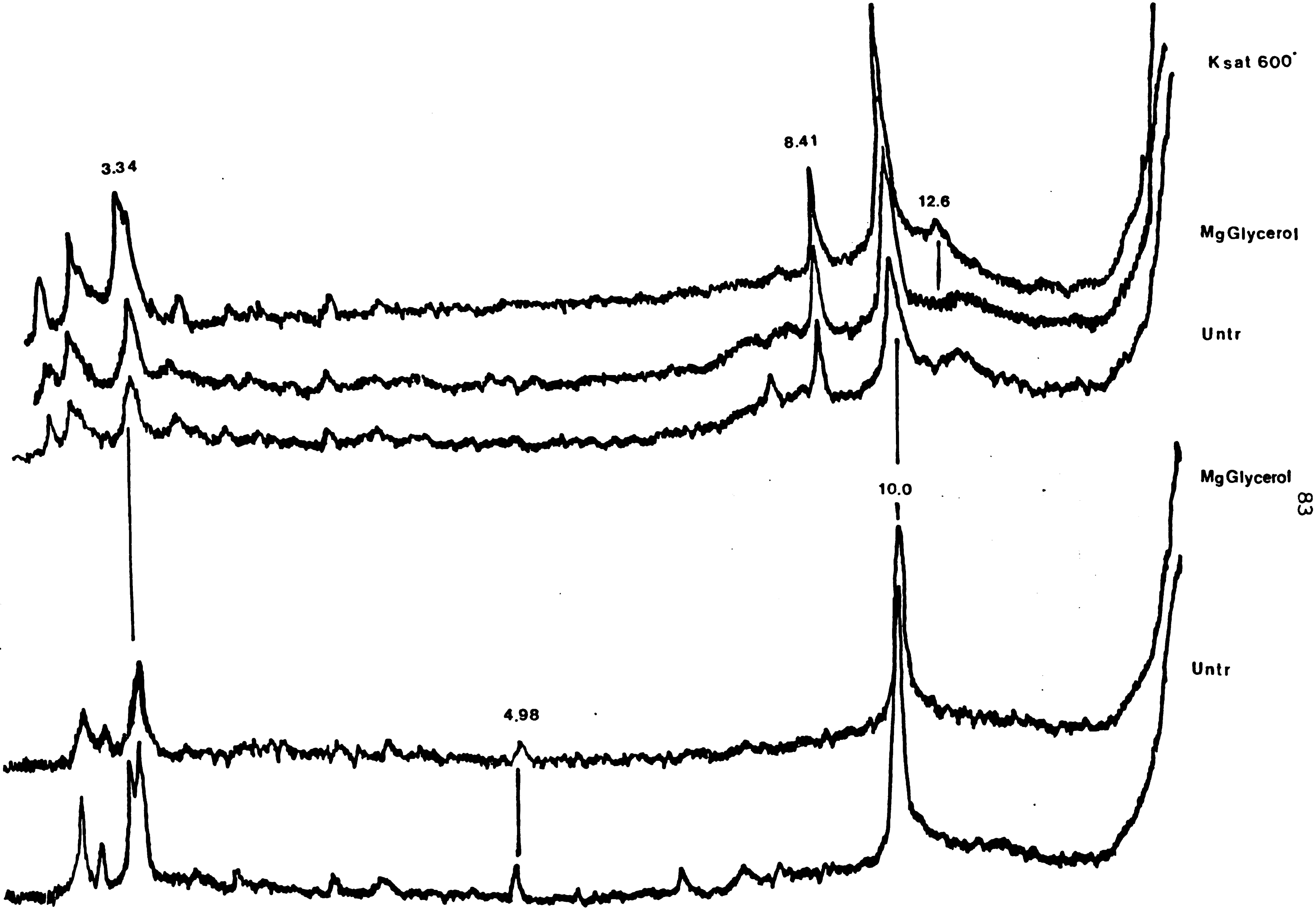


Figure 20.- Granite (FR-64)

