BEHAVIOR OF TRACE ELEMENTS IN ROCK WEATHERING AND SOIL FORMATION

by

NICHOLAS MARTIN SHORT

B.S., St. Louis University
(1951)

M.A., Washington University
(1954)

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF
PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June, 1958

Signature of Author______________________________
Department of Geology and Geophysics
May 19, 1958

Certified by______________________________
Thesis Supervisor

Accepted by______________________________
Chairman, Departmental Committee
on Graduate Students

BEHAVIOR OF TRACE ELEMENTS
IN ROCK WEATHERING AND SOIL FORMATION

by

Nicholas Martin Short

Submitted to the Department of Geology and Geophysics on May 13, 1958 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

The distribution within size fractions of the major elements Si, Al, Fe^{+3}, Mg, Ca, Na, K, and Ti (as oxides) and the minor elements Ba, Co, Cr, Cu, Ga, Mn, Ni, Pb, Sc, Sr, V, Zn, and Zr were studied within the soil and weathering products developed on 1) a granodiorite (Wyoming), 2) a basalt (Colorado), 3) a granite (Missouri), and 4) a metamorphosed andesite (N. Carolina). Samples of parent rock and from every horizon in each soil profile were taken.

Determinations of the particle size distribution and the mineralogy of the sand, silt, and clay fractions were made on each soil sample. Measurements of soil chemistry parameters, including %-H_2O, pH, E_h, soluble salts, % free iron oxide, organic matter content, and the cation exchange capacities of the silt and clay fractions were made on most samples.

Element concentrations were determined by spectrochemical analysis using the mutual standard method. Analyses were made on each total bulk soil sample, and on sand, silt, and clay fractions separated from these samples. From some of the samples, analyses of elements removed by acetic acid leaching were obtained. The precision of the analyses was ±7.5% for a single set of spectrographic arcings but was ±28.0% for arcings carried across several photographic plates.

From the analysis results 1) concentrations corrected to constant Al_2O_3, 2) net changes in element concentration in the total soil, 3) weathering indices, and 4) concentration (relative enrichments) and distribution indices, have been computed. Variations in major and minor element content were related to the particle size, mineralogy, and soil chemistry parameters by graphical and statistical methods. Several new methods were developed for testing the degree of association between geochemically similar elements.

Interpretation of the data has led to these general conclusions:

1.) No consistent pattern of distribution of most major and minor elements in either total bulk or size fraction samples is observed when analyses of the four soil suites are compared.

2.) The degree of enrichment or depletion for most trace elements in the four soils is directly proportional to the amount of clay and silt size particles produced by more intense and longer weathering.

3.) The magnitude of concentration changes for both major and minor elements is largest between "unweathered" parent rock and the bottom soil (C horizon) samples.

4.) Similarity of behavior during the weathering process is demonstrated for the element pairs: Al-Ga, Fe-Co, Fe-Mn, Fe-Ti, Fe-V, and Mg-Sc. Less definite associations are noted, both in the total soil and in size fractions, for the pairs: Fe-Cu, Fe-Cr, Mg-Cu, Ca-Sr, K-Ba, and K-Pb.

5.) The soil B horizon is usually the zone of maximum enrichment for the elements Co, Cr, Cu, Mn, Ni, Sc, Ti, and V; other minor elements have a more variable distribution.

6.) The sand and/or silt fractions often show enrichments of certain elements which are concentrated in unweathered or resistate minerals. The clay fraction may be enriched in elements which show depletion in the sand or silt fractions. Variations of enrichment in the clay fraction are less than in total soil or other size fractions because of the predominance of one or more clay minerals.

7.) Concentration changes of certain elements can be related to survival or destruction of minerals from the parent rock only when large sample to sample variations are detected in the sand or clay fractions.

8.) No clear-cut relation between minor element variations and pH, E_h, or free iron oxide values throughout a profile has been found in any of the four soils.

9.) The largest (leachable) amounts of an element available to plants occurs for most elements in the B horizon.

10.) Adsorption (cation exchange) is an important factor in controlling the leach extract composition but appears to have little influence on the trace element distribution in the total bulk soil.

11.) Possible association of such elements as Cr, Cu, Ni, Pb, and V with organic matter is indicated only in the A horizon samples in which the organic matter content exceeds 2% in all four soils.

12.) Climate appears to be more important than parent rock composition in affecting the pattern of trace element variations.

13.) It may be possible to deduce the chemical composition of an unsampled parent rock from the soil concentration of such indicator elements as Si, Fe, Cu, Sc, V, and Zr.

Thesis Supervisor: William H. Dennen

Title: Associate Professor
of Geology

ACKNOWLEDGEMENTS

I would especially like to express my gratitude to my thesis supervisor, Dr. William H. Dennen, for his advice and aid in several phases of this thesis. I wish also to extend thanks to my thesis advisers, Dr. Ely Mencher, Dr. John Winchester, and Dr. Robert R. Shrock for their many helpful suggestions.

I am grateful to the many others who have made contributions to the thesis. Specific mention and sincere thanks are due to:

Mr. William Grundmann for capable assistance during the sample collecting trip through the Rocky Mountains.

Dr. R. T. Martin, Soils Stabilization Lab, M.I.T., for his cooperation in providing facilities and suggestions for the soils chemistry tests and in serving as an *ex officio* member of my thesis committee.

Dr. Robert Ogilvie, Metallurgy Department, M.I.T., for guidance in the use of x-ray facilities.

Dr. William Johns and his assistant, Mr. Rodney Tettenhorst, Department of Geology, Washington University in St. Louis, for their aid in checking and interpreting the x-ray data.

Dr. Neil Shimp, Spectrographer at the Department of Soils, Rutgers University in 1956, for his generous cooperation in running spectrochemical analyses of several of my samples.

Mr. Erwin Strahl and his group at the Department of Mineralogy, Pennsylvania State University, for providing an invaluable cross-check of my data by carrying out chemical and x-ray fluorescence analyses of several selected samples.

Dr. E. E. Pickett, Department of Agricultural Chemistry, University of Missouri, for providing flame photometer analyses of sodium and potassium in these same samples.

The State Soil Scientists of Colorado, Missouri, North Carolina, and Wyoming for soils information relating to the sample sites.

The Department of Geology, Washington University, for permission to use its laboratory facilities during the summers of 1955, 1956, and 1957.

Personnel of the Geology and Geochemistry Division at the Gulf Research and Development Company, Pittsburgh, Pennsylvania, for assistance in the heavy minerals, redox potential, D.T.A., and x-ray studies, and for numerous suggestions relating to the preparation of this manuscript.

The secretarial staff at Gulf Research, for the typing of this thesis.

Mr. Paul Fiehler and Miss Theresa Provenzo of the Gulf Research Laboratories, for the final preparation of all figures and illustrations.

TABLE OF CONTENTS

APPENDICES

Appendix

Appendix

TABLES

Table

Table

FIGURES

INTRODUCTION

Geochemical studies of the occurrence and distribution of the minor or trace elements in rock systems have concentrated primarily on igneous rocks, ore deposits, and agricultural topsoils. In recent years the application of optical and mass spectrographic methods of analyses for groups of elements in rocks and minerals has provided considerable data regarding the role of trace elements in geologic processes. However, there are still few detailed investigations of the collective behavior of both major and minor elements during a geochemical process involving notable changes in concentrations and in chemical environment.

One aspect of geochemistry that stands in need of much further study is the process of weathering and rock decomposition. Specifically, attention should be given in future studies to such basic problems as 1) the detailed mechanisms of weathering, 2) the energies and thermodynamics involved in weathering, 3) equilibria and phase relationships, 4) the mobilities of elemental components, 5) the exact processes leading to enrichments and depletions of elements, 6) the identification of stages of weathering, and 7) the systematic classification of weathering processes and products.

Trace elements can be particularly useful in solving some of these problems. Trace elements serve as sensitive guides or "tracers" for the geochemical changes that are active during weathering because they are present in small but highly varying amounts while at the same time they follow or "mirror" the behavior of their correlative major elements. For example, a concentration change of 150 to 10 ppm (15x) for a particular minor element magnifies by ten-fold an associated change from 15 to 10% (1.5x) for a geochemically similar major element.

The few previous studies of trace element behavior in rock weathering have been limited insofar as they have not attempted to integrate major <u>and minor</u> element variations with such parameters as parent rock composition, the physical and geochemical environment, the distribution of elements among phases, and the physical, chemical, and mineralogical character of the weathered products during all stages of transformation from unaltered rock to an "old-age" soil.

It is the objective of this thesis to examine the minor element geochemistry of the rock weathering and pedological processes from the viewpoint of relating the concentration changes of selected trace elements to changes of the major elements found in the soils and to the above-mentioned dynamic parameters. Indirectly also, this investigation provides information which suggests at least partial answers to some of the basic problems of weathering enumerated in a preceding paragraph.

The method of investigation is comprised of a systematic analysis of four virgin soil profiles collected from various parts of the United States. All profiles extend into unweathered parent rock and hence cover a broad range of rock decomposition. Each profile was studied in detail in terms of its physical character, particle size distribution, mineralogy, soils chemistry, and stages of weathering. Major and minor element variations within each profile were obtained from the determination by means of emission spectrographic analysis of concentrations in representative samples taken from different horizons. These concentration changes were then related to the dynamic parameters by various interpretative devices.

GENERAL SUMMARY OF RESULTS AND CONCLUSIONS

The principal observations, interpretations, and conclusions resulting from this investigation of chemical weathering are presented below both as a preview and a summary of the main points developed in the thesis.

1.) Spectrochemical analysis has proved effective in detecting and analyzing quantitatively 21 elements. Relative compositional changes in a sample series were determined with very good precision (± 7.5%); absolute amounts in these samples were not determined with high accuracy.

2.) The apparent net gain or loss in concentrations with respect to parent rock composition of 20 elements in each soil is indicated below by + or - symbols for the four soil suites studied. The geographic location, parent rock type, and soils group classification for each soil is shown in parenthesis beneath the suite's locality letter.

	Si	Al	Fe	Mg	Ca	K	Na	Ti	Ba	Co	Cr	Cu	Ga	Mn	Ni	Pb	Sc	Sr	V	Zr
Suite G: (Colo; basalt; brown aridic)	+	+	+	-	-	-	-	+	-	-	-	-	+	-	+	+	+	+	+	-
Suite K: (Wyo; granodiorite; acid prairie)	-	+	+	+	-	-	-	-	-	+	+	+	-	-	+	+	+	-	+	+
Suite N: (Missouri; granite; gray-brown podzol)	+	-	+	+	-	-	-	+	+	+	+	+	-	+	+	+	+	+	+	+
Suite S: (N.C.; metam. andesite; red-yellow podzol)	+	-	+	-	-	-	-	+	+	+	+	+	-	-	+	?	+	-	+	+

3.) The parameter which most consistently correlates with enrichments and depletions of minor elements is the percentage of clay-sized particles. Clay percent can be taken as an indicator of the degree of weathering.

4.) A weathering index, based on the ratio: $\frac{100 \times \text{mols}(Ca + Mg + Na + K)}{\text{mols}\ (Si + Al + Fe + Ti)}$ (as oxides), also provides a measure of the extent of weathering and similarly can be correlated with variations in minor element concentrations.

5.) Because of losses during separation and also poor interplate precision during spectrographic analyses of different sample categories, it has proved impossible to achieve a "materials balance" for the various soil size fractions, i.e., the weighted sum of the analyses of these several fractions did not usually equal (within the tolerated experimental error) the analysis of the total (undivided) soil.

6.) Despite the errors affecting the analyses of the size fractions, the general patterns of relative concentration changes between fractions and of variations within fractions can be defined for most of the elements in the four suites. Enrichments in the clay fraction have not been as large as expected and variations within this fraction are less than in the total soil, sand, or silt fractions. The sand and/or silt fractions often show enrichments of certain elements which are concentrated in unweathered or resistate minerals. In some instances, the cause(s) of several element concentrations in one or more size fractions have not been satisfactorily explained. Certain elements which are supposed to show similar geochemical behavior do not alsays associate in the same manner or degree in these size fractions.

7.) Relationships between chemical and mineralogical changes were noted in all four soils. Striking changes were found when several minerals underwent rapid destruction during early stages of weathering. Enrichment of certain elements could be tied to survival of such minerals as the micas, magnetite, augite, and several accessories. Concentration changes related to development of identified secondary minerals (clay minerals, etc.) and colloidal material were not convincingly demonstrated.

8.) Associations of such parameters as cation exchange capacity, organic matter content, and free iron oxide with concentration variations could sometimes be established for individual elements in one or more profiles; however, direct control of the majority of the variation of an element by any of these parameters was not demonstrated.

9.) No clear-cut relation between minor element variations and pH or E_h was found. E_h and free iron oxide variations broadly coincided. A few minor ferride elements sometimes appeared to be influenced by these variations. Knowledge of pH and E_h values for a soil permits the probable ionic state of an element in the solution or in exchange positions to be predicted.

10.) The largest amounts of an element available to plants (maximum percent leachable by acetic acid) was determined for most elements to occur in the B horizon. A general positive correlation between leachable amount of an element and the degree of weathering was found; migrations of soluble elements to the B horizon layers may distort this relationship.

11.) Most of the minor elements tend to concentrate in the B horizon by precipitation or fixation on surfaces from downward moving soil solutions, although there are many individual exceptions due to such factors as caliche formation, concentration in organic matter, survival in resistate minerals, etc.

12.) The most pronounced chemical changes occur during the weathering of parent rock to C horizon soil.

13.) Observations by others of similarities of behavior in a geochemical system were confirmed for the weathering process for the element pairs: Al-Ga, Fe-Co, Fe-Mn, Fe-Ti, Fe-V, and Mg-Sc. Several other associations, namely between Fe-Cu, Fe-Cr, Mg-Cu, Ca-Sr, K-Ba, and K-Pb, were positive in some of the soils and indefinite or negative in the others. Associations between the above pairs in the several size fractions in a given soil were often both positive and negative; in some cases this is explained as due to selective concentration of one element with respect to the other or to the relative distribution of the two elements among several phases undergoing different degrees of decomposition or formation; in other cases, such opposing associations appear to be contradictory.

14.) The effect of climate differences (especially in rainfall) on the pattern of minor element variations appears to be more influential than the effect of initial parent rock composition.

15.) It is possible to roughly estimate the nature and chemical composition of the parent rock from the reported analysis of a soil alone. Si, Fe, Cu, Sc, V, and Zr are the most sensitive elements for this purpose.

16.) The geochemical variations of both major and minor elements within a soil profile are largely functions of 1) the degree of decomposition of the primary host minerals, 2) the relative proportions of the more resistant minerals which accumulate in the soil, 3) the amounts which can be accepted in secondary mineral structures, 4) the oxidation states of the released elements, and 5) the degree of leaching by natural solvents of the fraction of any element occupying exchange positions on mineral surfaces or held in readily soluble colloidal matter.

SURVEY OF PREVIOUS WORK

The problem of trace element behavior in chemical weathering processes has not yet received much attention from geochemists. In contrast, the pedologists have made thousands of surveys of the occurrence and distribution of individual or groups of trace elements in the strictly soil portion of the weathered mantle.

The principles of trace element occurrence and distribution in rocks have come primarily from studies of igneous rocks. The classic work on the Skaergaard intrusion of East Greenland (Wager and Deer, 1939) later led to a detailed determination by Wager and Mitchell (1951) of the distribution of trace elements in the intrusive differentiates. An earlier study, indicating major and minor element relationships, was made on some Caledonide plutonics by Nockolds and Mitchell (1948). An investigation of trace element distribution in Hawaiian lavas was carried out by Wager and Mitchell (1953). Sandell and Goldich's studies (1943) and Fairbairn, Ahrens, and Gorfinkles' work on the Ontario diabase (1953) should also be mentioned.

Even before these contributions, V. M. Goldschmidt had evolved and defined many of the basic principles of chemical element distribution in the earth's crust (1937, 1945).

There have been few comprehensive studies of trace element distribution in sedimentary rocks (see Krauskopf, 1955). Oil companies have recently investigated trace elements in sedimentary rocks and are only now publishing results. The search for uranium has also given impetus to such trace element work. Trace element behavior during metamorphism of shales has been treated by Shaw (1954-55).

Trace element studies in soils have been largely confined to certain elements (B, Cr, Co, Cu, Mo, Ni, Se, V, and Zn) of agricultural and biological importance. Usually only the topsoil or zone of tilth receives detailed attention. Commonly only a single minor element is studied at one time in relation to its distribution in different soil types. Many routine analyses have been published by the U. S. Department of Agriculture (e.g.: Slater, Holmes, and Byers, 1937). Soils scientists at many University Agronomy Departments and State Agricultural Surveys (e.g.: Allison and Gaddum, 1940) have added valuable information. In foreign endeavors, the English, Russians, Indians, and Japanese have been chief contributors to trace element knowledge.

R. L. Mitchell of the Macaulay Institute in Scotland is well known for his contributions to the field of trace element distribution in rocks and soils (1946, 1947, 1948, 1955, et al.). The Russian, A. P. Vinogradov, has written an important treatise (1950) on the principles of minor element distribution in soil systems. In 1955, D. J. Swaine published a much needed bibliography of all world-wide publications on trace elements in soils to that date, together with an annotated summary of information available for each of 44 minor elements.

Detailed studies of trace element distribution over the entire soil profile are uncommon and studies from the viewpoint of weathering processes, major-minor element relationships, mineralogical changes, and thermodynamics are rare indeed!

Most of the direct determinations of element distribution in the profile have been made during the recent upsurge of geochemistry in the 1950's. Gordon and Murata (1952) of the U.S.G.S. studied the behavior of minor elements during the weathering of nepheline sysnites to residual bauxites. An important contribution has been made by J. R. Butler (1954-55) of Rothhamsted Experimental Station, England. Butler investigated selected groups of trace elements in soils derived from a variety of parent rocks collected in Lancashire and the Caledonides of Norway. His study embraced both major and minor element determinations and soils mineralogy. The trace element analyses were limited, however, to topsoil and parent rock and do not therefore include a complete picture of profile changes. Yamasaki, Iida, and Yokoi (1955) of Nagoya University in Japan conducted a similar survey of granodiorite and its weathering products. The Canadians, Wright, Levick, and Atkinson (1955) examined the trace element distribution in virgin profiles taken from four great soil groups. Drs. N. Shimp and J. Connors of Rutgers have published (1957) results of perhaps the most thorough study up to that date. A total soil and a clay fraction sample from the A, B, and C horizons from six New Jersey soils of heterogenous parentage were analyzed for content of 4 major and 10 minor elements. From the resulting data concentration and distribution ratios of these elements were calculated. Some correlation with other soils properties was included.

In regard to providing data illuminating the principles of trace element behavior in weathering processes, all such previous work has been hindered by limitations in scope. These include:

1.) Generally few minor elements are determined.

2.) Specific correlations of minor-major element pairs and groups is not always made.

3.) Some of the profile horizons are not analyzed.

4.) The parent rock is usually not sampled.

5.) The parent rock is often of secondary origin.

6.) The soil usually is not residual.

7.) The pin-pointing of trace elements within phases or size fractions is not commonly attempted.

8.) Supporting data characterizing the soils (mineralogy, size distribution, soils chemistry) is not determined.

9.) The initial and early stages of weathering (reactions within and adjacent to the parent rock) are seldom considered.

In recognition of these omissions in previous studies, the plan of this thesis investigation has been designed to avoid some of these limitations.

LOCATION AND SELECTION OF SOIL SAMPLE SITES

Eighteen soil suites were sampled during the collecting trips of June and September, 1955 but time, cost of analysis, and uncertainties as to residual origin led to the elimination of all except four of these from the final investigation.

All soil sites were selected primarily from the geological rather than pedological standpoint, that is, with the objective of showing principles and phenomena of weathering and rock decomposition rather than soil-forming processes. Three specific restrictions governed the choice of the soil profile sites:

1.) The parent rock must be of igneous origin (or, if metamorphic, of igneous derivation).

2.) The developed profile must be residual.

3.) The profile must BE thin enough to be sampled with simple field tools.

Two other factors were kept in mind in selecting the sample sites. The first was to use soils from a variety of rock types, if possible showing extremes in compositional range. The second was to obtain soils developed under several different climates. These factors provide additional variables which, when determined, aid in the correlation of the chemical changes with their various causes.

On the basis of these conditions of sample selection, the final sites were taken either from flat uplands within or adjacent to more rugged topography or from low elevation hills and dissected plains. A soil originating from granodiorite was obtained from the northern Bighorn Mountains of Wyoming;

a soil derived from a basalt flow was collected near Denver, Colorado; a soil with a granite parent rock was sampled in the Missouri Ozarks near the village of Graniteville; and a soil developed on a metamorphosed andesite was collected in the Appalachian Piedmont near Asheboro, North Carolina.

During field work criteria were set up to distinguish residual from transported or secondary soils. Those favoring a residual history include:

1.) Development on gentle slopes without indication of slumping.
2.) General continuity of parent rock type (i.e., immediate locality consisted of dominantly uniform lithologic type).
3.) Outcrops of similar parent rock exposed within 100 feet of sample site.
4.) No glacial or alluvial deposits evident in near vicinity.
5.) Absence of rock rubble different from presumed parent rock, either on ground surface or within the profile as sampled (the presence of gravel like that of the parent rock is strong evidence of a residual nature).
6.) Relict texture (inherited from the parent rock) persisting through the soil profile.
7.) No abnormal soil horizons noted within the profile on exposure.

In addition, supplementary evidence supporting a residual origin for each of the four suites was provided later during laboratory analysis. Such features as relation and continuity of heavy minerals or index minerals with respect to parent rock and correlation of overall soils chemical composition to parent rock composition helped confirm the residual identifications.

An ideal sample site was one with only enough vegetative cover to prevent wind deflation. Road cuts, stream banks, and shallow test pits were examined prior to sampling to give a picture of a profile's suitability. Soils experts were consulted during the collecting trips in Colorado, Missouri, and Georgia for their opinions as to favorable soil sites.

The actual sample face was exposed in one of two ways. In Colorado, Wyoming, and Missouri (in part) test pits, roughly 2 x 5 feet in plan, were dug to decomposed bedrock. Digging difficulties prevented penetration to unaltered parent rock. In North Carolina, where the soil was too thick to be dug through, samples were collected from a stream gully adjacent to a road cut.

The sampling pattern depended on the appearance of the exposed profile. The pattern was chosen in accord with visual identification and separation of soil horizons on the basis of differences in color, texture, structure, or any other distinguishing features. At least one sample from the A, B, and C horizons, plus parent rock, was always taken. If a horizon was thicker than 8 inches, two or more samples were taken 6 inches or more apart. The sample point was actually a small zone, 2 to 3 inches in diameter and 4 to 6 inches in depth, within a horizon exposed on one face of the pit or cut; hence a given sample represents the average of soil variations within a small volume.

Each sample was removed with a metal trowel. Care was taken to make the sample representative by taking a large total amount (± 800 grams). After removal each sample was placed in a plastic bag and then in a labeled cardboard carton. Neither bag nor carton was sealed; thus the moisture content could change after collection.

No field measurements were made of such soil properties as moisture, pH, redox potentials, or bulk density. Minor contamination could have been produced by metal from the trowel, shovel, or pick, or by soil droppings from the surface or pit face.

DESCRIPTION OF SOIL PROFILES

The sample site for each of the 4 soil suites will be described in relation to 1) its specific location, 2) local physiography, 3) drainage, 4) pertinent climatic data, 5) associated vegetation, 6) regional and/or local geology (including immediate parent rock), 7) general soil description, 8) profile description, and 9) soil classification. The first six categories are summarized in Table 1. The slope classification and drainage class terminologies have been defined in the U.S.D.A. Soil Survey Manual (1951, pp. 160-63 and 169-72 respectively). Categories 7 and 8 are discussed on the following pages. Following each profile description is a statement of the probable soils group and soil type to which the suite has been correlated. Some of this information has been provided by state soils scientists; the remainder was obtained by consulting soils maps and soil survey descriptions published by the U.S.D.A. Bureau of Soils.

Each profile has been described according to the format and nomenclature recommended by the U. S. Department of Agriculture (see Soil Survey Manual, 1951, pp. 173-234). The color, texture, structure, and consistency were qualitatively appraised in the field and wherever possible revised and renamed later after laboratory studies. This information, together with horizon designations,[1] depth from surface to base of horizons, thicknesses,

---

[1] In this thesis, the C horizon (within the actual soil profile) is considered to be the disintegrated and superficially weathered parent rock rubble in which minor amounts of silt and clay particles may be admixed whereas the D horizon (sampled from the nearest exposed outcrop) is defined as the much less altered and more coherent parent rock.

TABLE 1

Descriptions of Soil Profiles

Suite	Location	Local Physiography	Drainage	Climate	Vegetation	Geology
G	North Table Mtn: 1 1/2 m. NNE of Golden, Colo; in Sec. 22, T 3 S, R 70 W (of 6th princ. meridian); about 500 ft SE of trap quarry and 300 ft E of mesa rim.	North Table Mtn = flat mesa, 1 1/2-2 m. long; elev. ± 6500 ft; 400-500 ft above Golden. Mesa relief: 40-50 ft; Class B complex slope; 1-5° grade; no glacial contamination.	Class 3, moderate to well drained; mesa drained by small, short usually dry master stream flowing SE & several gullied tributaries. Local perched water table.	Semi-arid. Nearby Denver: ann. ppt. = 13.4 in.; mean ann. T = 50.5° F.	Grass and weed covered; trees and bushes scarce; cattle-grazed.	Adjacent to Colo. Front Range; N. Table Mtn consists of 2 late Tertiary basalt flows ± 50 ft thick; intbd w. alluvial fan deposits. Basalt = augite & plag., w K-feldspar; numerous vesicules filled w. zeolites.
K	Northern Bighorn Mtns 28 m. (air) W of Sheridan, Wyom.; 150 ft above & 600 ft NE of U.S. Hiway 14, 2.1 m. S of junction with Wyom. Hiway 14; in T 55 N, R 88 W.	Locally: gently rolling meadows; relief 50-100 ft; irregular ridges of barren rock, relief 100-300 ft; elev: greater than 7500 ft; Class B & C complex slope; 1-10° grade; some glacial wash in vicinity	Class 4, well drained; internal drainage exceeds surface runoff local region drained by Owen Creek, flowing N to S. Fork of Tongue River.	Data for immed. area unavailable; locally semi-humid, mountainous climate; Sheridan to E is semi-arid, w. ann. ppt. = 15.1 in.; mean ann. T = 43.1° F.	Short grass & wild flowers; few trees or bushes; some nearby groves & patches of pines & aspen.	Precamb. igneous bands trending NNW; Camb. sedims. 1 m. to W. Rock types: 1. Normal Red Granite (± 10% biot; plag.) 2. Binary granite pegmatite (in dike-like bands 10-50 ft wide) 3. Binary granite aplite.
N	15 ft E of vertical E face of quarry 150 ft E of Mo. Hiway 21; 0.8 m. NNW of Post Office, Graniteville, Missouri; in SW 1/4 SW 1/4 Sec. 11, T 3 N R 3 E	Exhumed Precamb. granite hills; hills elongate; elev. ± 1300 ft; relief 500 ft; valleys underlain by Camb. sst & dolo.; immediate relief 30-50 ft; Class C complex slope; 10° grade.	Class 3, moderate to well drained; local intermittent streams; small, usally dry stream 200 ft W of quarry; internal drainage along soil-granite contact; semi-impervious clayey soil near bottom.	Area in humid-temperate zone; Ann. ppt. = 42-46 in.; mean ann. T = 50-51° F.; av. low = 23° F.; av. high = 91° F.	Hills forest-covered; immediate site grass-free, weed-covered; oak, walnut trees moderately dense, contribute to forest litter.	Massive binary red granite (Precamb), contains several types of feldspars; vertical jointing, weathers to pronounced spheroidal boulders; rhyolite and felsite flows occur less than 1 m. away.
S	400 ft NE of corner boundary betw. Davidson, Montgomery & Stanley Cos., N. Caro.; 25 ft W of point 1200 ft NE of bridge across Yadkin (Pee Dee) River at confluence with Badin Lake, 3 m. S of Newsom & 26 m. SW of Asheboro, N. Caro.	Site within dissected Appalachian Piedmont, local relief 50-75 ft; site on flat terrace within Class B simple slope, 6° grade to S.	Class 2, imperfectly drained; lower horizon impervious, upper better drained; local control by Yadkin River; a gully cuts thru site into road ditch.	Humid-temperate; Asheboro ann. ppt. = 46.0 in.; mean ann. T = 61.1° F.; av. low = 3° F.; av. high = 103° F.	Heavily forested by oak and nut trees, a few pines; heavy forest undergrowth & litter.	Region comprised of "Carolina slates": metamorphic slates, low-rank schists, & metavolcanics; at site: medium green, massive, fine-xline andesitic metavolcanic; epidote along fractures.

special soil features, and sample numbers, is summarized in Tables 2 A-D.

