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Geochemical and mineralogical studies
on the weathering of granitic rocks

by

Robert Curtis Harriss

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Thesis Director's Signature:

A handwritten signature in cursive script, reading "John A. S. Adams", is written over a horizontal line.

Houston, Texas

May, 1965

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INTRODUCTION

Weathering Reactions

Weathering reactions take place primarily as the result of disequilibria between the lithosphere and the hydrosphere, atmosphere, and biosphere. The rate of decomposition of a mineral or group of minerals is a reflection of the differential between physical and chemical conditions at the time of formation and those existing at the present surface.

For convenience three main types of weathering may be distinguished: physical, chemical, and biological. All these processes may take place side by side, and usually do, though their relative importance varies according to the characteristics of the local physio-chemical environment. In the extremes of arid and arctic regions, physical processes generally predominate, while in most other climates, chemical and biological weathering are the principal modes of rock decomposition. The present study is concerned primarily with the chemical weathering of igneous rocks in temperate regions and the processes which control the mobilization and redistribution of cations in soils.

Chemical weathering is primarily the result of four

major processes. These are:

- 1) Hydrolysis and hydration - hydrolysis is the incorporation of hydronium and hydroxyl ions into a mineral structure. Hydration is the adsorption and/or absorption of water molecules into a mineral structure.
- 2) Oxidation - oxidation reactions are of primary importance in minerals containing ferrous ion. The oxidation of ferrous to ferric ion disrupts the electrical and geometric balance of the crystal lattice and leaves it more susceptible to dissolution. For example, the conversion of biotite to vermiculite is initiated by the oxidation of ferrous to ferric ion (Walker, 1949).
- 3) Exchange reactions - ion exchange may be one of the most important types of reaction taking place during the early stages of chemical weathering. Exchange reactions are dependent on the concentration of solvent in contact with the mineral surface, the nature and number of exchange sites, and the availability of various types of ions.
- 4) Diffusion - diffusion may well be the rate limiting process during the intermediate and later stages of

weathering due to the formation of inert reaction rims that slow reactions. It has been demonstrated by Correns (1961) that during the early stages of alteration, rims of hydrous aluminum silicate are formed around feldspars and micas; thus the reaction interface moves inward and exchangeable ions and other reacting materials must diffuse through the thickening outer rim in order to react with the primary mineral structure.

The rate and nature of weathering processes in the natural environment can be discussed in terms of six closely interacting factors - parent rock type, topography, climate, organic activity, local physiochemical conditions, and time. However, the relative importance of these factors is a subject of controversy. For example, Short (1961) in a study of geochemical variations in four residual soils concluded that climate was apparently the principal factor controlling the rate of release and redistribution of certain major and trace cations during weathering. In contrast, Dennen and Anderson (1962) in a study of the weathering crusts on thirty-two selected rocks concluded that chemical changes during weathering are primarily controlled by the local physiochemical environment

and not by the parent rock type or climate. It should be noted, however, that in both of these studies a wide variety of rock types have been sampled in a number of different weathering environments resulting in a large and unevaluated number of variables, which limit the amount of conclusive information available. To evaluate the relative importance of various controlling factors on weathering reactions it is necessary to isolate and study the effects of as many individual variables as possible. Thus, it appears to this writer that the most profitable approach to the study of weathering reactions in nature is to study the alteration of a single rock group in a variety of different climatic regimes or a variety of rock types in a single climatic regime.

Rationale of the Present Investigation

- 1) The geochemistry and mineralogy of the weathering of a single rock group, granitic rocks, was investigated in several different environmental settings, with particular emphasis on the mobilization and redistribution of selected cations.
- 2) The effects of different types of regional weathering

and weathering environments on the chemistry of natural surface waters were investigated.

- 3) The role of weathering in the biogeochemical dynamics of an ecosystem were considered.
- 4) Experiments were designed to investigate the kinetics of mineral dissolution and to study the effects of exchange reactions on the composition of natural waters.

PREVIOUS WORK

General

From the early work on rock weathering and soil genesis by Merrill (1897) up to the review of weathering processes by Reiche (1950), little attempt was made to investigate the behavior of individual chemical elements during the decomposition of silicate rocks. Due to the lack of adequate analytical techniques, early workers on this subject were limited to descriptive studies which concerned primarily the geomorphological aspects of weathering. Particularly noteworthy of mention are papers by Merrill (1897), Polynov (1937), and Jenny (1941). More recent papers of interest include those by Ruxton and Berry (1957) and Ruxton (1958).

Goldich (1938) was one of the first geologists to investigate chemical changes occurring during weathering. Subsequent workers who have published information on the chemistry of rock weathering include Brock (1943), Wahlstrom (1948), Butler (1953, 1954), McLaughlin (1955), Keller et.al. (1955), Yamasaki, Iida, and Yokoi (1955), Anderson and Hawkes (1958), Bolter (1961), Short (1961),

Kelly and Zumberge (1961), Dennen and Anderson (1962), Pliler and Adams (1962), and Richardson and Adams (1963). The pedologists have published a large amount of data on the distribution of major and trace elements in the soil portion of the weathered mantle. Excellent reviews of the pedological literature have been presented by Swaine (1955) and Vinogradov (1959).

Weathering of Granitic Rocks

Brock (1943) presented some of the first analyses of fresh granite and its weathered equivalent. The granite was collected from a locality near Hong Kong, a humid-temperate climatic zone. Brock noted an early and complete loss of calcium and sodium. Potassium was next depleted with iron and titanium being reduced only in the advanced stages of decomposition. A loss of silica was noted in the final stage of weathering. The residual weathering deposits contained quartz, sericite, kaolinite, and a little chlorite.

Wahlstrom (1948) investigated a granodiorite near Boulder, Colorado. Examples of both pre-Pennsylvanian and recent weathering were well exposed. The chemical changes

as a result of pre-Pennsylvanian weathering show an apparent enrichment of the upper portion of the weathered mantle in total iron, titanium, and aluminum and a progressive decrease in silica, calcium, sodium, and potassium with increased stages of decomposition. Magnesium shows an apparent increase in concentration during the intermediate stages of weathering and becomes abruptly depleted in the final stages of decomposition. Secondary minerals resulting from pre-Pennsylvanian weathering include iron oxides, hydrated mica, clay minerals (not identified), and dolomite. Of the original minerals in the granodiorite, quartz and microcline proved the most resistant to weathering.

The chemical changes resulting from recent weathering of the granodiorite are not as pronounced as those resulting from pre-Pennsylvanian weathering. The major change during recent weathering is the oxidation of iron and an apparent increase in aluminum. Secondary minerals formed during weathering include kaolinite, iron oxide, and vermiculite.

On the basis of the above described results, Wahlstrom concluded that pre-Pennsylvanian weathering took place in a

humid-temperate climate with laterization being the dominant process, whereas the recent weathering has taken place in a semi-arid climate with oxidation being the dominant process.

Butler (1953) investigated, with spectrographic techniques, the geochemistry and mineralogy of rock weathering in the Lizard area, Cornwall. Butler was the first investigator to study the behavior of minor elements during weathering in any detail. Granodiorite was among the rock types studied and in the transformation of rock to soil there was an apparent decrease in silica, sodium, potassium, and lithium. Aluminum, iron, magnesium, calcium, titanium, barium, chromium, nickel, and strontium were selectively concentrated in the weathering products. Vanadium, lead, and rubidium decreased during intermediate stages of weathering and increased in the final stages of decomposition, relative to the parent-rock. The geochemical behavior of the elements is what might be expected from the simple chemical properties of the elements with the obvious exception of the dissimilarity in the behavior of potassium and rubidium

and the immobility of calcium and strontium. There was a notable decrease in the potassium/rubidium ratio and an increase in the nickel/cobalt ratio with increased weathering. The soils over the granodiorite were a complex mixture of illite, vermiculite, kaolinite, chlorite, and quartz.

Yamasaki, et.al. (1955) in a spectrographic study of trace elements in a granodiorite and its weathering products found a decrease in silica, calcium, potassium, sodium, titanium, barium, and strontium and an increase in aluminum, chromium, and vanadium with increased weathering. Iron, magnesium, manganese, nickel, and zirconium showed an apparent increase during the intermediate stages of decomposition and decrease in the final stage relative to the parent-rock. Cobalt remained nearly constant throughout the course of weathering. The principal alteration product formed was hydrated halloysite.

The most comprehensive study to date by Short (1961) concerned a spectrographic study of geochemical variations in four residual soils. Of the four profiles investigated, two are of particular interest to this study, a profile on a granodiorite from Wyoming and a profile on a granite from

Missouri. The granodiorite is being decomposed in a semi-humid, mountainous climate and shows a continuous decrease in calcium, potassium, sodium, barium, and strontium, and a continuous increase in silica, titanium, cobalt, chromium, copper, nickel, lead, zinc, and zirconium throughout the profile from rock to soil. Aluminum, magnesium and iron are concentrated during the intermediate stages and depleted in the final stages of weathering relative to the parent-rock. The granite on the other hand was decomposed in a humid-temperate zone. In this case there was an increase in silica, titanium, chromium, copper, and nickel and a decrease in aluminum and calcium with increased weathering. Iron, magnesium, barium, cobalt, manganese, lead, strontium, zinc, and zirconium show an initial increase in concentration in the intermediate stages of weathering and a decrease in the following final stages. Potassium and sodium show a decrease in concentration during the intermediate stages of weathering, followed by an increase in concentration relative to the parent-rock in the final stage of decomposition. Short noted that the largest percentage gains or losses occur during the initial stages of

weathering. Short also noted a distinct difference in the geochemical behavior of several elements during the decomposition of the various rock types and concluded that climate appeared to be the dominant factor influencing the redistribution of cations during weathering.

A spectrographic study by Dennen and Anderson (1962) of thirty-two selected weathering crusts from a variety of rock types indicated the chemical changes in incipient rock weathering are primarily controlled by local physical-chemical conditions rather than climate or parent-rock type. Dennen and Anderson state that apparently the mineral assemblages of common rocks represent a highly similar chemical substance. On the basis of the analyses presented, the relative chemical activity or tendency to be mobilized during incipient weathering was, from most to least active, nickel, chromium, vanadium, calcium, magnesium, copper, iron, titanium, zirconium, manganese, sodium, silica, potassium, and aluminum.

Pflizer and Adams (1962) and Richardson and Adams (1963) investigated the effect of weathering on the uranium and thorium distributions in a granodiorite and granite respectively. Both of these studies have demonstrated that

uranium is much more mobile during weathering than thorium. This fractionation of uranium and thorium during weathering is thought to be due to the fact that, although the two elements have very similar properties under reducing conditions, uranium is easily oxidized to the soluble uranyl form during weathering, whereas thorium remains in its relatively insoluble tetravalent state. Pliler and Adams also noted an increase in the relative concentration of uranium and thorium with increased weathering and attributed this to the concentration of insoluble resistate minerals containing relatively large amounts of radioactivity in the weathering products.

In summary, the following generalizations appear valid on the basis of previous studies.