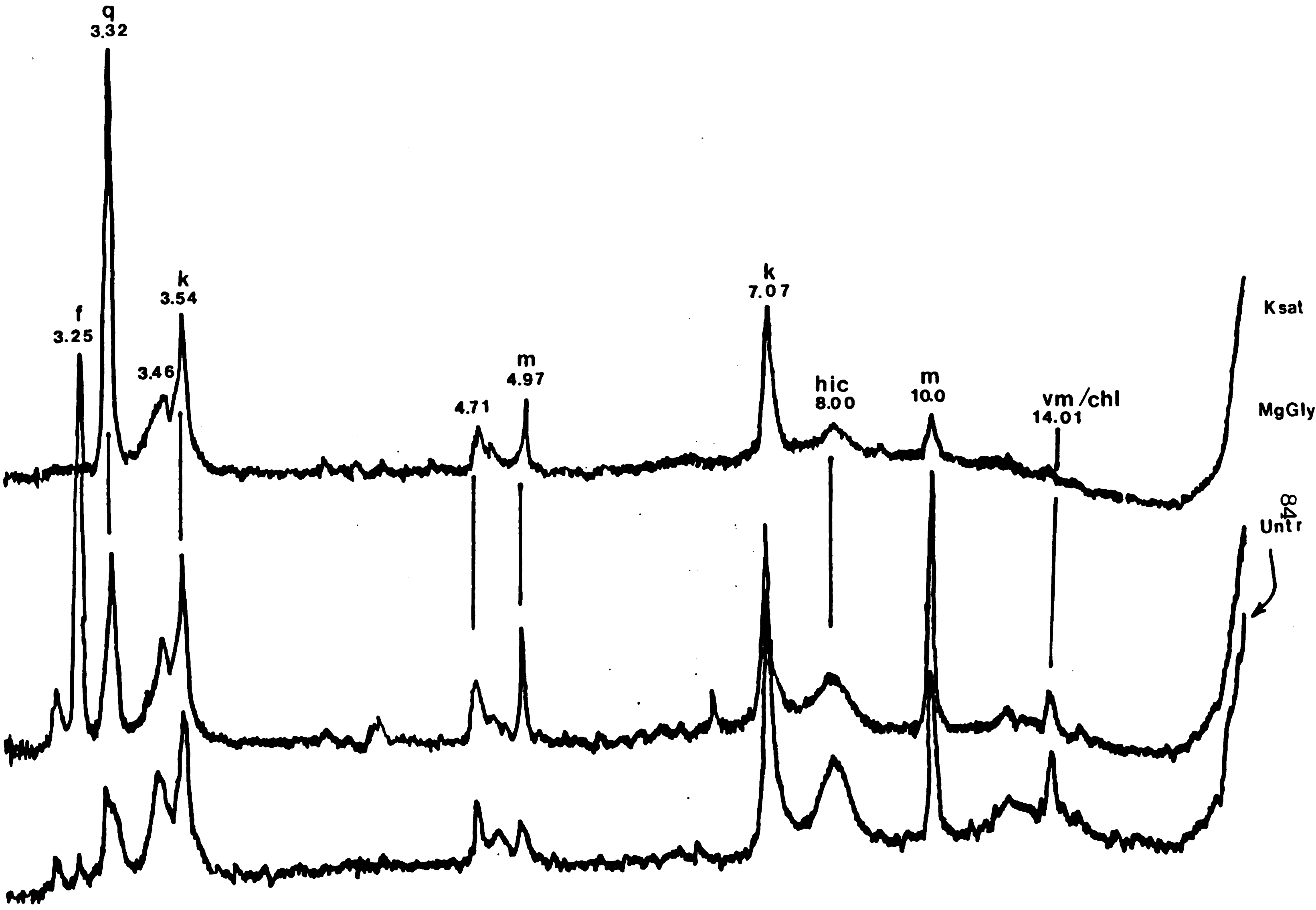


Figure 21.- Hand Picked Micas from Granite (HP-M)