If a horizon within the profile was sampled, the corresponding sample number is underlined. This number consists of a letter assigned to the soil site in the field followed by a number which lists the sequence in which the sample was collected (for example: G-3, the third sample from the top of the profile at locality G). The depth in inches below the surface at which the sample was taken is shown in parenthesis below the sample number.

The color of each sample was determined in direct sunlight on the finely ground total bulk samples (TBS) (see p.166) by comparison to standard colors in the Munsell Soil Color Charts. The color terms and symbols follow the classification described in the Munsell Charts text (see also, Soil Survey Manual, 1951, pp. 194-203). The textural classification used is that presented in Table 4, page 39, of this thesis.

Suite G:

General Soil Description: The soil cover over most of North Table Mountain is thin (in places less than 4 inches). Lava bedrock lies immediately beneath. Near low spots and drainage gullies the soil may attain a thickness of 2-3 feet. Some of this soil may represent slope wash accumulation.

The soil at the sample site is clearly residual as indicated by a relict texture comprised of *in situ* laths of weathered plagioclase. This texture is evident up to 3-4 inches from the present surface. No distinct soil horizons are developed. Very little gravel or rock fragments are present except near bedrock. The soil-bedrock transition is sharp, occurring over a 2-4 inch zone of mixed soil and thin rock ledges. Grass roots penetrate the soil to a depth of 12-18 inches.

TABLE 2 A-D

List of Abbreviations
Used in Soil Descriptions

ang	-	angular	rky	-	rocky
blky	-	blocky	sa.	-	subangular
frbl.	-	friable	sft	-	soft
gran.	-	granular	sl.	-	slightly
hrd.	-	hard	stky	-	sticky
lse	-	loose	v.	-	very
pl.	-	plastic	w.	-	with
rk.	-	rock			

Color Terms:

P	-	pale	Yell	-	yellow, yellowish
Dk	-	dark	Brn	-	brown, brownish
Str	-	strong	Red	-	red, reddish
Gry	-	gray, grayish	L.	-	light

TABLE 2A

Suite G:

Horizon	Depth to base (inches)	Thickness (inches)	Color	Size Classif.	Soil Structure	Soil Consistency Dry	Moist	Wet	Special Features	Samples
A_0	1	1							Largely organic matter mixed with soil	
A_1	4	3	Dk Gry Brn (10 YR 4/2)- Dk Brn (10 YR 4/3)	Sandy clay loam	sa. blky-gran.	sl. hrd.	firm	stky	Faint relict texture	G-1 (2 ")
A_2	9	5							Similar to A_1 but less blackish	
B_1	20	11							Prominent relict texture; mottled	
1. Upper			Brn (10 YR 5/3)	Clay loam	blky - sa. blky	hrd.	firm	stky-sl. pl.		G-2 (11 ")
2. Lower			P Brn (10 YR 6/3)	Sandy clay loam	blky	sl. hrd.	frbl.	stky-sl. pl.		G-3 (18 ")
B_2	28	8	P Brn (10 YR 6/3)- L Yell-Brn (10 YR 6/4)	Sandy loam	sa. blky-gran.	sl. hrd.	firm	stky	Prominent relict texture, partly unweathered hornblende & plagiocl. phenocrysts; gravelly rubble	G-4 (26 ")
C_1	32		P Brn (10 YR 6/3)- V P Brn (10 YR 7/3)						Highly weathered parent rk; breakable w. fingers; in loose rubble and thin ledges	G-6 (29 ")
D									Parent rock	G-9 From nearby quarry

Profile: The immediate profile was exposed by digging 2.6 feet to bedrock near the bottom of a 2° slope inclined to the southeast. The profile description is summarized in Table 2 A.

Soil Classification: The soil atop North Table Mountain lies very close to the boundary between the zonal Chestnut and Brown Aridic great soils groups typical of the western Great Plains and the shallow Lithosol soils of much of the higher Rocky Mountains. Characteristics of the soil and its vegetation indicate it to be a variant of the Aridic Brown soils group (also called the Northern Dark Brown soils). The regional soils map places the Daniels series in the vicinity of the sample site. A Soil Survey around the Brighton, Colorado area (Harper, Scott, and Frahm, 1932) designates the soil formed on the Table Mountain lavas as the Table Mountain loam.

Suite K:

General Soil Description: The sampled soil appears to be developed on the normal granite (see Table 1). The depth of soil development varies laterally in a hundred feet from 0 to 3 feet. Contamination from sources outside the sample site is nil but a mixture of several granite types in the surface and soil rubble indicates some nearby wash and mass movement activity.

Profile: The profile exposed by digging 1.7 feet to apparent bedrock showed several separable horizons. Grass root penetration extended to about 12 inches. The description is given in Table 2 B.

Soil Classification: On the soils map of the U. S., the Northern Bighorn Mountains region appears to be located within the shallow azonal Lithosols great soils group of the western United States. However, the Soil Survey report on Sheridan County, Wyoming (Thorp, Glassey, Dunnewald, and Parsons,

TABLE 2B

Suite K:

Horizon	Depth to base (inches)	Thickness (inches)	Color	Size Classif.	Soil Structure	Soil Consistency			Special Features	Samples
						Dry	Moist	Wet		
A_1	3	3	Dk Brn (10 YR 4/3)- Dk Yell Brn (10 YR 4/4)	Loam	gran.	sft	frbl.	stky	Upper layers v. dark; few rk. fragments	K-1 (2 ")
A_2 grades into	10	7	L Yell Brn (10 YR 6/4)	Sandy loam	gran.	sft	v. frbl.	sl. stky	A few rk. fragments; some roots	K-2 (6.5 ")
B_1 changes abruptly to	16	6	L Red Brn (5 YR 6/4)- Red Yell (5 YR 6/6)	Loamy sand	gran.	sft-lse	v. frbl.	sl. stky	Some gravel & rk. fragments	K-3 (12 ")
C_1	18	2	Pink (5 YR 7/3 - 7/4)	Sand	gran.-rky	lse	lse	non-stky	Mostly gravelly rk. fragments w. some silt & clay; red-stained	K-4 (17 ")
C_2	21	3	Pink (7.5 YR 7/4) V P Brn (10 YR 7/4)	Sand	gran.-rky	lse	lse	non-stky	Highly fragmented yellow-stained bed-rock w. interstitial silty soil	K-5 (20 ")
D									Parent rock	K-7 From near-by otc.

1939) classifies the soils in the vicinity of the sample site within the dark acid Prairie soils group. The map in this report shows the exact site to be in either the Burgess fine gravelly loam or Woodrock loam types. Both series are Podzolic but since the Woodrock forms under heavily forested cover, it is concluded that the grass-covered Suite K belongs to the Burgess series.

Suite N:

General Soil Description: The soil about the Graniteville quarry varies from 0 to 5 feet in thickness, with an average of 2 feet. The soil, where thick, shows a well-developed profile. Slopewash is evident in the immediate area but the normal profile and sharp diminution of rubble within the profile indicate the soil to be residual.

Profile: The profile is five feet thick. The upper 3 feet were sampled from a pit dug 10 feet east of the quarry face; the lower 2 feet were sampled from an exposed embankment 5 feet closer to the quarry. Table 2 C presents the summary data for this profile.

Soil Classification: The granite soils of the Missouri Ozarks have been correlated with the Ashe series developed on igneous terranes in the central Appalachians. In Missouri, these form a part of the zonal Gray-Brown Podzolic soils group. Around Graniteville, Mo., the soils have been assigned to the Ashe stoney loam type, described in the Soil Survey of Reynolds County, Missouri (Krusekopf, De Young, Walkins, and Deardorff, 1918).

Suite S:

General Soil Description: Most of the soils of the Piedmont show, irrespective of parent rock, strongly differentiated A and B horizons, the latter

TABLE 2C

Suite N:

Horizon	Depth to base (inches)	Thickness (inches)	Color	Size Classif.	Soil Structure	Soil Consistency			Special Features	Samples
						Dry	Moist	Wet		
A_o	1	1							Humus zone; organic matter & twigs	
A_1	6	5	V. P Brn (10 YR 7/3)	Loam	gran.	sft	v. frbl.	sl. stky	Roots; porous	N-1 (2 ")
B_1	31	25								
1. Upper			L. Yell Brn (10 YR 6/4)	Silt loam	gran.	sft	v. frbl.	sl. stky-sl.pl.	Roots	N-2 (11 ")
2. Middle			Yell (10 YR 8/6)	Silt loam	gran.-sa. blky	hrd.	frbl. firm	stky-sl.pl.		N-3 (22 ")
3. Lower			V. P Brn (10 YR 7/4)	Silty clay loam	sa. blky	sl. hrd.	frbl. firm	v. stky-sl.pl.	More cohesive; very little gravel	N-4 (32 ")
Transitional to										
B_2	44	13	V. P Brn (10 YR 7/4)	Loam	gran.-sa. blky	sft	frbl.	v. stky-sl.pl.	Higher clay content	N-6 (54 ")
Transitional to										
C_1	56	12							Highly weathered granite; fragmented; some powdery clay	
C_2									Weathered granite	
D									Parent rock	N-9

marked by a rich red-brown color. Many of the soils developed on granites can be classed as saprolites.

The sampled profile follows this pattern in a general way but the red, iron-rich B horizon is much less conspicuous. The soil, in contrast to a saprolite, actually becomes finer and more clayey with depth. The bottom soil is a hard, compact clay mass which retains much of the texture of the underlying parent rock. This represents complete decomposition <u>in situ</u> of the originally fine-grained metavolcanic parent rock to a clay-like residue. Relict texture persists, with decreasing definition, almost to the top of the profile. A remarkable feature is the secondary development of black shot- or nut-like iron-manganese concretions which appear prominently in the middle two-thirds of the profile.

Most signs indicate this soil to be residual. However, several quartzite rock fragments in the topsoil from an undiscovered source indicate possible contamination from slopewash.

<u>Profile</u>: The profile was described and sampled from an exposure along a dry gully. A vertical trench 6 inches deep was cut into this gully to expose fresher soil. The description is given in Table 2 D.

<u>Soil Classification</u>: The soils developed in the southern Piedmont belong to the Red-Yellow Podzolic soils group. Reference to the soils map (#11) accompanying the U.S.D.A. Soil Survey report for Davidson County, North Carolina (Hardison and Brinkley, 1915) shows the sample site apparently to fall within the Georgeville silty clay loam or clay loam series. However, the Survey text description (p. 484) does not conform to the soil character and properties determined for Suite S. A recheck of the soils map showed that, within the immediate area of the sample site, there are several

TABLE 2 D

Suite S:

Horizon	Depth to base (inches)	Thickness (inches)	Color	Size Classif.	Soil Structure	Soil Consistency			Special Features	Samples
						Dry	Moist	Wet		
A_1	8	8	Yell Brn (10 YR 5/6)	Sandy clay loam	gran.	sft-sl. hrd.	v. frbl.	sl. stky	Twigs, roots, pebbles (a few of quartzite)	S-1 (5 ")
Grades into										
A_2	16	8	Str Brn (7.5 YR 5/6)	Clay loam	gran.-sa. blky	hrd.	frbl.	stky	Patches and seams of red-brown clay. Small blackish concretions, faint residual texture.	S-2 (12 ")
Grades into										
B_1	48	32							Blackish concretions numerous in upper part; scattered in lower. Relict texture increases in lower; soil breaks into chunky to nodular fragments; more clayey with depth.	
1. Upper			Red-Brn (7.5 YR 6/6) Str Brn (7.5 YR 5/6)	Loam	gran. sa. blky	hrd.	frbl.	sl. stky		S-3 (24 ")
2. Lower			Yell (10 YR 7/6) Brn Yell (10 YR 6/6)	Clay	sa. blky-ang blky	hrd.	firm	stky-sl.pl.		S-4 (36 ")
B_2	60	12	Yell (10 YR 7/6)	Silt loam	sa. blky-ang blky	hrd.	frbl.-firm	sl. stky	Noticeable relict texture; blackish spots diminish; resembles highly weathered bedrock.	S-5 (51 ")
Grades into										
C_1	60+		Yell (2.5 YR 7/6)						Weathered, yellow-stained chunky fragments of bedrock.	S-6 (61 ")
D									Fresh bedrock	S-7

patches of soil classed as the Iredell loam. The text description (p. 483-84) of this soil type agrees more closely with the nature of Suite S. The soil is described as brown to gray-brown in the upper 10 inches, iron concretion-bearing in the upper layers, and composed dominantly of plastic clay in the lower layers; the parent rocks are described as metamorphosed diorites and gabbros.

The clay mineral assemblage for Suite S (see p. 61) when compared with that found by Rolfe (1954) in the Iredell loam of North Carolina confirms the correlation of this suite with that series.

SOIL PARTICLE SIZE ANALYSIS

I. Methods:

A mechanical analysis of particle size distribution was made on each sample from the four soil profiles following the procedure set up by Kilmer and Alexander (1949). The soil was pretreated for removal of organic matter, soluble cements, and free iron oxide by addition of H_2O_2 and weak acetic acid. Sodium hexametaphosphate was used as the dispersing agent. The sand and gravel fractions were sized by sieving on Tyler screens; the silt and clay fractions were sized by pipette analysis. The fraction finer than 1/4096 has been termed the ultraclay fraction.

The Wentworth grade scale has been used as the basis of all size calculations. The raw size analysis data is presented as histograms showing the frequency distribution of particles in these grade divisions (Figure 1 A-D). The combination of these data into the Wentworth gravel, sand, silt, clay and ultraclay divisions is summarized in Table 3. These larger divisions (with ultraclay added to clay) were used to plot a cumulative curve, on an arithmetic scale, for each sample (Figure 2 A-D). From these curves, the median diameters Q_2 and the Trask Sorting Coefficient S_o (Krumbein and Pettijohn, 1938, pp. 229-31) were calculated and are given in Table 3. Variations in sand-silt-clay percentages, recalculated to 100% because of omission of gravel and ultraclay, within each profile are shown in triangle diagrams in Figures 3 A-D.

Frequency percentages of the major divisions recalculated according to the U.S.D.A. Bureau of Soils size scale (sand-silt division at 1/2 mm.; silt-clay at 1/200 mm.) and classification (U.S.D.A. Soil Survey Manual, 1951, pp. 209-211) are presented in Table 4.

TABLE 3

Soil Particle Size Data

Sample No.	% Gravel	% Sand	% Silt	% Clay	% Ultraclay	Q_2	S_o
G-1	1.8	46.1	21.7	9.1	19.7	.045	14.8
G-2	5.9	31.9	17.0	20.9	24.1	.011	27.4
G-3	21.6	39.7	14.2	10.6	14.0	.135	17.9
G-4	28.8	40.7	15.8	9.1	5.9	.270	30.4
K-1	20.2	38.5	31.7	7.2	3.0	.130	9.0
K-2	24.4	51.7	17.4	4.1	2.1	.330	5.6
K-3	40.6	47.9	8.0	2.1	1.4	.850	5.7
K-5	41.1	53.5	3.4	1.7	0.2	.900	5.1
N-1	8.7	39.3	39.3	9.5	2.8	.050	16.7
N-2	5.1	22.3	47.6	19.0	5.6	.010	12.9
N-3	1.3	14.7	51.1	18.6	14.0	.009	11.6
N-4	0.1	9.8	51.3	20.7	17.3	.007	11.8
N-6	11.5	33.4	34.7	10.5	11.7	.040	24.0
S-1	19.4	39.4	13.1	15.5	7.6	.150	21.6
S-2	17.4	33.4	19.5	19.8	9.7	.060	18.6
S-3	18.3	37.5	26.2	17.2	2.8	.105	10.8
S-4	7.3	27.7	18.8	25.0	21.0	.006	25.7
S-5	-	18.5	66.5	14.7	0.3	.041	2.6

TABLE 4

Size Data According to Bureau of Soils Classification

Sample No.	% Sand* (2 - 0.05 mm.)	% Silt* (0.05 - 0.002 mm.)	% Clay* (0.002 mm.)	Soil Class.
G-1	49	24	27	Sandy clay loam
G-2	35	25	30	Clay loam
G-3	51	21	28	Sandy clay loam
G-4	59	22	19	Sandy loam
K-1	52	40	8	Loam
K-2	71	22	7	Sandy loam
K-3	83	12	5	Loamy sand
K-5	92	5	3	Sand
N-1	46	45	9	Loam
N-2	25	59	16	Silt loam
N-3	18	59	23	Silt loam
N-4	11	60	29	Silty clay loam
N-6	41	44	15	Loam
S-1	50	20	30	Sandy clay loam
S-2	42	29	29	Clay loam
S-3	48	38	14	Loam
S-4	31	26	43	Clay
S-5	22	71	7	Silt loam

*Because the Wentworth gravel fraction is excluded and ultraclay is combined with clay, the sand, silt and clay percentages are recalculated to 100.

FIGURE I A-D

HISTOGRAMS SHOWING PARTICLE SIZE DISTRIBUTION

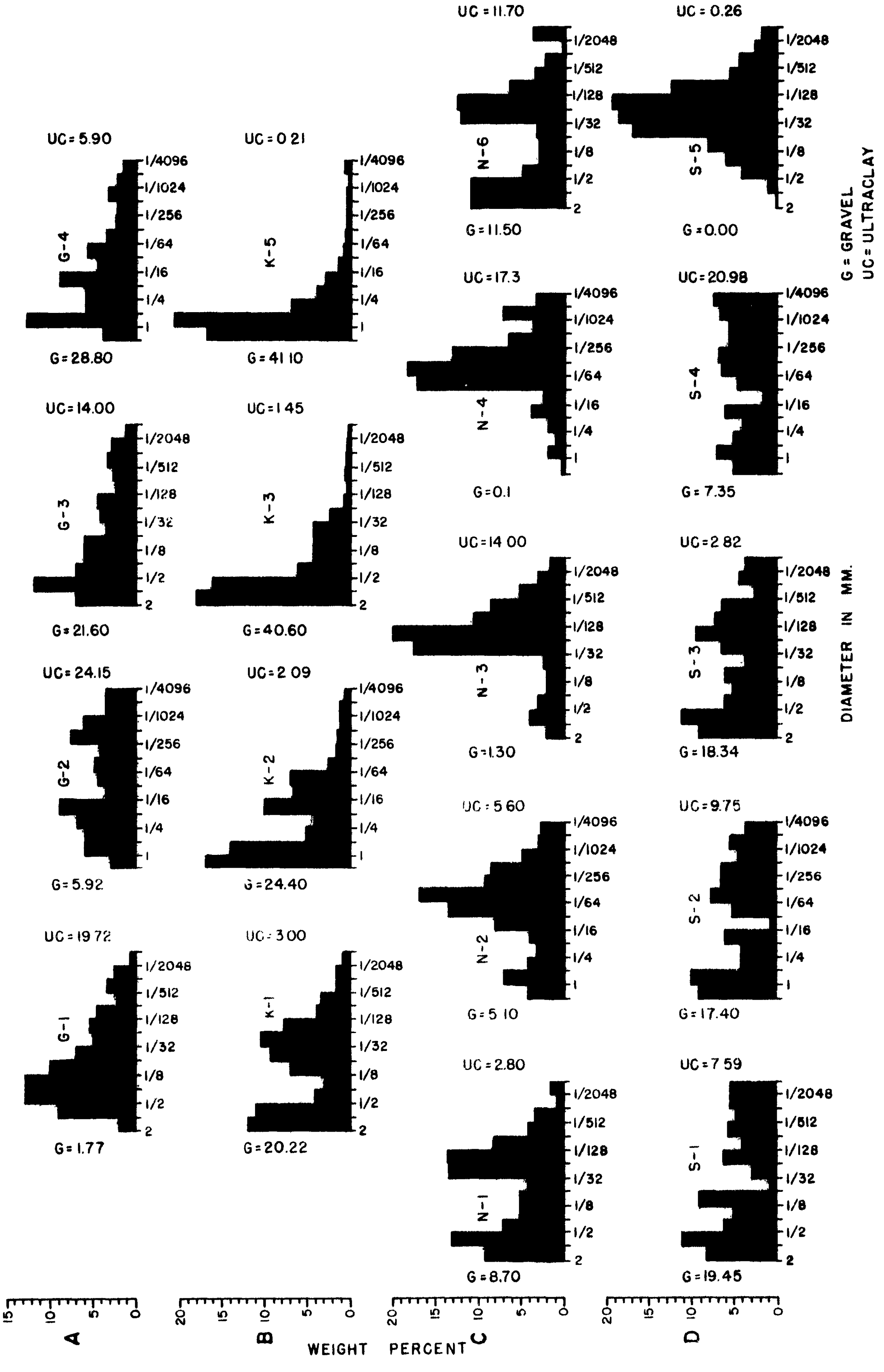


FIGURE 2

CUMULATIVE CURVES

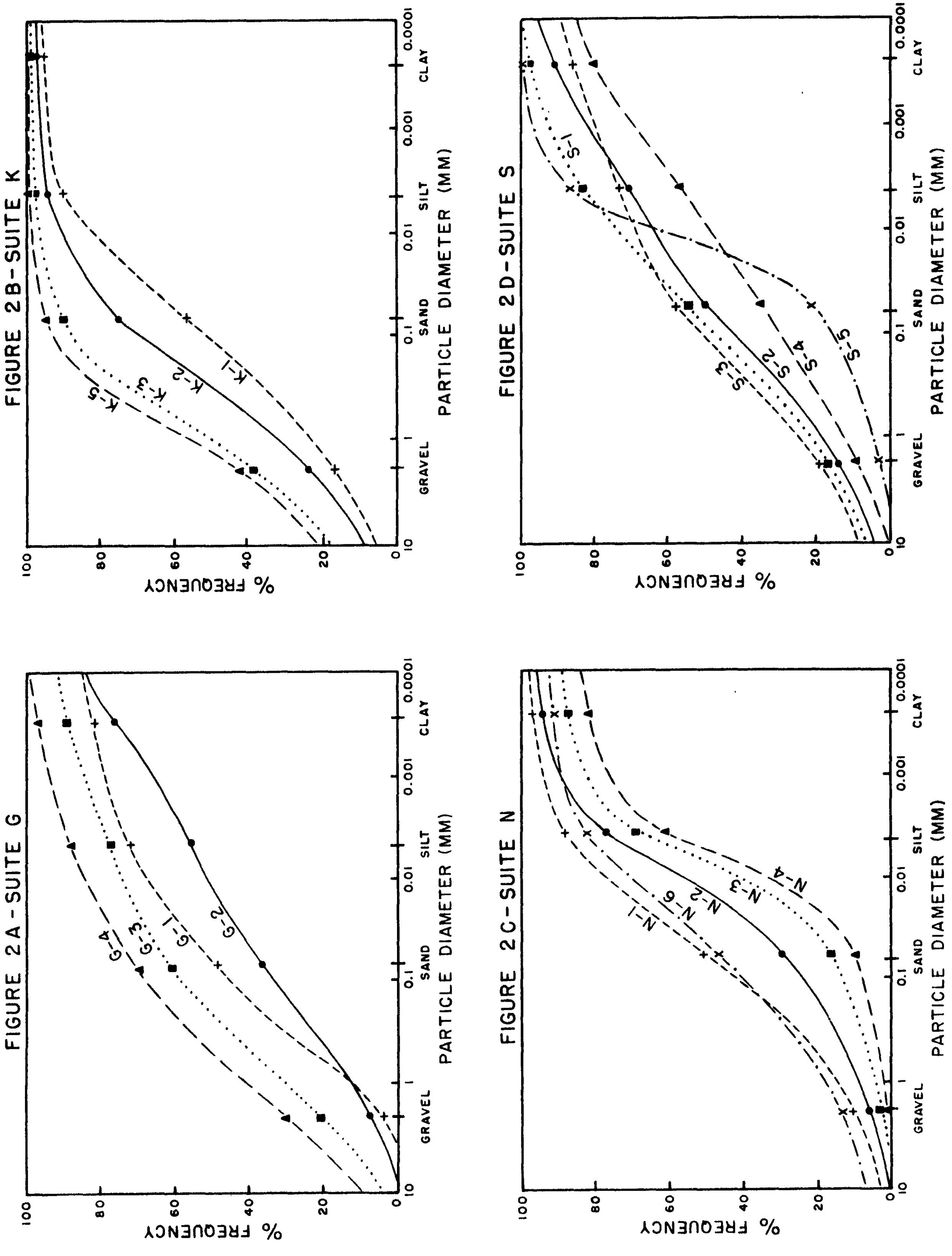


FIGURE 2A - SUITE G

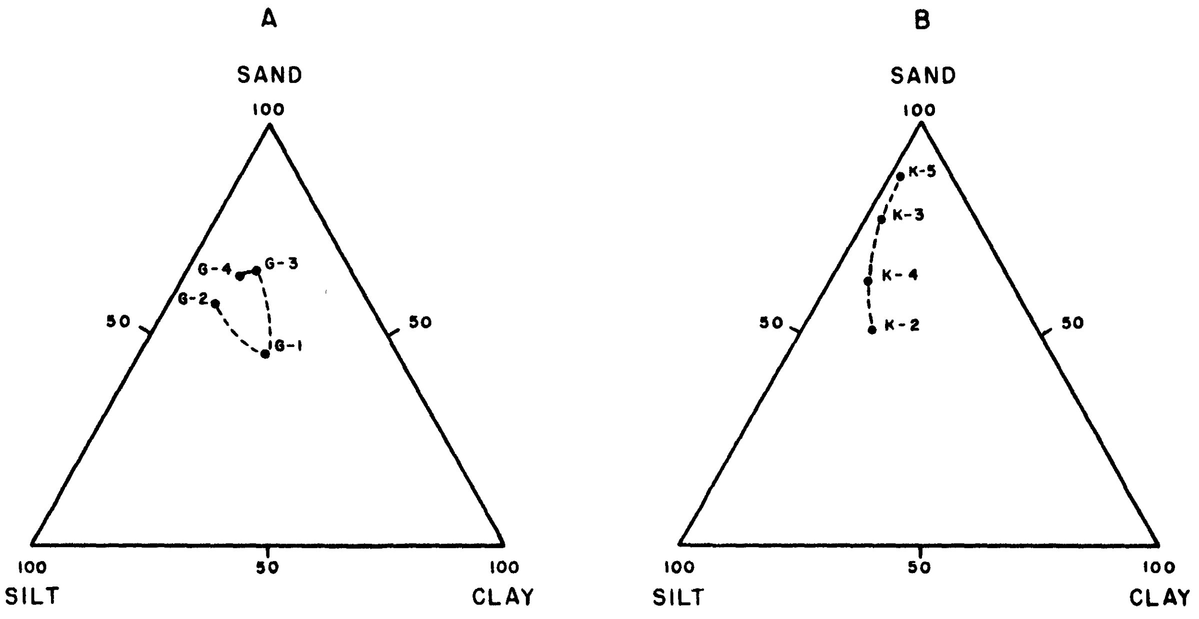
FIGURE 2B - SUITE K

FIGURE 2C - SUITE N

FIGURE 2D - SUITE S

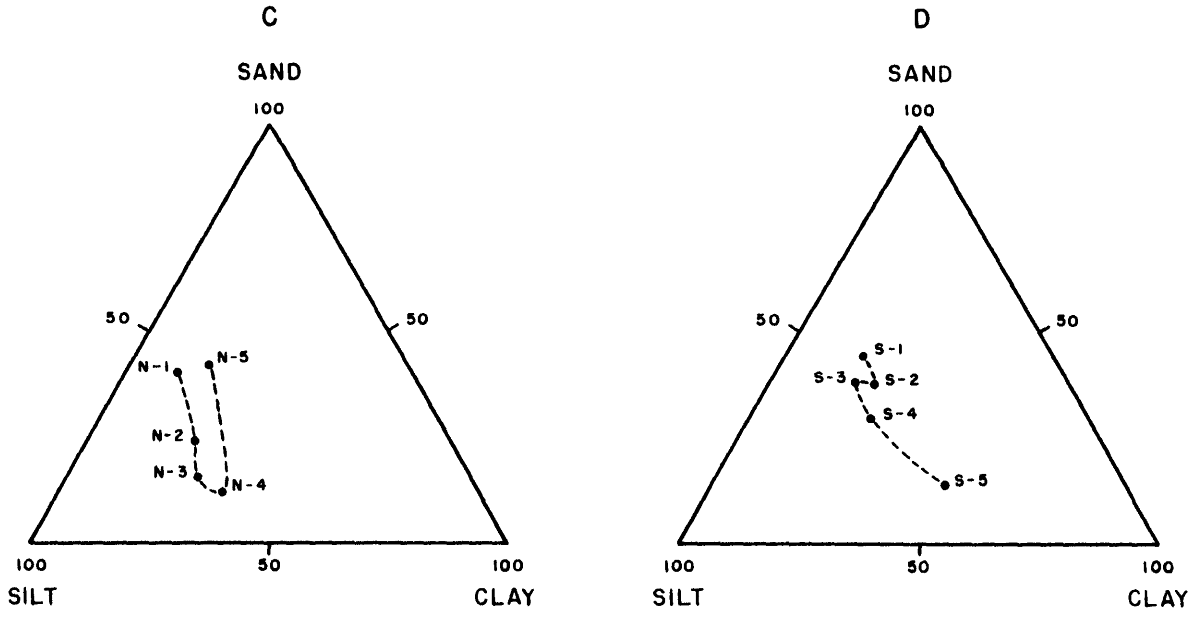
FIGURE 3

TRIANGLE DIAGRAMS OF SIZE VARIATIONS



G-SUITE

K-SUITE



N-SUITE

S-SUITE

II. Discussion and Interpretation:

A. General:

Certain characteristic patterns of size distribution are common to all four suites:

1.) The sand and silt fractions comprise the majority of the particles by weight.