- 1) The behavior of major and trace elements during weathering cannot be predicted on the basis of present knowledge. It would appear from the majority of published studies that the alkalies and alkaline earths are, in general, more mobile during weathering than the other cations commonly found in silicate lattices; however, the study by Dennen and Anderson (1962) complicates the picture by suggesting that

nickel and chromium are among the more mobile cations and sodium and potassium among the least mobile cations during the decomposition of silicate minerals.

- 2) Under humid weathering conditions mineral stability to weathering generally follows the sequence proposed by Goldich (1938), which is merely the reverse of the normal sequence of crystallization of minerals from an igneous melt.
- 3) The lattice site of an element is often an important factor in determining its relative mobility during weathering. This is particularly well demonstrated in the case of uranium, thorium, and zirconium which are often located in insoluble resistate minerals which tend to be concentrated in weathering products.
- 4) The relative importance of factors such as parent-rock type, climate, topography and biological activity on chemical weathering is highly variable and must be evaluated for each case investigated. Almost all of the data available to date is from humid-temperate regions.
- 5) The mineralogy of residual soils formed on granites is generally very complex, containing quartz, iron oxides, and a variety of clay minerals.

FIELD AND LABORATORY METHODS

Field Collections

The first stage in a geochemical investigation of this type is the selection of sample sites. In this investigation, in order to study the weathering of a single rock type in some detail, it was necessary to sample with the idea of having as much control as possible on the relative differences in climatic and local physiochemical factors between each collection locality.

The criteria used in selecting suitable residual soils for study were: (1) textural similarity to parent-rock, (2) favorable geomorphic setting, and (3) mineralogical data. Any one of these criteria alone would not be satisfactory; however, if all three criteria, when applied to a particular profile, indicate in situ weathering, then one can be fairly certain that the profile is residual. For example, if a soil has a texture very similar to the underlying rock then in situ alteration of the rock is indicated; however, mineralogical studies of the soil are necessary in order to determine whether the alteration is a result of hydrothermal activity of surficial weathering.

In certain cases it is impossible to separate the two types of alteration. The most favorable geomorphic setting is a relatively flat topographically high area where the likelihood of contamination and removal of material is minimized.

During the Fall of 1963 and the Summer of 1964, five weathering profiles were collected on granitic rocks. Brief general descriptions of these profiles are given in Table 1 and more detailed petrographic descriptions are given in Appendix I.

The nomenclature used in this study to describe the various horizons observed in the profiles under investigation is as follows:

A-horizon - the eluviated (leached) top layers.

B-horizon - the illuviated (enriched) layers.

C-horizon - altered parent material.

D-horizon - unaltered parent material.

All of these horizons do not necessarily occur in every soil profile.

It should be noted from Table 1 that several profiles collected short distances from each other, for example, the two profiles on the Tishomingo granite and the two on the Mount Scott granite, were taken from distinctly

TABLE 1

Generalized Description of Weathering Profiles

Profile T-1

Location - Eastern Arbuckle Mountains; on State Highway 7, 1.7 miles west of intersection with State Highway 99 between Tishomingo and Connerville, Johnson County, Oklahoma.

Local Physiography - Deeply eroded continental craton; elevation ± 1000 ft.; gently rolling topography with relief of 25-50 ft.; profile collected from local topographic high.

Drainage - Well drained; internal drainage probably exceeds surface runoff.

Climate - Semi-humid, with annual mean precipitation of 35 inches; average annual number of times of freeze and thaw is 70.

Vegetation - Grass and weed covered; trees scarce; plant roots seldom extend more than six inches into soil.

Profile Maturity - Profile consists of A, B, C₀, C₁, C₂, and D horizons; total thickness from the top of the C horizon to the surface is 60 inches.

Agricultural History - Local cultivation and interference with natural drainage.

TABLE 1 (cont'd)

Profile T-2

Location - Eastern Arbuckle Mountains; on State Highway 7, 2 miles east of intersection with State Highway 99 between Tishomingo and Connerville, Johnson County, Oklahoma.

Local Physiography - Flat planar surface interrupted by small erosional remnants of granite with relief of 5-15 feet; collection site on flat terrace with little or no slope.

Drainage - Imperfectly drained as a result of flat topography.

Climate - Semi-humid, with annual mean precipitation of 35 inches; average annual number of times of freeze and thaw is 70.

Vegetation - Sparse covering of grass, weeds, and small bushes; trees scarce.

Profile Maturity - Profile consists of A, B, C₀, C₁, C₂, and D horizons; total thickness from the top of the C horizon to the present surface is 35 inches.

Agricultural History - Local cultivation and interference with natural drainage.

TABLE 1 (cont'd)

Profile S-1

Location - Wichita Mountains; Mount Scott, Wichita Mountains Wildlife Refuge, Comanche County, Oklahoma.

Local Physiography - Mount Scott dominates the eastern part of the Wichita Mountains, rising 1118 feet above Lake Lawtonta and is the highest point in southern Oklahoma. Very irregular granite surface with relief of 10-200 ft.

Drainage - Well drained; surface drainage exceeds internal drainage.

Climate - Semi-humid, with annual mean precipitation of 25 inches; average annual number of times of freeze and thaw is 80.

Vegetation - Patchy distribution of grass, weeds, and small trees, intersperced with bare granite surfaces.

Profile Maturity - Profile consists of A, B, C₀, C₁, C₂, and D stages of weathering; total thickness of weathered rock is 10-15 inches.

Agricultural History - None.

TABLE 1 (cont'd)

Profile S-2

Location - Wichita Mountains, Mount Scott, Wichita Mountains Wildlife Refuge, Comanche County, Oklahoma.

Local Physiography - Profile was collected from flat surface on top of Mount Scott.

Drainage - Imperfectly drained, moisture is lost from soil mainly by evaporation.

Climate - Semi-humid, with annual mean precipitation of 25 inches; average annual number of times of freeze and thaw is 80.

Profile Maturity - Profile consists of A, B, C, and D horizons; total thickness of the weathered material is 6-8 inches.

Agricultural History - None.

TABLE 1 (cont'd)

Profile E-1

Location - Elberton granite, quarry adjacent to Highway 72 approximately 10 miles west of Elberton, Elbert County, Georgia.

Local Physiography - Eastern edge of Appalachian province, gently rolling topography with local relief up to 15 feet. Profile was collected from wall of granite quarry.

Drainage - Well drained by surface and internal runoff.

Climate - Humid-temperate, with annual mean precipitation of 50 inches; annual number of times of freeze and thaw is 50.

Vegetation - Dense growth of grass; scattered pine and oak trees.

Profile Maturity - Profile consists of A_0 , A_1 , C_0 , C_1 , C_2 , and D horizons; total thickness of the weathered mantle is 30-35 feet.

Agricultural History - Unknown.

different physical settings with regard to drainage and, presumably represent different local physiochemical environments. The profile on the Elberton granodiorite from Georgia may be the result of weathering under climatic conditions quite different from those associated with the Oklahoma granites.

General Laboratory Procedure

Major and trace element analyses were performed by rapid analysis (Shapiro and Brannock, 1962), atomic absorption spectrophotometry, and gamma-ray spectrometry on approximately 150 rock samples, artificially leached rock samples, and leachate solutions. Details of sample preparation and analytical techniques are given in Appendix II.

Clay minerals present in the soils were identified by standard x-ray diffraction techniques discussed by Warshaw and Roy (1961), Biscaye (1964), and Brown (1961). Detailed methods are discussed in Appendix II.

The two most complete and well developed profiles, T-1 on the Tishomingo granite in Oklahoma, and E-1 on the Elberton granodiorite in Georgia, were investigated

in detail. Several different size fractions of the soil were separated from each profile and studied chemically.

Reaction pH's were determined on bulk samples from various horizons of profiles T-1, S-1, and E-1 on the Tishomingo, Mount Scott, and Elberton granites, respectively. Reaction pH determinations were made by adding 50 ml. of distilled water (pH of approximately 5.0, similar to that of rain water) to 10 grams of disaggregated sample in a polyethylene beaker. The beaker was agitated for several minutes, then 24 hours later the pH of the solution was measured with a Beckman model G laboratory pH meter.

In reporting the data obtained in the present investigation digits which are not significant and which are not reproducible are enclosed in parentheses.

PETROGRAPHY

The three granite rocks under investigation can be distinguished petrographically, petrologically, and chemically.

This section will discuss in general the macroscopic

and microscopic characteristics of the unaltered and partially altered samples. Detailed descriptions of individual samples from the various horizons in the weathering profiles developed on these granites are presented in Appendix I.

Tishomingo granite

The Tishomingo granite is located in the Eastern Arbuckle Province of Oklahoma. These rocks represent deeply eroded batholiths which have been dated at 1.0 to 1.3 billion years old (Ham, 1965). The granites of this area are generally coarse-grained, biotite-plagioclase-microcline, mesozone granites (ibid).

The unaltered Tishomingo collected with profiles T-1 and T-2 is nearly identical at the two collection localities. Both samples are coarse-grained and porphyritic. In hand specimen, large crystals of microcline, from 0.5 to 1.5 inches long, are visible in a matrix of finer grained quartz, biotite, and feldspar. In thin section microcline-perthite makes up approximately 50 percent of the rock, oligoclase 20 percent, quartz 20 percent, and biotite 6 percent. Magnetite, apatite, zircon,

and sphene are present as accessory minerals.

During the early stages of alteration there appears to be a general dissolution and etching along twin planes and grain boundaries. In thin section this dissolution is particularly noticeable along perthite boundaries and on plagioclase surfaces. The next stage of alteration is characterized by the appearance of micaceous minerals on feldspar surfaces and an increase in the 2V and darkening of biotite. The alteration of the plagioclase often reflects original zoning within the individual crystals. The almost complete dissolution of plagioclase and biotite result in a general disaggregation of the rock. On the basis of microscope examination the relative mineral stabilities in the Tishomingo granite, from least to most stable, are: oligoclase, biotite, microcline, and quartz.

Mount Scott granite

The Mount Scott granite is medium grained and porphyritic. Micropegmatites make up approximately 50 percent of the rock, microperthite 6 percent, orthoclase 12 percent, oligoclase 14 percent, quartz 11 percent, and ferromagnesium

minerals 3 percent. Accessory minerals present include magnetite and zircon. Biotite is present in trace amounts.

Hornblende is the major ferromagnesium mineral present and is the most easily altered mineral in the rock. In samples of relatively fresh rock hornblende is often altered to epidote. Plagioclase is altered to sericite and clay minerals in the early stages of weathering. Potassium feldspar is only slightly altered during the disaggregation of this granite and is often found in crystalline form in the overlying residual soils. The relative mineral stabilities in the Mount Scott granite, from least to most stable, are: hornblende, oligoclase, orthoclase, and quartz.

Elberton granodiorite

Macroscopically, the Elberton granodiorite is a medium-grained, light-gray, biotite granodiorite. The major constituents of the rock are quartz 32 percent, oligoclase 32 percent, orthoclase 24 percent, and biotite 12 percent. Magnetite, sphene, and epidote are present in trace quantities. In thin section, its texture results

from an aggregate of interlocking grains of quartz and feldspar, with filaments of a somewhat idiomorphic biotite which is often partially altered to chlorite even in relatively fresh rock. The feldspars are usually twinned, and, in the case of orthoclase, show a strong development of cleavage. Apatite and zircon are present as accessories.