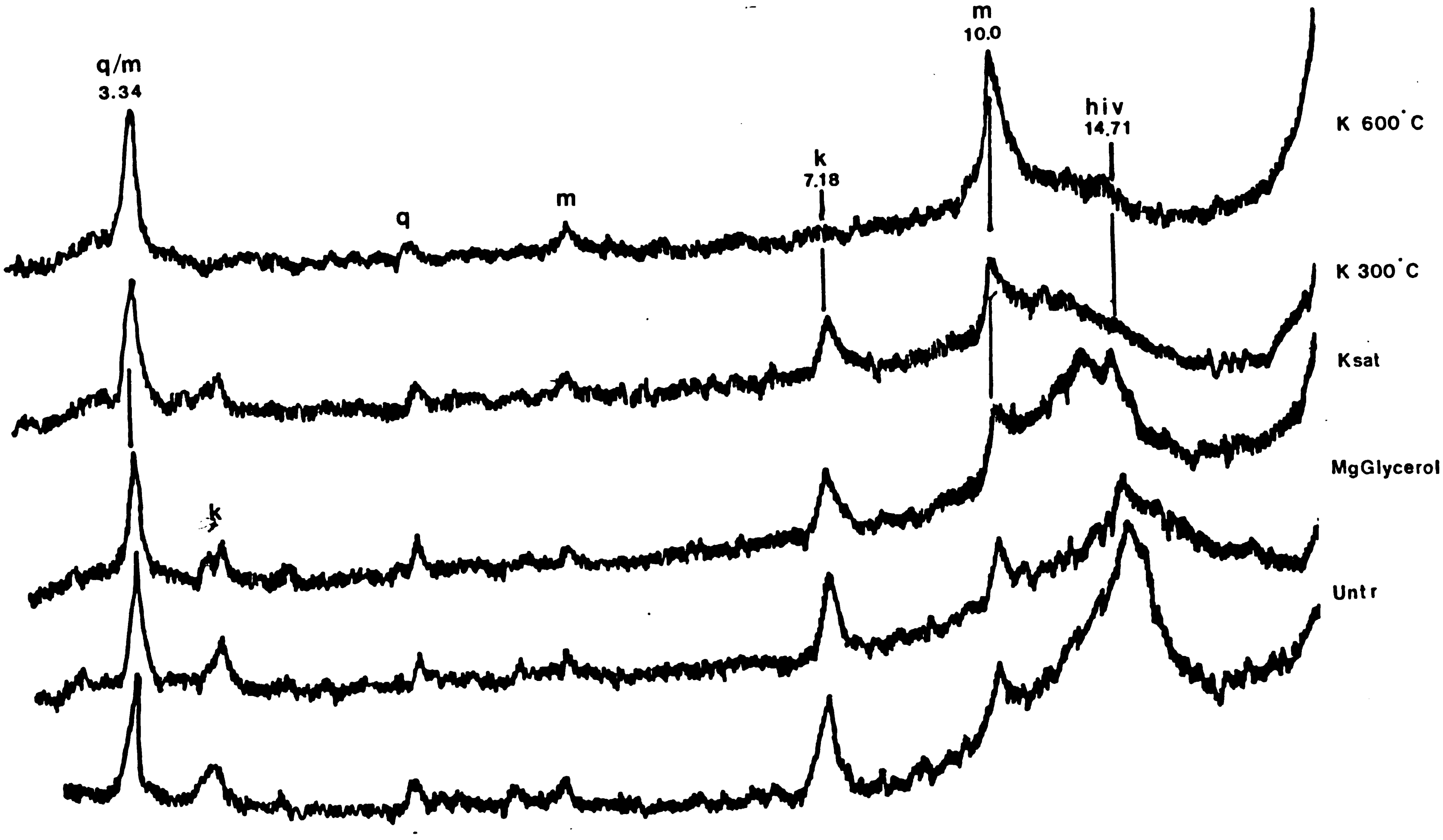


Figure 22.- Soil Sample (LV-7)