2.) Most individual samples show bimodal maxima. In many samples the 1/2 - 1 mm. class in the sand fraction produces one of the maxima. This is primarily due to a large number of particles in this size class accumulating either from 1) direct release from the parent rock during weathering of crystalline grains initially of this size (Suites K and N), or 2) a tendency of weathered rock fragments to reduce to this size during disintegration (Suites G and S), or 3) authigenic build-up of small shot-like concretions (Suite S).

3.) Corresponding to the double maxima, the particle frequencies of the sieve and the pipette fractions, taken separately, each show a tendency to form a normal distribution curve. Examination of the histograms, which roughly outline the curve slopes, indicates the distribution to be skewed in most samples.

4.) There is often an abnormally low percentage frequency within the 1/16 - 1/32 mm. class. This is caused in part by the inability of coarser silt particles to pass freely into the pipette orifice during the sampling of that size range.

5.) All four suites are characterized by Trask Sorting Coefficients slightly to much larger than the coefficients (1 to 4) determined for sedimentary rocks. This is to be expected from soils because the great range of soil particles produced during weathering have undergone little of the sorting or size differentiation that sediments experience during transportation and deposition.

6.) The Sorting Coefficients of the two granite soils (K and N) indicates them to be better sorted than the two soils derived from basic parents (G and S).

B. Specific:

Each of the 4 suites possesses individual peculiarities of distribution which warrant comment:

Suite G: This soil has the highest average Sorting Coefficient (most poorly sorted) of the four studied. Sand particles make up the dominant size fraction, even though the soil was derived from a fine-grained (basaltic) parent rock. Some of the particles correspond to phenocrysts of feldspar and hornblende found in the parent; others are rock fragments. Both the gravel fraction percentages and the median diameters increase in the direction of parent rock, as is the common case in soils. The triangle diagram (Figure 3 A) shows all G-samples to be relatively uniform in size distribution. This corresponds to the appearance of this soil in the field, for the profile displayed less visible differences than commonly encountered.

The cumulative curves for the G-samples are more nearly linear than in the other suites, which further substantiates the indication of uniformity and also reveals that there is less contrast between size classes than usually observed in soils.

The cumulative curves show the sequence G-1 to G-4 to be irregular in that G-2 plots below G-1 rather than between G-1 and G-3 (i.e., is composed of finer sizes on average). This anomaly is emphasized by the decrease in the median size and the increase in Sorting Coefficient with respect to G-1 and G-3. G-2 shows a conspicuous increase in clay and ultraclay percentages (indicating a high degree of weathering), partly at the expense of the sand fraction. G-2 also shows anomalies in the soils chemistry and spectrochemical analyses.

Suite K: In the field this soil exhibited a well-developed (although thin) profile considered to be typical of that produced from granites in the Rocky Mountain Regions. The regularity of profile development is further demonstrated by the size distribution. This is markedly indicated by the plot on the triangle diagram which shows a steady increase in sand down the profile. The other major size fractions also show regular patterns of change through the profile.

Samples K-3 and K-5 are similar to each other in size character as are, to a lesser extent, K-1 and K-2. These two pairs, however, are distinctly different, as is especially notable from a comparison of the median diameters.

In all samples the clay and ultraclay fractions make up only a minor part of the total. Only in K-1 and K-2 does the silt fraction constitute a major portion. The gravel fraction is fairly high whereas the sand fraction dominates in all samples. From this it is concluded that Suite K is not strongly weathered, even in the upper horizons. The lower horizons (K-3 and K-5) represent typical saprolitic weathering of granites, in which disintegration is the main process in the earlier stages.

The comparatively high degree of sorting (low Coefficient) further supports the conclusion regarding the limited extent of weathering. In this case the sorting is caused by lack of production of finer sizes rather than by any winnowing effect from a fluid medium.

Suite N: The triangle diagram for this suite indicates a down-profile trend toward finer sizes which becomes sharply reversed in sample N-6. The cumulative curves show that the top sample N-1 and bottom sample N-6 are closely similar, except that N-6 has higher percentages both of gravel and ultraclay.

The median diameter values when compared to the grain size values in the parent rock indicate the soil to be highly weathered. The silt fraction dominates; however, the clay and ultraclay fractions also are high. The Sorting Coefficient tends to follow the change in median diameters, i.e., the increase in finer sizes leads to an improvement in the degree of sorting.

The peculiar trend in size distribution may be due to several causes. N-6 occurs just above weathered parent rock and hence a high gravel content and minimum development of fine sizes is expected. The downward increase in clay coupled with a decrease in gravel to N-4 is however anomalous. Such a condition could be produced by:

1.) Deflation of finer sizes near the surface, leading to relative increase in coarser particles.
2.) Translocation downward of clay particles during internal drainage.
3.) Concentration of groundwater and consequent location of zone of most active weathering above a relatively impervious parent rock-weathered C horizon interface.

Suite S: The size distribution within the Suite S profile is the most irregular of the four studied. Several anomalies are difficult to explain.

The cumulative curves, triangle diagrams, histograms, and summary data all indicate abnormal fluctuation downward in sorting, median size, and in percentage distribution of all major size classes. S-1, S-2, and S-3 are generally similar to each other, although S-2 has an average finer size than S-3. In the cumulative curves, the sequence S-1 - S-3 is inverted in the coarse and intermediate size ranges and the entire sequence S-1 - S-2 - S-3 is reversed in the finer sizes with respect to the common pattern for most soils in which the curves for the lower soil layers plot above those of successively higher layers. The high proportion of gravel sizes in these three, compared to the bottom two samples, is distinctive.

S-4 is distinctly finer-sized than the samples taken above it. The size distribution corresponds to the physical appearance, like that of a hard fire-clay, of this sample.

S-5 shows an absence of gravel fragments, a dominance of silt size particles, and a near absence of very fine particles. A very high degree of sorting is confirmed by the Sorting Coefficient.

These peculiarities of distribution are explained by the evidence from the field examination of the profile:

1.) Sample S-5 represents parent rock in the incipient or early stages of weathering. The prevalence of silt size particles partly reflects the initial grain sizes of the parent rock.

2.) Sample S-4 indicates a more advanced stage of weathering.

3.) Samples S-1 through S-4 show a relative increase in gravel and sand sizes at the expense of finer sizes because of the authigenic development of iron-cobalt-manganese concretions.

PARENT ROCK MINERALOGY

The minerals comprising the parent rock of each soil suite were identified by a petrographic examination of thin sections and mineral grains. An estimate of mineral composition was made by a point count (200 points) of the mineral categories set up for each thin section. The composition of each parent rock is presented in Table 5.

Rocks from areas which include the parent rock of each soil suite have been described in the literature. On the bases of these descriptions and of the petrographic results given in Table 5, each parent rock has been classified as to probable rock type. The rock name assigned is included in Table 5. The references to the published descriptions are also given in this table.

TABLE 5

Suite G: G-9 = Orthoclase-bearing basalt (trachybasalt ?) (Waldschmidt, 1939)

Plagioclase ($Ab_{40}An_{60}$) = 65.0% Olivene = 1.0%

Orthoclase = 7.0% Biotite = 1.0%

Augite = 14.0% Magnetite = 12.0%

Accessory minerals: Pyrite, Apatite.

Alteration products: Epidote, Calcite, Sericite (?), Hematite

Suite K: K-7 = Granodiorite (Osterwald, 1955)

Microcline = 45.0% Biotite = 3.0%

Oligoclase ($Ab_{76}An_{24}$) = 30.5% Chlorite (altered from biotite) = 3.0%

Quartz = 16.0% Magnetite = 1.5%

Accessory minerals: Zircon, Rutile, Topaz, Apatite, Garnet (rare).

Alteration products: Kaolinite "dust", Sericite, Hematite, Leucoxene.

Suite N: N-9 = Binary granite (Tolman and Goldich, 1935)

Quartz = 45.0% Muscovite (secondary?) = 3.5%

Feldspar: Biotite-Chlorite = 1.0%
  Unidentified = 15.0%
  Perthite = 24.0% Magnetite = 0.5%
  Albite-Oligoclase = 11.0%

Accessory and alteration minerals: Calcite, Sericite, Fluorite (?).

Suite S: S-7 = Metamorphosed andesite tuff (metavolcanic greenstone) (Councill, 1953; Stuckey, 1928, p. 21)

Feldspar (orth:plag::1:7) = 53.0% Calcite = 1.0%

Epidote and Zoisite = 25.5% Quartz = 0.5%

Chlorite = 14.0% Andalusite = 1.0%

Accessory and alteration minerals: Unidentified clay mineral, a micaceous mineral (?), Titanite-Leucoxene, Mica (sp?), Magnetite, Hematite = 5.0%

SOIL MINERALOGY

I. Introduction:

The mineral phases in a soil provide indicators for determining the degree of weathering, the probable chemical changes, the proof of a residual origin, and the extent of possible contamination (see: Haseman and Marshall, 1945; Jackson et al., 1948). The phases which comprise the bulk of the soil fall into seven categories (see also: Keller, 1955):

1.) Unweathered to highly altered grains of primary phases released from the parent rock.

2.) Heavy minerals.

3.) Secondary crystalline phases: concretionary growths, authigenic grains, tiny flakes of alteration products spalled off from weathered grains, crystalline cements, clay minerals, and mineral coatings formed *in situ* during weathering by a variety of processes.

4.) Secondary amorphous phases: "silicate wreakage" (see Keller, 1955), mineral gels, stains, coatings, and cements.

5.) Foreign phases: mineral grains resulting from contamination, etc.

6.) Organic phases: twigs, macerated leaves and grass, spores, much altered coaly matter, skeletons, shells, chitinous insect covers, excretory matter, and amorphous, gelatinous organic stains and cements (often finely intergrown with secondary phyllosilicates).

7.) Gas and liquid phases: oxygen, CO_2, etc.; adsorbed and pore water.

The mineral content of the sand, silt, clay, and heavy mineral fractions from each of the four suites were examined in detail for representatives of some of these categories by methods described in the following pages. The results of these studies are also summarized, along with an interpretation of their meaning in regard to the nature and degree of weathering.

II. Sand Fraction:

The +170 and +35 sieve fractions separated during the particle size analyses were examined for mineral content under the binocular and petrographic microscopes. Two hundred grains from the +170 fraction of selected sand samples were point-counted to provide an estimate of the variation in mineral proportions caused by varying degrees of weathering within the soil profile. For this point count several mineral categories were set up for each suite on the basis of shape, color, cleavage, and characteristic optical properties.

The results of the point count analyses are presented in Table 6. The parent rock percentages of minerals corresponding to these categories are also included. The probable horizon represented by each sample is indicated by the horizon letter in parenthesis.

By comparing the percentage of a mineral in each horizon to the parent rock percentage, it is possible to evaluate the relative change in intensity of weathering throughout the profile. A further indication of the degree of weathering is provided by computing the ratio of weathered or altered feldspar to fresh feldspar. Table 6 shows this ratio for Suites G, N, and S samples. The indicated changes are not absolute because the changes in volume of each soil horizon relative to parent rock have not been ascertained.

Interpretations of the mineral changes in the sand fraction in relation to weathering are summarized for each suite as follows.

Suite G: The decrease in the combined percentages of plagioclase from 82% to 67% from C to A horizons indicates the relative instability of Ca-feldspars during weathering. The initial increase in percent plagioclase between G-9

TABLE 6

Sand Fraction Composition

Suite G:

	Clear Plagiocl.	Altered Plagiocl.	$\frac{\text{Clear}}{\text{Altered}}$ Pl.	Orthocl.	Biotite	Augite	Magnetite
G-1(A)	43.5%	24.0%	(.552)	-	7.5%	14.0%	5.0%
G-2(B)	47.5%	26.0%	(.547)	2.0%	9.5%	8.0%	6.0%
G-4(C)	50.5%	32.0%	(.634)	1.0%	7.5%	7.0%	2.0%
G-9(Par)	65.0%			7.0%	1.0%	14.0%	12.0%

Suite K:

	Biotite-Chlorite	Magnetite
K-1(A)	32%	2%
K-2(B)	23%	-
K-3(B)	23%	3%
K-5(C)	25%	4%
K-7(Par)	6%	1.5%

Feldspar and Quartz were not point counted

Suite N:

	Clear Feldsp.	Altered Feldsp.	$\frac{\text{Clear}}{\text{Altered}}$ Feld.	Quartz	Biotite	Opaques
N-1(A)	47.0%	24.0%	(.511)	20.0%	1.0%	4.0%
N-3(B)	24.5%	58.5%	(2.39)	13.5%	1.0%	2.0%
N-6(C)	33.5%	45.5%	(1.36)	19.5%	1.0%	0.5%
N-9(Par)	50.0%			45.0%		

Suite S:

	Epidote	Clear or twinned Plagioclase.	Altered Plagiocl.	$\frac{\text{Clear}}{\text{Altered}}$ Pl.	Quartz	Opaques
S-1(A)	1.0%	16.0%	77.5%	(4.84)	4.5%	1.0%
S-3(B)	2.0%	11.0%	78.0%	(7.09)	9.0%	0.5%
S-4(B)	4.0%	9.0%	81.5%	(9.06)	5.0%	0.5%
S-5(C)	26.0%	10.5%	61.4%	(5.86)	0.5%	0.5%
S-7(Par)	23.0%	53.0%			0.5%	

and G-4 is partly the effect of the relative decrease of other minerals. The large decrease in orthoclase most likely reflects the inability to distinguish it from plagioclase during the point count. The sharp increase in biotite flakes in the soil is explained as a physical comminution of easily cleaved mica rather than survival as a stable mineral. The apparent decrease in augite in G-4 and G-2 is caused by selective concentration of parent rock crystals larger than .088 mm. (+170) in the coarser fractions; the augite increase in G-1 therefore indicates both reduction in size and survival during weathering. Magnetite, a resistate mineral, increases upward after a sharp initial decrease for the same reasons as augite. Evidence that G-2 represents the most weathered horizon (B) in the profile is given by the maximum percentage of magnetite and biotite and by the lowest ratio of fresh to weathered feldspar in that sample.

Suite K: The Suite K sand fraction indicates that the soil follows the "normal" weathering pattern for granitic rocks. Conformity to the Goldich Stability Series (Goldich, 1938) during weathering is well illustrated by the behavior of the parent rock minerals as observed in the +35 fraction.

1.) Plagioclase is more completely weathered than microcline.
2.) Stable quartz increases in the more weathered samples.
3.) Biotite is readily altered to chlorite.
4.) Kaolinite and sericite form directly from feldspar.
5.) Iron release and migration is indicated by the appearance of stains on iron-free minerals and by partial destruction of biotite.

The pronounced increase in biotite-chlorite in the soil results both from particle comminution and greater stability relative to the more weathered feldspars. The up profile decrease in magnetite shows that this resistate mineral can be affected by weathering.

Suite N: The decrease in quartz and increase in altered feldspars in N-3 support the particle size and soil chemistry indications that the middle horizons in this profile are more highly weathered. The reversal of the ratio of unaltered to weathered feldspar in N-1, such that unaltered feldspar now dominates, indicates that the mineral species comprising it (microcline ?) is more stable than the species (plagioclase ?) making up the bulk of the altered feldspar. Thus, in the topsoil, part of the altered feldspar has been destroyed, leading to relative enrichment of the unaltered feldspar.

Comparison of parent rock to soil composition shows the quartz to have apparently decreased from 45% to 20-13% whereas feldspar increases from 50% to 72-82%. This is hard to explain and may be due largely to the inability to distinguish between quartz and feldspar in the +170 fraction. Mica shows a decrease from 3.5% to 1.0% which may be due to comminution of the sand size flakes to smaller flakes concentrating in the silt-clay fractions.

Suite S: Epidote persists throughout the profile, thus supporting the identification of the profile as residual; however, the sharp decrease in epidote percentage between S-5 and S-4 shows its high instability. Assuming only a small volume change, the close agreement between epidote percentage in S-5 (26.0%) and the parent rock S-7 (23.0%) shows that S-5 is essentially a strongly weathered portion of the actual parent rock.

The absence of recognizable chlorite, which composes 14.0% of the parent rock, in all the sand samples can be explained in one or both of two ways.

1.) The chlorite is highly unstable and is easily destroyed during the early stages of weathering.

2.) The chloritic masses readily break down into finer size particles which accumulate in the silt and clay fractions.

The feldspars follow an unusual trend. Their combined percentages are all greater than the parent rock percentage and they also increase up profile. The increase upward is due to the loss of chlorite and the pronounced reduction in epidote, such that the percentages of all remaining soil minerals show a relative increase. The increase in clear over altered plagioclase may be, as in the case of the Suite N sand fraction, a relative enrichment resulting from more complete destruction of less stable feldspars.

The quartz noted in all horizons is largely introduced through contamination. This is best supported by the occasional presence of well-rounded grains probably carried in by the winds. The occurrence of wind-blown quartzitic surface deposits 35-50 miles southeast of the sample site (see G.S.A. map: Pleistocene Aeolian Deposits of the U.S., Canada, and Alaska) lends credence to this interpretation. The slightly biaxial character and undulatory extinction observed in many of the quartz grains indicates that much of the quartz may have been derived from the Paleozoic metamorphics of the eastern Piedmont.

An upward increase, observed in the +35 fraction, in the proportion of the secondary black concretions relative to other minerals reflects 1) actual increase in the number of concretions formed, 2) probable comminution of the larger, gravelly concretions, and 3) continued destruction of unstable minerals.

III. Silt and Clay Fractions:

Identification of the minerals present in the silt and clay fractions in the soils was made by x-ray diffraction and differential thermal analysis (D.T.A.) methods.

The initial x-ray analyses were carried out at M.I.T. using a Norelco low angle x-ray diffractometer equipped to produce copper Kα radiation. X-ray mounts of a silt (1/128 - 1/256 mm.) and a clay (1/2048 - 1/4096 mm.) fraction were prepared from the residue of the Na-dispersed soils used in the pipette analysis of particle size. Some of these mounts were treated with glycol to induce expansion of the (001) layers of any montmorillonoids present. Other mounts were slowly heated to 550°C to facilitate recognition of chlorites.

As a further check on the mineral content of the clay fractions, one set of the soil samples was x-rayed by Mr. Rodney Tettenhorst of Washington University and another set by Mr. W. T. Caneer of the Gulf Research Laboratory in Pittsburgh.

An unsuccessful attempt was made to obtain a quantitative estimate of mineral composition in the clay fraction by comparing x-ray peak heights of the soils fractions with peak heights of clay mineral and quartz standards mixed in known proportions. Only the quartz percentage could be estimated within acceptable accuracy by this method. A general estimate of the changes in proportions of several minerals within a soil profile was made by a comparison of relative peak heights of selected d spacings in a series of samples from different horizons.

The minerals found by x-ray analyses of the four soil suites are listed in Table 7. Characteristic x-ray diffractometer patterns, showing the principal diagnostic peaks, are illustrated in Figure 4.

TABLE 7

Clay-sized Minerals Identified by X-ray Analysis

Suite G:

1. Feldspar
2. Montmorillonite
3. Chlorite (minor)
4. Mica
5. Quartz (?)

Suite K:

1. Quartz
2. Kaolinite
3. Illite-chlorite mixed layer
4. Illite-mica
5. Feldspar
6. Montmorillonite (?)

Suite N:

1. Quartz
2. Feldspar
3. Kaolinite
4. Illite-mica*
5. Chlorite (?)*

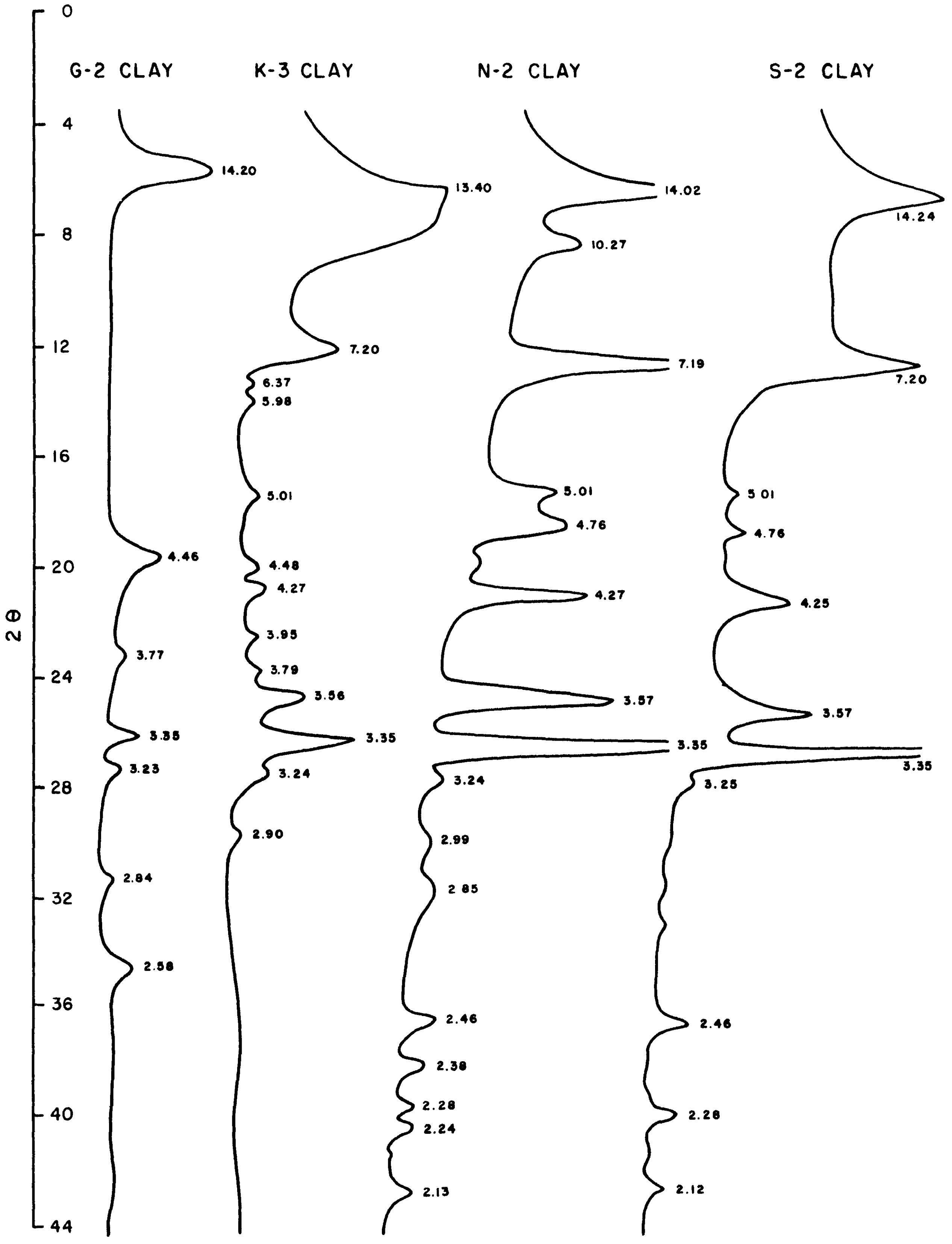
Suite S:

1. Quartz (contaminant)
2. Feldspar
3. Chlorite (iron-rich)
4. Mica
5. Calcite (?)

*Possibly mixed layer.

FIGURE 4

X-RAY DIFFRACTOMETER PATTERNS



A differential thermal analysis was made on at least one sample from each soil suite. The D.T.A. patterns thus produced are shown in Figure 5.

Interpretation of the x-ray and D.T.A. results are presented in the following pages.

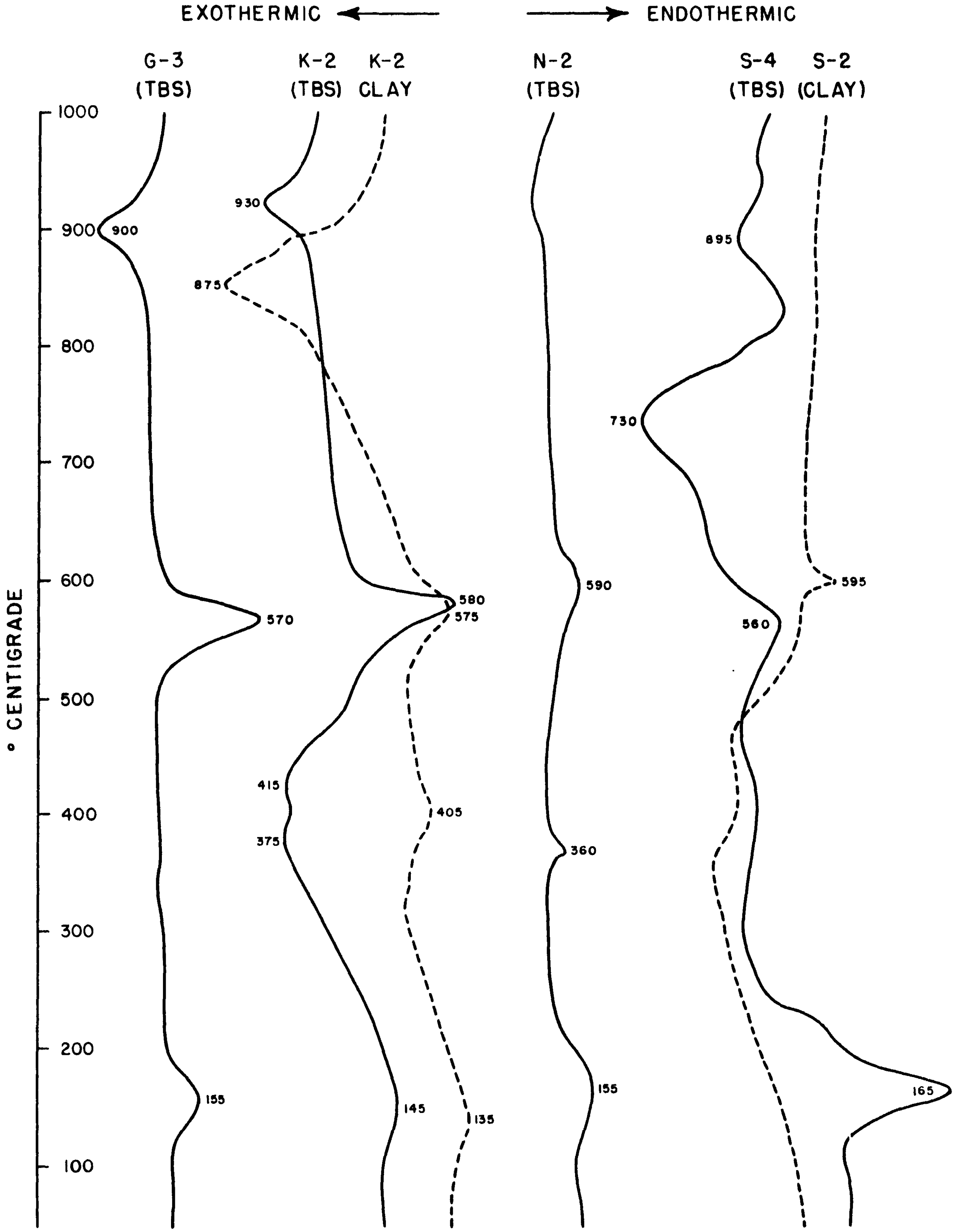
Suite G: The patterns produced by Suite G silt and clay fractions were generally poor. Glycol treatment did not reveal the presence of montmorillonite. However, an x-ray analysis under controlled humidity (Milne and Warshaw, 1956) at Gulf Research demonstrated montmorillonite to be the dominant clay mineral. This was confirmed by the D.T.A. run and by the high cation exchange capacities of 55-63 me/100 g (see page 65) for samples in this suite. Chlorite is suggested by the 13.7 and 4.48 A peaks but its amount is too small to show response to heat treatment.

The diminution of some peak heights and absence of others indicate that the secondary minerals formed have a low degree of crystallinity. This may be interpreted as evidence either of an incipient or early stage of secondary mineral formation or of more complete destruction of these minerals by intense weathering. The latter view is supported by a correlation in G-2 of the most subdued peaks in the series with increase in silt and clay particle percentage (page 44) and with the greatest chemical changes (page 65) in the suite.