Upon weathering, the original texture is very well preserved in the residual soil. The initial stages of weathering are accompanied by an etching of plagioclase surfaces and leaching of biotite. Iron leached from biotite is oxidized and liberated as yellow staining, particularly on quartz surfaces. The next observable stage in the weathering sequence is the appearance of patches of kaolinite (?) and sericite on the plagioclase surfaces. The alteration in the feldspars progresses mainly along twinning and cleavage planes. In the final stages of weathering, the orthoclase begins to show evidence of major alteration in the form of ragged edges and dissolution pits in the crystal surfaces. The relative mineral stabilities in the Elberton granodiorite, from least to most stable, are: plagioclase, biotite, orthoclase, and

quartz.

RESULTS

Soil Mineralogy

The residual soils developing on the Tishomingo granite and Mount Scott granite in southern Oklahoma are a complex mixture of quartz, potassium feldspar, iron oxides, illite, kaolinite, and montmorillonite; however, several distinct mineralogical differences can be observed in the four weathering profiles investigated (see Table 2). In profile T-1 on the Tishomingo granite illite is the most abundant clay mineral present accompanied by lesser amounts of kaolinite and montmorillonite. The kaolinite is poorly crystallized (very broad x-ray diffraction peaks) throughout the entire profile. In contrast, in profiles T-2, S-1, and S-2, kaolinite predominates and illite, montmorillonite, and mixed layer clays are less abundant. Also, in the latter three profiles, the kaolinite is well crystallized.

The residual soils on the Elberton granodiorite in eastern Georgia are almost entirely composed of kaolinite, quartz, and iron oxides with minor amounts of illite and chlorite present. In contrast to the Oklahoma soils,

TABLE 2

Mineralogy of the less than two micron fraction of the residual soils.*

Profile: T-1	T-2	S-1	S-2	E-1
1) Illite	1) Kaolinite	1) Kaolinite	1) Kaolinite	1) Kaolinite
2) Kaolinite	2) Illite	2) Illite	2) Illite	2) Quartz
3) Montmorillonite	3) Montmorillonite	3) Montmorillonite	3) Montmorillonite	3) Chlorite
	4) Mixed layer	4) Mixed layer	4) Orthoclase	4) Illite
			5) Quartz	

*The minerals are listed in order of approximate relative abundance as determined by relative peak heights on the x-ray diffraction record. The size fractionation was made in settling tubes.

potassium feldspar is not found in the surface soils of the Elberton profile. It appears from the x-ray diffraction patterns that the amount of illite present relative to kaolinite decreases with increasing weathering in the less than 2 micron size fraction. As will be noted in the profile descriptions in Appendix I the thickness of the soil mantle in Georgia is an order of magnitude greater than that found on either of the Oklahoma granites investigated.

In all of the soils investigated, it appeared that the majority of the iron oxide present was associated with other minerals, primarily as surface coatings, rather than being present as separate grains.

Treatment of chemical data

The determination of absolute chemical changes involved in the alteration of fresh rock to residual soil is at best very difficult. Several complicating factors must be taken into account such as the change in volume which occurs when a given soil is produced from an equivalent amount of rock and the effects of the removal of unknown amounts of material from an open system.

Four different methods of evaluation have been used by various investigators and will be discussed in the following paragraphs.

Goldich (1938), Butler (1953, 1954), Short (1961), and others attempted to compensate for changes in volume and removal of material by assuming that one major element, aluminum, remains constant during the course of weathering. On this basis a correction factor is computed by dividing the percent aluminum oxide in the parent rock by the percent aluminum oxide in any weathered horizon and multiplying the weight percent of all the other constituents in that particular horizon by this factor. Bolter (1961) used a similar technique assuming titanium oxide to be constant throughout the course of weathering. These methods are somewhat limited, because they are dependent on the immobility of aluminum or titanium, both of which are leached to some extent during weathering. However, since these elements are among the least mobile of the constituents in a rock, under most natural weathering conditions, the application of this technique provides an estimate of the mobility of the other elements relative to aluminum or titanium.

Adams and Richardson (1960), in a study of bauxites, concluded that the thorium, uranium, and zirconium contents of the bauxites were related to the type of source rock. The immobility of alpha emitters under severe leaching and the fact that thorium was found in equilibrium with its daughters led the authors also to conclude that the entire radioactive decay series were within resistate minerals an essentially closed system during weathering. It is likely on the basis of Adams and Richardson's data that one of the best methods of determining absolute chemical changes during weathering may be to assume a minor element such as thorium constant, providing that the element can be shown to be in a resistate site in the primary material.

Wahlstrom (1948) and Dennen and Anderson (1962) discussed chemical changes during rock weathering in terms of the variation in weight percent metal or oxide in the various weathered horizons relative to the parent-rock composition. This approach seems to provide very useful information on the mineralogical controls on chemical weathering when the chemical data are combined with petrographic observations.

A fourth method previously used for the evaluation of

chemical changes during weathering involved the selection of an index of weathering. Jackson (1964) uses an index based on the relative stability of common minerals to weathering. Numbers are assigned to various minerals with increasing index number indicating increasing relative stability to weathering. The weighted average of the index numbers calculated for the minerals present in the clay fraction is the weathering mean, and this decreases as a function of the intensity and degree of weathering. This method is particularly useful for studying the soil portion of the weathered mantle. Grant (1963, 1964) used changes in bulk density as an index of the degree of weathering with some success.

Reiche (1950) devised a chemical index, but it has not proven very useful in most weathering studies.

The applicability of any of these methods of interpretation depends, in part, on the nature of the problem under study. In the present investigation, the method utilizing compositional comparison relative to the parent-rock composition will be primarily utilized. This method is considered superior to the other methods when applied to the study of chemical changes during the early stages of

granitic rock weathering, prior to the actual disaggregation of the rock.

Elemental concentration changes during weathering

The chemical analyses of the five weathering profiles investigated are given in Tables 3 - 11 at the end of the text. The variation in weight percent metal at various stages of profile development, in both total bulk samples of all five profiles and the less than 44 micron fraction of the soil portion of profiles T-1 and E-1 are presented graphically in Figures 1 - 7.

Silicon - The geochemical distribution of silicon is similar in all five weathering profiles investigated. The weight percent silicon per unit volume in any sample always decreases with increasing weathering regardless of variations in the parent-rock mineralogy, climatic conditions, or local physiochemical parameters. The largest percentage loss of silicon generally occurs during the transition from the C-horizon to the B-horizon, corresponding to the transition from weathered rock to a completely disaggregated and leached soil. The total amount of silicon lost (a few percent) in the transition

Figure 1 - Chemical variation in weathering profile T-1 on the Tishomingo granite, Oklahoma.

Figure 2 - Chemical variation in weathering profile T-2 on the Tishomingo granite, Oklahoma.

Figure 3 - Chemical variation in weathering profile S-1 on the Mount Scott granite, Oklahoma.

Figure 4 - Chemical variation in weathering profile S-2 on the Mount Scott granite, Oklahoma.

Figure 5 - Chemical variation in weathering profile E-1 on the Elberton granodiorite, Georgia.

Figure 6 - Chemical variation in the less than 44 micron fraction of the weathered horizons of profile T-1 on the Tishomingo granite, Oklahoma.

Figure 7 - Chemical variation in the less than 44 micron fraction of the weathered horizons on the Elberton granodiorite, Georgia.

from rock to soil was also similar in the five profiles investigated, with the exception of the very immature profile on the Mount Scott granite.

Aluminum - A strong inverse relationship in the geochemical distribution of aluminum relative to silicon was noted in each of the weathering profiles investigated (see Figure 8). However, the changes in aluminum concentration were not as uniform through each stage of weathering as was the case with silicon. It should be emphasized that the apparent increase in aluminum is not due to the addition of material, but rather is the result of the loss of other constituents, yielding an increase in the weight percent aluminum per unit volume of sample. The largest percentage gain in aluminum occurred in the profile on the Elberton granite in Georgia.

Iron - The distribution of iron during weathering is very irregular in bulk samples from all five profiles and in the less than 44 micron fraction of two selected profiles. In general, iron tends to be slightly concentrated in intermediate horizons; however, several exceptions are apparent in figures 1 - 5. The weight percent iron in the bulk sample generally increases slightly in the transition

Figure 8

from rock to soil; the inverse occurs in the less than 44 micron fraction of the soil with increased weathering.

Magnesium - The tendency for a depletion of magnesium during the transformation of rock to soil was noted in each of the profiles investigated; however, the depletion was pronounced only in the case of the profile on the Elberton granodiorite and in the less than 44 micron fraction of the soil portion of the weathered mantle on the Tishomingo granite. The distribution of magnesium in the various weathering horizons of the Oklahoma profiles is very irregular. A much larger weight percentage of magnesium is removed from the Georgia granodiorite during soil formation than either of the Oklahoma granites. A major portion of the magnesium removal in the Georgia profile occurs in the transformation from weathered granite (C₂-horizon) to disaggregated soil (A₀ horizon).

Calcium - A definite loss of calcium during weathering occurs in each of the profiles studied. The three well drained profiles T-1, S-1, and E-1 show the largest removal of calcium from the bulk rock. Mobilization and removal appears to occur throughout the course of weathering; however, calcium generally exhibits much

greater mobility during the early stages of weathering than any of the other elements investigated. It is also interesting to note that the three well drained profiles show a slight concentration of calcium in the B-horizon, relative to adjacent horizons, whereas the two imperfectly drained profiles (T-2 and S-2) show a slight enrichment of calcium in the A-horizon.

Potassium - The two profiles on the Mount Scott granite and the single profile on Elberton granodiorite show a slight increase in potassium content during the early stages of weathering, followed by a decrease in potassium with increased weathering. The potassium variations in the two profiles on the Tishomingo granite are more irregular and show an apparent increase in potassium with increased weathering in T-1, and only a slight decrease with increased weathering in T-2. Hence, the total loss of potassium is much more pronounced in the weathering of the Mount Scott granite and Elberton granodiorite than in the case of the Tishomingo granite. The largest change in weight percent potassium in bulk samples generally occurs in the intermediate and final stages of alteration (A- and B-horizons).

Sodium - The geochemical distribution of sodium is similar in each of the weathering profiles investigated. Sodium content in each case decreases during the transformation of rock to soil, with significant leaching in both the bulk sample and the less than 44 micron fraction of the soil. The graphical presentation of sodium versus potassium variations (figure 9) shows clearly that sodium is mobilized at a much earlier stage of weathering than potassium.