APPENDIX B

Hand Calculations of Clay Structural Formulas

APPENDIX C

Hydrogeochemical Flux Data

HALF CELL Formula:

$$[M^{+}]_{x}[\underbrace{Al^{+3}_{a-y} + Fe^{+3}_{b} + Mg^{+2}_{d}}_{\text{OCTAHEDRAL}}][\underbrace{Al^{+3}_{y} + Si^{+4}_{4-y}}_{\text{TETRAHEDRAL}}]O_{10}[OH]_{2}$$

FRESH BIOTITE (From Microprobe Data - ISHERWOOD + Street)

	%	FACTOR	Proportions	SYMBOL	VALENCE
SiO_2	39.60	60	.660	Z	4
TiO_2	2.13	79.9	.0266		4
Al_2O_3	11.20	51	.2196	A	3
FeO	14.04	71.8	.1955	B	2
Fe_2O_3	3.95	80	.0494	B	3
CaO	trace	56		X	2
MgO	13.75	40	.3438	D	2
Na_2O	.....	31			1
K_2O	10.35	47.1	.2198	N	1
H_2O	4.98	6.0	.8300		

K = prop constant

$$= \frac{22}{4(.660) + 4(.0266) + 3(.2196) + 2(.1955) + 3(.0494) + 2(.3438) + 1(.2198)} = 4.5344$$

$$Y = 4/4.5344 - .660 = 4/K - Z$$

$= .222$ Al in tetrahedral layer

$A - Y = .2196 - .222 = -.0025$ Aluminium in octahedral layer

$$a - y = (A - Y)K = (-.0025)(4.5344) = 0$$

$$b = BK = (.1955)(4.5344) = .886 \qquad b_{Fe^{+++}} = .224$$

$$d = DK = (.3438)(4.5344) = 1.559$$

$$y = YK = (.222)(4.5344) = 1.06$$

$$n = NK = (.2198)(4.5344) = .9967$$

WEATHERED BIOTITE

	%	FACTOR	Proportions	SymBOL	VAlence
SiO_2	40.78	60	.6797	Z	4
TiO_2	1.82	79.9	.0228		4
Al_2O_3	11.71	51.	.2296	A	3
FeO	1.42	71.8	.0198	B	2
Fe_2O_3	17.58	80	.2198	B	3
CaO	1.40	56	.0250	X	2
MgO	9.95	40	.2488	D	2
Na_2O	....				1
K_2O	5.70	47.1	.1210	$\overline{N}$	1
H_2O	9.64	6.0	1.606	—	1

$K = 22/4.866 = 4.521$

$Y = 4/4.521 - .6797 = .2051$

$A\text{-}Y = .2296 - .2051 = .0245$

$a - y = .110$

$b = .089$

$b_{Fe^{+++}} = .994$

$d = 1.125$

$y = .927$

$x = .113$

$n = .547$

CALC. FRESH BIOTITE
(ISHERWOOD + STREET, 1976)

HALF CELL:

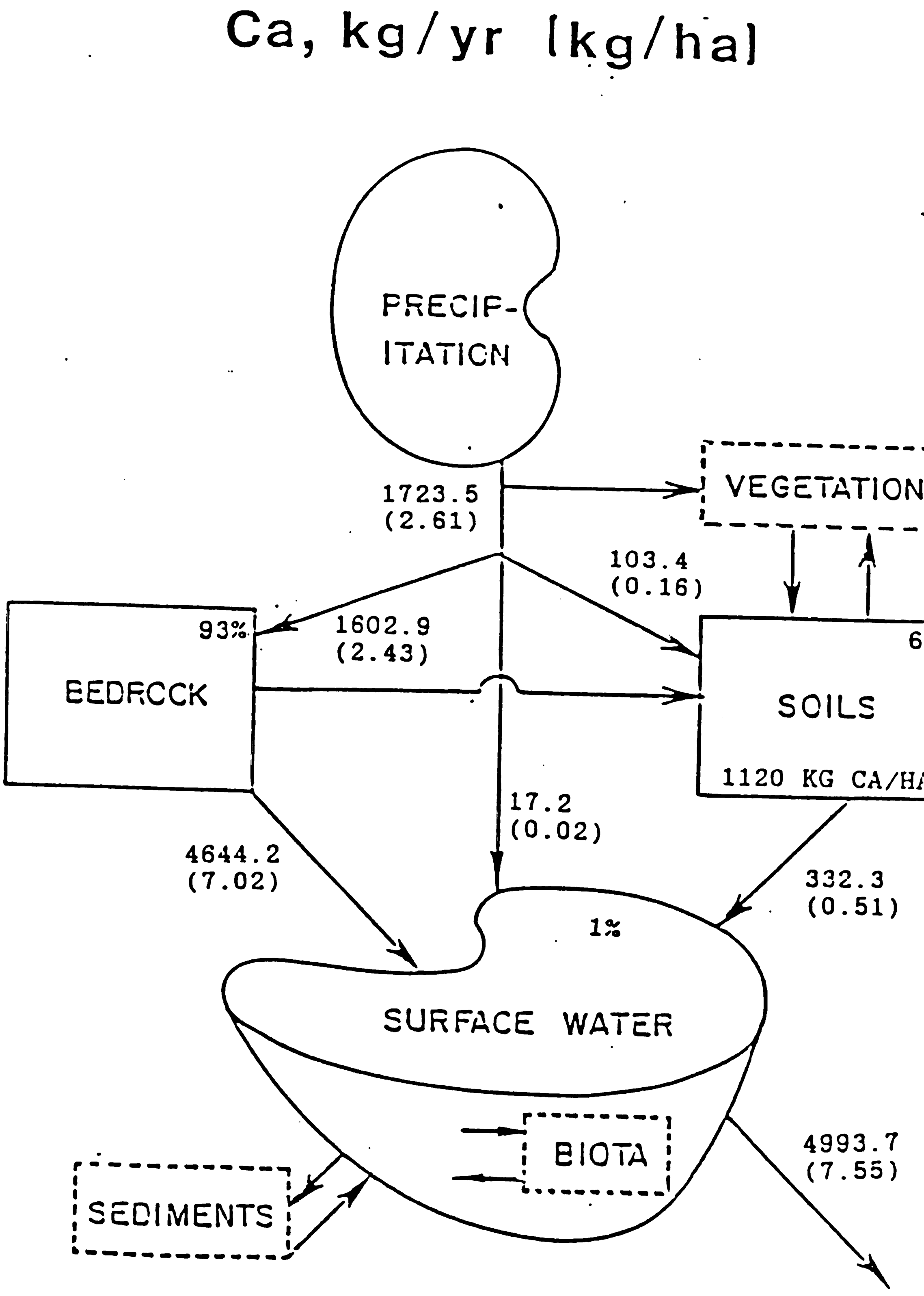
$$K^{+}_{.997}\left[Fe^{2+}_{.886}\ Fe^{3+}_{.229}\ Mg^{2+}_{1.559}\ Ti^{4+}_{.121}\right]\left[Al^{3+}_{1.006} + Si^{3+}_{2.994}\right]\left[OH\right]_{2}\ O_{10}$$

CAL. WEATHERED BIOTITE
(ISHERWOOD +STREET, 1976)

$$Ca^{2+}_{.113}\ K^{+}_{.597}\left[Fe^{2+}_{.089}\ Fe^{3+}_{.994}\ Mg^{2+}_{1.125}\ Ti^{4+}_{.103}\ Al^{3+}_{.110}\right]\left[Al^{3+}_{.927}\ Si^{4+}_{3.073}\right] O_{10}\ \left[OH\right]_{2}$$