Suite K: A mixed layer intergrowth of illite and chlorite is indicated by a broad peak between 13.4 and 10.1 A which collapses on heat treatment to 10.2 A. An endothermic peak around 600°C and a stronger exothermic peak around 900°C in the D.T.A. pattern for K-2 clay can be caused by both of these minerals.

FIGURE 5

D.T.A. CURVES



The amount of quartz is uniform in the silt fraction and shows a slight increase in the clay fraction samples from the A and upper B horizons. Feldspar diminishes toward the profile top. Mixed layer illite-chlorite is more prominent in the clay fraction.

The x-ray evidence fails to offer an adequate explanation of the high exchange capacities of 39-59 me/100 g (page 65) noted in the clay fraction. The gradual exothermic rise between 600 and 900°C in the D.T.A. pattern for K-2 is likely the effect of hydrated iron oxide.

Suite N: A nonexpanding peak at 14 A which partly disappears on heating in some samples and a broad peak between 14 and 10°A in others indicates the possibility of a mixed layer illite-chlorite. Quartz, feldspar, and kaolinite produce prominent peaks which are strongest from the middle horizon samples.

Suite S: A weak nonexpanding 13.6 A peak which diminishes upon heating together with a strong 7.15 A peak which completely disappears at 550°C has been interpreted by Dr. William Johns of Washington University (personal communication) as due to an iron-rich chlorite (Brindley and Gillery, 1956). Rolfe (1954) has found a similar chlorite in a study of the clay minerals in the Iredell loam of North Carolina (to which Suite S has been correlated). Chlorite was found in the parent rock S-7 but is absent in all sand fraction samples.

Quartz appears in the silt and clay fractions of samples S-1 through S-4. This quartz is introduced as a wind-blown contaminant (page 55).

The peak heights of all sample patterns show little variation except for a much stronger 13.6 A chlorite peak in S-5. Cation exchange data for the Suite S samples indicates the absence of high exchange capacity minerals such montmorillonite and vermiculite (found by Rolfe in his investigation).

The D.T.A. pattern for S-2 clay shows a broad exothermic reaction between 250 and 450° C. The pattern for S-4 shows a broad but sharper exothermic peak around 720° C. Both such reactions can be ascribed to hydrated iron, aluminum, and manganese oxide. The silt and clay fractions from Suite S appear to be composed largely of poorly crystalline or amorphous phases, among which these hydrated oxides probably predominate.

IV. Heavy Minerals Fraction:

Heavy minerals (specific gravity greater than 2.85) were recovered from the +170 mesh sand fraction of two samples from each suite by separation in bromoform. The heavy mineral assemblages were identified by petrographic techniques and the proportion of each mineral determined by a point count of 100 grains. A list of the heavy minerals found in each suite is presented in Table 8, along with the percentage of the total sand fraction comprised by the heavy minerals and the proportion (in percent) of each mineral in the assemblage.

TABLE 8

Suite G:	Augite	Magnetite	Rutile	Leucoxene	Apatite	Zircon	Mica
G-2 (32.5%)	61%	32%	2%	1%	2%	-	2%
G-4 (16.9%)	72%	17%	3%	3%	3%	1%	1%

Suite K:	Topaz	Magnetite	Leucoxene	Rutile	Chlorite	Hornblende	Zircon	Apatite
K-2 (4.0%)	32%	35%	13%	8%	9%	-	3%	-
K-5 (7.7%)	37%	32%	22%	2%	3%	1%	2%	1

Suite N:	Hematite	Magnetite	Leucoxene	Tourmaline	Rutile	Zircon	Apatite	Hypersthene(?)
N-1 (0.8%)	15%	69%	3%	2%	2%	1%	7%	1%
N-6 (1.0%)	79%	13%	2%	1%	2%	1%	2%	-

Suite S:	Epidote	Fe-Mn-Co Concretion	Actinolite	Andalusite	Rutile	Zircon
S-3 (7.6%)	73%	20%	4%	2%	-	1%
S-5 (34.5%)	99%	-	-	-	1%	-

SOIL CHEMISTRY

Measurements of soil moisture ($-H_2O$), pH, E_h (redox potential), salt content (conductivity), organic matter, free iron oxide, and cation exchange capacities (C.E.C.) were made on most soil samples from the four suites. The methods used are described in Appendix A. Table 9 gives the results of these measurements. Interpretation and discussion of these results follows.

I. General Features:

1.) The percentage of pore and adsorbed water in all samples generally tends to follow the percentage variations of clay and ultraclay.

2.) The pH for all suites lies on the acid side of 7.0. This is the general case for most soils. The pH of the two soils derived from the acid (granitic) rocks is as expected lower than the pH characterizing the intermediate (andesitic) derived soil from Suite S and is even lower than that produced in the soil coming from the basic parent (basalt) for Suite G. In all four suites, the parent rock is one or more pH units more basic than the soil derived from it.

3.) The low conductivity values for all soils shows the soils to be devoid of noteworthy amounts of soluble salts.

4.) The E_h values for all four soils indicate their present redox states to be moderately to strongly oxidized. In Suites K and N the highest E_{h_7} values coincide with the zone of iron enrichment in the B horizon. The higher $+E_h$ values for the parent rocks is contrary to the expectation of a lower degree of oxidation in the less altered source material.

TABLE 9

Soil Chemistry

Sample No.	% -H_2O	pH	Redox Potential			Conductivity (me. NaCl/100)	% Organic Matter	% Free Iron Oxide	C.E.C. (me/100 g.)		
			pH	E_h	E_{h_7}				Silt	Clay	Total Soil
G-1	4.64	5.8	6.3	+.642	+.616	0.12	4.53	1.16	20	55	20
G-2	8.57	6.4	6.6	+.628	+.617	0.12	2.40	1.21	36	61	35
G-3	5.95	6.7	-	-	-	0.19	1.80	1.15	27	63	19
G-4	2.63	7.0	7.2	+.587	+.615	0.16	1.69	0.93	25	58	12
G-9			9.0	+.551	+.671						
K-1	3.47	4.6	4.9	+.367	+.258	0.37	5.86	0.69	14	38	8
K-2	2.30	4.6	-	-	-	0.08	2.65	0.95	15	47	6
K-3	1.69	4.4	5.1	+.634	+.533	0.04	1.07	1.02	12	59	3
K-4	0.65	4.4	-	-	-	0.03	0.54	0.79	14	35	-
K-5	0.37	4.6	5.5	+.592	+.515	0.05	0.20	0.24	19	44	2
K-7			6.3	+.642	+.616						
N-1	0.72	4.1	4.5	+.582	+.450	0.12	4.71	0.83	-	-	-
N-2	1.32	4.1	-	-	-	0.07	0.76	1.14	-	-	-
N-3	2.82	4.2	4.3	+.627	+.478	0.05	0.82	1.56	-	-	-
N-4	3.84	4.2				0.05	0.44	-	-	-	-
N-6	2.40	3.9	4.1	+.580	+.422	0.07	0.16	-	-	-	-
N-9			6.7	+.477	+.442						
S-1	1.54	5.3	6.0	+.700	+.650	0.10	2.21	0.59	11	7	2
S-2	1.70	5.1	-	-	-	0.08	1.00	3.99	9	17	6
S-3	2.78	4.7	5.8	+.689	+.617	0.08	0.80	2.22	12	21	7
S-4	3.92	5.1	-	-	-	0.06	0.70	5.19	24	28	18
S-5	4.56	5.3	6.1	+.710	+.670	0.07	0.35	3.42	-	-	-
S-7			8.0	+.757	+.830						

5.) As is typical of soils, the majority of the organic matter is concentrated in the topmost horizon(s).

6.) There seems to be no significant correspondence between pH and percent organic matter.

7.) In the two granite-derived soils, free iron oxide concentrates in the B horizon and thus confirms this generalization. There is a less distinct relation between maximum iron oxide percentages and position in the profile in the two other soils.

8.) The cation exchange capacity of the silt fractions seems to be higher than would be expected from reference to other reported values. This may indicate that separation of silt from clay in the sample preparation was incomplete.

II. Specific Features:

A few comments are appropriate for each of the four suites:

Suite G: The soil reaction for this soil is more basic than for the other suites. This may represent the joint contribution of both parent rock and the relatively high organic matter content. The nearly constant E_{h7} soil values indicate little variation in the oxidation level throughout the profile. The free iron oxide content is rather low for a soil formed from a parent rock containing 9.22% total ferric iron oxide. C.E.C. also is high both for the soil as a whole and for the clay fraction. This is in part the result of the presence in the finer fractions of 1) the high exchange clays montmorillonite and chlorite, 2) the organic matter content, and 3) the possible presence of zeolites.

Sample G-2 reflects in the $+H_2O$, free iron oxide, and C.E.C. values the anomalies noted for this sample in the particle size and mineral composition analyses. This provides a further indication that this horizon is more highly weathered than those above and below.

Suite K: The uniformity of pH in all K-samples is mainly controlled by the prevalence of almost unweathered gravel, sand, and silt particles which have a constant composite pH similar to that of the parent rock. The lower $+E_{h_7}$ value for K-1 is produced by the increase in unoxidized (and strongly reducing) organic matter in the surface layers. The free iron oxide content conforms with the visible evidence of maximum iron staining in the B horizon. The exchange capacity of the total soil is low. The cation exchange capacity values appear to follow the variation in organic matter. The C.E.C. values of the clay fraction are rather high and cannot be adequately accounted for by those minerals found in the x-ray analysis.

Suite N: Only some of the soil chemistry measurements were made on these samples. As with Suite K samples, the pH is nearly constant. In this suite however, the unweathered fractions comprise only a minor part. This uniformity is not explained but it does not seem to have any relation to the organic matter or to variations in the proportions of the finer size particles. The changes in adsorbed water content closely parallel the variations in the clay and ultraclay percentages. The incomplete set of free iron oxide values shows an increase downward which agrees with the increase in yellow-brown soil coloration in the middle of the profile.

Suite S: Some of the peculiarities of size distribution noted for this suite have a counterpart in the free iron oxide values which show the same erratic variations as do the median diameters and clay and ultraclay classes. The high free iron oxide values demonstrate the ready release of iron to solution and its greater mobility in this profile. This helps to account for the presence of the iron concretions in the upper profile. However, the near absence of these concretions in the S-4 horizon does not correspond with the maximum value for free iron oxide found for the sample from this horizon.

The $-H_2O$ increase downward coincides with the increase in finer sizes except for sample S-5. The pH values do not seem to follow either size or any other of the soil chemistry parameters.

The C.E.C. values for the silt and the clay do not show large differences. Both sets of values are low. Only the chlorite noted in these fractions during the x-ray studies would be expected to make any significant cation exchange contribution.

SPECTROCHEMICAL ANALYSES

The chemical composition of all soil and rock samples was obtained by emission spectrographic analyses using the mutual standard method (Dennen and Fowler, 1955). The concentration of the major elements S_i, Al, Fe, Mg, Ca, K, Na, and T_i as oxides and the minor elements Ba, Co, Cr, Cu, Ga, Mn, Ni, Pb, Sc, Sr, V, Zn and Zr were determined in the total bulk soil and parent rock samples from all four soil suites and in addition in sand, silt, clay, and leach extract fractions from Suites G, K, and N.

The principle of the mutual standard method, the bases of selection of analysis elements, the preparation of samples, and the methods of calculation are discussed in detail in Appendix B. This appendix also includes a complete presentation of spectrographic procedures and conditions used in the soil chemical analysis. Many of these conditions are summarized in Table 10 on the following page.

The precision of the spectrographic analyses was, for the average of all elements, 7.4% (relative error) for a series of samples run on a single plate (intraplate precision) and 28.0% between sets of samples run on several plates (interplate precision). As designed, the analysis procedure involved the arcing of each entire series of one sample type (e.g., total bulk, silt, clay) from a profile on a single plate. Thus, because of the poorer interplate precision, relative concentration changes between different sample types from a soil suite could be determined with less certainty. Such changes should exceed 28% between samples to be considered valid. A summary of all tests and cross-checks made to assess both precision and accuracy of the analyses is given in Appendix C.

TABLE 10

Spectrographic Conditions

Method - Mutual standard; ratios to Al

Standardization - Standards G-1 (granite) and W-1 (basalt) run on each plate

Arc Charge Preparation - 1:1 by volume ground sample to carbon

Pre-arcing Treatment - Arc charge heated for 5 minutes over a burner

Electrodes - 3/16 in. diameter "specpure" carbon. Sample electrode bored to depth of 6.35 mm. and inner diameter of 2.30 mm.; electrode charge not weighed

Spectrograph - Hilger 3 meter quartz prism; Littrow mount

Excitation - Anode excitation, 220 volts, 6 amps, 14 mm. arc gap

Slit and Sector - 10.5 mm.; rotating 7 step sector; step sector ratio 2^{-n}

Optics - Arc source focused on collimator lens by 150 cm. spherical condenser

Wave Length Region - 2750-4575 A^{o}

Exposure - Total energy method; 230-265 seconds; sample arced in duplicate with spectra superimposed

Plates - Eastman-Kodak S.A. 1 4 x 10" glass plates

Processing - 270 seconds in Kodak D-19 developer at 20^{o}C; 10 second wash; 15 minute acid fix; 1 hour wash

Calibration - Rotating step sector method (Ihrens, 1950, pp. 127-29)

Analysis Lines - See Table 20.

Line Density Measurement - Density measured as deflection d by a Jarrell-Ashe Model 200 Microphotometer

PRESENTATION OF ANALYSIS DATA

The results of the spectrochemical analyses of samples from the four soil suites are summarized in Tables 11 A-D on the following pages.

The TBS, sand, silt, and clay concentrations of each element given in these tables have been plotted on a log scale as a function of the depth in inches, on an arithmetic scale, for each sample of a soil profile. These plots, each for a separate profile, are shown graphically in Figures 6 through 9. For comparison, the size and soil chemistry data have been plotted on a similar scale on the right side of each graph. The depth scale has been condensed to vertically exaggerate the concentration scale. The relative error of the analysis of each element is shown as a circle, whose radius is proportional to that error, around the point plotted for each parent rock; the proportional effect of this error varies slightly for each other analysis point, depending on its actual value (radius of circle = R.E./100 x concentration). A similar plot of the leach data for Suites G, K, and S is presented in Figure 10. The analyses of Suite N include only total bulk soil and parent rock samples.

All concentrations (in percent for major elements and ppm for minor elements) are reported on an anhydrous and carbon-free basis. The effect of omitting the major constituent H_2O does not distort the calculations of other element concentrations because 1) water and volatiles are largely removed by pre-arcing heating and 2) the mutual standard method of calculation, by the use of ratios (to Al) and summation of all concentrations arbitrarily to 100, removes the "dilution" effect of water, organic matter, etc. The concentrations as reported in this thesis do not compare directly with most soil analyses which show percentages of all constituents computed on the basis of inclusion of water and often organic matter.

TABLE 11 A

Spectrochemical Analyses of Suite G

	G-1				G-2					G-3			G-4					G-9
Element	TBS	Silt	Clay	Leach	TBS	Sand	Silt	Clay	Leach	TBS	Silt	Clay	TBS	Sand	Silt	Clay	Leach	Parent
%																		
SiO_2	59.81	56.30	70.35	2510	60.16	64.26	57.20	72.67	2605	64.28	59.95	74.67	57.79	58.86	64.00	72.68	1678	50.56
Al_2O_3	16.65	18.53	10.60	686	19.80	15.23	15.70	10.45	504	14.45	17.72	9.17	15.75	12.48	17.02	10.46	561	14.14
Fe_2O_3	11.27	12.49	10.04	53	9.85	10.69	12.60	9.63	352	9.87	9.22	8.68	10.73	13.97	5.70	8.95	40	8.95
MgO	2.08	2.11	2.86	3290	2.11	3.75	2.56	2.58	3390	2.55	2.00	2.80	3.09	2.59	1.22	3.25	2380	4.70
CaO	4.29	7.13	1.47	5705	3.09	2.71	6.91	1.47	10590	4.54	5.85	1.48	5.58	4.17	3.40	1.37	8900	11.00
K_2O	3.07	0.91	2.65	571	2.70	2.32	1.21	1.68	955	2.02	1.59	1.35	3.88	3.06	3.08	1.56	455	5.45
Na_2O	1.37	1.07	0.53	1533	1.22	1.26	1.82	0.49	1132	1.00	2.30	0.60	2.02	2.07	4.34	0.61	1343	4.01
TiO_2	1.27	1.15	1.07	n.d.	0.92	0.72	1.49	1.00	n.d.	0.85	1.19	0.98	1.08	0.80	0.75	0.68	n.d.	0.85
Ppm																		
Ba	1470	686	821	58	963	1145	910	413	68	1280	1062	421	1370	1050	1426	527	63	1453
Co	9	40	22	0.11	8	13	47	16	0.06	17	36	14	19	25	11	13	0.09	23
Cr	20	18	27	0.36	14	20	30	23	0.23	24	27	23	24	35	10	28	0.14	95
Cu	53	22	83	0.83	50	118	23	56	2.84	58	29	60	65	104	5	85	1.15	83
Ga	13	25	16	n.d.	18	11	26	15	n.d.	12	25	12	14	14	26	13	n.d.	11
Mn	1260	870	1760	24	750	1236	880	1250	31	1150	177	1320	1495	1522	205	1430	25	1505
Ni	10	1	16	0.70	6	15	2	15	0.59	9	2	14	16	15	2	19	0.48	6
Pb	24	7	240	0.24	14	8	9	40	n.d.	n.d.	7	32	12	11	5	29	n.d.	10
Sc	28	27	30	n.d.	29	6	24	33	n.d.	25	18	30	26	21	6	29	n.d.	12
Sr	445	290	181	15	408	170	418	88	17	480	461	158	540	393	902	192	16	408
V	218	237	108	0.36	174	128	276	97	0.29	185	143	110	218	195	112	94	0.34	159
Zn	n.d.	n.d.	123	n.d.	n.d.	n.d.	n.d.	124	n.d.	n.d.	n.d.	103	n.d.	n.d.	n.d.	83	n.d.	n.d.
Zr	411	435	214	n.d.	453	135	630	197	n.d.	363	575	180	518	138	425	152	n.d.	552

TABLE 11 B

Spectrochemical Analyses of Suite K

	K-1				K-2				K-3				K-4			K-5					K-6
Element	TBS	Silt	Clay	Leach	TBS	Sand	Silt	Clay	TBS	Silt	Clay	Leach	TBS	Silt	Clay	TBS	Sand	Silt	Clay	Leach	Parent
%																					
SiO_2	74.82	81.83	71.86	281	72.19	72.50	79.53	71.53	70.83	75.65	69.93	242	70.58	71.07	68.86	67.45	68.73	71.44	71.26	80	67.16
Al_2O_3	13.81	10.43	13.56	685	14.38	13.19	10.97	13.74	15.22	11.91	15.44	1790	15.40	12.30	15.53	18.11	12.58	11.95	15.99	503	13.60
Fe_2O_3	3.79	3.49	8.27	44	4.36	7.24	4.24	8.91	4.89	4.48	8.69	32	4.05	6.64	8.54	3.68	8.80	6.44	6.80	15	3.68
MgO	1.03	1.57	2.14	440	1.37	1.70	1.84	2.04	1.42	2.02	2.19	320	0.92	2.83	2.76	1.39	2.64	3.21	2.24	161	1.01
CaO	0.90	0.40	0.39	2375	0.89	0.80	0.45	0.63	0.68	1.10	0.41	1070	0.86	1.57	0.75	1.63	1.77	2.01	0.48	531	2.21
K_2O	2.71	1.33	2.73	1540	3.33	1.59	1.34	2.31	3.21	2.71	2.18	191	3.40	2.50	2.71	3.36	1.79	1.66	2.35	27	6.38
Na_2O	1.70	0.79	0.38	428	2.14	2.20	0.82	0.37	2.63	1.40	0.40	179	3.04	1.83	0.39	3.08	2.77	1.67	0.37	75	4.11
TiO_2	0.59	0.48	0.42	n.d.	0.62	0.46	0.61	0.50	0.54	0.74	0.73	n.d.	0.42	0.91	0.59	0.53	0.66	0.95	0.50	n.d.	0.52
Ba Ppm	1788	935	785	37	1916	860	900	680	2612	1005	526	73	2638	1578	592	2930	1150	2250	648	14	3015
Co	7	7	6	0.5	7	5	11	7	6	8	4	0.03	4	10	5	5	9	13	6	0.02	3
Cr	24	47	61	0.3	26	11	58	55	10	46	42	0.15	9	26	38	10	2	46	37	0.03	10
Cu	18	26	19	1.0	12	60	17	19	8	23	22	0.35	5	44	21	11	39	220	53	0.11	7
Ga	18	8	35	n.d.	19	12	9	31	19	15	37	n.d.	16	29	54	21	18	30	30	n.d.	17
Mn	578	404	545	13	543	629	566	475	450	435	355	5	432	942	400	394	930	1170	423	2	702
Ni	15	28	31	0.4	14	22	28	54	12	49	15	0.16	5	24	35	7	15	33	15	0.07	2
Pb	22	15	60	n.d.	15	9	14	47	18	25	53	n.d.	18	27	61	20	12	21	44	n.d.	12
Sc	8	10	n.d.	n.d.	9	6	13	n.d.	7	18	n.d.	n.d.	7	20	n.d.	7	8	23	n.d.	n.d.	2
Sr	214	166	30	3.7	254	184	134	37	397	253	39	1.4	403	304	46	529	217	323	51	0.8	690
V	73	45	133	n.d.	73	57	57	152	108	88	185	0.08	95	196	254	102	95	176	102	0.03	57
Zn	66	86	109	n.d.	73	n.d.	98	108	80	213	n.d.	n.d.	72	n.d.	n.d.	77	n.d.	n.d.	n.d.	n.d.	n.d.
Zr	980	364	188	0.15	1108	300	474	210	1170	1058	262	0.10	692	1032	299	594	322	1210	252	n.d.	309

TABLE 11 C

Suite N - Total Bulk Sample

Element	N-1	N-2	N-3	N-4	N-6	N-9
SiO_2	84.45	83.55	83.40	83.50	82.00	80.00
Al_2O_3	8.98	9.35	10.22	10.15	10.31	11.50
Fe_2O_3	1.72	2.01	3.09	3.66	3.28	1.82
MgO	0.16	0.33	0.56	0.82	0.26	0.03
CaO	tr	0.09	0.07	0.06	0.04	0.60
K_2O	2.42	2.22	1.27	0.93	1.98	2.32
Na_2O	1.62	1.62	0.86	0.45	1.63	3.69
TiO_2	0.42	0.58	0.37	0.45	0.42	tr
Ba	322	585	572	578	330	435
Co	5	5	8	8	n.d.	n.d.
Cr	89	34	58	57	24	n.d.
Cu	17	17	18	19	11	8
Ga	14	17	16	11	12	17
Mn	20	28	53	122	36	3
Ni	24	27	27	14	9	10
Pb	9	10	12	13	9	7
Sc	4	7	8	9	6	n.d.
Sr	40	54	48	56	32	25
V	30	48	47	60	45	n.d.
Zr	331	704	420	377	316	92
	99.88	99.90	100.07	100.15	100.00	100.01

TABLE 11 D

Spectrochemical Analyses of Suite S

			S-1				S-2			S-3				S-4								
Element	TBS	Sand	Silt	Clay	Leach	TBS	Silt	Clay	TBS	Silt	Clay	Leach	TBS	Sand	Silt	Clay	TBS	Silt	Clay	Leach	S- Nodule	S- Parent
%																						
SiO_2	67.20	75.45	84.90	72.25	396	64.65	82.20	62.20	59.90	67.00	55.55	1330	56.50	67.15	51.05	50.45	55.10	59.00	49.00	892	59.80	49.10
Al_2O_3	13.48	11.85	8.48	17.50	773	14.78	9.84	21.60	18.12	15.55	24.78	296	19.51	12.31	23.80	29.50	20.42	20.60	27.70	262	14.20	20.23
Fe_2O_3	15.10	9.61	4.54	6.56	62	16.60	5.90	11.44	18.11	14.60	14.10	182	19.13	15.74	21.20	15.00	15.55	13.40	15.80	72	19.90	15.75
MgO	0.92	0.29	0.28	0.49	680	0.65	0.32	0.70	0.80	0.61	0.89	1440	1.27	1.35	0.90	1.38	2.86	1.19	3.25	4160	1.65	5.57
CaO	0.32	0.30	0.74	0.24	1028	0.30	0.44	0.38	0.16	0.26	0.45	899	0.14	0.17	0.36	0.31	2.74	3.30	1.02	2160	0.19	4.90
K_2O	0.74	1.07	0.44	0.62	154	1.01	0.48	0.65	1.07	1.00	0.77	183	1.04	1.87	1.05	0.97	1.24	1.26	1.27	180	1.61	1.70
Na_2O	0.38	0.48	0.15	0.39	316	0.22	0.16	0.30	0.25	0.28	0.37	336	0.47	0.46	0.40	0.41	0.69	0.60	0.47	1138	0.60	1.15
TiO_2	1.21	0.42	0.33	1.61	n.d.	1.33	0.51	2.44	1.38	0.79	2.98	n.d.	1.43	0.50	0.76	1.88	0.96	0.62	1.57	n.d.	1.72	1.03
Ppm																						
Ba	455	295	490	170	26	575	488	145	486	525	129	33	406	363	332	83	511	495	185	29	636	282
Co	164	50	34	50	2.9	171	60	78	168	53	58	1.9	56	19	67	54	39	48	85	0.2	706	43
Cr	226	131	29	23	0.09	221	30	51	177	68	58	0.06	152	81	94	66	110	144	72	0.1	65	127
Cu	126	126	36	50	2.4	153	61	78	170	112	58	1.9	138	221	160	54	203	206	85	2.1	193	29
Ga	8	6	4	2	0.01	11	5	9	13	14	13	n.d.	14	n.d.	24	14	18	23	4	0.03	9	24
Mn	2570	712	2125	910	9.5	2720	2920	1030	3040	2940	620	11.1	1210	1168	2640	239	735	1910	1450	14.2	8200	2450
Ni	7	25	2	5	0.6	9	4	7	7	5	9	0.3	22	6	6	7	6	7	9	0.9	16	10
Pb	14	11	7	8	0.06	15	8	6	12	8	6	0.06	8	5	11	5	5	8	n.d.	0.05	32	n.d.
Sc	14	10	8	14	0.07	12	9	18	19	14	21	0.5	53	25	24	28	53	23	34	0.6	47	45
Sr	67	74	196	66	0.8	60	146	57	60	119	63	0.9	93	61	157	48	266	866	133	3.0	19	330
V	432	142	145	194	0.04	504	166	350	520	387	420	0.04	414	174	470	386	338	101	243	0.14	240	253
Zn	129	n.d.	162	200	n.d.	149	146	216	112	185	190	n.d.	90	n.d.	169	170	88	n.d.	94	n.d.	n.d.	n.d.
Zr	407	110	510	438	0.31	400	530	443	383	695	384	0.13	137	54	357	230	48	134	158	n.d.	13	20