Rubidium - In profiles S-1 and E-1 rubidium shows a tendency to be enriched in the slightly weathered rock and then depleted in the intermediate and late stages of weathering relative to the parent-rock composition. In profile T-1 on the Tishomingo granite rubidium content increases with increased weathering, while in profiles T-2 and S-2 rubidium shows little or no variation in concentration throughout the course of weathering. The graphical presentation of potassium versus rubidium (figure 10) shows several interesting features. The general trend in the potassium-rubidium concentration changes in profiles T-1 and T-2, both of which are developed on the Tishomingo granite and only a short

Figure 9

Figure 10

distance apart, is in opposite directions. However, it should be noted that the initial stages of weathering in profile T-1 give a similar trend to that observed in the complete suite from profile T-2. This evidence, in addition to the fact that T-1 has a considerably thicker A and B horizon, would suggest that T-2 may have only reached a maturity stage equivalent to the early stages of development of T-1. The most mature profile, E-1 on the Elberton granodiorite, shows a distinct decrease in potassium-rubidium with increased weathering. These data imply that there are several reversals in the potassium-rubidium concentration changes during the various stages of weathering and with further work it is possible that these elements might be utilized as indicators of soil maturity. The analyses of different size fractions from T-1 and E-1 show a definite tendency for an enrichment of rubidium relative to potassium in the less than 44 micron fraction of the soil. This decrease in the potassium-rubidium ratio in the fine fraction of soils developed on granites has also been noted by Butler (1953).

Manganese - During weathering manganese is enriched in

the intermediate C- and B-horizons and depleted in the A-horizons of the profiles on the Tishomingo granite and Elberton granodiorite, relative to the parent-rock compositions. The two profiles on the Mount Scott granite show a continuous loss of manganese with increased alteration. The iron/manganese ratios are not constant, nor consistent in directional variation in any of the profiles investigated.

Copper - The distribution of copper within the weathering profiles is very irregular. Profiles T-2, S-1, and E-1 on the Tishomingo and Mount Scott granites, and Elberton granodiorite respectively, show an enrichment of copper in the A-horizons. Profiles T-1 and S-2 show a depletion of copper in the A-horizon. In the less than 44 micron fraction of soils on the Tishomingo granite and Elberton granodiorite copper consistently decreases with increasing weathering.

Zinc - The variation in parts per million zinc per unit volume of material is generally rather small in the five profiles studied. The redistribution of zinc during weathering follows a pattern similar to that of manganese with an enrichment in the B- and/or A-horizons

of the profiles. The less than 44 micron fraction of soils on the Tishomingo granite and Elberton granodiorite show a continuous decrease in zinc content with increasing alteration.

Thorium - The four Oklahoma profiles studied generally showed a slight increase in parts per million thorium with increasing alteration, whereas in the Georgia profile thorium increased during the intermediate stages of weathering and was depleted in the A-horizon.

Uranium - Although the distribution of uranium in the various weathering horizons of the profiles studied is somewhat irregular, the uranium content of the A-horizon is invariably less than that of the parent granite. The thorium/uranium ratios of the residual soils were consistently higher than those of the parent granite. The uranium values obtained for the petrographically "fresh" samples appear lower than the average for granites, suggesting that rather significant amounts of uranium might be removed from granite during the very early stages of weathering.

Principal characteristics of elemental distributions

A detailed examination of the data in Tables 3-11 reveal certain characteristics in the geochemical distribution of both major and trace elements which recur in each of the soils investigated. These observations in addition to those made on the size fraction study are summarized below.

- 1) Several elements, notably silicon, aluminum, magnesium, calcium, sodium, and zinc exhibit similar distributions in each of the five profiles investigated. Silicon, calcium, and sodium decreased with increased alteration in all five profiles. Magnesium and zinc were concentrated in the partially altered C₂ and B-horizons of the profiles. Aluminum increased with increasing degree of weathering in each of the five profiles.
- 2) Zinc and copper show consistent differences in geochemical distribution during the weathering of a total bulk sample and the less than 44 micron portion of the sample. In the bulk samples from various horizons, zinc and copper are generally enriched in the less than 44 micron fraction of these same samples,

zinc and copper decrease with increased weathering.

- 3) Zinc, copper, and lithium were found concentrated in the less than 44 micron portion of the soils, while the remaining elements investigated were distributed more evenly in the various size fractions of the bulk soil.
- 4) The largest percentage loss in material from bulk samples generally occurs in the transition from the weathered rock or C-horizon to the B-horizon. However, different elements are mobilized and removed at different stages of alteration depending on their lattice site and the chemistry of the weathering solution. For example, the majority of the mobile calcium in a granitic rock is generally localized in hornblende and/or plagioclase feldspar, two relatively unstable minerals under surface conditions, while potassium is generally mobilized in the later stages during soil formation, as a result of its concentration in the relatively stable potassium feldspar minerals.

Relative mobility of the individual elements

Relative mobility is used in the present study as an

index of the final distributions of individual elements during the transformation of a rock into a soil. The most complete and mature profile from each of the three granites under investigation was selected, and the relative mobility of the individual elements from each profile calculated by obtaining the ratio of the concentration of each element in the soil to the concentration of the element in the parent granite. Thus, the numerical value of the ratio is inversely proportional to the relative mobility of the element (Tables 12 - 14).

The results obtained in the relative mobility calculations are in general agreement with the calculations of Smýth (1913), Polynov (1937), Anderson and Hawkes (1958), and Feth et.al. (1964).

The most consistant features of the mobility calculations indicate that calcium and sodium in every case are the most mobile elements, and aluminum, iron, and copper the least mobile elements at the weathering site. Potassium, rubidium, silicon, magnesium, manganese, and uranium show an intermediate mobility. The behavior of lithium, thorium, and zinc is highly irregular and inconsistent at the three different weathering sites.

TABLE 12

Relative mobility of cations during the weathering of the Tishomingo granite, Oklahoma.

Element	Site	Concentration	Ratio $\frac{\text{Soil}}{\text{Rock}}$
Si (%)	Soil	24.(04)	0.71
	Rock	34.(10)	
Al	Soil	15.(90)	2.15
	Rock	7.(40)	
Fe	Soil	2.4(0)	2.42
	Rock	0.9(9)	
Ca	Soil	0.21	0.002
	Rock	1.2(9)	
Mg	Soil	0.18	0.58
	Rock	0.31	
Na	Soil	0.92	0.27
	Rock	3.4(0)	
K	Soil	3.7(0)	1.20
	Rock	3.2(0)	
Rb (ppm)	Soil	78	1.30
	Rock	60	
Li	Soil	14	0.39
	Rock	36	
Mn	Soil	23(5)	1.10
	Rock	21(0)	
Cu	Soil	10	1.30
	Rock	8	
Zn	Soil	56	1.70
	Rock	34	
Th	Soil	9.1	1.10
	Rock	8.5	
U	Soil	0.9	0.53
	Rock	1.7	

Relative Mobility:

Ca > Na > Li > U > Mg > Si > Th > Mn > K > Cu > Rb > Zn > Al > Fe

Relative mobility of cations during the weathering of the Mount Scott granite, Oklahoma.

Element	Site	Concentration	Ratio <u>Soil</u> Rock
Si (%)	Soil Rock	22.(37) 35.(60)	0.63
Al	Soil Rock	17.(34) 7.(90)	2.20
Fe	Soil Rock	4.4(0) 3.6(0)	1.20
Ca	Soil Rock	0.09 1.2(9)	0.007
Mg	Soil Rock	0.43 0.52	0.83
Na	Soil Rock	0.65 2.9(6)	0.22
K	Soil Rock	1.9(0) 3.6(0)	0.53
Rb (ppm)	Soil Rock	55 72	0.76
Li	Soil Rock	26 18	1.40
Mn	Soil Rock	35(1) 93(3)	0.38
Cu	Soil Rock	11 8	1.40
Zn	Soil Rock	93 15(3)	0.61
Th	Soil Rock	16.6 13.2	1.26
U	Soil Rock	3.2 3.4	0.94

Relative Mobility:

Ca > Na > Mn > K > Zn > Si > Rb > Mg > U > Fe > Th > Cu > Li > Al

TABLE 14

Relative mobility of cations during the weathering of the Elberton granodiorite, Georgia.

Element	Site	Concentration	Ratio <u>Soil</u> Rock
Si (%)	Soil	21.(56)	0.67
	Rock	32.(40)	
Al	Soil	20.(10)	2.40
	Rock	8.(44)	
Fe	Soil	3.0(8)	1.80
	Rock	1.7(6)	
Ca	Soil	0.04	0.002
	Rock	1.7(0)	
Mg	Soil	0.18	0.040
	Rock	0.52	
Na	Soil	0.12	0.005
	Rock	2.5(5)	
K	Soil	1.8(3)	0.47
	Rock	3.8(6)	
Rb (ppm)	Soil	66	0.64
	Rock	10(3)	
Li	Soil	23	1.40
	Rock	16	
Mn	Soil	11(0)	0.55
	Rock	20(0)	
Cu	Soil	18	1.30
	Rock	14	
Zn	Soil	64	0.97
	Rock	66	
Th	Soil	39.8	0.84
	Rock	47.6	
U	Soil	2.7	0.55
	Rock	4.9	

Relative Mobility:

Ca > Na > Mg > K > Mn > U > Rb > Si > Th > Zn > Cu > Li > Fe > Al

Autoradiographs

A series of fresh and partially altered rock samples and associated residual soils were studied with autoradiographic techniques in order to determine the effects of weathering on the distribution of uranium and thorium. One inch thick rock slabs were placed adjacent to Kodak type KK industrial x-ray film and exposed for approximately thirty days. Photographic prints of the autoradiographs are shown in figures 11 and 12.

The widely distributed light gray areas in the photographs represent feldspar grains whose main radioactive component is potassium-40. The black point sources represent concentrations of uranium and/or thorium, generally associated with biotite or accessory grains. For a complete discussion of the distribution of radioactivity in granites the reader is referred to Richardson (1963) and Ragland (1964).

The autoradiographs show a definite decrease in the density of concentrated radioactive sources with increased weathering. However, the radiometric data presented in tables 3 and 7 indicate only a small loss in uranium and little or no significant change in the relative concentration

Figure 11 - Autoradiographs of fresh and partially altered Tishomingo granite, Oklahoma.

Profile
position

C₂

C₁

C₀

D

Figure 12 - Autoradiographs of fresh and partially altered Elberton granodiorite, Georgia.

Profile position

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of thorium throughout the profile.

It may be concluded from these preliminary studies that although there is a redistribution of radioactivity during weathering there is apparently only localized mobilization, particularly in the case of thorium.

DISCUSSION

Mineralogical control on cation mobility

Calcium and sodium show the greatest relative mobility during the weathering of granitic rocks, the primary reason being their rather high concentration in relatively unstable minerals and their high solubility in natural waters. These elements are localized primarily in the plagioclase feldspars and mafic minerals which are the first minerals to show signs of alteration in a granitic rock. Thus, the majority of the calcium and sodium in a granitic rock is released into solution in the early stages of weathering, prior to extensive soil formation. If sufficient water is available and drainage is good, then the calcium and sodium will be transported out of the environment and will not be incorporated into the residual soils formed in the later stages of weathering.

Although all the soils studied in the present investigation are depleted in calcium and sodium relative to the parent granites, the Georgia soils, located in an area of relatively high, year around rainfall are particularly deficient in these elements. Climatic factors play an important secondary role in the mobility of these elements.