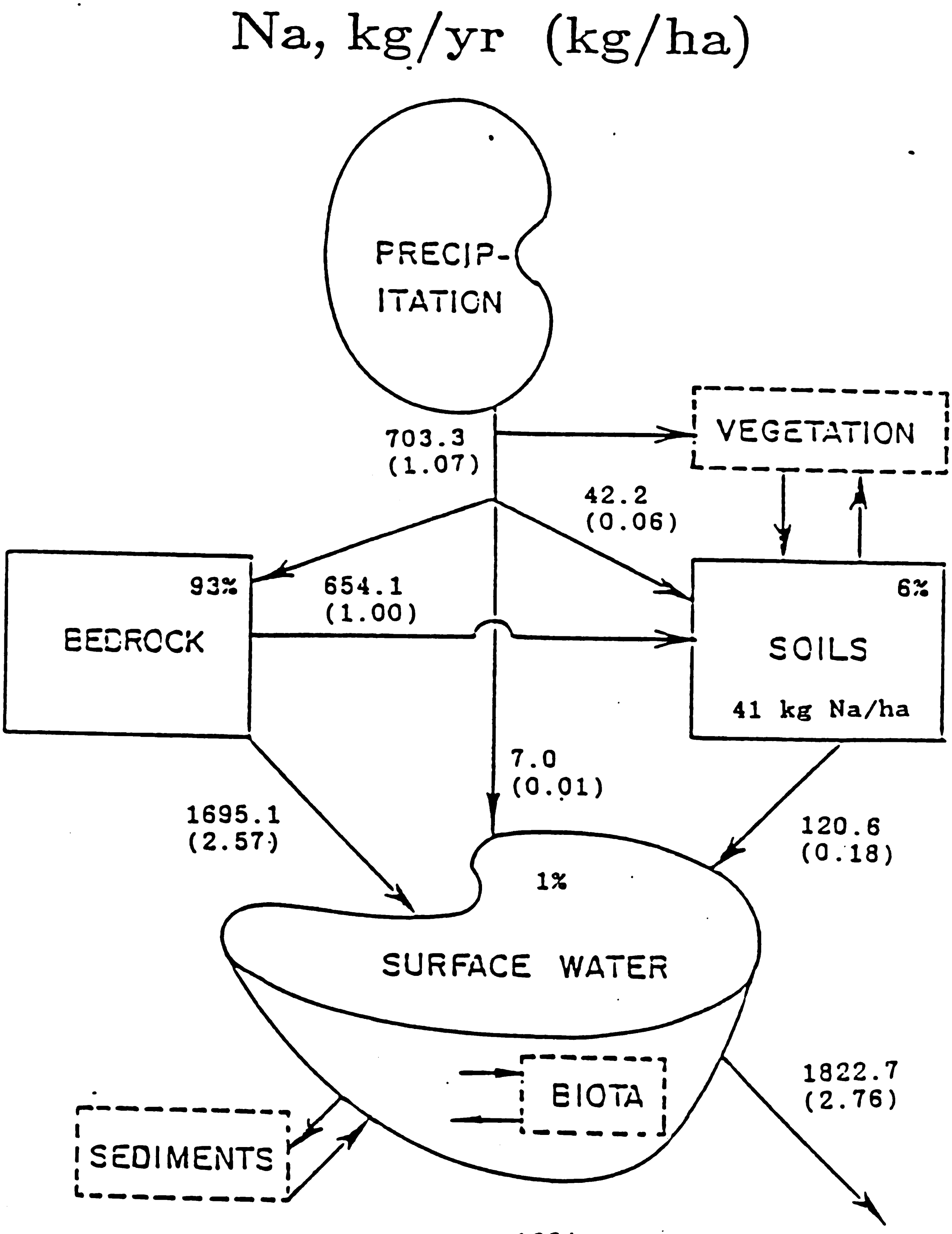
APPENDIX C

Hydrogeochemical Flux Data



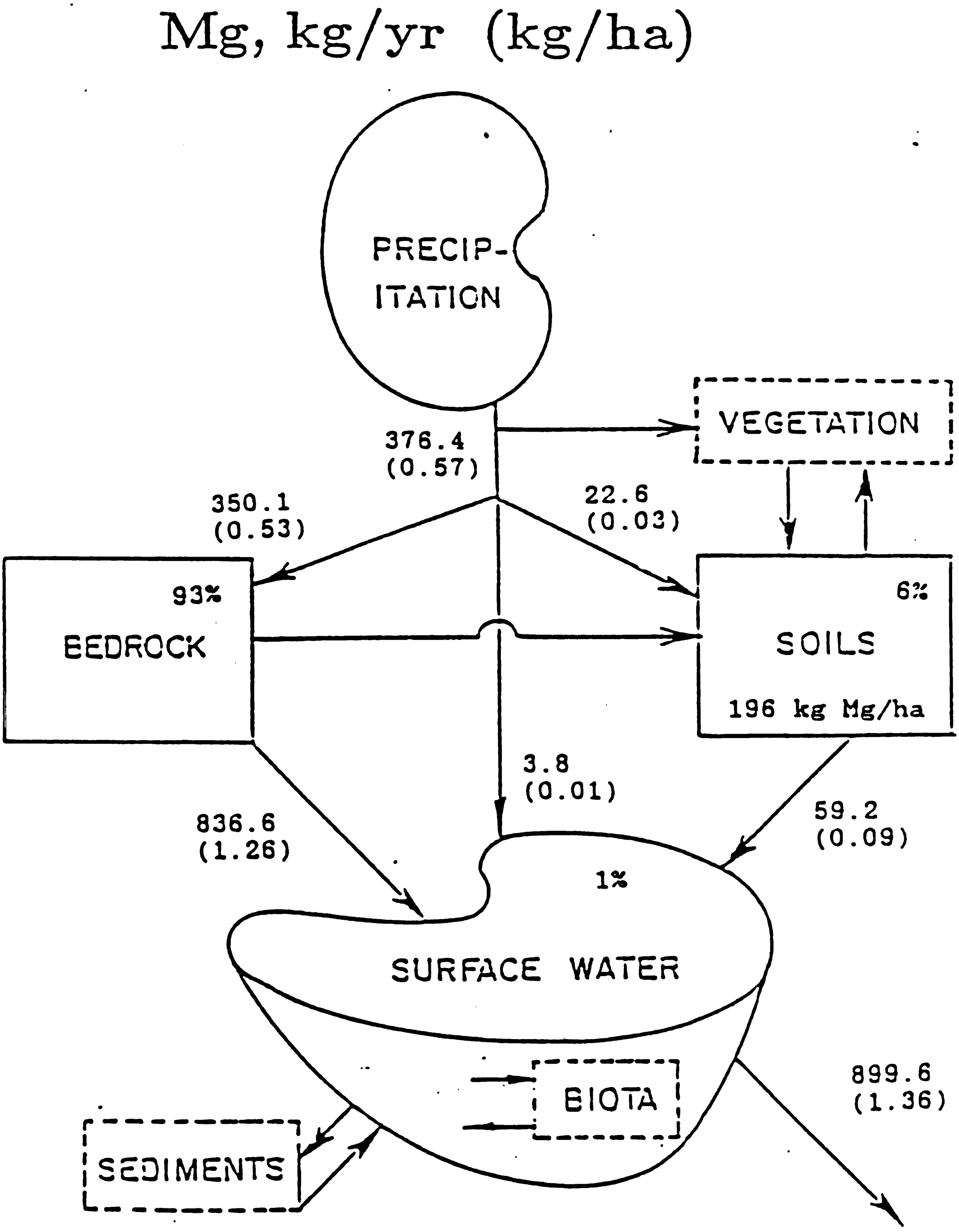
1984

Figure 23.- Calcium Flux Diagram for Lochvale
(from Baron, personal communication)



1984

Figure 24.- Sodium Flux Diagram for Lochvale
(from Baron, personal communication)



1984

Figure 25.- Magnesium Flux Diagram for Lochvale (from Baron, personal communication)