FIGURE 6

GRAPHIC PRESENTATION OF SPECTROCHEMICAL ANALYSES OF SUITE G

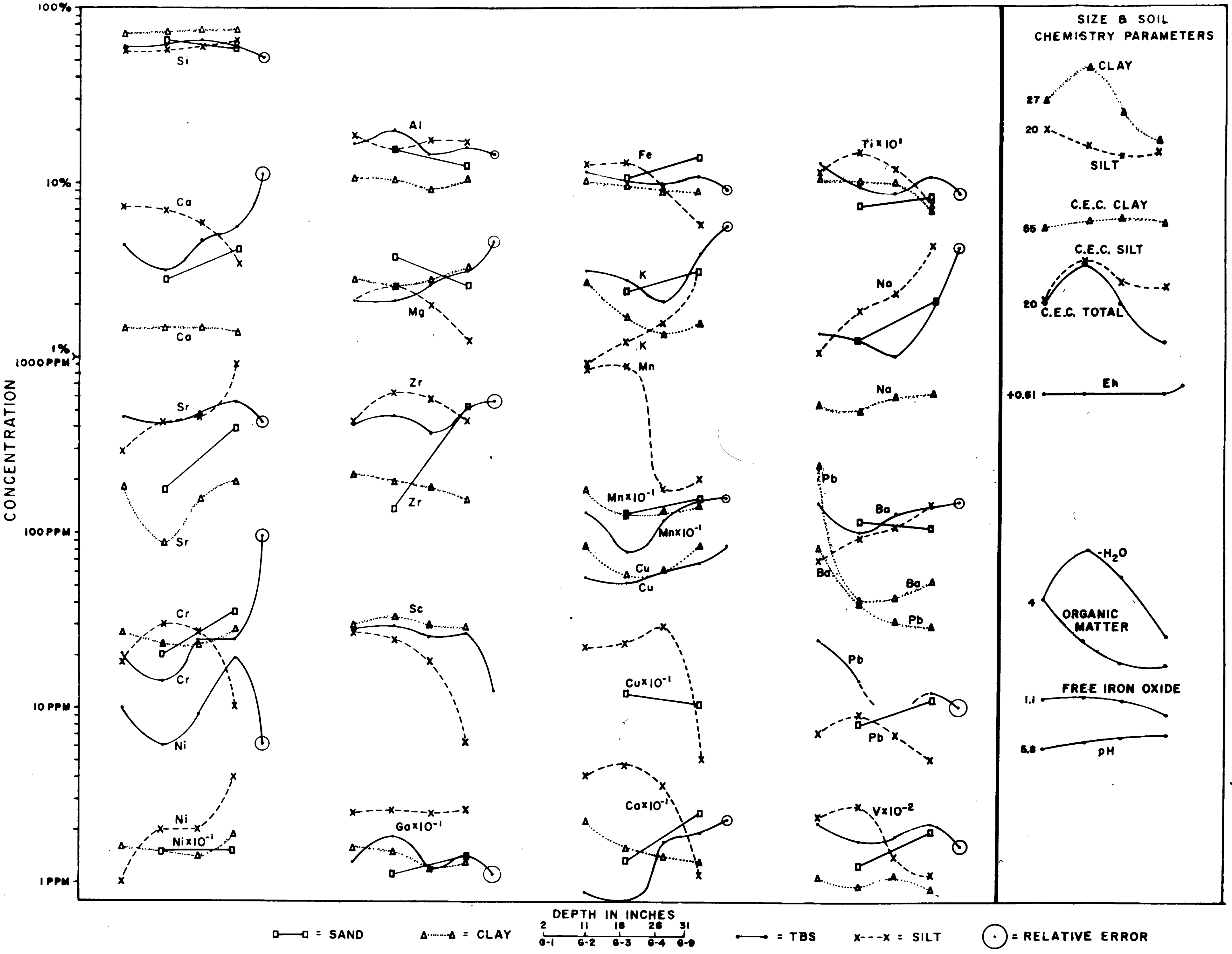


FIGURE 7

GRAPHIC PRESENTATION OF SPECTROCHEMICAL ANALYSES OF SUITE K

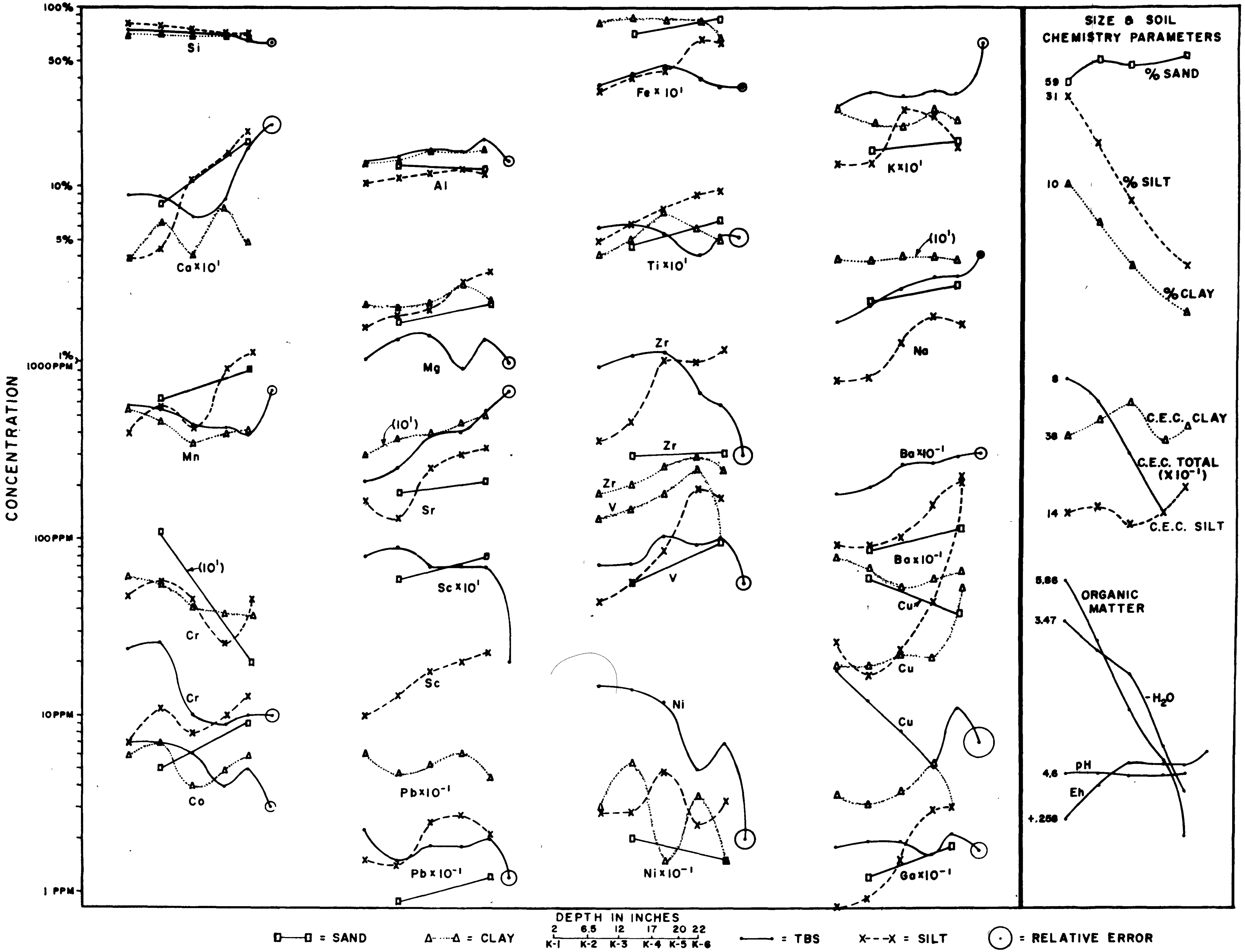


FIGURE 8

GRAPHIC PRESENTATION OF SPECTROCHEMICAL ANALYSES OF SUITE N

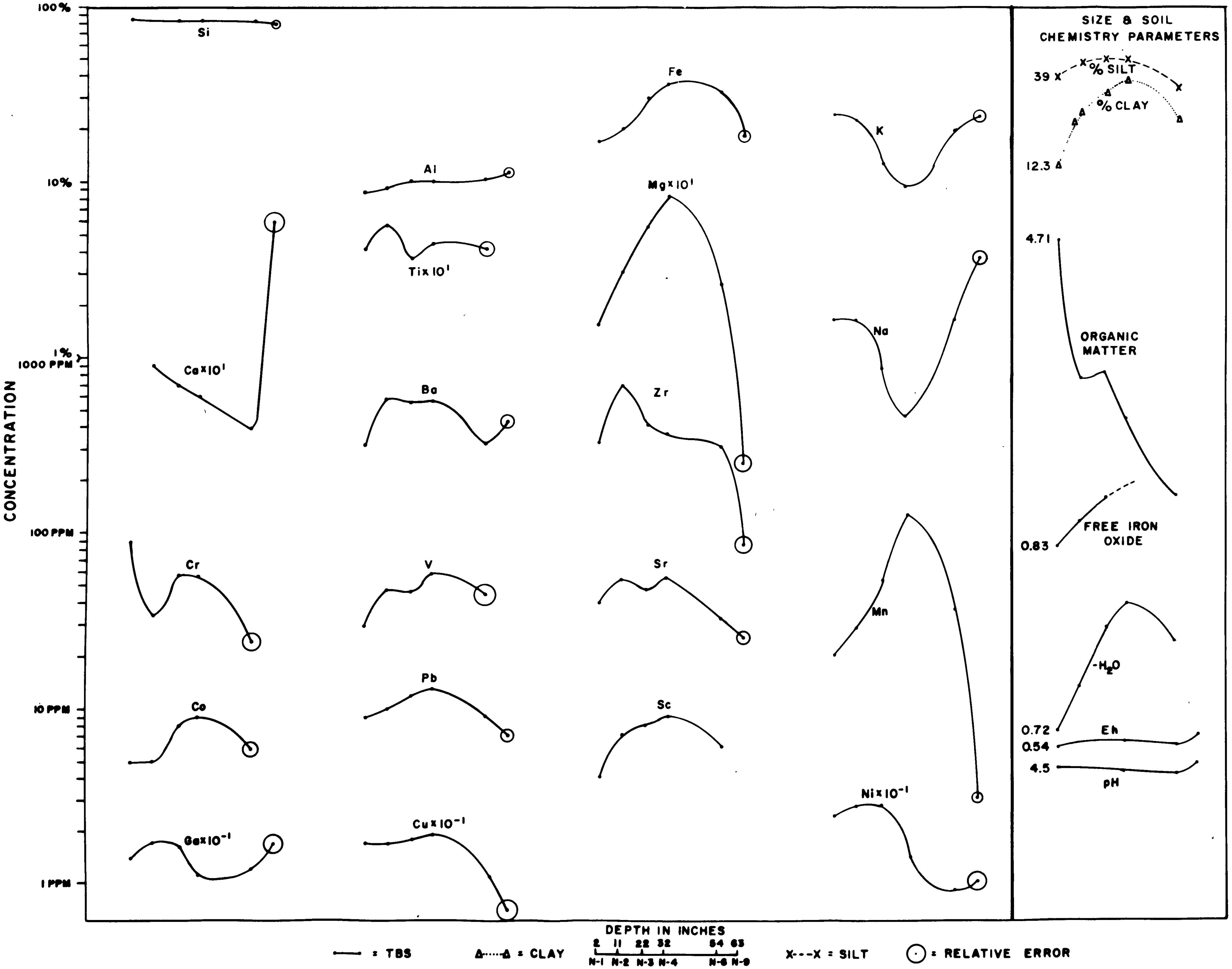


FIGURE 9

GRAPHIC PRESENTATION OF SPECTROCHEMICAL ANALYSES OF SUITE S

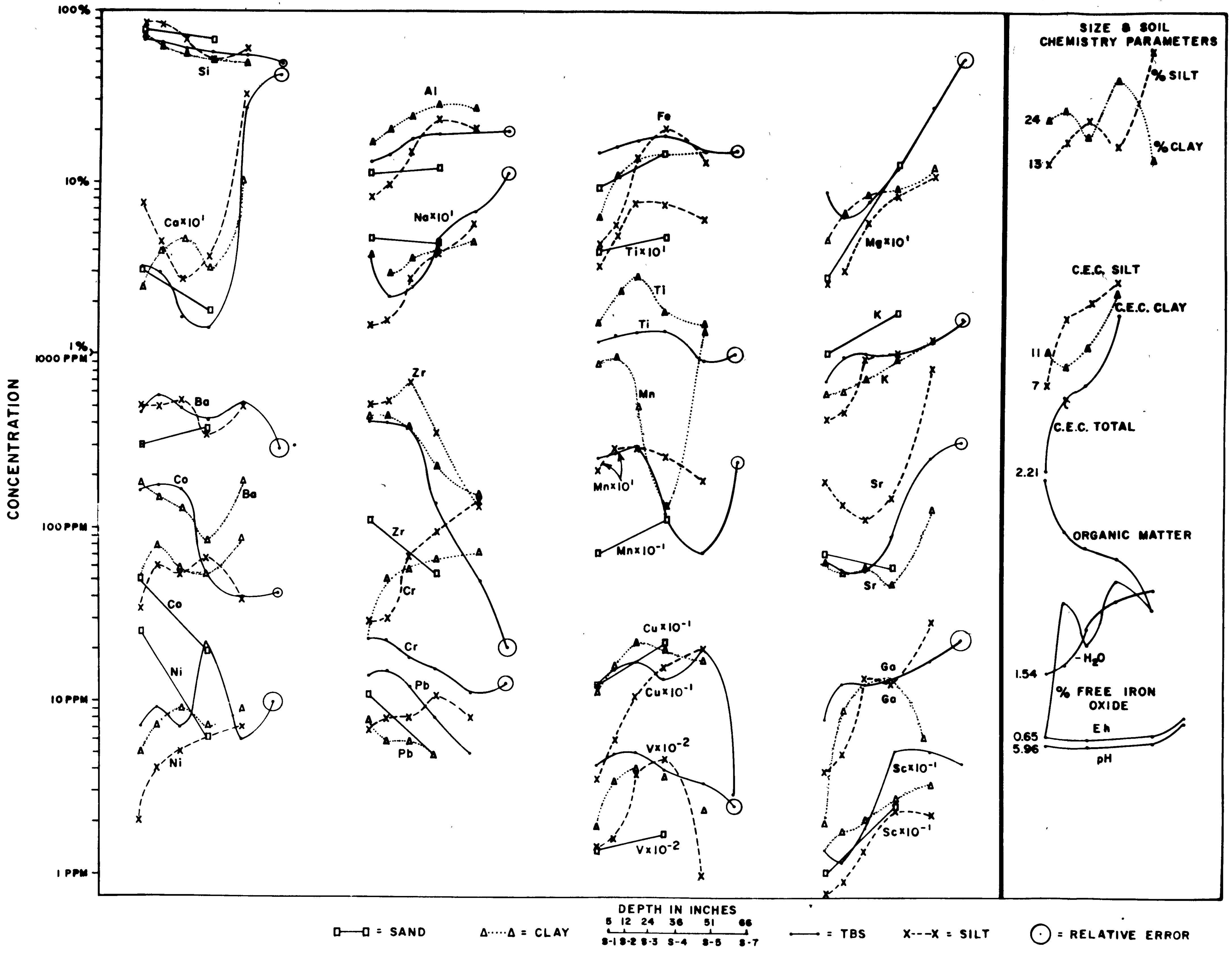
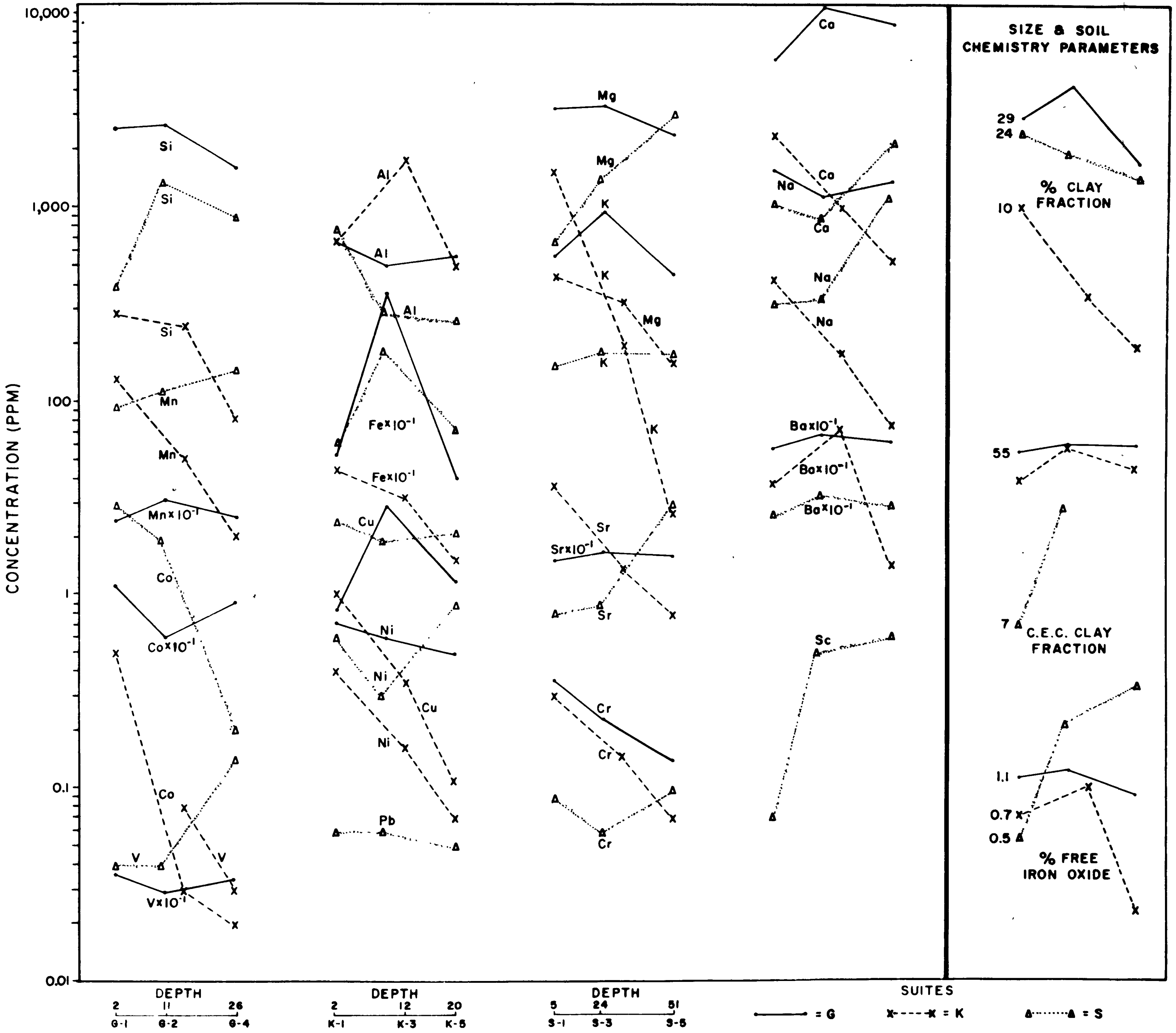


FIGURE 10

GRAPHIC PRESENTATION OF SPECTROCHEMICAL ANALYSES OF ACETIC ACID LEACHATES



INTERPRETATION OF DATA

I. Introduction:

The data presented in Tables 11 A-D and in Figures 6-10 can be treated in many ways to provide additional information on the geochemical behavior of major and minor elements during weathering. In the first part of this section, the methods and results of analyzing the data, both through treatments previously developed by other workers and through new treatments devised by the writer, are explained and presented. In the rest of this section, the raw spectrochemical data and the various analytical treatments are specifically interpreted in terms of 1) a summary of certain element behavior characteristics common to all four soils, 2) the pattern of major and minor element behavior in each soil suite, and 3) a comparison of individual element behavior in these soils to the behavior expected on the basis of other reported investigations and of geochemical principles of occurrence and distribution. In each case, the behavior is also related to size, mineralogy, and soil chemistry variables whenever possible.

II. Methods of Interpretation:

A. Absolute Chemical Changes and Relative Gains and Losses:

On page 71 it was pointed out that the mutual standard method of calculations permits direct comparison of the chemical changes between various samples by eliminating the effects of variable water, organic matter, etc. on the total percentage of elements reported. Changes within a series of related samples are therefore expressed in terms of varying proportions of a fixed number of composition variables which always add to 100.

When the chemical changes from parent rock to soil are considered with respect to the volumes occupied by the materials involved, the results of the spectrochemical analyses are clearly relative rather than absolute values. In the weathering of rock to soil, constituents are added or lost and total volumes and mineral densities are changed. The absolute gain or loss of any constituent relative to its original amount in the parent rock can be specified only if the volume of soil equivalent to the same volume of parent rock is known and the total mass of each constituent element in each volume is accurately determined.

The distinction between relative and absolute concentrations can be illustrated by a simple hypothetical example. Let a 1:1:1 by volume mixture of salt, anhydrite, and quartz be subjected to the action of water. Let it further be assumed that the water then completely dissolves the salt and additional water reacts with the anhydrite to form gypsum. In response to the volume reduction by removal of salt, the apparent increase in the calcium sulphate and SiO_2 phases goes from 33% to 50% for each (if water is not analyzed for) even though their absolute amounts have not changed. However, the increase, if measured with respect to volume, will not be 1:1 for these two phases, because the anhydrite will also have changed its volume in conversion to gypsum.

In a more complex way, similar changes affect rock transformations to soil. Absolute changes cannot be determined unless 1) equivalent volumes are known and 2) the effects of gains or losses of material on the proportions of remaining constituents (always reported as percentages totaling 100%) can be removed or corrected for.

The effect of volume changes can be determined by an involved set of calculations (Barshad, Chemistry of the Soil, 1955, pp. 17-20) requiring the use of bulk density and clay translocation data. Because sample volumes were not measured in the field, bulk densities could not be determined; hence, this correction cannot be applied to the thesis samples.

The effect of relative gains or losses, when volume corrections are not made, can be largely removed by the method described by Goldich (1938) and others. This method also tends to compensate for volume changes as well. The method assumes that one element remains constant during the course of weathering. Aluminum oxide is chosen as most likely to fulfill this condition. Any change, say an increase from 15% to 20% in Al_2O_3, represents therefore the effects both of its apparent enrichment relative to constituents removed from the system and of volume changes (which usually oppose the apparent enrichment effect). A correction factor $= \frac{Al_2O_3 \text{ in original rock}}{Al_2O_3 \text{ in any weathered horizon}}$ is applied by multiplication to all other constituents to reduce the effects of the relative changes. The sum of all the corrected concentrations, when compared to the original 100% represents the apparent total gain or loss of all constituents. The percentage net gain or loss of any constituent relative to the parent is the difference between the corrected concentration of that constituent and its concentration in the original rock divided by this original concentration, times 100 (see Pettijohn, 1949, pp. 377-79, for further details). For simplicity, the original 100% can be imagined to be equivalent to 100 grams of parent material; the corrected concentrations are then considered to be the amount of grams of each constituent remaining after weathering in any sampled horizon.

Such a correction has been applied to the raw analysis data for the TBS samples. The new concentrations relative to constant Al_2O_3 are shown in Tables 12 A-D. The percentage net change is recorded in parenthesis next to each new concentration. A more exact picture of changes would have resulted if data for $-H_2O$ and several other constituents had been available for inclusion in the calculations. However, comparison of the Table 12 values to the original TBS values shows that this correction has brought about a more regular pattern of change and has emphasized the magnitude of some depletions or enrichments.

It is also possible to compute an average net change for the total soil relative to the parent rock composition. Because at least part of the gained or lost element concentrations in a given horizon do not actually correspond to introduction or complete removal from the soil system but represent redistributions from elsewhere in the profile, an averaged total percent gains or losses for each element will tend to reduce some of the extreme variations noted in some samples. This average will therefore reflect more closely the gross changes in weathering from parent rock to a soil, irrespective of spatial redistribution of the elements in the chemically "stratified" profile. The average net change for each element has been calculated by taking the algebraic sum of its weighted (according to the interval thickness for which each sample is representative, expressed as its fraction of the total profile thickness) percentage gain or loss for all samples in a profile. The results are shown in the appropriate columns in Table 13. The percentage gain or loss of each element in the individual samples and for the average net change have been plotted in diagrams similar to those of Goldich (1938).

TABLE 12 A

Concentrations Relative to Constant Al_2O_3

Suite G

	G-1		G-2		G-3		G-4		G-7
	%	% N.C.	%	% N.C.	%	% N.C.	%	% N.C.	%
SiO_2	50.79	(+0.45)	42.64	(-15.7)	62.90	(+24.4)	51.88	(+2.61)	50.56
Fe_2O_3	9.57	(+6.92	7.58	(-15.3)	9.66	(+7.93)	9.63	(+7.60)	8.95
MgO	1.77	(-62.3)	1.50	(-68.1)	2.50	(-46.8)	2.77	(-41.1)	4.70
CaO	3.64	(-66.9)	2.19	(-80.1)	4.44	(-59.6)	5.01	(-54.4)	11.00
K_2O	2.61	(-52.1)	1.91	(-64.9)	1.98	(-63.7)	3.48	(-36.1)	5.45
Na_2O	1.16	(-71.1)	0.86	(-78.5)	0.98	(-75.6)	1.81	(-54.9)	4.01
TiO_2	1.08	(+27.1)	0.65	(-23.5)	0.83	(-2.35)	0.97	(+14.1)	0.85
	PPM		PPM		PPM		PPM		PPM
Ba	1248	(-14.1)	683	(-53.0)	1252	(-13.8)	1230	(-15.4)	1453
Co	8	(-65.2)	6	(-73.9)	17	(-21.7)	17	(-21.7)	23
Cr	17	(-82.1)	10	(-89.5)	23	(-75.8)	22	(-76.8)	95
Ga	11	(0)	13	(+18.2)	12	(+9.09)	13	(+18.2)	11
Mn	1070	(-28.9)	532	(-64.6)	1125	(-25.2)	1342	(-4.19)	1505
Ni	8	(+33.3)	4	(-33.3)	9	(+50.0)	14	(+133)	6
Pb	20	(+100)	10	(+70.0)	-		11	(+10.0)	10
Sc	24	(+100)	21	(+75.0)	24	(+100)	23	(+91.7)	12
Sr	378	(-7.35)	289	(-29.2)	470	(+15.2)	485	(+18.9)	408
V	185	(+16.3)	123	(-20.7)	181	(+13.8)	195	(+22.6)	159
Zr	349	(-37.8)	321	(-41.8)	355	(-35.7)	465	(-15.8)	552

% N.C. = Percent Net Change

TABLE 12 B

Concentrations Relative to Constant Al_2O_3

Suite K

	K-1		K-2		K-3		K-4		K-5		K-7
	%	% N.C.	%	% N.C.	%	% N.C.	%	% N.C.	%	% N.C.	%
SiO_2	73.68	(+9.71)	68.28	(+1.67)	63.01	(-6.18)	62.33	(-8.71)	50.65	(-24.6)	67.16
Fe_2O_3	3.73	(+1.36)	4.14	(+12.5)	4.37	(+18.7)	3.58	(-2.71)	2.76	(-25.0)	3.68
MgO	1.01	(0)	1.30	(-28.7)	1.27	(+25.7)	0.81	(-19.8)	1.04	(+2.97)	1.01
CaO	0.89	(-59.7)	0.84	(-62.0)	0.61	(-72.4)	0.76	(-65.6)	1.22	(-44.8)	2.21
K_2O	2.67	(-58.1)	3.15	(-49.8)	2.87	(-55.0)	3.00	(-53.0)	2.52	(-60.1)	6.38
Na_2O	1.67	(-59.4)	2.02	(-50.8)	2.35	(-42.8)	2.68	(-34.8)	2.31	(-43.8)	4.11
TiO_2	0.58	(+11.5)	0.59	(+12.1)	0.48	(-6.90)	0.37	(-25.9)	0.40	(-20.7)	0.52
	PPM		PPM		PPM		PPM		PPM		PPM
Ba	1761	(-41.6)	1812	(-39.9)	2336	(-22.7)	2330	(-22.9)	2200	(-27.0)	3015
Co	7	(+133)	7	(+133)	5	(+66.6)	4	(+33.3)	4	(+33.3)	3
Cr	24	(+140)	25	(+150)	9	(-10.0)	8	(-20.0)	8	(-20.0)	10
Cu	18	(+157)	11	(+57.1)	7	(0)	4	(-42.9)	8	(+14.3)	7
Ga	18	(+5.88)	18	(+5.88)	17	(0)	14	(-17.6)	16	(-5.88)	17
Mn	569	(-18.9)	514	(-26.8)	402	(-42.7)	381	(-45.7)	296	(-57.8)	702
Ni	15	(+650)	13	(+550)	11	(+450)	4	(+100)	5	(+150)	2
Pb	20	(+66.6)	14	(+16.7)	16	(+33.3)	16	(+33.3)	15	(+25.0)	12
Sc	8	(+300)	9	(+350)	6	(+200)	6	(+200)	5	(+150)	2
Sr	211	(-69.4)	240	(-65.2)	355	(-48.6)	356	(-48.4)	397	(-42.5)	690
V	72	(+26.3)	69	(+21.0)	96	(+68.4)	84	(+47.4)	76	(+33.3)	57
Zr	965	(+212)	1048	(+239)	1045	(+238)	611	(+97.7)	446	(+44.3)	309

% N.C. = Percent Net Change

TABLE 12 C

Concentrations Relative to Constant Al_2O_3

Suite N

	N-1		N-2		N-3		N-4		N-6		N-9
	%	% N.C.	%	% N.C.	%	% N.C.	%	% N.C.	%	% N.C.	%
SiO_2	108.2	(+35.2)	102.2	(+27.7)	93.82	(+17.3)	94.60	(+18.2)	91.43	(+14.3)	80.00
Fe_2O_3	2.20	(+20.9)	2.46	(+35.2)	3.48	(+90.1)	4.15	(+128)	3.66	(+101)	1.82
MgO	0.20	(+567)	0.40	(+1233)	0.63	(+2000)	0.93	(+3000)	0.29	(+867)	0.03
CaO	-		0.11	(-81.7)	0.08	(-86.7)	0.07	(-88.3)	0.04	(-93.3)	0.60
K_2O	3.10	(+33.6)	2.72	(+14.7)	1.43	(-38.4)	1.05	(-54.7)	2.21	(-4.74)	2.32
Na_2O	2.08	(-43.6)	1.98	(-46.3)	0.97	(-73.7)	0.51	(-86.2)	1.82	(-50.7)	3.69
TiO_2	0.54		0.71		0.42		0.41		0.47		-
	PPM		PPM		PPM		PPM		PPM		PPM
Ba	412	(-5.29)	715	(+64.4)	643	(+47.6)	655	(+50.6)	368	(-15.4)	435
Co	6		6		9		9		-		-
Cr	114		42		65		65		27		-
Cu	22	(+175)	21	(+162)	20	(+150)	22	(+175)	12	(+50.0)	8
Ga	18	(+5.88)	21	(+23.5)	18	(+5.88)	12	(-29.4)	13	(-23.5)	17
Mn	26	(+767)	34	(+1053)	60	(+1900)	138	(+4500)	40	(+1233)	3
Pb	12	(+71.4)	12	(+71.4)	13	(+85.7)	15	(+114)	10	(+42.9)	7
Sc	5		9		9		10		7		-
Sr	51	(+104)	66	(+164)	54	(+116)	63	(+152)	36	(+44.0)	25
V	38		59		53		68		50		-
Zr	424	(+353)	860	(+835)	472	(+391)	427	(+364)	352	(+283)	92
Ni	31	(+210)	33	(+230)	30	(+200)	16	(+60.0)	10	(0)	10