Mineralogy plays an entirely different role in controlling the mobility of potassium and rubidium. In granitic rocks, potassium and rubidium are primarily localized in the potassium feldspar and micas. Petrographic observations (Appendix I) indicate that potassium feldspar remains relatively unaltered until the intermediate and final stages of weathering, particularly in the Oklahoma soils where slightly altered potassium feldspar is found in the A-horizon. The chemical data indicate a relative increase in the amount of potassium and rubidium during the early and intermediate stages of weathering which results from the dissolution and removal of mafic minerals and plagioclase and a relative increase in the amount of potassium and rubidium bearing feldspar per unit volume of rock.

The distribution of thorium in the five profiles is somewhat irregular; however, the amount of thorium in the soils is always greater than or approximately equal to the amount in the parent granite.

Chemical control on cation mobility

The mobility in a time independent system of several common rock forming elements, notably silicon, aluminum, and iron, is primarily controlled by their low solubility in natural waters. Once an initial equilibrium is attained at the rock-water interface, further dissolution of the rock is dependent on the recharge characteristics of the hydrologic system.

In the five profiles investigated in the present study, silicon exhibited a much greater relative mobility than aluminum throughout the course of weathering. To explain the differences in relative mobility of these two elements during weathering, it is necessary to consider the factors which govern the solubility of a particular element; namely, matrix, pH, composition of the weathering solution, and temperature. Krauskopf (1959) and Correns (1949) have investigated the solubility relationships

of silica and alumina as a function of pH (Figure 13). If the data on the reaction pH's of the three granite weathering profiles under investigation (Table 15) are applied to the diagram constructed from Krauskopf's and Correns' data, then it becomes readily evident that under the pH conditions which would be expected to result from the reaction of rain water with granite, silica would be much more soluble than aluminum. As Keller (1963) has pointed out, these solubility relationships are slightly complicated by secondary interaction effects such as the enhancement of silica solubility by dissolved sodium and potassium and tendency of dissolved calcium and magnesium to reduce the solubility of silica. The well drained soils generally show the greatest loss of silica during soil formation as would be expected because the faster circulating weathering solutions have less chance of reaching equilibrium with the coexisting mineral assemblage.

The immobility of iron in the weathering environment is a result of the low solubility of the iron hydroxides and hydrated oxides which form quickly after the release of iron from the weathering of minerals such as biotite.

Figure 13 - Solubility relationships in the systems $\text{SiO}_2 - \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 - \text{H}_2\text{O}$ (data from Krauskopf, 1959; Correns, 1949).

TABLE 15

Reaction pH Measurements of Weathering Profiles

<u>Weathering Horizon</u>	<u>Tishomingo Granite</u>	<u>Mount Scott Granite</u>	<u>Elberton Granodiorite</u>
A ₀	6.3	7.3	5.2
A ₁	6.3	--	4.8
B	6.2	4.8	6.5
C ₂	6.5	6.0	5.9
C ₁	6.5	6.6	5.9
C ₀	7.0	6.9	5.5
D	7.6	7.6	8.7

The question of the removal of iron in colloidal form must be considered, however, because the formation of iron colloids is a well documented phenomenon. The apparent reason for the ineffectiveness of colloids in iron transport is the presence of abundant charged surfaces, particularly quartz surfaces, which serve as nucleation agents for iron precipitates. This also explains the abundance of iron coated quartz grains observed in the weathered rock and soils (see Appendix I).

Adsorption is also an important chemical control on cation mobility. Noll (1931) concluded that the adsorbability of ions in the natural environment increases with (a) increasing charge on the ion, (b) decreasing hydrated volume, (c) increasing polarizability, and (d) increasing dipolar properties. The clay minerals and fine-grained iron oxides constitute the main inorganic exchange materials in most soils. These materials generally have a very high surface area and negatively charged surfaces. In the present investigation, it appears that during weathering the redistribution of lithium, copper, and zinc are strongly influenced by adsorption and surface exchange. These elements are all concentrated in

the less than 44 micron fraction of the soils. With the possible exception of lithium, these elements are not common structural components of clays, particularly kaolinite, which is the most abundant clay present.

Biological control on cation mobility

One biological control on cation mobility is expressed in the surface enrichment of cations which are taken up by plants, including microorganisms. Calcium and sodium often show a slight enrichment in the A-horizon which could possibly be attributed to organic agents.

Lovering (1959) has demonstrated the ability of some plants to accumulate significant amounts of certain major elements, such as silicon, aluminum, calcium, and iron. Lovering calculates that a forest of silica-accumulator plants averaging 2.5 percent silica and 16 tons dry weight new growth per year would extract about 2000 tons of silica from the underlying soil in 5000 years. Keller (1957) discussed the exchange of hydrogen ions from plant rootlets for nutrient cations such as calcium, magnesium, and potassium held in exchange positions in silicate minerals.

The decay of plant materials also undoubtedly enhances the solubility of mineral structures by the release of the general class of humic acids, including oxalic and citric acids. Soil organic matter can complex with metals by ion exchange, surface adsorption, chelation and peptization reactions increasing the solubility and correspondingly the mobility of many metals in nature. The formation of such complexes may be partially responsible for the irregular behavior of such elements as thorium and zinc; however, there is no proof to support such a conclusion.

A thorough investigation of biological effects on weathering, where such effects are at a maximum, is needed.

GEOCHEMICAL IMPLICATIONS

Water chemistry

The chemical constituents of natural inland surface waters are derived from a variety of sources including:

- (1) atmospheric materials, such as dust, salt particles from the sea, volcanic debris, and industrial pollution,

which are transferred to surface waters by rain or snow; (2) ground water discharge; and (3) mineral dissolution and the release of solutes during chemical weathering.

The chemistry of rain water has been summarized by Gorham (1961), Carrol (1962), and Junge (1963). These authors have concluded that differences in the composition of rain water are caused by several factors, principally by the atmospheric conditions and amount of rainfall, nearness to the ocean, and amount of contamination in the local atmosphere. However, a total of approximately eighteen rain water samples from the United States have been analyzed in detail, and the relative importance of the numerous variables is unknown for the North American continent. As pointed out by Carrol (1962), rain water is potentially a very effective agent in geologic processes, but its effectiveness has been evaluated for only a few arid areas.

The effects of rock weathering on the composition of natural waters begins when rain water initially comes into contact with mineral surfaces. Strongly alkaline conditions are indicated by studies on the reaction pH of fresh rock (Keller et.al., 1963; this paper, Table 15).

Under these conditions, silica is relatively mobile and is released from the more soluble minerals along with associated alkali and alkaline earth cations. Alumina is relatively insoluble in the pH range of 7.0 - 9.0, and experimental studies by Correns (1963) indicate that hydrated aluminum minerals often form rims around partially weathered crystals. Once the weathering solution comes to equilibrium with the adjacent mineral assemblage, weathering processes are minimized. The question which now arises is how to determine whether, on a regional scale, a water - soil equilibrium exists.

Equilibrium diagrams

The use of equilibrium diagrams as an approach to the understanding of water - soil relationships has been demonstrated by Feth et.al. (1964). However, as noted by Feth et.al., the elucidation of the principles behind the construction of equilibrium diagrams and their potential applicability to geochemical studies must be attributed mainly to Garrels (1960). The following brief discussion will concern construction of equilibrium diagrams for the systems $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ and

$K_2O - Al_2O_3 - SiO_2 - H_2O$. For a more detailed treatment, the reader is referred to Garrels (1960) and Feth et.al. (1964).

Stability diagrams which demonstrate equilibrium relationships between various minerals under different physiochemical conditions can be constructed using the equilibrium constant for a particular reaction calculated from the free energy of formation of the constituents involved in the reaction.

The primary assumptions made in the construction and application of the diagrams is that the activity of any solid is unity and that the molarity of soluble constituents equals the activity.

For the system $K_2O - Al_2O_3 - SiO_2 - H_2O$, the following equations are used to determine the fields of stability of the different phases.

From these equations, the stability relations can be written as functions of $\left[\text{K}^+\right] / \left[\text{H}^+\right]$ and $\left[\text{H}_4\text{SiO}_4\right]$ as demonstrated in figure 14.

Figure 14 - System $K_2O - Al_2O_3 - SiO_2 - H_2O$ at $25^\circ C$ and 1 atm. total pressure (diagrams from R.M. Garrels, personal communication).

Similarly, in the system, $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$, the equilibrium diagram for different phases can be constructed from the following equations:

Figure 15 - System $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ at 25°C and 1 atm. total pressure (diagrams from R.M. Garrels, personal communication).

single year were chosen in order to include the extremes in chemical variation.

The equilibrium diagrams suggest that kaolinite should be the stable mineral in the Georgia soils. A mixture of kaolinite and montmorillonite is predicted for the Oklahoma soils if equilibrium exists between the soils and surface waters. Gibbsite, K-mica or illite, albite and K-feldspar are presumably unstable in both regions and montmorillonite should be unstable in the Georgia soils overlying the Elberton granodiorite. A comparison of these results with the mineralogical analyses of the soils (Table 2) suggests several interesting implications.

- 1) The Georgia soils, which are composed almost entirely of kaolinite, are very close to equilibrium with the natural surface waters. These results imply that weathering processes are not presently very active in the residual soils overlying the Elberton granodiorite and, thus the quality of the surface waters should remain rather stable.
- 2) The residual soils on the Oklahoma granites which are a mixture of illite and kaolinite with small

amounts of other clays present, are not in equilibrium with the natural surface waters. Illite is an unstable constituent of the soils and should eventually weather to kaolinite unless a change in the $\left[K^+ \right] / \left[H^+ \right]$ and $\left[H_4SiO_4 \right]$ of the waters occurs so that illite can be included in the equilibrium assemblage.

The above results are consistent with field observations, the soil mantle on the Elberton granodiorite being much more mature and several orders of magnitude thicker than that on the Oklahoma granites. There are several possible explanations for the differences in the degree of weathering in the two areas.

First, the more extensive weathering of Georgia granite could possibly be attributed to present-day climatic conditions. Although the average annual rainfall and number of frost-free days in east-central Georgia and southern Oklahoma are similar, the distribution of annual rainfall is quite different. In Georgia the rainfall is distributed fairly evenly throughout the year, resulting in a rather constant supply of moisture in the soil, whereas in Oklahoma, rainfall is generally limited to

the fall and winter months. Thus, four to five months out of every year, Oklahoma is characterized by an arid climate. The more extensive soil-water contact in the Georgia soils possibly promotes a greater annual rate of weathering and more rapid profile development than found in the Oklahoma soils where soil moisture is absent for a significant portion of each year.

A second possibility is that the more extensive weathering of the Georgia granites occurred under slightly different meteorological conditions than presently exist. The major portion of profile development in the Georgia soils may have occurred during the last postglacial temperature maximum, some 5500 years before present. This explanation would require the development of warmer and more humid conditions along the Atlantic coast and relatively arid conditions in the south-central United States.

Biogeochemical effects of weathering

The importance of certain trace metals in biological and physiological processes has been well documented by Hutchinson (1943), Herriott (1953), Stiles (1961), Warren

(1962), and numerous other authors. Deficiencies in elements such as zinc, cobalt, manganese, iron, and copper, to name only a few, generally result in easily recognizable pathologic and/or metabolic irregularities in the associated food chain. Cobalt deficiency is a nutritional problem in animals grazed on plants grown in certain areas of New Hampshire and Massachusetts (Kubota, 1964) and zinc deficiencies are widespread in fruit trees grown in certain portions of Florida and California (Stiles, 1961), to name only a few specific examples.