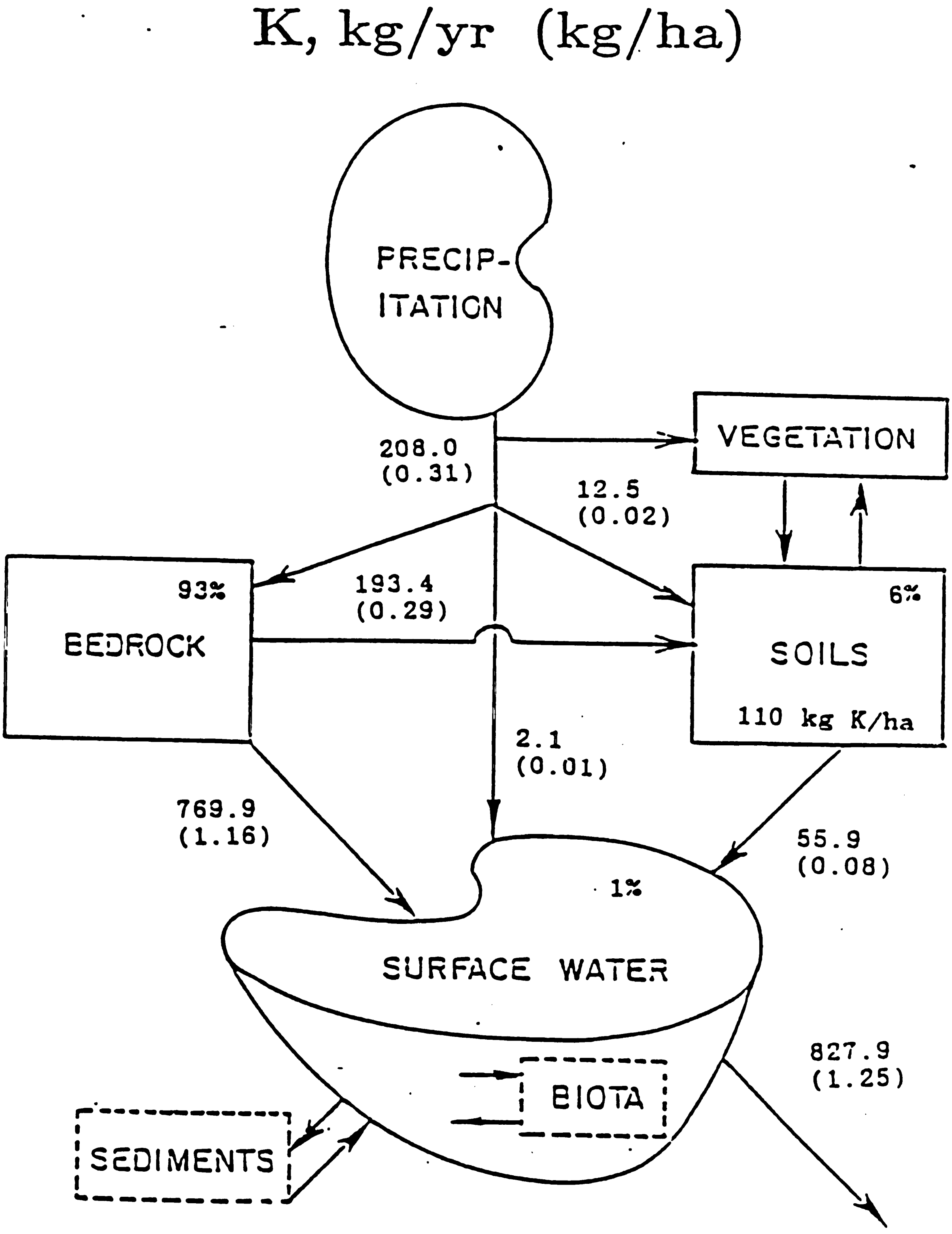


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Figure 26.- Potassium Flux Diagram for Lochvale (from Baron, personal communication)