% N.C. = Percent Net Change

TABLE 12 D

Concentrations Relative to Constant Al_2O_3

Suite S

	S-1		S-2		S-3		S-4		S-5		S-7
	%	% N.C.	%	% N.C.	%	% N.C.	%	% N.C.	%	% N.C.	%
SiO_2	100.6	(+105)	88.51	(+80.3)	66.85	(+36.1)	58.59	(+19.3)	54.60	(+11.2)	49.10
Fe_2O_3	22.67	(+43.9)	22.73	(+44.3)	20.21	(+28.3)	16.32	(+3.62)	15.41	(-2.16)	15.75
MgO	1.38	(-75.2)	0.89	(-84.0)	0.89	(-84.0)	1.32	(-76.3)	2.83	(-49.2)	5.57
CaO	0.48	(-90.2)	0.41	(-91.6)	0.18	(-96.3)	0.15	(-96.9)	2.72	(-44.5)	4.90
K_2O	1.11	(-34.7)	1.38	(-18.8)	1.19	(-30.0)	1.08	(-36.5)	1.23	(-27.6)	1.70
Na_2O	0.57	(-50.4)	0.30	(-73.9)	0.28	(-75.6)	0.49	(-57.4)	0.68	(-40.9)	1.15
TiO_2	1.82	(+76.7)	1.82	(+76.7)	1.54	(+49.5)	1.48	(+43.7)	1.95	(+89.3)	1.03
	PPM		PPM		PPM		PPM		PPM		PPM
Ba	683	(+142)	787	(+179)	542	(+92.2)	421	(+84.7)	506	(+79.4)	282
Co	246	(+472)	234	(+444)	187	(+335)	58	(+32.6)	39	(-9.30)	43
Cr	339	(+164)	303	(+138)	198	(+55.9)	158	(+24.4)	109	(-14.2)	127
Cu	189	(+552)	209	(+621)	190	(+555)	143	(+393)	201	(+593)	29
Ga	12	(-50.0)	15	(-37.5)	15	(-37.5)	15	(-37.5)	18	(-25.0)	24
Mn	3857	(+57.4)	3724	(+56.1)	3392	(+38.4)	1255	(-48.8)	728	(-70.3)	2450
Ni	11	(+10.0)	12	(+20.0)	8	(-20.0)	23	(+130)	6	(-40.0)	10
Pb	21		21		14		8		5		-
Sc	21	(-53.3)	16	(-65.4)	21	(-53.3)	55	(+22.2)	53	(+17.8)	45
Sr	101	(-69.4)	82	(-75.1)	67	(-79.7)	96	(-70.9)	264	(-20.0)	330
V	648	(+156)	690	(+173)	580	(+129)	429	(+70.0)	335	(+32.4)	253
Zn	194		204		125		93		87		-
Zr	611	(+2950)	547	(+2635)	427	(+2075)	142	(+610)	48	(+140)	20

% N.C. = Percent Net Change

TABLE 13

Average Net Change For Total Soil

	Suite G %	Suite K %	Suite N %	Suite S %
SiO_2	+ 4.51	- 5.81	+ 21.00	+ 42.54
Fe_2O_3	+ 3.83	+ 1.77	+ 85.00	+ 19.56
MgO	- 58.42	+ 11.23	+1751.0	- 73.62
CaO	- 63.29	- 60.62	- 78.05	- 84.36
K_2O	- 52.10	- 55.08	- 17.60	- 30.17
Na_2O	- 68.38	- 46.88	- 64.79	- 59.64
TiO_2	+ 7.12	- 4.36	+	+ 63.89
Ba	- 20.66	- 31.41	+ 33.90	+108.69
Co	- 42.22	+ 83.26	+	+211.84
Cr	- 65.98	+ 53.60	+	+ 61.04
Cu	+	+ 39.83	+151.60	+524.91
Ga	+ 10.82	- 1.05	- 7.32	- 36.64
Mn	- 36.84	- 38.28	+2242.0	- 4.51
Ni	+ 57.79	+358.22	+123.15	+ 31.70
Pb	+ 31.13	+ 32.74	+ 80.85	+
Sc	+ 93.45	+245.20	+	+ 13.55
Sr	+ 2.68	- 55.18	+127.14	- 63.03
V	+ 11.88	+ 38.50	+	+103.17
Zr	- 31.10	+173.46	+445.00	+1458.0

B. Distribution and Concentration Indices:

Connor, Shimp, and Teddrow (1957) have established and defined the concepts of distribution ratio and concentration ratio as applied to soils. In their definition the *distribution ratio* is "obtained by dividing the amount of each element in the A horizon of any soil by that in the C horizon". The concentration ratio is found by "dividing the amount of element in the clay fraction of the A or B horizon by that in the entire soil of the C horizon".

To avoid confusion with these terms, the analogous terms Distribution Index (D.I.) and Concentration Index (C.I.) are introduced and defined as follows:

Distribution Index: the ratio of an element amount in a specified soil horizon to the amount in the parent rock.

Concentration Index: the ratio of an element amount in any size fraction (gravel, sand, silt, or clay) in a specified horizon to the amount in the total bulk soil of that horizon.

A D.I. or C.I. value greater than 1 implies a relative enrichment whereas a value less than 1 indicates a depletion.

If C.I. values for all size fractions obtained from the total bulk sample are determined, the weighted (percentage of each size fraction expressed as a decimal) values of each fraction when summed should equal 1.000. Thus, ideally, if all C.I. values are known with perfect accuracy, a total bulk sample fractionated into sand (30%, C.I. = 0.4), silt (40%, C.I. = 0.7), and clay (30%, C.I. = 2.0) would produce a sum as follows:

$$.3(0.4) + .4(0.7)m + .3(2.0) = 1(1.0)$$

A departure from 1.000 would indicate an error which can be due to many, often undetermined, causes.

D.I. and C.I. values for Suites G, K, N, and S are presented in Tables 14 A-D on the following pages. The general character of the C.I. and D.I. changes throughout each soil profile has been illustrated by a set of descriptive symbols (Figure 11). The symbols used and their meanings are presented on page 96.

Examination of the data shows that, for some of the elements in each suite, the summed C.I. values are nearly always less than or greater than 1.000. This seemingly implies a large error in the spectrochemical data and/or in the assumptions used in calculating the indices. Deviations from 1.0 as low as 0.3 and as high as 3.0-4.0 in these sums would seem to cast strong doubt on the validity and usefulness of the results.

When the analysis program was planned, it was concluded that the gravel fraction (which often comprised 20-40%) would have, because it is much less weathered, little influence on the overall geochemical variations. It was therefore omitted in the spectrochemical analysis program.

After the C.I. values were computed, it was found that inclusion of (weighted[1]) gravel values in many cases produced sums much closer to 1.000. Because no actual gravel samples were analyzed spectrographically, an estimate of their composition had to be made by this reasoning:

Let it be assumed that the residual gravel fraction is composed largely of unweathered rock fragments very similar to the parent rock. For any horizon sample, the reciprocal of the D.I. value = $\frac{\text{total bulk}}{\text{parent rock}}$ would then be $\frac{\text{parent rock} = \text{gravel}}{\text{total bulk}}$ which is then equivalent to a C.I. value by definition

---

[1] Gravel percentages estimated from data obtained in the sieve analysis of the coarse soil fractions.

TABLE 14 A

Distribution and Concentration Indices

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	Ba	Co	Cr	Cu	Ga	Mn	Ni	Pb	Sc	Sr	V	Zr
Distribution Index																				
TBS:																				
G-1	1.180	1.178	1.258	.443	.389	.341	.564	1.495	1.021	.392	.211	.639	1.181	.838	1.666	2.400	2.333	1.090	1.370	.636
G-2	1.198	1.400	1.100	.449	.261	.304	.495	1.082	1.116	.348	.147	.603	1.636	.498	1.000	1.400	2.415	1.000	1.094	.720
G-4	1.140	1.112	1.200	.653	.506	.503	.712	1.270	.980	.826	.253	.783	1.272	.993	2.666	1.200	2.168	1.321	1.370	.710
Concentration Index																				
Gravel:																				
G-2	.835	.714	.910	2.225	3.560	3.290	2.020	.924	.896	2.875	6.800	1.660	.611	2.010	1.000	.715	.414	1.000	.915	1.390
G-4	.877	.898	.834	1.531	1.978	1.990	1.404	.788	1.020	1.210	3.950	1.278	.785	1.008	3.374	.832	.461	.756	.730	1.409
Sand:																				
G-2	1.015	.907	1.082	1.225	.876	1.032	.860	.783	1.122	1.625	1.430	2.360	.611	1.650	2.500	.573	.207	.925	.736	.529
G-4	.976	.934	1.299	1.220	.749	1.034	.789	.740	1.173	1.315	1.458	1.600	1.000	1.017	.939	.916	.808	.728	.895	.524
Silt:																				
G-1	.886	1.310	1.109	1.013	1.661	.781	.296	.905	.736	4.449	.900	.415	1.920	.690	.100	.291	.965	.652	1.087	1.750
G-2	.905	.936	1.289	1.211	2.240	1.491	.448	1.620	.891	5.880	.467	.461	1.443	1.172	.333	.642	.829	1.026	1.585	2.410
G-4	1.061	1.290	.858	.397	.610	2.142	.794	.695	1.560	1.892	.416	.077	1.858	.137	.250	.416	.231	1.668	.514	1.645
Clay:																				
G-1	1.128	.750	.894	1.374	.343	.387	.864	.844	.883	2.450	1.350	1.562	1.230	1.398	1.600	10.000	1.072	.407	.495	.864
G-2	1.150	.622	.979	1.222	.475	.401	.624	1.088	.404	2.000	1.642	1.120	.835	1.665	2.500	2.850	1.138	.215	.557	.755
G-4	1.204	.781	.832	1.060	.245	.302	.772	.630	.588	.685	1.166	1.306	.930	.960	1.185	2.418	1.115	.356	.431	.419

G-3 not included in the ratios because of an uncertainty in the original values

TABLE 14 B

Distribution and Concentration Indices

Distribution Index

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	Ba	Co	Cr	Cu	Ga	Mn	Ni	Pb	Sc	Sr	V	Zr
TBS:																				
K-1	1.111	1.018	1.030	1.020	.407	.413	.425	1.133	.591	2.333	2.400	2.578	1.059	.825	7.500	1.834	4.000	.310	1.281	3.079
K-2	1.076	1.068	1.186	1.356	.398	.530	.530	1.191	.635	2.333	2.600	1.715	1.119	.775	7.000	1.250	4.500	.369	1.281	3.580
K-3	1.053	1.120	1.329	1.406	.308	.640	.504	1.040	.865	2.000	1.000	1.140	1.119	.642	6.000	1.500	3.500	.576	1.896	3.781
K-4	1.051	1.132	1.100	.911	.390	.739	.533	.809	.875	1.333	.900	.715	.944	.616	2.500	1.500	3.500	.585	1.670	2.240
K-5	1.004	1.331	1.000	1.373	.740	.749	.526	1.018	.971	1.666	1.000	1.571	1.236	.561	3.500	1.668	3.500	.769	1.791	1.920

Concentration Index

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	Ba	Co	Cr	Cu	Ga	Mn	Ni	Pb	Sc	Sr	V	Zr
Gravel:																				
K-2	.924	.936	.843	.737	2.520	1.886	1.487	.839	1.575	.427	.384	.558	.894	1.291	.144	.800	.225	1.710	.780	.278
K-5	.996	.751	1.000	.728	1.352	1.355	1.479	.982	1.030	.600	1.000	.637	.809	1.783	.286	.600	.286	1.300	.554	.518
Sand:																				
K-2	1.002	.917	1.655	1.240	.899	1.027	.477	.741	.449	.715	.077	5.000	.631	1.158	1.570	.600	.666	.725	.780	.272
K-5	1.019	.695	2.386	1.890	1.086	.899	.533	1.245	.392	1.880	.200	3.540	1.625	1.323	2.140	.600	1.142	.410	.931	.542
Silt:																				
K-1	1.091	.755	.921	1.525	.455	.465	.490	.814	.524	1.000	2.040	1.443	.444	.696	1.865	.681	1.250	.775	.616	.372
K-2	1.101	.763	.970	1.341	.506	.383	.415	.985	.470	1.570	2.228	1.415	.473	1.043	2.000	.934	1.445	.528	.781	.427
K-3	1.070	.783	.918	1.421	1.620	.532	.845	1.369	.385	1.333	4.460	2.875	.790	.968	4.080	1.389	2.570	.638	.815	.904
K-4	1.006	.799	1.635	3.080	1.825	.603	.736	2.161	.600	2.500	2.890	8.800	1.810	2.181	4.800	1.500	2.860	.756	2.160	1.492
K-5	1.059	.659	1.745	2.310	1.232	.406	.494	1.791	.770	2.600	4.600	10.000	1.431	1.670	4.720	1.051	3.290	.612	1.725	2.040
Clay:																				
K-1	.960	.980	2.180	2.079	.433	.221	.992	.712	.439	..857	2.541	1.054	1.942	.942	2.060	2.720	--	.137	1.824	.192
K-2	.990	.958	2.041	1.489	.707	.173	.695	.806	.355	1.000	2.110	1.582	1.630	.875	3.859	3.130	--	.145	2.082	.190
K-3	.986	1.013	1.775	1.543	.604	.152	.659	1.350	.202	.666	4.200	2.752	1.945	.789	1.250	2.950	--	.098	1.713	.224
K-4	.974	1.010	2.105	3.000	.873	.112	.797	1.112	.199	1.255	4.220	4.200	3.368	.925	7.000	3.390	--	.114	2.090	.431
K-5	1.057	.871	1.845	2.222	2.942	.120	.699	.961	.215	1.166	3.700	7.560	1.430	1.071	2.140	3.670	--	.097	1.000	.435

TABLE 14 C

Distribution Index

TBS - Suite N

	N-1	N-2	N-3	N-4	N-6
SiO_2	1.056	1.044	1.042	1.044	1.025
Al_2O_3	.781	.813	.889	.883	.897
Fe_2O_3	.945	1.104	1.698	2.011	1.802
MgO	5.333	10.000	18.667	27.333	8.667
CaO	-	.150	.117	.100	.067
K_2O	1.086	.956	.547	.401	.853
Na_2O	.439	.439	.233	.122	.442
TiO_2			INCREASES		
Ba	.740	1.345	1.315	1.329	.759
Co			INCREASES		
Cr			INCREASES		
Cu	2.125	2.125	2.250	2.375	1.375
Ga	.824	1.000	.941	.647	.705
Mn	6.667	9.333	17.667	40.677	12.000
Ni	2.400	2.400	2.700	1.400	.900
Pb	1.286	1.429	1.714	1.857	1.286
Sc			INCREASES		
Sr	1.600	2.160	1.920	2.240	1.280
V			INCREASES		
Zr	3.598	7.652	4.565	4.097	3.435

TABLE 14 D

Distribution and Concentration Indices

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	Ba	Co	Cr	Cu	Ga	Mn	Ni	Pb	Sc	Sr	V	Zr	Zn
Distribution Index																					
TBS:																					
S-1	1.365	.655	.958	.165	.065	.330	.435	1.174	1.611	3.830	1.780	4.350	.333	1.050	.700	-	.311	.203	1.708	20.350	
S-2	1.314	.729	1.031	.116	.061	.191	.595	1.291	2.039	3.980	1.740	5.290	.438	1.112	.900	-	.267	.182	1.976	20.000	
S-3	1.215	.896	1.151	.143	.033	.217	.630	1.340	1.725	3.910	1.392	5.860	.541	1.240	.700	-	.423	.182	2.049	19.150	
S-4	1.146	.964	1.214	.228	.029	.408	.612	1.388	1.440	1.300	1.196	4.760	.584	.494	.600	-	1.176	.282	1.630	6.850	
S-5	1.120	1.008	.986	.513	.560	.600	.730	.931	1.811	.907	.867	7.000	.750	.306	.600	-	1.176	.806	1.334	2.400	
Concentration Index																					
Gravel:																					
S-1	.732	1.504	1.044	6.050	15.400	3.060	2.300	.852	.620	.263	.562	.230	3.000	.952	1.429	-	3.215	4.960	.586	.049	
S-4	.871	1.037	.824	4.380	34.450	2.452	1.634	.720	.694	.768	.836	.210	1.712	2.050	1.666	-	.850	3.550	.613	.146	
Sand:																					
S-1	1.120	.880	.636	3.100	.937	1.260	1.446	.347	.649	.305	.580	1.000	.750	.286	3.572	-	.715	1.102	.329	.271	
S-4	1.189	.631	.833	1.062	1.212	.999	1.795	.471	.891	.339	.598	1.601	-	.965	3.670	-	.471	.656	.421	.394	
Silt:																					
S-1	1.260	.630	.300	.304	2.310	.395	.595	.272	1.076	.207	.128	.286	.500	.830	.287	.500	.571	2.925	.335	1.255	
S-2	1.270	.665	.335	.492	1.464	.729	.475	.383	.849	.350	.136	.399	.455	1.071	.455	.532	.750	2.435	.330	1.322	
S-3	1.118	.857	.805	.750	1.622	1.120	.935	.571	1.078	.315	.384	.660	1.075	.967	.712	.666	.738	1.985	.744	1.812	
S-4	.905	1.218	1.105	.708	2.570	.851	1.010	.530	.816	1.195	.620	1.159	.930	2.183	1.000	1.375	.453	1.688	1.135	2.600	
S-5	1.070	1.005	.862	.416	1.202	.870	1.016	.645	.969	1.230	1.296	1.014	1.720	2.600	1.444	1.600	.433	3.242	.299	2.790	
Clay:																					
S-1	1.078	1.300	.435	.532	.750	.816	.837	1.330	.374	.305	1.018	1.105	.250	.353	.715	.571	1.000	.986	.449	1.078	
S-2	.961	1.461	.691	1.075	1.265	1.362	.643	1.834	.252	.460	.230	1.077	.818	.379	.776	.400	1.500	.950	.695	1.107	
S-3	.928	1.362	.779	1.111	2.810	1.480	.720	2.158	.255	.345	.328	1.322	1.000	.204	1.283	.500	1.105	1.050	.809	1.000	
S-4	.891	1.509	.784	1.087	2.210	.871	.932	1.314	.204	1.039	.434	1.489	1.000	.198	1.164	.625	.529	.516	.934	1.678	
S-5	.888	1.351	1.015	1.137	.372	.681	1.022	1.634	.362	2.175	.654	.871	.222	1.975	1.500	-	.642	.500	.720	3.329	
Concretion:																					
S-3	1.001	.783	1.096	2.060	1.186	2.400	1.504	1.245	1.310	4.200	.367	1.135	.691	2.695	2.290	2.665	2.470	.317	.462	.034	

Explanation of Symbols in Figures 11 & 12

1.) ▼ = The values increase toward the top of the profile, i.e., the element becomes more concentrated.

2.) ▲ = The values decrease toward the top of the profile, i.e., the element is depleted.

3.) ⧗ = The values show a minimum in the center or B horizon.

4.) ◆ = The values show a maximum in the center or B horizon.

5.) ⬮ = The values are relatively constant, i.e., vary by less than 10%.

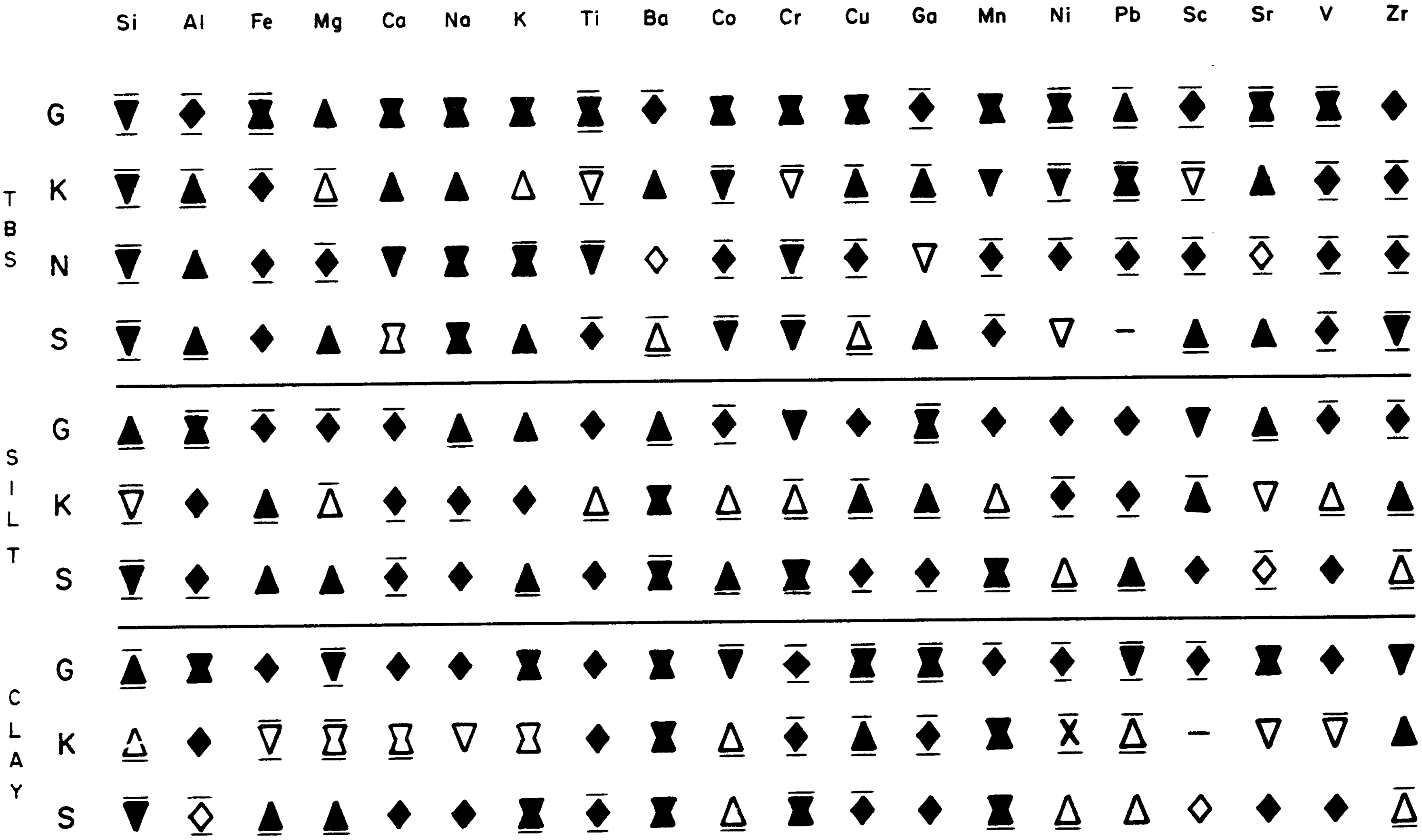
6.) X = No definite pattern can be specified.

7.) – = The initial or final value is greater than 1.000, depending on whether this symbol is below or above any of the other symbols.

8.) ▽ = If any of the first six symbols are not blackened, the symbol has this added meaning: the pattern of change is definite but variable, i.e., one or more of the indices or ratios is anomalously high or low with respect to the values adjacent to it in the sequence.

FIGURE II

SYMBOLIC REPRESENTATION OF DISTRIBUTION INDEX VARIATION OVER A PROFILE



When such values, along with two sand values obtained from each suite and the two corresponding C.I. values for silt and clay, are totaled[2], originally abnormal sums in most cases approach 1.000.

These resulting sums for six samples were treated statistically for mean and relative error as described on pages 186-87 (see Table 25). Although individual element C.I. sums often sharply departed from 1.000, the averages for the six samples, (1.045) and for the individual elements (1.016) both closely approach the theoretical 1.000. The relative error of 28.95% for the six samples is remarkably close to the interplate precision estimate of 28.0%. This may be coincidence or it may reflect the same errors that produce the interplate error.

There are many reasons why most of the individual element C.I. sums would not consistently be close to 1.000. Among these can be cited:

1.) The error in equating gravel to parent rock.

2.) The loss of certain soluble constituents present in the total bulk sample when the size fractions are produced.

3.) Errors in determining the weight percentages of each size fraction.

4.) Loss of very fine clays and colloids during fractionations.

5.) Intraplate and interplate errors (the C.I. values will include these).

Examination of the index data for a given element shows that the variations in the C.I. values over the profile for a given size fraction do not always follow the trend set by the D.I. values. Furthermore, a value in a

---

[2] After recalculating sand, silt, and clay percentages to 100% with the inclusion of the gravel percentages.

sequence will occasionally seem reversed from the apparent trend (e.g.: .45; .63; .57; .72; .86). Such a value is more likely a reflection of precision than of a real geochemical change.

The close agreement between interplate precision and the relative error of the C.I. sums is interpreted as an indication that the C.I. error is largely due to the interplate error. The approach of the mean of the C.I. errors to the expected sum of 1.000 is taken as evidence that the individual element errors effectively cancel out when all element errors are grouped and that the method as a whole (and assumptions applied to it) is in control.

C. Weathering Potential Index and Weathering Index:

Reiche (1945) has formulated a weathering potential index which describes the stability of rocks and minerals and denotes the degree of weathering. This index is defined as:

$$\text{W.P.I.} = \frac{100 \times \text{mols}(K_2O + Na_2O + CaO + Mg) - H_2O)}{\text{mols}(SiO_2 + Al_2O_3 + Fe_2O_3 + CaO + MgO + Na_2O + K_2O)}$$

A high index is associated with rocks or minerals of low stability; as weathering proceeds the index will decrease and the weathered products become relatively more stable with respect to further weathering.

Analyses of total bulk soil samples from the A, B, and C horizons and of parent rock have been used to compute a similar index for the four soil suites. The index values differ from Reiche's in that H_2O is not included in the calculations.

A refinement of Reiche's weathering potential index has been devised by the writer. Each soil index is divided by the parent rock index to provide a new value defined as the *weathering index*. This value can range from 0 to 1. An arbitrary scale of the degree of weathering, based on this index, has been set up as follows:

.000 - .200 = intense weathering
.200 - .400 = strong weathering
.400 - .600 = moderate weathering
.600 - .800 = mild weathering
.800 - 1.00 = slight weathering

Both the weathering potential index (in parenthesis) and the weathering index for selected samples are shown below:

TABLE 15

A		B	C	Parent
G-1		G-2	G-4	G-7
(12.80)		(10.93)	(17.27)	(29.16)
.439		.375	.592	
K-1		K-3	K-5	K-7
(5.84)		(8.75)	(10.06)	(13.41)
.435		.652	.750	
N-1	N-3	N-4	N-6	N-9
(3.59)	(2.37)	(2.08)	(4.38)	(6.14)
.585	.386	.339	.713	
S-1	S-3	S-4	S-5	S-7
(3.03)	(2.89)	(3.97)	(10.51)	(18.86)
.161	.153	.210	.557	

Both indices have proved to be sensitive indicators of the degree of weathering in the four soil suites. The chief merit of the weathering index is that it removes the effects of differing initial compositions in the parent rocks and therefore allows all soils to be compared directly to each other.

D. Relative Geochemical Associations:

Certain elements in igneous rocks associate with or follow geochemically certain other elements. The principles underlying these associations of element pairs were clearly stated by Goldschmidt (1937) and have been summarized by Mason (1952, pp. 114-18).

It is probable that similar associations persist in sedimentary rocks and in the chemical environment characteristic of weathering and soil formation. In fact, numerous references to positive associations of Ca-Mg, Ca-Sr, K-Ba, Fe-Mn, Fe-V, and Al-Ga and other pairs can be found in the literature on sediments and soils.

In order to test for such associations and to discover possible new ones, ratios of concentrations of various elements to other elements with which it is arbitrarily assumed they associate have been calculated for parent rock, each total bulk soil sample and clay fraction samples in every sampled horizon within the four soil profiles. The basis of selecting which elements are to be ratioed to one another is simply the observed and definitely established associations already noted in igneous rocks, regardless of whether similar associations have been demonstrated for sedimentary rocks or soils.