Weathering processes control the release of metals into soils and subsequently into the biosphere. The purpose of this section is to determine what role weathering would be expected to have in the production of nutritionally deficient soils developed on granitic rocks.

A compilation of the existing data on the chemical weathering of granitic rocks is presented in Table 17. These data indicate that, for soils of temperate semi-humid to humid environments, iron, vanadium, cobalt, nickel and copper are always found in quantities equal to or greater than those found in the parent-rock. Thus,

TABLE 17

Summary of gains (x) and losses (-) of biologically important metals during the weathering of granitic rocks.

Reference*:	1	2	3	4
Rock Type:	Granodiorite	Granodiorite	Granodiorite	Granodiorite
Si (%)	x	-	-	-
Al	x	x	x	x
Fe	x	x	x	x
Mg	x	-	x	x
Ca	-	-	-	-
K	-	-	-	-
Na	-	-	-	-
Co (ppm)	x		0	0
Cu	x	0		
Mn	-	-	x	x
Ni	x	x	x	x
V	x		x	0
Zn	x	0		

*: 1 - Short (1961).
 2 - Present study.
 3 - Yamasaki (1955).
 4 - Butler (1953).

TABLE 17 (cont'd)

Summary of gains (x) and losses (-) of biologically important metals during the weathering of granitic rocks.

Reference*:	1	2	2	2	2
Rock Type:	Granite	Granite	Granite	Granite	Granite
Si (%)	x	-	-	-	
Al	-	x	x	x	
Fe	x	x	x	x	x
Mg	x	x	-	-	-
Ca	-	-	-	-	-
K	x	x	-	-	-
Na	-	-	-	-	-
Co (ppm)	x				
Cu	x	0	x	x	x
Mn	x	x	x	-	-
Ni	x	x	x	x	x
V	x				
Zn	x	x	x	-	-

*: 1 - Short (1961).

2 - Present study.

deficiencies in iron, vanadium, nickel, cobalt, and copper in residual soils overlying granites must be attributed to the absence or very low concentration of the particular element in the parent granite. In contrast, weathering processes may or may not be effective in producing soils deficient in zinc, manganese, potassium, magnesium and silica. Calcium and sodium are, in all cases, mobilized and removed from residual granitic soils during weathering.

The above considerations should be taken into account when treating nutritionally deficient soils. For example, if a residual soil on a granite is deficient in copper, then the addition of a copper containing substance to the soil should overcome the deficiency. However, if a granitic soil is deficient in manganese, an additive may not solve the problem since the weathering processes active in leaching the original soil manganese may also be effective in mobilizing and removing any manganese additive. Where weathering processes are active in producing nutritional deficiencies in soils, the physio-chemical nature of the soil must be considered.

CONCLUSIONS

The following conclusions pertain specifically to the granitic rocks studied in the present investigation.

- 1) Petrographic observations and chemical analyses indicate that the relative mineral stabilities in the three granites under investigation generally follow the sequence: plagioclase feldspar, biotite, potassium feldspar, quartz, from least to most stable respectively. This relative stability sequence is consistently observed regardless of climatic and/or local physiochemical variations.
- 2) The largest physical and chemical changes occur in the transition from the C-horizon (weathered rock) to the B-horizon (soil).
- 3) Mineralogy is the predominant factor controlling the mobility of calcium, sodium, potassium, rubidium, and thorium during weathering. Calcium and sodium are concentrated primarily in the plagioclase feldspars and are released and mobilized during the early stages of weathering. Potassium, rubidium, and thorium are concentrated in the relatively stable

orthoclase feldspars and resistate minerals and are mobilized only in the intermediate and final stages of weathering.

- 4) Lithium, copper, and zinc are generally enriched in the soil portion of the weathered mantle as a result of adsorption and surface exchange with clay minerals.
- 5) Kaolinite is the predominant clay mineral present in the Georgia soils. Kaolinite and illite are both present as major constituents in the Oklahoma soils. The quantitative importance of the various clays is a function of the degree of weathering of the soils.
- 6) Stability diagrams indicate that the natural surface waters of east-central Georgia are in equilibrium with kaolinite, the major clay mineral present in the soils. In contrast, the natural surface waters of southern Oklahoma are in equilibrium with kaolinite and montmorillonite, but not illite which is a major constituent of the Oklahoma soils. Thus, the diagrams indicate that a disequilibrium relationship exists between the Oklahoma

soils and coexisting natural waters.

- 7) Combined field and theoretical evidence indicates that the Georgia soils have reached maturity and are probably the result of extensive weathering during the last post-glacial temperature maximum, approximately 5500 years ago. The Oklahoma soils are very immature and are presently undergoing active alteration.

TABLE 3

Chemical analyses of weathering Profile T-1 on the Tishomingo granite.

Sample No.: Profile pos.	W-61 D	W-61A C ₀	W-54 C ₁	W-53 C ₂	W-52 B	W-50 A
Si (%)	34.(10)	32.(00)	30.(80)	30.(82)	25.(41)	24.(42)
Al	7.(40)	7.(80)	9.(21)	10.(40)	13.(58)	16.(14)
Fe	0.99	1.7(4)	2.3(0)	2.3(0)	2.4(0)	2.2(0)
Ca	1.2(9)	1.6(2)	0.76	0.31	0.23	0.18
Mg	0.31	0.44	0.42	0.38	0.43	0.17
Na	3.4(0)	3.3(8)	2.6(6)	1.5(9)	0.9(2)	0.9(0)
K	3.2(0)	2.3(7)	3.3(7)	3.8(6)	3.8(0)	3.7(0)
Rb (ppm)	60	52	74	80	89	78
Li	36	41	17	20	11	14
Mn	21(0)	29(2)	38(0)	33(7)	23(5)	20(0)
Cu	8	9	9	9	10	6
Zn	34	45	48	48	56	39
Th	8.5	5.2	11.9	9.6	9.1	8.1
U	1.7	1.4	2.1	1.6	1.3	0.9

TABLE 4

Chemical analyses of weathering profile T-2 on the Tishomingo granite.

Sample No. Profile pos.	W-61 D	W-60		W-60A		W-59		W-58		W-57	
		C ₀		C ₁		C ₂		B		A	
Si (%)	34.(16)	32.(70)		32.(01)		28.(10)		23.(10)		23.(12)	
Al	7.(40)	6.(93)		8.(17)		9.(72)		16.(00)		16.(94)	
Fe	0.98	1.0(5)		1.4(2)		1.1(0)		1.4(1)		1.2(2)	
Ca	1.2(9)	1.7(7)		1.4(2)		0.91		0.40		0.76	
Mg	0.32	0.37		0.25		0.23		0.32		0.27	
Na	3.4(0)	3.2(8)		3.4(4)		2.8(3)		1.4(2)		1.6(5)	
K	3.2(2)	2.9(0)		2.8(3)		3.4(3)		2.3(8)		2.2(7)	
Rb (ppm)	60	58		63		69		58		60	
Li	36	41		40		38		41		33	
Mn	21(0)	27(0)		29(1)		31(1)		32(3)		20(0)	
Cu	8	8		8		5		11		10	
Zn	34	53		40		40		50		45	
Th	8.5	6.2		9.4		7.9		12.3		8.6	
U	1.7	1.4		1.6		1.7		1.6		1.2	

TABLE 5

Chemical Analyses of Weathering Profile S-1 on the Mount Scott granite.

Sample No. Profile pos.	W-67 D	W-62 C ₀	W-63 C ₁	W-69 C ₂	W-65 B	W-68 A
Si (%)	35.(60)	35.(04)	32.(10)	31.(32)	25.(60)	22.(37)
Al	7.(90)	9.(21)	8.(81)	12.(83)	16.(01)	17.(34)
Fe	3.6(0)	3.8(3)	2.9(3)	3.4(0)	4.4(0)	3.0(7)
Ca	1.2(9)	0.23	0.23	0.31	0.09	0.09
Mg	0.52	0.13	0.12	0.42	0.49	0.43
Na	2.9(6)	2.8(3)	2.5(5)	0.78	0.57	0.65
K	3.6(0)	3.8(6)	3.7(5)	3.2(0)	2.3(8)	1.9(0)
Rb (ppm)	72	83	78	72	66	55
Li	18	16	17	28	23	26
Mn	93(3)	36(9)	36(8)	33(7)	35(1)	28(0)
Cu	8	5	6	11	11	10
Zn	15(3)	72	88	88	93	80
Th	13.2	16.5	13.9	16.1	16.6	16.0
U	3.4	4.6	3.1	3.6	2.9	3.2

TABLE 6

Chemical analyses of weathering Profile S-2 on the Mount Scott granite,
Oklahoma

Sample No. Profile Position	W-21		W-21c		W-21b		W-21a	
	D		C		B		A	
Si (%)	35.(12)		32.(49)		32.(13)		31.(07)	
Al	7.(80)		8.(23)		8.(21)		8.(90)	
Fe	3.6(0)		3.8(3)		4.0(0)		3.7(0)	
Ca	1.3(0)		1.0(0)		0.86		1.0(2)	
Mg	0.50		0.40		0.55		0.31	
Na	2.9(0)		2.8(2)		2.7(5)		1.7(2)	
K	3.2(7)		3.8(0)		3.1(1)		2.7(5)	
Rb (ppm)	74		78		70		74	
Li	18		16		21		18	
Mn	97(8)		85(2)		83(6)		83(0)	
Cu	14		11		17		8	
Zn	18(4)		14(9)		17(5)		16(1)	
Th	15.0		14.2		15.1		14.8	92
U	2.8		3.4		3.2		2.0	

TABLE 7

Chemical analyses of weathering profile E-1 on the Elberton granite.

Sample No. Profile pos.	E-7 D	E-2 C ₀	E-3 C ₁	E-4 C ₂	E-5 A ₁	E-6 A ₀
Si (%)	32.(40)	29.(89)	29.(67)	30.(51)	24.(00)	21.(56)
Al	8.(44)	11.(35)	13.(56)	15.(18)	19.(56)	20.(10)
Fe	1.7(6)	2.2(5)	2.1(9)	1.9(7)	2.5(0)	3.0(8)
Ca	1.7(0)	0.66	0.86	1.1(6)	0.05	0.04
Mg	0.52	0.56	0.52	0.52	0.26	0.18
Na	2.5(5)	2.1(5)	1.8(5)	2.4(1)	0.14	0.12
K	3.8(6)	4.5(0)	4.6(2)	4.3(0)	3.0(8)	1.8(3)
Rb (ppm)	10(3)	11(2)	10(6)	10(3)	92	66
Li	16	20	18	17	20	23
Mn	20(0)	23(0)	23(5)	20(0)	18(0)	11(0)
Cu	14	16	14	17	14	18
Zn	66	78	80	75	61	64
Th	47.6	53.0	53.8	48.0	36.6	39.8
U	4.9	2.4	1.6	1.8	2.7	3.3

TABLE 8

Chemical analyses of various size fractions from
profile T-1 on the Tishomingo granite.