The various pairs selected and their ratios are presented in Tables 16 A-D. The number in parenthesis next to each ratio designation represents the power of 10 by which the initial ratio (produced by dividing the actual

TABLE 16 A

Relative Geochemical Associations

Suite G

		TBS						Clay			
Ratio		G-1	G-2	G-3	G-4	G-9		G-1	G-2	G-3	G-4
Fe/Mg	(0)	5.41	4.66	3.87	3.48	1.90	(0)	3.51	3.72	3.10	2.75
Fe/Ti	(+1)	8.90	10.70	11.50	10.00	10.50	(0)	9.41	9.63	8.85	13.10
Fe/Co	(0)	1.25	1.23	5.80	5.65	3.89	(+1)	4.56	6.04	6.18	6.88
Fe/Cr	(+1)	5.62	7.01	4.10	4.47	0.94	(+1)	3.71	4.18	4.15	3.19
Fe/Cu	(+1)	2.13	1.97	1.70	1.65	1.08	(+1)	1.21	1.72	1.45	1.05
Fe/Mn	(+3)	9.00	13.10	8.60	7.20	5.90	(+3)	5.70	7.70	6.60	6.20
Fe/Ni	(0)	1.13	1.64	1.09	0.67	1.49	(+1)	6.26	6.44	6.20	4.65
Fe/V	(+2)	5.20	5.70	5.30	4.90	5.60	(+1)	9.30	9.94	7.87	9.52
Mg/Cu	(+2)	3.92	4.22	4.39	3.98	5.66	(+2)	3.44	4.61	4.67	3.82
Mg/Ni	(+1)	2.08	3.52	2.83	1.93	7.83	(+1)	1.79	1.72	2.00	1.71
Mg/Sc	(+2)	7.40	7.30	10.20	11.80	39.10	(+2)	9.50	7.80	9.30	11.20
Al/Ti	(-1)	1.31	2.16	1.70	1.45	1.66	(0)	9.92	10.04	9.35	15.32
Al/Ga	(0)	1.28	1.10	1.20	1.12	1.28	(+1)	6.63	6.98	7.65	9.51
Ca/Mg	(0)	2.06	1.46	1.78	1.80	2.34	(+1)	5.15	5.70	5.30	4.22
Ca/K	(0)	1.39	1.14	2.24	1.43	2.02	(+1)	5.56	8.76	10.90	8.78
Ca/Na	(0)	3.13	2.53	4.54	2.76	2.75	(0)	2.78	3.00	2.47	2.25
Ca/Sr	(+3)	9.60	7.60	9.50	10.40	27.00	(+3)	8.10	16.70	9.40	7.20
K/Na	(0)	2.24	2.21	2.02	1.92	1.35	(+1)	5.00	3.43	2.25	2.56
K/Ba	(+3)	2.10	2.80	1.60	2.80	3.70	(+3)	3.20	4.00	3.20	3.00
K/Pb	(+1)	1.28	1.93	-	3.24	5.45	(+3)	11.00	4.20	4.20	5.40
Ni/Co	(0)	1.11	0.75	0.53	1.19	3.84	(0)	0.73	0.94	1.00	1.46

TABLE 16 B

Relative Geochemical Associations

Suite K

				TBS							Clay		
Ratio		K-1	K-2	K-3	K-4	K-5	K-6		K-1	K-2	K-3	K-4	K-5
Fe/Mg	(0)	3.68	3.18	2.65	4.40	2.65	3.64	(0)	3.85	4.36	3.96	3.09	3.02
Fe/Ti	(0)	6.41	7.05	9.02	9.65	6.95	7.07	(-1)	1.97	1.78	1.19	1.44	1.36
Fe/Co	(+1)	5.40	6.20	8.10	10.10	7.30	12.20	(0)	1.37	1.27	2.17	1.70	1.13
Fe/Cr	(+1)	1.58	1.67	4.89	4.52	3.68	3.68	(+1)	1.35	1.62	2.06	2.24	1.84
Fe/Cu	(+1)	2.10	3.53	6.12	8.10	3.34	5.25	(+1)	4.35	4.68	3.94	4.05	1.28
Fe/Mn	(+3)	6.56	8.05	10.80	9.40	9.35	5.24	(+2)	1.52	1.87	2.45	2.13	1.60
Fe/Ni	(+1)	2.52	3.11	4.07	8.10	5.26	18.40	(+1)	2.66	1.65	5.79	2.44	4.54
Fe/V	(+2)	5.20	6.00	4.50	6.60	3.60	6.40	(+2)	6.20	5.90	4.70	3.40	6.60
Mg/Cu	(+2)	5.70	11.40	17.80	18.40	12.60	14.40	(+1)	1.12	1.07	1.00	1.31	0.42
Mg/Ni	(+2)	6.70	9.80	11.80	18.40	19.80	5.00	(+2)	6.90	3.80	14.60	7.90	6.40
Mg/Sc	(+1)	1.90	1.52	2.03	1.31	1.26	5.00	-	-	-	-	-	-
Al/Ti	(-1)	2.35	2.32	2.82	3.67	3.42	2.62	(-1)	3.23	2.25	2.11	2.63	3.20
Al/Ga	(+1)	7.71	7.56	8.01	9.65	8.63	8.00	(+1)	3.87	4.44	4.19	2.88	5.34
Ca/Mg	(+1)	8.74	6.50	4.78	9.35	11.70	21.90	(+1)	1.80	3.10	1.90	2.70	2.10
Ca/K	(+1)	3.31	2.67	2.11	2.52	4.85	3.46	(+1)	1.40	2.70	1.90	2.80	2.00
Ca/Na	(+1)	5.29	4.15	2.58	2.82	5.30	5.38	(0)	1.02	1.70	1.02	1.92	1.29
Ca/Sr	(+3)	4.20	3.50	1.70	2.10	3.10	3.30	(+2)	1.30	1.70	1.05	1.63	0.94
K/Na	(0)	1.59	1.56	1.22	1.12	1.09	1.54	(0)	7.20	6.25	5.45	6.95	6.35
K/Ba	(+3)	1.51	1.74	1.23	1.29	3.92	9.02	(+3)	3.48	3.40	4.14	4.56	3.64
K/Pb	(+1)	1.23	2.22	1.79	1.89	1.66	5.30	(+2)	4.56	4.91	4.12	4.45	5.35
Ni/Co	(0)	2.14	2.00	2.00	1.20	1.40	0.66	(0)	5.16	7.71	3.75	7.00	2.50

TABLE 16 C

Relative Geochemical Associations

Suite N

TBS

Ratio		N-1	N-2	N-3	N-4	N-6	N-9
Fe/Mg	(0)	10.75	6.10	5.50	4.50	12.60	60.00
Fe/Ti	(0)	4.10	3.46	8.35	8.12	7.80	-
Fe/Co	(+1)	3.44	4.02	3.87	4.57	-	-
Fe/Cr	(+2)	1.90	5.90	5.30	6.40	14.00	-
Fe/Cu	(+1)	1.01	1.18	1.71	1.92	2.97	2.30
Fe/Mn	(+2)	8.60	7.20	5.80	3.00	9.10	30.60
Fe/Ni	(+2)	7.20	7.50	11.40	26.20	35.20	18.20
Fe/V	(+2)	5.70	4.20	6.60	6.10	7.30	-
Mg/Cu	(+3)	9.40	19.40	31.00	43.30	23.20	3.80
Mg/Ni	(+3)	6.60	12.20	20.70	58.50	28.90	3.00
Mg/Sc	(+2)	4.00	4.70	7.00	9.10	4.30	-
K/Ba	(+3)	7.50	3.80	2.20	1.60	6.00	5.30
K/Na	(0)	1.50	1.37	1.48	2.03	1.21	0.63
K/Pb	(+1)	2.69	2.22	1.05	0.72	2.20	3.32
Al/Ti	(-1)	2.14	1.61	2.76	2.26	2.45	-
Al/Ga	(+1)	6.40	5.50	6.40	9.20	8.60	6.80
Ca/Mg	(+1)	-	2.70	1.25	0.73	1.53	200.0
Ca/K	(+2)	-	4.40	5.50	6.50	3.00	25.80
Ca/Na	(+2)	-	5.50	8.10	13.30	2.50	16.20
Ca/Sr	(+3)	-	2.20	1.50	1.10	1.20	24.00
Ni/Co	(0)	4.80	5.40	3.40	1.70		

TABLE 16 D

Relative Geochemical Associations

Suite S

		TBS							Clay				
Ratio		S-1	S-2	S-3	S-4	S-5	S-7		S-1	S-2	S-3	S-4	S-5
Fe/Mg	(-1)	1.64	2.55	2.27	1.51	5.45	2.83	(-1)	1.34	1.63	1.59	1.09	0.48
Fe/Ti	(-1)	1.25	1.25	1.31	1.34	1.62	1.53	(0)	4.07	4.70	4.73	7.98	10.05
Fe/Co	(+2)	9.20	9.70	10.80	34.10	39.80	36.60	(+1)	1.31	1.47	2.43	2.78	1.81
Fe/Cr	(+2)	6.70	7.50	10.20	12.60	14.10	12.40	(+1)	2.85	2.25	2.43	2.28	2.20
Fe/Cu	(+1)	1.20	1.08	1.06	1.38	0.76	0.77	(+2)	5.75	6.93	6.27	7.28	10.89
Fe/Mn	(+3)	5.89	6.10	5.95	15.80	21.20	6.32	(+3)	7.21	11.10	22.80	62.90	10.90
Fe/Ni	(0)	2.16	1.84	2.59	0.87	2.59	1.57	(0)	1.27	1.63	1.57	2.14	1.76
Fe/V	(+2)	3.50	3.30	3.50	4.60	4.60	6.20	(+2)	3.38	3.27	3.36	3.89	6.51
Mg/Cu	(+3)	7.30	4.25	4.70	9.20	13.80	192.0	(+3)	4.30	4.24	3.95	6.70	18.40
Mg/Ni	(+1)	1.29	0.72	1.14	0.58	4.76	5.57	(+1)	0.98	1.00	0.99	1.97	3.61
Mg/Sc	(+2)	6.60	5.40	4.20	2.40	5.40	12.30	(+2)	3.50	3.88	4.24	4.93	9.55
Al/Ti	(-1)	1.11	1.11	1.31	1.36	2.13	1.97	(-1)	1.09	0.89	0.83	1.57	1.76
Al/Ga	(0)	1.68	1.34	1.39	1.39	1.14	0.84	(0)	8.75	2.40	1.91	2.26	0.89
Ca/Mg	(+1)	3.50	4.60	2.00	1.10	9.60	8.80	(+1)	4.90	5.40	5.00	2.20	3.00
Ca/K	(+1)	4.30	3.00	1.50	1.30	26.20	28.80	(+1)	3.90	5.90	5.90	3.20	8.00
Ca/Na	(+1)	8.43	13.60	6.41	2.97	39.70	48.40	(+1)	6.15	12.70	12.10	7.57	21.70
Ca/Sr	(+3)	4.77	5.00	2.67	1.56	10.30	16.90	(+2)	3.64	6.67	7.14	6.45	7.70
K/Na	(0)	1.94	4.60	4.29	2.21	1.80	1.48	(0)	1.59	2.16	2.08	2.36	2.70
K/Ba	(+3)	1.62	1.76	2.20	2.56	2.50	6.04	(+3)	3.64	4.48	5.97	11.70	68.60
K/Pb	(+2)	5.30	6.75	8.92	13.00	25.00	-	(+2)	7.75	10.80	12.80	19.40	-
Ni/Co	(+2)	4.30	5.30	4.20	39.00	15.00	23.0	(+2)	10.00	9.00	15.50	13.00	10.60

numerical value, irrespective of whether in % or ppm, of one element concentration by the value of the other) is multiplied to obtain a series of numbers within the range 0 to 10. This facilitates direct comparison of various values which otherwise might differ by several orders of magnitude.

The ratio change sequence in TBS samples compared to parent rock and in clay fraction samples compared to the clay fraction sample in the lowest sampled horizon represent in effect the relative enrichment or depletion through the profile of one element with respect to the other. Because a given change can result either from opposing changes or from different rates of change in the same direction in the numerator and denominator element values, the original raw data must be consulted to determine which of the two elements has the larger responsibility for the observed change.

The variations of these association ratios within each profile have been shown symbolically in Figure 12. The symbols have the same meaning (except No. 7 which is omitted) as those in Figure 11, except that they are here applied to ratios rather than to indices.

The following are some of the factors which can produce ratio changes throughout a soil profile.

1.) Relative mobilities of different elements moving through the soil, as functions of different solubilities and different degrees of fixation on particle surfaces.

2.) Relative distribution of an element among several mineral phases which undergo different degrees and rates of weathering.

3.) Selective incorporation of certain elements in secondary phases, both as essential constituents and as isomorphous substitutes.

FIGURE 12

SYMBOLIC REPRESENTATION OF RELATIVE GEOCHEMICAL ASSOCIATION VARIATION

	G		K		S		N
	TBS	CLAY	TBS	CLAY	TBS	CLAY	TBS
Fe/Mg	▼	▼	X	▼	△	◆	⧗
Fe/Ti	◆	▲	◆	▼	▲	▲	◆
Fe/Co	◆	▲	▲	◆	▲	◆	△
Fe/Cr	X	◆	◆	◆	▲	●	▲
Fe/Cu	▼	◆	◆	●	▽	▲	▲
Fe/Mn	◆	◆	◆	◆	◆	◆	⧗
Fe/Ni	⧖	●	▲	△	X	△	▲
Fe/V	X	●	X	▽	▲	▲	△
Mg/Cu	▲	◆	◆	▼	⧗	⧗	◆
Mg/Ni	X	●	◆	◇	⧗	▲	◆
Mg/Sc	▲	●	⧗	-	⧗	△	◇
Al/Ti	◆	▲	◆	⧗	▲	⧗	X
Al/Ga	●	▲	◆	X	▼	▽	◇
Ca/Mg	⧗	◆	⧗	◇	⧗	▽	⧗
Ca/K	X	◆	X	X	⧗	△	△
Ca/Na	X	▼	⧗	●	⧗	⧖	◆
Ca/Sr	▲	◆	⧗	▽	⧗	▲	⧗
K/Na	▼	▼	▼	●	◆	▲	◇
K/Ba	△	◆	⧗	●	▲	▲	⧗
K/Pb	▲	⧗	△	⧗	▲	▲	⧗
Ni/Co	⧗	▲	▽	X	◆	◆	◆

The exact cause(s), if determinable, of any change in ratio must be assessed individually in every case in terms of all the evidence bearing on these and other factors.

E. Observed Geochemical Associations and Correlation Coefficients:

The geochemical association ratios described above neither directly confirm nor disprove any positive or negative associations of elements in soils and weathering. As a rule of thumb, a fairly constant ratio series may indicate a tendency for two elements to behave alike but the association could also be due to both elements being principally in one mineral or could even be only fortuitous.

Positive associations are more definitely established when two element concentrations tend to increase or decrease together during weathering with respect to position in the soil profile (horizon depth) or some other variable common to them. The change need not be of the same magnitude (i.e., may be only proportional) but must be in the same direction. For example, a decrease in Fe and V in the A horizon and a corresponding increase in the iron enrichment zone of the B horizon would demonstrate a probable association.

The simplest and most direct way of noting any sympathetic or antipathetic associations is by inspection of the curves in Figures 6-9. Those elements whose curves when compared have similar trends, similar inflections, and similar (or proportionately related) slopes may be geochemically related. Similarity in the curves does not however constitute by itself sufficient proof of a definite geochemical relationship.

On the basis of such visual inspection of these curves, a generalized system of rating the degree of association was set up. The rating is dependent entirely on a broad, qualitative "eyeball" comparison of the curves and hence reflects the subjective judgment of the writer. The rating scale ranged from 0 (no association), 1 (slight association), 2 (moderate association), to 3 (strong association). Positive or negative associations were indicated by the appropriate + or - signs. When decisions were difficult, the direction and degree of changes of all corresponding points in compared curves were individually scrutinized.

The possible associations of all curves in the figures number in the hundreds. Therefore the numerical results of this system of associations are not reported in this thesis. A sample association analysis of A1 in Suite S showing the various combinations of associations that were set up, is shown below:

		Sand	Silt	Clay	% Silt	% Clay	Free Iron Oxide	C.E.C.
A1	TBS:	+3	+2	+3	+1	-2	+1	+2
	Silt:	+2		+3	+1	-2	+2	+2
	Clay:	+3			+1	-2	+1	+2

In reporting the results of this association analysis in the soil suite interpretations on pages 115-34, only certain of the associations having ratings of ±3 (those considered meaningful and noteworthy) will be discussed. Five rules or guides for making interpretations by this association analysis are given in Appendix D.

In an attempt to put the associations on a quantitative basis, various element pairs were compared with each other by a statistical device known as the *correlation coefficient*. In effect, the correlation coefficient indicates the degree of association (or correlation) of two variables. For the two variables X and Y (e.g., two element concentrations), when N is the number of samples, the correlation coefficient *r* is defined as:

$$r = \frac{(\Sigma X \cdot Y - N \Sigma X \cdot \Sigma Y)^2}{(N \Sigma X^2 - (\Sigma X)^2)\ (N \Sigma Y^2 - (\Sigma Y)^2)}$$

A value of r = +1 indicates perfect positive correlation; r = -1 indicates perfect negative correlation; and r = 0 indicates no correlation.

Correlation coefficients were calculated for various groupings of selected element pairs. The only grouping for which meaningful correlation coefficients were obtained was that in which all values of the analyses of TBS, sand, silt, and clay for all suites were combined. The resulting coefficients r were tested for significance by Student's t test at the 50%, 10%, 5%, and 1% levels (see Mood, 1950, p. 206).

The correlation coefficient r for each tested pair in this grouping, rated as to level of significance for N = 52, is presented in Table 17.

TABLE 17

Fe-Co = +.425****
Fe-Cr = +.024
Fe-Cu = +.028
Fe-Mn = +.257**
Fe-Ni = +.192*
Fe-Ti = +.510****
Fe-V = +.481****
Mg-Cu = +.398****
Mg-Ni = +.169*
Mg-Sc = +.413****
K-Ba = +.334***
K-Sr = +.354****
K-Pb = +.026
Ca-Sr = +.332***
Al-Ga = +.592****
Al-Ti = +.048

Significance: * 50% level ** 10% level *** 5% level **** 1% level

In the discussion that follows on the interpretation for individual suites, all specified associations between geochemically related elements are based primarily on the writer's visual correlation of the curves in Figures 6-9, aided in some instances by these calculated correlation coefficients.

F. Correlations Between Chemical and Several Soil Chemistry Variations:

Relationships and associations between major-minor element variations within a soil profile and other varying parameters such as pH, E_h, $-H_2O$, organic matter, etc. were demonstrated or implied by the same method of visual comparison between curves plotted in Figures 6-9 as previously described. Relative comparisons on the ordinate scale can be made directly between concentrations and those parameters expressed in percent. The pH and E_h values are based on narrower scale limits and hence their variations along the ordinate are subdued.

G. Percent Leachable Element:

The leach values in Tables 11 A-D represent the total amount of any element (in ppm) that was removed by acetic acid from a given amount of soil. This amount is dependent on the fractions of an element held in soluble cements, in exchange positions, in easily destroyed mineral phases or colloidal gels, etc. It is also related to the total amount of the element present in the entire TBS soil sample. An estimate of the amount of an element readily removed by leaching relative to the total amount can be obtained by computing the <u>percent leachable element</u>, which is defined as:

$$\% \text{ leachable element} = 100 \times \frac{\text{leach value (ppm)}}{\text{TBS value (expressed as ppm)}}$$

The percent leachable element values computed from all the leachate concentrations in Suites G, K, and S are presented in Table 18.

As a first approximation, it would be expected that the fraction of an element available for leaching is directly proportional to the total present. Several complicating factors can alter this. A more thoroughly weathered rock or soil should have a greater amount of most of its constituent elements removed than a moderately or slightly weathered rock or soil. On the other hand, stronger weathering usually leads to increased clay mineral formation which provides for higher cation exchange activity and therefore greater fixation of certain elements. Many of these fixed elements are removable by acetic acid leaching. Stronger weathering may also produce a higher proportion of colloidal gels and "silicate wreakage" that collect or selectively incorporate some elements only to release them readily upon leaching.

Examination of the percent leachable element data and of the curves in Figure 10 shows a pronounced tendency for the maximum or minimum leach concentrations or relative amounts available to be in the B horizons. The maxima can be explained for many of the elements, especially the ferrides, as due to reconcentration by natural leaching down profile of elements removed from the usually more weathered A horizons and re-precipitated or adsorbed in the B horizons. A minimum in the B horizons for certain elements may be due to one or several causes, including 1) re-precipitation in topsoil by upward capillary movement of solutions (caliche formation), 2) concentration by translocation processes in the B horizons of clay minerals deficient in the particular element(s), and 3) impeded drainage leading to excessive ground water (and solvent action) in the B horizons (gleying effects).

TABLE 18

Percent Leachable Element

Element	% G-1	% G-2	% G-4	% K-1	% K-3	% K-5	% S-1	% S-3	% S-5
SiO_2	.423	.435	.296	.038	.035	.0019	.059	.225	.166
Al_2O_3	.417	.253	.369	.495	1.18	.179	.574	.167	.136
Fe_2O_3	.047	.365	.037	.116	.065	.041	.041	.102	.046
MgO	15.8	16.1	7.7	4.27	2.25	1.89	5.53	18.0	14.5
CaO	13.3	34.2	15.9	26.4	15.7	3.25	32.2	56.6	7.9
K_2O	1.85	4.34	1.17	5.68	.598	.080	2.10	1.70	1.45
Na_2O	11.2	9.30	6.65	2.54	.681	.142	8.32	13.4	16.5
Ba	3.94	7.05	4.60	2.14	1.79	.478	5.72	6.80	5.68
Co	1.22	.756	.475	7.14	.428	.400	1.76	1.13	.051
Cr	1.80	1.64	.587	1.25	1.50	.304	.041	.034	.091
Cu	1.57	5.68	1.77	5.55	4.37	1.00	1.90	1.12	1.03
Ga	-	-	-	-	-	-	.012	-	.022
Mn	1.90	4.13	1.67	2.22	1.11	.508	.369	.365	1.95
Ni	7.00	9.82	3.00	2.66	1.25	1.00	8.57	4.26	15.0
Pb	1.00	-	-	-	-	-	.427	.500	1.00
Sc	-	-	-	-	-	-	.500	2.64	1.13
Sr	3.37	4.16	2.96	1.73	.352	.156	1.19	1.58	6.25
V	.165	.167	.156	-	.074	.029	.009	.008	.042
Zr	-	-	-	.015	.008	-	.076	.034	-

Because of the above implications (and others) it appears difficult to correlate the degree of weathering with the relative (or absolute) leachable element values. However, despite anomalies, a general rule that stronger weathering is indicated from the percent leachable data by increases in ferrides, Al, and Si and decreases in alkalis and alkaline earths (and minor element associates) seems valid for most of the samples examined.

Most of the leach data contradicts the conclusion often reported in studies of minor element availability to plants that the A horizon layers contain the maximum amounts. The B horizon layers in all four suites contain richer supplies of some of these desired available elements.

H. Trace Element Content of Minerals and Rocks:

The trace element content of individual minerals in both parent rock and soils was not determined in this spectrochemical study.

In the discussion that follows comparisons of the trace element content of the parent rocks with that of rocks of similar lithology and origin are based on reported analyses in Goldschmidt (1955) and Rankama and Sahama (1950). Average trace element concentrations for some of the igneous minerals noted in the four soils have been determined by Nockolds and Mitchell (1948, p. 572) and Wager and Mitchell (1948, p. 144). Semi-quantitative values of trace element content of the A.P.I. clay mineral standards is presented in the American Petroleum Institute Project No. 49 Report No. 7 (1950, pp. 71-90). These values are useful in estimating the general range of trace element content expected in the minerals found in the four soil suites.

III. Specific Interpretations:

A. Element Behavior Characteristics Common to the Four Soils:

Several characteristics in the behavior of some of the major and minor elements recur in all soils studied in this thesis. Some of these features have been mentioned before but are briefly reviewed here in order to coordinate the discussion that follows on behavior in the individual suites. Evidence for and some aspects of these characteristics will be further treated in this discussion.

1.) All four soils undergo a net loss in Ca, Na, and K and a net gain in Fe, Ni, Pb, Sc (?), and V.

2.) The largest percentage gain or loss occurs between parent rock and the bottom soil or C horizon.

3.) Enrichments are most prominent in the B horizon. Fe and V consistently showed maximum concentrations in this horizon; none of the elements attained a maximum in the A horizon in all four soils.

4.) Several elements, notably Al, K, Na, Ca, Ba, and Sr, usually decrease in the A horizon; however, in every soil at least one of these elements shows a gain in the A horizon relative to its amount in the B horizon.

5.) There is a strong direct correlation between concentration changes of certain elements and an increase in clay size; this association is less definite for the silt fraction.

6.) In composition, the clay fraction is most typical of the nature of chemical changes resulting from formation of secondary minerals and weathering by-products; the silt fraction is most typical of the average weathered character of the parent rock because it contains both decomposed primary minerals and some of the coarser secondary minerals; the sand fraction is most typical of the nature of enrichment caused by survival of the more stable and resistant minerals; and the gravel fraction is most typical of slightly altered or weathered parent rock.

7.) The variations throughout the profile of most major and minor elements are generally less in the clay fraction than in other fractions or the total soil because this fraction is composed dominantly of one or more clay minerals containing these elements.

8.) For many of the elements in each of the soils there is not a "material balance" when the individual fractions are added together in proportion to their relative amounts. In a few cases, the concentration index of an element is greater or less than 1.000 for all its size fractions. Possible causes of these discrepancies were discussed on page 98. Often, when an element enriches in one or two of the size fractions, a corresponding depletion in the other size fraction(s) is not commensurate. The largest differences in concentrations are usually (as expected) between gravel and the other fractions.

9.) Except for Cu in the A horizon, no horizon consistently contains the same maximum % leachable amount of an element in all four soils.

10.) All soils showed some degree of positive association between Fe-Co, Fe-Cu, Fe-Mn, Fe-Ti, Fe-V, Mg-Cu, Mg-Sc, K-Pb, K-Sr and Al-Ga in the silt fraction and Fe-Cr, Fe-Ni, K-Ba, and Al-Ga in the clay fraction.

11.) Possible associations between cation exchange capacity or free iron oxide variations and concentration changes of those elements commonly influenced by these variations in most cases have not been supported by data from the four soils.

12.) Specific changes in concentration cannot be certainly nor consistently related to pH or E_h variations. All soils become more acid (lower pH) and more oxidized (higher E_h) relative to their parent rocks.

13.) The two soils (N and S) from the more humid eastern U.S. show greater relative (to parent rock) percent gains (see Table 13) in Si, Ti, Ba, Co, Cr, Cu, Mn, Pb, V, and Zr than the two soils (G and K) from the semiarid western U.S. All four soils show generally similar losses in Na, Ca, and K. The two acid soils (K and N) show only a greater relative gain in Mg and Ni as compared to the more basic soils (G and S). The chemical distinction between these four soils, in terms of their pattern of element behavior, seems more a function of climatic differences than of parent rock.

14.) From the preceding, it is evident that it is not a simple matter to deduce the probable parent rock type directly from the chemical analysis of a soil. In the two basic soils, lower Si and higher Fe and usually higher Cu, Sc, V, and lower Zr were the only consistent concentration changes that might serve to distinguish acid and basic-derived soils in other areas. The uniformly low concentrations of Ca, Na, and K and the wide and overlapping ranges of variation of most of the minor elements in all four soils would appear to preclude use of these elements as indicators of parentage.

B. Pattern of Element Behavior in Each Soil Suite:

Suite G: The soil from locality G weathers in a more arid climate than those climates affecting the other three suites. Several of the elements behave according to a different pattern than in these other suites. A single sample, G-2, from this locality convincingly demonstrates the relationship between selective enrichments or depletions of elements and the degree of weathering as evidenced by clay content, water content, free iron oxide, C.E.C., etc.

The weathering index for this suite shows it to be moderately to strongly weathered. The difference in degree of weathering between top and bottom soils is not as pronounced as in soils formed in humid climates. The lower index for G-2 confirms the greater degree of weathering assigned to it on the basis of other measurements.

The average net change for the total soil shows gains in Si, Fe, Ti, Ga, Ni, Pb, Sc, Sr, and V and losses in Mg, Ca, K, Na, Ba, Co, Cr, Mn, and Zr. This soil differs from Suites K, N, and S in showing losses in Co, Cr, Cu, and Zr, and a gain in Ga. It is possible that a humid climate is more effective in concentrating these elements.