Sample No. Size fraction	W-50 420-1680 μ	W-50 <44 μ	W-50 Bulk	W-51 420-1680 μ	W-51 <44 μ	W-51 Bulk
Fe (%)	0.68	1.9(3)	1.5(2)	0.31	1.8(6)	1.5(2)
Ca	0.09	0.40	0.15	0.04	0.31	0.23
Mg	0.07	0.31	0.18	0.04	0.30	0.19
Na	0.52	1.0(4)	0.87	0.48	0.95	0.92
K	5.0(0)	1.9(0)	4.7(0)	4.7(9)	1.9(4)	3.9(1)
Rb (ppm)	97	52	89	63	55	78
Li	4	20	10	3	16	14
Mn	84	38(0)	19(1)	71	33(7)	22(2)
Cu	8	65	5	20	10(4)	2
Zn	26	92	40	20	96	37

TABLE 9

Chemical analyses of various size fractions from
profile T-1 on the Tishomingo granite.

Sample No. Size Fraction	W-52 420-1680 μ	W-52 < 44 μ	W-52 Bulk	W-53 420-1680 μ	W-53 < 44 μ	W-53 Bulk
Fe (%)	2.6(2)	2.9(3)	2.4(0)	4.4(0)	2.6(2)	2.3(0)
Ca	0.09	0.56	0.23	0.46	0.91	0.31
Mg	0.42	0.40	0.43	0.78	0.58	0.38
Na	0.61	1.0(0)	0.92	1.0(0)	2.0(0)	1.5(9)
K	3.2(8)	1.9(4)	3.8(0)	2.3(8)	1.2(6)	3.8(6)
Rb (ppm)	78	58	89	60	43	80
Li	21	34	24	30	27	20
Mn	26(6)	35(1)	23(5)	69(2)	47(0)	33(7)
Cu	17	13(1)	8	38	23(1)	5
Zn	56	12(0)	56	93	19(2)	48

TABLE 10

Chemical analyses of various size fractions from
profile T-1 on the Tishimingo granite.

Sample No.	W-54	W-54	W-54	W-54	W-54	W-54
Size fraction	1680-420 μ	420-250 μ	250-149 μ	149-62 μ	<44 μ	Bulk
Fe (%)	3.5(0)	6.6(3)	7.5(1)	5.6(8)	2.9(3)	2.3(0)
Ca	1.0(0)	1.0(0)	1.1(6)	1.6(1)	1.3(9)	0.76
Mg	0.84	1.0(7)	0.97	0.79	0.67	0.42
Na	2.2(9)	2.4(9)	2.5(5)	2.6(8)	2.6(8)	2.6(6)
K	2.3(8)	1.6(7)	1.8(0)	1.3(1)	1.2(2)	3.3(7)
Rb (ppm)	66	63	60	46	37	74
Li	30	35	38	31	48	17
Mn	75(0)	11(20)	10(64)	93(3)	81(6)	38(0)
Cu	38	59	67	96	194	5
Zn	90	14(0)	11(2)	98	17(3)	48

TABLE 11

Chemical analyses of the less than 44 micron size fraction from profile E-1 on the Elberton granodiorite, Georgia.

Sample No.	E-3	E-4	E-5	E-6	E-7
Profile Position	C ₀	C ₁	C ₂	A ₁	A ₀
Fe (%)	1.9(0)	1.6(2)	1.5(3)	1.8(1)	1.7(6)
Ca	0.81	0.74	0.21	0.24	1.7(0)
Mg	0.68	0.61	0.11	0.09	0.52
Na	1.2(6)	1.0(0)	0.42	0.10	2.5(5)
K	2.0(6)	1.8(6)	1.0(3)	0.54	3.8(6)
Rb (ppm)	65	60	43	32	10(3)
Li	37	21	26	23	16
Mn	26(5)	26(1)	20(9)	14(7)	20(0)
Cu	17(9)	16(4)	13(1)	92	14
Zn	28(5)	24(6)	20(3)	18(0)	66

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Appendix I

Description of weathering profile T-1 on the Tishomingo granite, located in roadcut on Oklahoma highway 7, 1.7 miles west of intersection with Oklahoma highway 99, between Tishomingo and Connerville, Johnson County, Oklahoma.

Sample No. and Location	Weathering Horizon	Description
0 W-50	A ₁	Highly weathered, brown soil; contains illite, kaolinite, montmorillonite, iron oxide, abundant iron-stained quartz, and weathered K-feldspar crystals. Slight amount of organic matter in top few inches.
10" W-51	A ₀	Highly weathered, buff colored soil; mineralogy similar to W-50 with exception of slightly greater amounts of K-feldspar. Textural resemblance to parent-rock begins to disappear.
20"		
W-52	B	Highly weathered, dark red soil; rock completely disaggregated; plagioclase absent and biotite highly altered, K-feldspar shows evidence of extensive dissolution on edges, iron oxide stains on quartz.
30"		
W-53	C ₂	Partially weathered rock; easily disaggregated; small cracks filled with micaceous minerals and iron oxide; plagioclase and biotite are very highly altered.
40"		

Description of weathering profile T-1, continued.

Sample No. and Location	Weathering Horizon	Description
50" W-54	C ₁	Partially weathered rock; dull pink color; plagioclase grains show extensive alteration to micaceous minerals; iron oxide stains on quartz.
60" W-61A	C ₀	Slightly weathered rock; plagioclase shows partially altered surfaces, biotite shows an increase in 2 V and a decrease in refractive index.
W-61	D	Coarse grained, reddish-pink, porphyritic granite; contains perthite, plagioclase, K-feldspar, quartz, biotite, and accessory minerals.

Description of weathering profile T-2 on the Tishomingo granite, located in roadcut on Oklahoma highway 7, 1.7 miles west of intersection with highway 99, between Tishomingo and Connerville, Johnson County, Oklahoma.

Sample No. and Location	Weathering Horizon	Description
0		
10" W-57	A	Reddish-brown soil; contains kaolinite, illite, montmorillonite, mixed layer clays, quartz, weathered K-feldspar, and iron oxide.
20" W-58	B	Brown soil; mineralogy similar to W-57, plagioclase absent; slight textural similarity to parent granite.
30" W-59	C ₂	Partially altered rock; plagioclase and biotite highly weathered; rock easily disaggregated.
40" W-60A	C ₁	Partially altered rock; plagioclase shows extensive alteration to micaceous minerals on surfaces, grain boundaries deeply etched.
W-60	C ₀	Weathering crust on parent granite; only plagioclase shows microscopic evidence of alteration.
W-61	D	Coarse grained, porphyritic, pinkish-red, granite; contains perthite, K-feldspar, plagioclase, quartz, biotite, and accessory minerals.

Description of weathering profile S-1 on the Mount Scott granite, located in the Wichita Mountains Wildlife Refuge, Comanche County, near Lawton, Oklahoma.

Sample No. and Location	Weathering Horizon	Description
0		
W-68	A	Gray soil; contains kaolinite, illite, quartz, iron oxide and montmorillonite; organic matter relatively abundant.
10"		
W-65	B	Black soil; mineralogy similar to W-68; several very small rock fragments present; iron stains present on rock and mineral fragments.
20"		
W-69	C ₂	Highly weathered rock; easily disaggregated; plagioclase almost completely removed, K-feldspar shows fairly extensive alteration.
30"		
W-63	C ₁	Partially weathered rock; plagioclase surfaces altered to micaceous minerals, K-feldspar slightly altered.
W-62		
W-67	C ₀	Weathering crust on parent granite; slight alteration on feldspar surfaces; iron oxide present in microcracks and along quartz-feldspar grain boundaries.
	D	Medium grained and porphyritic; contains micropegmatite, orthoclase, oligoclase, quartz, and altered hornblende.

Description of weathering profile S-2 on the Mount Scott granite, located in the Wichita Mountains Wildlife Refuge, Comanche, County, near Lawton, Oklahoma.

Sample No. and Location	Weathering Horizon	Description
0 W-21 _A	A	Reddish-brown soil; contains kaolinite, illite, montmorillonite, mixed layer clays, quartz, iron oxide, and K-feldspar; weak textural resemblance to parent granite.
W-21 _B	B	Brown soil; mineralogy similar to W-21 _A , small rock fragments also present; extensive iron staining on rock and mineral fragments.
10" W-21 _C	C ₀	Partially weathered rock; feldspars show alteration to micaceous minerals on surfaces, small fractures filled with iron oxide present.
W-21	D	Medium grained and porphyritic; contains micropegmatite, orthoclase, oligoclase, quartz, and altered hornblende.
20"		

Description of weathering profile E-1 on the Elberton granodiorite, located in quarry adjacent to U.S. highway 72 about 10 miles west of Elberton, Georgia.

Sample No. and Location	Weathering Horizon	Description
0		
E-6	A ₁	Red saprolite; contains iron oxide, kaolinite, illite, chlorite, and quartz; organic matter prominent in top four inches.
10' E-5	A ₀	Buff saprolite; contains kaolinite, illite, chlorite, quartz, and altered K-feldspar; retains parent-rock texture very well.
E-4	C ₂	Highly weathered rock; plagioclase feldspar and biotite highly altered; easily disaggregated.
20' E-3	C ₁	Highly weathered rock; plagioclase feldspar and biotite highly altered; iron stains prominent on mineral surfaces.
E-2	C ₀	Slightly weathered rock; plagioclase feldspar and biotite altered; iron stains on quartz; K-feldspar unaltered.
30' E-7	D	Medium grained, light gray, biotite granodiorite; contains quartz, plagioclase, orthoclase, and biotite.

APPENDIX II

Sample Preparation

Approximately 500-600 grams of sample were collected in the field and returned to the laboratory for analysis. The samples were split into three separate fractions for clay mineral identification, size analysis, and chemical analysis. Standard accepted procedures were used for size analysis and clay mineral identification. Sample preparation for chemical analysis was carried out as described in the following paragraph.

For atomic absorption spectrophotometric analysis rock samples weighing several hundred grams were ground to pass 100 mesh. A 0.5 gram sample was weighed out and placed in a teflon beaker. Ten mls. of concentrated nitric acid were added, and the beaker was covered and placed under heat lamps for about two hours. The covers were next removed and 5 mls. of concentrated hydrofluoric acid were added, and the mixture was evaporated to dryness. The addition of nitric acid and hydrofluoric acid was then repeated, and the sample again evaporated to dryness. Next, 1.5 mls. of concentrated nitric acid and 50 mls. of water were added, and the sample was evaporated to about 20 mls. The sample was then transferred to a 25 ml. volumetric flask and made to volume

with double-distilled water. Dilutions of 100-fold, 5000-fold, and 20,000-fold were made.

Chemical Analysis

Analyses for Fe, Ca, Mg, Na, K, Rb, Li, Mn, Ni, Cu, and Zn were performed on the Perkin-Elmer Model 214 Atomic Absorption Spectrophotometer. The precision and sensitivity for each element are given in Table 16. Precision was determined by analyzing approximately 10% of the rock samples in duplicate and calculating the average deviation from the mean of each sample pair.

Chemical and optical interferences are often a problem in atomic absorption spectrometry; however, the magnitude of such interferences is generally small and steps may be taken to correct them. For example, aluminum apparently forms complexes in aqueous solution with alkaline earth ions. Those elements present in complex form do not absorb light characteristically when introduced into the flame. David (1960) demonstrated that buffer solutions of lanthanum could be used to preferentially complex the aluminum and thus release the alkaline earths. An error in the determination of iron

TABLE 16

Element	Precision	Sensitivity
Si	$\pm 2\%$	n.d.
Al	$\pm 2\%$	n.d.
Fe	$\pm 4\%$	1 ppm
Ca	$\pm 5\%$	1 ppm
Mg	$\pm 2\%$	0.5 ppm
Na	$\pm 1\%$	0.5 ppm
K	$\pm 5\%$	1 ppm
Rb	$\pm 3\%$	0.5 ppm
Li	$\pm 2\%$	0.5 ppm
Mn	$\pm 3\%$	0.5 ppm
Cu	$\pm 3\%$	1 ppm
Zn	$\pm 5\%$	0.5 ppm
Th	$\pm 2\%$	n.d.
U	$\pm 5\%$	n.d.

may result from light scattering by excess amounts of sodium in the flame. Light scattering apparently does not affect the analysis of iron in silicate samples, but it is a very important consideration in the analysis of sea water. Several of the transition elements are subject to significant interferences, particularly nickel and cobalt. Several methods may be used to reduce the magnitude of such interferences. These are:

- (1) chemical separation of certain elements by ion exchange, solvent extraction, or paper chromatography;
- (2) the use of rock standards to determine all working curves; and, (3) the use of artificial standards whose composition is similar to that of the rocks under investigation and which are spiked with known amounts of certain trace elements.

Silicon and aluminum were determined by the rapid analysis methods developed by the U.S. Geological Survey. A complete discussion of rapid analysis is given by Shapiro and Brannock (1962).

Uranium and thorium determinations were made by gamma-ray spectrometry. The equipment and methods used have been well described by Adams (1964).

Clay mineral analysis

Sedimented slides were made from a less than 2 micron fraction of each soil sample. The clay mineralogy of each sample was determined using a Phillips Norelco x-ray diffractometer, copper K α radiation, and a nickel filter. Samples were scanned from 2° to 30° two-theta for untreated and ethylene glycol treated samples and from 2° to 15° two-theta for heat treated samples. All samples were run at a goniometer speed of ½°/ minute. Each slide was analyzed in an untreated condition, after saturation in an ethylene glycol atmosphere at 60° centigrade for 1½ hours, and finally after heat treatment to 600° centigrade for 1½ hours.

Mineral identifications were made as follows:

- 1) Chlorite is indicated by 7.08Å and 3.54Å peaks and a variable peak (13.8Å - 14.2Å) on untreated and glycolated records. After heating the sample to 600° centigrade, chlorite is indicated by a sharp peak at 14.0Å (Brown, 1961).
- 2) Illite is identified by major 10.0Å, 5.0Å, and 3.33Å peaks. These peaks are not effected by ethylene glycol saturation.

- 3) Kaolinite was identified using the $7.16\text{\AA}$ and $3.58\text{\AA}$ peaks as discussed by Biscaye (1964).
- 4) Mixed layer clays are generally indicated by small broad asymmetrical peaks between $10.0\text{\AA}$ and $17.0\text{\AA}$ on the record of a glycolated slide.
- 5) Montmorillonite is identified as the $14.0\text{\AA}$ clay which expands to $17.0\text{\AA}$ with ethylene glycol saturation and collapses to $10.0\text{\AA}$ with heating to 600° centigrade.
- 6) The feldspars are characterized by peaks in the $3.28\text{\AA}$ - $3.16\text{\AA}$ region. According to Goodyear and Duffin (1954), a plagioclase feldspar can usually be identified and at the same time distinguished from potassium feldspar by two very strong peaks in the $3.17\text{\AA}$ - $3.22\text{\AA}$ region, medium sized peaks in the $6.40\text{\AA}$ - $6.50\text{\AA}$ region and three medium to strong reflections with spacings of $4.03\text{\AA}$ - $4.05\text{\AA}$, $3.74\text{\AA}$ - $3.78\text{\AA}$, and $3.61\text{\AA}$ - $3.67\text{\AA}$. Orthoclase feldspars are much more common in soil samples than the plagioclase feldspars.
- 7) Quartz is often present in soil samples and is characterized by peaks at $3.34\text{\AA}$ and $4.26\text{\AA}$. The $3.34\text{\AA}$ peak coincides with one of the illite peaks and should not be used for identification.

APPENDIX III

EXPERIMENTAL STUDIES

A series of experimental studies have been designed and initiated in order to evaluate the relative importance of several types of weathering reactions in the release and redistribution of cations during the dissolution of igneous rocks and minerals. Experiments were carried out under controlled conditions which simulate two weathering environments commonly found in nature. The studies were conducted as follows:

- 1) Closed system experiments were designed to study the kinetics of mineral dissolution and solid-liquid equilibria under conditions which simulate a natural system characterized by limited hydrologic recharge.
- 2) Open system experiments were conducted in order to study weathering reactions in a situation where the leaching solutions circulate through the material rather rapidly, so that a solid-liquid equilibrium is seldom reached.

The following paragraphs will discuss the methods, results, and significance of the preliminary experiments.

Closed system experiments

A variety of unaltered granitic rocks and minerals were ground to pass through a -100 mesh screen. The ground samples were then washed with acetone and distilled water to remove dust, and subsequently dried under infrared lamps. Four ten gram samples of each of the various rocks and minerals were placed in individual polyethylene bottles and fifty milliliters of conductivity grade distilled water (pH 4.8 - 5.0) added. At intervals of 10, 50, 100, and 150 days, a sample of each rock and mineral was removed and the coexisting solution analyzed by atomic absorption spectrophotometry and absorption spectrophotometry.

The results of the closed system experiments were quite unexpected. In every case an apparent "equilibrium" was established in less than ten days. For example, the amount of magnesium leached from biotite in 10 days was equal to the amount leached in 150 days. The concentrations of dissolved cations in the various systems investigated are given in Table 18. The results may be summarized as follows:

- 1) Silicon and aluminum exhibit the smallest concentration

TABLE 18

Concentrations of dissolved cations in closed system leaching solutions (all values in parts per million).

Sample	pH	Si	Al	Ca	Mg	Na	K
Orthoclase	8.3	7.6	0.41	0.80	0.16	3.4	32.6
Microcline	8.0	7.8	0.61	0.93	0.20	4.6	35.3
Oligoclase	8.4	7.6	0.47	15.00	1.20	16.6	4.2
Muscovite	8.1	7.1	0.42	0.24	0.14	5.1	18.5
Biotite	8.4	7.2	0.46	0.66	2.00	4.0	21.6
Conway granite	9.0	8.4	0.51	9.60	0.40	15.1	10.6
Tishomingo granite	8.7	7.9	0.56	4.80	0.23	19.0	13.5
Mount Scott granite	8.7	7.8	0.47	2.80	0.26	21.4	16.1
Elberton granodiorite	9.1	8.0	0.45	13.10	7.40	18.6	9.4
Fitzwilliam granite	8.5	7.6	0.58	11.55	8.54	13.1	10.7

ranges in the various solutions. These elements reach an apparent equilibrium rather rapidly and are limited by their low solubility in water.

- 2) The concentrations of dissolved cations other than silicon and aluminum are highly variable from sample to sample, but show little variation in concentration with increasing time (over 10 days) in individual samples.
- 3) None of the minerals investigated dissolved stoichiometrically; however, the composition of the solid phase plays an important role in determining the equilibrium concentrations of dissolved products other than silicon and aluminum.

These above results would seem to indicate that the primary rate-limiting factor in the early stages of mineral dissolution is the low solubility of silicon and aluminum. Once the leaching solutions reach an equilibrium with respect to silicon and aluminum, the release of cations from the mineral structures is effectively stopped. Hydrolysis and diffusion are not effective weathering processes unless the main structural components of the silicate lattices can be broken down.

Thus, the reactions of feldspar and mica with water, discussed by Garrels and Howard (1957), are effective in mobilizing potassium by hydrolysis only as long as the water is under-saturated with respect to silicon and aluminum. It has been suggested by Correns (1963) that during mineral dissolution, thin decomposition layers of SiO_2 and Al_2O_3 form around individual mineral grains, reducing the diffusion of other cations, so that their rate of release roughly equals the decomposition of the SiO_2 - Al_2O_3 decomposition layer. The present results add support to Correns' proposal.

Open system experiments

Experiments by Correns and von Englehardt (1938) and Correns (1963) have demonstrated that particle size, pH of the leaching solutions, and flow rate play a significant role in the alteration of minerals in open systems. The primary purpose of the present study is to examine the kinetics of mineral dissolution in a system with a constant flow rate and approximately equigranular material.

All of the present experiments were carried out in

polyethylene columns, with the flow rate determined by the porosity of the filter used at the bottom of the column. Thus, a constant flow rate can be maintained throughout a single experiment, but the flow rates may vary slightly for different experiments depending on the characteristics of the particular filter system. Potassium feldspar was selected for these preliminary experiments because of its common occurrence in granitic rocks. The feldspar was ground to pass through a -100 mesh screen, subjected to an x-ray analysis to determine purity and subsequently packed in the polyethylene leaching columns. Distilled water with a pH of 5.0 was used as a leaching solution.

The results of this experiment are presented in Figure 16. The following features should be noted:

- 1) In the initial stages of alteration, there is a rapid removal of material. As pointed out by Correns (1963), this is probably due to the dissolution of rough edges and very small particles which result from the grinding process.
- 2) The removal of potassium, sodium, and silicon during the majority of the first forty hours of

Figure 16 - Open system leaching experiments on potassium feldspar using distilled water and a flow rate of approximately 1.5 ml/minute.

open system leaching approximates a zero order reaction.

- 3) After several days of leaching, the dissolution rate of potassium feldspar is considerably reduced.

The present results indicate that during the early stages of mineral dissolution, while the removal of the constituents is a zero order process, that transport of material to the reaction interface is not a rate limiting process. However, after a certain period of alteration, which is dependent on the previously mentioned factors of pH, flow rate, and grain size, the rate of leaching reactions become considerably reduced. In the open system experiments this reduction in leaching rate cannot be attributed to the development of an equilibrium as the silicon contents of the leaching solutions seldom exceed 3.0 parts per million. The results indicate that some mechanism, similar to that observed in the closed system experiments, is active in reducing the dissolution rate of feldspars in open systems. Thus, it appears that the formation of SiO_2 - Al_2O_3 decomposition layers around individual mineral grains is not an equilibrium phenomenon. The decomposition

rims form in both open and closed systems and are important as rate limiting factors. However, once an equilibrium is reached in a closed system and the decomposition layers can no longer be broken down, weathering is effectively stopped, whereas in open systems following the formation of decomposition rims an equilibrium is not generally attained and the solubility of the SiO_2 - Al_2O_3 layer controls the rate of subsequent alteration.