The pattern of D.I. changes in the TBS series is the same as above when corrected to constant Al_2O_3 and differs only in Ba showing a slight increase in the raw TBS values.

The C.I. values of the individual size fractions show in common increases in Fe, Mg, Co, and Zr and decreases in K, Ti, Pb, Sc, and Sr. Increases in Na and Fe and decreases in Si and Sc are noted in the sand and silt fractions whereas these elements show opposite changes in the clay fraction. An increase in V and decreases in Ba and Mn occur in the silt and clay fractions with opposite changes in the sand. The sand and clay show an increase in Cr and a decrease in Al with respect to opposite changes in the silt fraction.

A pronounced enrichment of Ni, Pb, and Sc and a large depletion of Co and Cr marks the TBS series. Co, Cr, and Ni appear to concentrate largely in the gravel and sand fractions, although striking enrichments of Co appear in both silt and clay fractions as well. Pb strongly concentrates in the clay fraction. Zr appears dominantly in the silt fraction which implies that any zircons, if present, have their average size within this range. The decrease in Zr in the TBS series may indicate that this element is present as soluble zirconate removable during hydrolysis.

Maximum concentrations of Ti and Pb in the A horizon and Si, Fe, Ga, Ni, Sc (?), Sr, and V in the B horizon and minimum concentrations of Mg, Ba (?), Ca, Co, Cr, Mn, Sr, and Zr in the A horizon and K and Na in the B horizon are characteristic of this suite.

If the D.I. values of the more weathered G-2 are compared to those of G-1 and G-3, it is seen that this greater weathering leads to an enrichment of Al and Ga and a depletion of Si, Fe, Ca, K, Na, Ti, Ba, Co, Cr, Mn, Ni, Pb, Sc, Sr, V, and Zr in G-2. This one sample affords the best indication of the pattern of chemical weathering in this profile. Thus, as weathering intensifies, most of the elements are removed, leaving behind a residue richer in Al. A possible end product would be a kaolinite or diaspore clay mineral; however, such Al-rich clay minerals were not detected by the x-ray analysis.

A study of the distribution of maximum values of the leachable elements finds Na, Al, Cr, and Co in the A horizon and Ca, Mg, Si, K, Fe, Ba, Mn, Ni, Sr, and V in the B horizon (G-2). When the A and C horizons are compared, maximum values of Mg, Si, Na, Al, K, Fe, Co, Cr, Mn, Ni, Sr, and V occur in the A horizon whereas maxima for Ca and Ba are found in the C horizon. On the whole, the B horizon provides the largest amounts of leachable elements.

The curve association analysis led to these conclusions:

1.) Variations in Ca, K, Na, Cr, and V are controlled by the sand content. This is explained as due to the prevalence of feldspars and magnetite in this fraction.

2.) Variations in Si, Al, Mg, K (in part), Ga, and Sc are largely functions of the clay fraction composition.

3.) As the percentage of clay increases, there appears to be a corresponding decrease in Ti, Ca, K, Sr, Mn, Ba, Cr, Co, and Ni in the total soil. Only V appears to increase with clay percent.

4.) Silt percent increase favors an increase in Fe (magnetite ?) and a decrease in Ti and Mg in the total soil.

5.) An increase in the percentage of silt is associated with a decrease in the silt fraction composition in Ca, Na, Ni, Co, and Zr.

6.) An increase in the percentage of clay leads to an increase in the clay fraction composition in Sc and Pb and a decrease in K, Na, Ba, Cr, Cu, Mn, Ni, and Cu.

7.) The free iron oxide values are inversely proportional to the total iron content (i.e., greater weathering and removal of iron leads to more free iron in cements, etc.).

8.) Positive associations between free iron oxide variation and ferrides are found for no elements in the TBS samples, only for Cr and Co in the silt, and for no elements in the clay. A negative association in the clay is noted for Co, Cr, Mn, and Ni, implying that these do not follow iron closely in cementing and staining processes.

9.) An increase in C.E.C. seems partly responsible for decrease in K, Sr (?), Fe, Cr, Mn, and Ni concentrations in the clay fractions. Only Ca appears to follow increases in the exchange capacity.

10.) Free iron oxide tends to follow the C.E.C. of the clay fraction. The total C.E.C. is also a function of clay percent.

Pronounced positive associations between geochemical pairs are found in the TBS samples for Fe-Ni, Fe-Ti, Mg-Cu, and Al-Ga; in the silt for Fe-Co, Fe-Ti, Fe-V, Mg-Sc, and K-Sr; and in the clay for Mg-Ni, K-Ba, K-Pb, and Al-Ga. Strong negative associations are evident in TBS for Fe-Co, Fe-Cr, Fe-V and Mg-Sc; and in the silt for Fe-Ni, Mg-Ni, and Ca-Sr.

In both TBS and clay, the relative geochemical associations of Fe with the various minors show few conspicuous variations; Fe/Cr is nearly constant except for the parent rock - C horizon transition. Fe/Mg increases towards the top of the profile, reflecting the enrichment of Fe from magnetite, coupled with weathering of augite and biotite. The Mg/minors ratios in TBS decrease primarily because of relative enrichment of the minors in the soil. The Na/Ca ratio is quite constant in both TBS and clay. The decrease in Ca/K and increase in K/Na reflects the greater stability of orthoclase and mica relative to the plagioclase. The drops in the K/Pb ratios in both TBS and clay are caused by the enrichment of Pb in the topsoil. Several conspicuous changes in ratios between parent rock and C horizon samples are noted: 1) a rise in Fe/Cr due to sharp drop in Cr, 2) a drop in Mg/Sc due to big increase in Sc in the soil, and 3) a drop in Ca/Sr due to the large loss in Ca relative to Sr, which remains fairly constant throughout the profile.

In comparison with trace element content of basalts, the parent rock appears to be high in Ba and Mn, low in Cr, Ni, and Sr, and about normal in Ga, Co, Pb, Sc, and V. Weathering of the feldspars involves removal of Sr, Ba, Pb, and Ga. Weathering of augite should cause loss of Cr, V, Ni, Sc, Co, and Mn. Survival of the resistate magnetite would produce an enrichment in Cr, Cu, Ni and V. The development of montmorillonite (the predominant clay mineral in the G suite) would normally lead to concentration of Cr, Mn, Ni, and Ti and depletion of Ba, Cu, Pb, and Zn.

Such predictions are not borne out by the observed changes in the G suite. The gains in Sr, Ga, and Pb actually observed imply either some selective adsorption process, incorporation within secondary phases, or original location in orthoclase or mica which relatively increase up profile. The actual loss of Cr, Co, Cu, Mn, and Ni implies that loss through the weathering of augite is more predominant than gains from the preservation of magnetite or formation of montmorillonite. The concentrations of most minor elements in the montmorillonitic clay fraction do not differ significantly from the concentrations in TBS, partly because the high proportion of clay in the soil probably controls the TBS composition. Relative to the parent rock, montmorillonite is enriched only in Pb and Sc (and Mg).

Suite K: The decomposition of the granodiorite at the K locality forms a typical mountain soil, in which only the upper layers show features, such as production of clay minerals and clay-size particles, destruction of unstable minerals, and iron enrichment, comparable to the degree of weathering associated with soil formation in more humid climates. The rock rubble which comprises the C horizon is similar in appearance to a saprolite, which is the characteristic product of granite weathering in mountainous terranes. Saprolite is often little more than disintegrated granite fragments and mineral grains held in a loose matrix of slightly weathered silt. Comparison of the analyses of the C horizon samples (K-4 and K-5) with that of the parent rock will therefore give an approximate indication of the character of saprolite weathering.

The weathering indices for Suite K indicate only mild weathering in the B and C horizons increasing to moderate weathering in the A horizon. The value of .750 for K-5 is probably a typical value for a saprolite. The appearance of the A horizon is that of a rather strongly weathered and comminuted soil; the weathering index is however not as low as in the A horizon of the other three soil suites.

The average net change for the total soil indicates gains in Fe, Mg, Co, Cr, Cu, Ni, Pb, Sc, V, and Zr and losses in Si, Ca, K, Na, Ti, Ba, Ga, Mn, and Sr. Si is lost in the B and C horizons whereas it increases in the A horizon. Such behavior may reflect the combination of removal of mechanically comminuted quartz grains from the parent rock - C horizon zone and removal of some silica released in feldspar weathering, accompanied by a relative concentration of quartz in the upper horizons as other elements are leached away. Mg increase is readily explained as a result of the survival and increase in biotite-chlorite in the upper horizons.

The D.I. changes for both raw and corrected to Al_2O_3 data are identical to each other but differ from the pattern for the total soil (above) in showing an increase in Si, Ti, and Ga in the upper horizons.

The C.I. values indicate that all fractions increase in Mg, Cu, and Ni and decrease in Al, Ca, K, Na, Ba, Sr, and Zr relative to the total soil. The sand and silt share increases in Si, Co, and Mn and decreases in Ga, Pb, and V; the opposite holds for the clay fraction. The silt shows an increase in Ti relative to a decrease in the sand and clay; Cr increases in the clay and decreases in the sand and silt.

The total soil exhibits pronounced enrichments in Co, Cr, Cu, Ni, Sc, and Zr. Cu becomes enriched in the sand of the A horizons and in the silt and clay of the C horizons. Similar enrichments of Mg, Cr, Ni, and Sc in the silt and Mg, Cr, Ga, Pb, Ni, and V in the clay are also notable.

The A horizon shows concentration maxima of Si, Co, Cr, Cu, Mn, Ni, Pb, Sc, and Ti and minima of Al, K, Na, Ba, and Sr; the B horizon contains maximum amounts of Fe, Mg, V, and Sr and a minimum of Ca.

Sample K-4 exhibits anomalies in D.I. and C.I. trends when compared to K-3 and K-5. This is indicated by a relative decrease in Mg, Ti, Co, Cr, Cu, Ga, Ni, and V in the TBS sample and is further reflected by increases in Mg, Ca, Ti, Mn, Ni, Sr, and V in the silt and Fe, Mg, Co, Ga, Ni, and V in the clay. These chemical anomalies have not been adequately explained. Their pattern could be due to an increase in weathering and/or enrichment in elements leached from above. K-4 is slightly higher in sand and lower in silt and clay and has a lower C.E.C. for its clay fraction than its two adjacent samples; this appears to discount the increase in weathering. The raw soil sample is noticeably redder (more free iron oxide ?) than either K-3 or K-5 but the Fe_2O_3 content in the TBS analysis and the free iron oxide value are not abnormal.

All elements except Al, Cr, and V attain maximum percent leachable amounts in the A horizon. The three exceptions are found in the B horizon. This observation coincides with the evidence that the A horizon is most weathered and further reveals that there has not been much downward migration of these elements upon release.

From the analysis of curve associations, these conclusions can be stated:

1.) Increases in Ca, Na, Ba, and V in the total soil are strongly influenced by the composition of the sand fraction.

2.) Both silt and clay composition have a positive effect on the total soil composition for Si and Al. The total Fe concentration is in part directly related to the amount in the clay whereas Ni and Ga are inversely related.

3.) As silt percent increases, there is a corresponding increase in Si and a decrease in Al, Ca, Ti, Ba, Cu, Ga, Sc, and V in the composition of the silt fraction. This strongly implies that as weathering breaks down feldspar, biotite, and magnetite to finer sizes, the principal residue in the silt size range is resistant quartz.

4.) Development of clay sizes leads to an enrichment in Si and Cr and depletion in Al, Cu, and Sr in the clay fraction.

5.) For the ferrides, there is direct correlation of Fe and inverse correlation of Cr, Mn, and Ni with free iron oxide in the total soil and direct correlation of Fe and V and inverse correlation of Mn, Ni (?), Cu, and Co with free iron oxide in the clay. The positive association of total Fe and free iron oxide indicate this element to be enriched as iron hydroxides and hydrolysates.

6.) Only Si, Ni, Co, Cr, Cu, and Mn show any positive association with C.E.C. Increase in C.E.C. is accompanied by decreases in Al, K, Na, Ba, Cu, Sr, and Sc in certain sample categories. Irregularities of pattern indicate that many of these associations are fortuitous. Cation fixation seems definite only for Co and possibly Ni. The association between K content in TBS, silt, and clay and the C.E.C. values was strongly negative.

7.) The rise in Cr, Cu, and Ni, in the top three samples may possibly be accounted for (in part) by the corresponding sharp rise in organic matter.

8.) The variations in percent silt and percent clay are similar to each other. C.E.C., percent organic matter, and percent $-H_2O$ all tend to closely follow silt and clay percentages.

Significant positive associations include in the TBS samples Mg-Cu, K-Sr, and Ca-Sr; in the silt Fe-Co, Fe-Cu, Fe-Mn, Fe-Ti, Fe-V, Mg-Sc, K-Pb, Ca-Sr, Al-Ga, and Al-Ti; and in the clay Fe-Cu and K-Pb. Negative associations are noted for K-Pb in TBS and Fe-Cr in the clay.

The relative geochemical associations of Fe to minors decrease up profile but usually show maxima in the B horizon. This pattern results from the combined effect of Fe increase in the B horizon and a corresponding increase in minor elements and decrease in Fe in the A horizon. Mg/Cu and Mg/Sc decrease upward by virtue of a relative increase in the minor elements whereas Mg/Ni decreases in the B horizon due to improverishment of Ni. Both Al/Ti and Al/Ga remain nearly constant. Ca ratios show decreases in the B horizon because of the relative increase of this element in the A horizon as a result of incipient caliche development. Most ratios in the clay fraction are generally more constant. Largest ratio changes, especially for Fe/Cu, Fe/Ni, Fe/V, Mg/Cu, Ca/Sr and Ni/Co, occur between samples K-4 and K-5 and are caused mainly by increases in the minor elements in K-4.

Comparison of the parent rock K-7 composition with a typical granodiorite indicates normal values for most of the minor elements. Ba is low and Sr high in K-7 which can be considered as evidence that the plagioclase is probably either more calcic and/or more abundant than indicated from the petrograpic study.

Weathering of granodiorite minerals should involve loss in Ga, Cr (?), Ba, and Sr and gain in Co, Mn, Ni, Sc, and V. Formation of kaolinite would enrich the soil products in Ti and Zr. Except for losses in Ti, Mn, and Cr, the above predicted changes actually occurred. Those three elements all are found in magnetite-ilmenite. Decrease up profile in leucoxene indicate a Ti loss. The Mn and Cr losses might be explained as due to a *relative* decrease in magnetite in a volume-increased soil even though the heavy mineral counts show it to have increased somewhat in proportion. The gain in some of the ferride minor elements may be correlated with the increase in biotite-chlorite in the sand fraction, although the absolute change of these minerals in the whole soil is not known.

Suite N: The soil from locality N is remarkable for its pronounced enrichment of certain minor elements during the weathering of a granite containing very small, sometimes undetected, amounts of these elements. The correlation between element enrichment and soil particle size is also well illustrated in this soil. Unfortunately, this soil was not subdivided into size and leach fractions nor were several of the soils chemistry tests made; inspection of the well-defined results of the TBS spectrochemical analysis indicates this to have been a soil deserving of a more thorough study.

The weathering index for Suite N shows the soil as a whole to be moderately weathered. The C horizon index lies at the borderline between mild and moderate weathering. The B horizon samples give strong weathering indices. The A horizon sample is only moderately weathered. The weathering index ratings closely follow the pattern of weathering intensity variation given by the percent clay and $-H_2O$ values. The probable causes for the increase in weathering in the middle horizons have been discussed on page 46. The rise in the weathering index for the topsoil sample N-1 can be explained as due to the increased amount of Na and K and probable decrease in Fe present in that horizon as the result of a relative feldspar accumulation consequent upon removal of clay particles to the B horizon.

The average net change data for the total soil indicates gains in Si, Fe, Mg, Ti (?), Ba, Co, Cr, Cu, Mn, Ni, Pb, Sc, Sr, V, and Zr and losses in Ca, K, Na, and Ga. Such a general pattern would result from the decomposition of the feldspars accompanied by a relative enrichment in magnetite and other heavy minerals and by strong adsorption on and/or incorporation in secondary clay minerals.

The D.I. values for this suite show an identical composite pattern of gains and losses as that of the total soil. Al decreases in all soil horizons relative to the parent rock. There are very large enrichments of Mg, Co, Cr, Mn, Ni, Ti, V, and Zr; several of these increase by factors of 10 to 40 times. The sharp drop in Ca from parent rock to soil is also conspicuous.

The greatest degree of enrichment occurs in the B horizon samples N-3 and N-4 which are also the most weathered. Na and K however increase again in the A horizon after undergoing apparent (?) decreases in the B horizon. The steady increase in Si towards the profile top coincides with the observed increase in quartz percentage. The Cr gain in the A horizon (especially N-1) could be due to increase in Cr-bearing magnetite and/or to selective association with organic matter. A similar explanation may also hold for Ni.

Direct comparison of concentration depth and particle size curves in Figure 8 shows striking parallel associations between Mg, Fe, Co, Mn, Pb, and

Sc and percent clay (and to a lesser extent silt) and between Ca, K, and Na and percent sand. Positive but less definite associations are noted between Ba, Cr (in part), Cu, Sr, V, and Zr and percent silt or clay. The association of these first and third element groups implies a direct relation both with clay mineralogy and with adsorption or exchange processes. The association of Ca, K, and Na with sand is obviously due to the importance of feldspars in this fraction.

The incompleteness of the free iron oxide curve allows only a suggestion of a positive relation between that parameter and increases in the first three samples in Fe, Co, Cu (?), Mn, Ni, and V. The slight rise in E_h (increased oxidation) in the B horizon fits the indicated trend of greater iron oxidation given by the free iron oxide curve.

Positive associations are evident for Fe-Co, Fe-Cu, Fe-Mn, Fe-V, Mg-Cu, and Mg-Sc. Negative associations are found for Fe-Cr and K-Pb. Ca and Sr tend to oppose each other in behavior, indicating Sr to be adsorbed selectively on the clays whereas Ca is easily leached from the profile.

Most of the relative geochemical association ratios clearly indicate the effects of selective enrichments and depletions in the middle horizons. The Ca/Na, Ca/K, and Na/K ratios all substantiate the general observation that feldspar stabilities increase in the order of their Ca-Na-K contents. Therefore, relative to the oligoclase and albite generations noted in the parent rock, orthoclase increases upward through the profile and reaches a maximum in N-3 and N-4.

Prediction of very low amounts of Co, Cr, Mn, Sc, and V, because of the scarcity of Fe-Mg minerals in the parent rock, is confirmed by the N-9 analysis.

Both Ba and Sr are low for an orthoclase and sodic-feldspar rich rock. Ni is unusually high. The kaolinite developed in this suite may account for some of the Ti and Zr enrichment. The possible presence both of chlorite and illite in the fine fractions may provide the hosts for those ferride minor elements which associate with these ferromagnesian clays.

Suite S: The soil from this North Carolina locality is developed under higher rainfall and wider temperature range conditions than the other three soils studied. This soil displays the extreme leaching and iron enrichment that are characteristic of most soils in the southeastern U.S. The most notable feature of the Suite S soil is the very marked enrichment of several minor elements in the upper horizons. Another noteworthy feature is the evident correlation that can be made between the rapid diminishing of several parent rock minerals in the developing soil and a sharp reduction in the concentrations of several elements which compose them. One feature that has not been adequately explained is the source or location of Fe in the parent rock; the apparent enrichment of Fe in the soil is visibly conspicuous but actually represents only a slight percent increase over the parent rock concentration.

The weathering indices for the soil show a pronounced increase in the degree of weathering between parent rock and C horizon (S-5) and very strong weathering in all overlying layers. The A and B horizons are rated as intensely weathered.

The average net change values for the total soil show gains in Si, Fe, Ti, Ba, Co, Cr, Ni, Pb, Sc, V, and Zr and losses in Mg, Ca, K, Na, Ga, Mn, and Sr.

The D.I. sequences for the raw data do not change in pattern when corrected to constant Al_2O_3. The grouped D.I. values differ from the total soil pattern (Table 13) in showing a decrease in Mn (except middle horizon layers), Ni, and Sc (except lower horizon layers). Al shows an over-all decrease. Inspection of the C.I. values indicates that, for most of the sand, silt, and clay samples, there is a general increase in Mg and decrease in Fe, Ba, Cr, Ga, and V. The sand and silt together have increases in Si, possibly Ca, and decreases in Al and Ti, coupled with opposite changes in the clay. Silt and clay show a gain in Zr and a loss in K relative to the sand. Sand and clay both exhibit increases in Mg and Cu and decreases in Mn and Sr in comparison to opposite changes in the silt. For Na, Co, Ni, and Sc, irregular gains and losses relative to a C.I. value of 1.000 in a series of values in one or more of the fractions indicates indefinite trends. On the whole, the Na values are similar in all 3 fractions; Co and Ni decrease in lower and increase in upper horizons in each fraction and Sc does the reverse.

Quite striking enrichments in Co, Cu, V, and Zr are evident in this soil both from C.I. and D.I. values and from the total soil net changes. The sand fraction shows a strong enrichment in Ni but in general shows only slight enrichment in Co, Cu, and V. The value of Ni in S-4 appears to be too high compared to its values in the other samples and is probably due to a precision fluctuation. The Zr rise is very large, considering that zircons are very scarce in either of the heavy mineral residues. As in Suite G, Zr may be largely present as the zirconate which can concentrate in the hydrolysates under certain conditions.

The analysis of the black concretion from the S-3 sample reveals it to be strongly enriched in Mg, Na, Co, Mn, Ni, Pb, and Sc, poor in Cr and V, and exceedingly low in Zr. The Fe content, relative to that in the parent rock, shows no increase. Visual examination of the concretion showed a blackish pigment-like coloration and occasional cores or splotches of bright pinkish-orange. The Mn content would explain the first color and the high Co content has led the writer to postulate the second color as indication of some secondary "cobalt bloom" mineral such as erythrite or bieberite. The enrichment of alkalis and alkaline earths along with the ferrides has not been explained but it is possible that these were adsorbed by the colloidal manganese wad that is presumed to comprise much of the concretion.

Maximum concentrations are found in the A horizon for Si, Co, Cr, Mn, and Zr and in the B horizon for Fe, Ti, Cu (?), Ni (?), and V. Minima in the A horizon include Al, Mg, K, Ga, and Sc and in the B horizon Ca, Na, and Sr.

There are sharp concentration changes for several elements between parent rock and S-5 and again between S-5 and overlying layers. These changes can be readily related to observed changes in mineral proportions due to rapid destruction of several unstable minerals as weathering proceeds from the moderate to the intense stage. Both chlorite and epidote are largely removed in the transition - parent rock to S-4. The destruction of most of the epidote between S-5 and S-4 (page 54) is accompanied by a pronounced decrease in Ca and Sr; the parallelism of behavior for these two elements suggests that most of the Sr is tied up with the epidote rather than the feldspar. The destruction of chlorite, a Mg-rich mineral, is chemically indicated by a sharp decrease in Mg in the soil and a nearly parallel decrease in Sc.

The increase in Si is partly the effect of contamination by windblown quartz grains. Some of the Si increase is a residual effect, as indicated by a corresponding decrease in Al.

The percent leachable element data shows maxima for Al, K, Co, Cu, and Zr (?) in the A horizon, for Si, Fe, Mg, Ca, Ba, and Sc in the B horizon, and Na, Cr, Ga, Mn, Ni, Pb, Sr, and V in the C horizon. The presence of a large amount of leachable elements in this "C horizon" differs from the other three suites. The sample S-5 from the C horizon has a clay-like appearance but is actually moderately weathered parent rock with only a small percentage of clay particles. It is difficult to explain the high leachability of several of these elements in S-5. Fixation of Mn, Ni, Na, and Pb in concretions in the upper horizons may be responsible for a "relative" rise in S-5 of the leachable amounts of these elements.

These possible associations are deduced from inspection of the curves in Figure 9:

1.) The nature of the sand fraction exerts a direct influence on the total bulk soil concentration changes of Si, Al, Fe, Ca, K, Ti, Co, Cr, Pb, Sc, and Zr; the silt fraction has a positive effect on the TBS changes of Fe, Ca, Ti, Ba, Cu, Sr, and V, and Zr and a negative effect on Mn changes; and the clay fraction shows a positive relation to the TBS changes of Si, Al, Na, Ti, Mn, V, and Zr.

2.) In general, concentration changes appear most strongly influenced by the silt fraction.

3.) Variations in Co, Ga, and Mn in the silt fraction correspond with variations in silt percent; most of the clay fraction concentration changes vary inversely with clay percent.

4.) The only elements to follow free iron oxide values are Ni and Cu in the TBS samples and Co in the silt fraction.

5.) Positive correspondence between C.E.C. and Na, Mg, K, and Ni in the silt fraction and negative correspondence between C.E.C. and Ti and V in the clay fraction are noted.

6.) Cr, Pb, and V (?) concentrations in the TBS samples show rises toward the top of the profile in accord with the increase in organic matter. These three elements are often associated with organic matter in sediments.

Strong positive associations have been found in the TBS samples for Fe-Ti, Ca-Sr, Al-Ga; in the silt for Fe-Cu, Fe-Ti, Fe-V, Mg-Cu, Mg-Ni, Mg-Sc, Ca-Sr, Al-Ga, Al-Ti; and in the clay for Fe-Cr, Fe-Ni, Mg-Ni, Mg-Sc, K-Sr, Ca-Sr, and Al-Ga. A negative association is noted for Mg-Cu in the TBS and K-Pb in the clay.

The up profile decrease in the relative geochemical association ratios of Fe/Cu, Fe/Cr, and Fe/Mn are caused by the large enrichments of the minor elements in the A and B horizons. The upward decrease in Mg and increase in Cu brings about the very striking decrease in Mg/Cu. Al/Ti and Al/Ga are generally constant over the profile. The behavior of Ca closely controls its ratios with Mg, K, Na, and Sr. K/Ba and K/Pb in both TBS and clay diminish because of the relative increase in the two minor elements. Both Fe/Cr and Fe/V (except in S-5) are nearly constant in the clay fraction.

Lack of data on trace elements in andesites and epidote and chlorite prevents an estimate of the expected composition of the parent rock. Most of the Fe is in the chlorite. Some Fe is probably also in the epidote. Magnetite is absent. The abnormally high iron percentage in the parent rock can be partly attributed to its calculation as Fe_2O_3 rather than as FeO, the form in which most of the iron occurs in the above two minerals.

C. Behavior of Individual Elements:

Table 19 summarizes data taken from Swaine (1955) on 1) the average trace element content of the lithosphere (Goldschmidt's estimates), 2) the normal range of trace element in soils of all types, 3) the average trace element content in soils, 4) the average amount of trace elements leached by 0.5 N acetic acid, 5) the range and average of trace element content in 43 profiles studied by Swaine (1951), listed in surface and subsurface categories, and 6) the trace element range in each of the four soil suites studied in this thesis.

Comparison of the analyses of the four soil suites with Swaine's data and also with data given by Butler (1954), Shimp et al. (1957), Allison and Gaddum (1940), and Wright, Levick, and Atkinson (1955) shows that the values obtained in this thesis are consistent with these studies of element distribution in soil profiles. Co, Cr, Cu, Ga, Ni, and Pb (which tend to enrich with increase in weathering intensity and duration) are lower in Suites G, K, and N than the averages in 3) and 5), probably because these three soils are less weathered and well-developed than most soils. The acetic acid leach values (Tables 11 A-D) agree very closely with the amounts indicated in 4) in Table 19.

One feature evident from examination of both the thesis data and these other studies is that the concentration, distribution range, and patterns of change of the individual trace elements show wide and often dissimilar variations among different soil types. It appears impossible to single out any element which consistently behaves in a like manner in all soils or which follows generally in all soils the known geochemical principles of its distribution. The geochemical behavior of any element must be studied and

TABLE 19

(All values in ppm)

	(1) Av. in Lithosphere	(2) Range In Soils	(3) Av. in Soils	(4) Av. Leached Acetic Acid	(5) Swaine's Av. & Range		(6) The Range in Four Soil Suites			
					Surface	Subsurface	G	K	N	S
Ba	430	100-300	100	± 30	300-3000 (1200)	500-5000 (1600)	683-1252	1761-2336	368-715	421-787
Co	40	1-40	10	0.1-1.0	<3-140 (20)	<3-200 (40)	6-17	4-7	6-9	39-246
Cr	200	5-1000	<100	0.3	15-500 (140)	200-800 (210)	10-23	8-24	27-114	109-339
Cu	70	2-100	20	1.0	10-140 (30)	10-250 (55)	50-65	4-18	12-22	143-209
Ga	15				12-70 (40)	20-70 (40)	11-13	14-18	12-21	12-18
Mn	1000	200-3000	600		50-7000 (1900)	70-7000 (2400)	532-1342	296-569	26-138	728-3857
Ni	100	5-500	35	0.1-6.0	5-100 (40)	10-150 (70)	4-14	4-15	10-33	8-23
Pb	16	2-200		0.2-6.0	20-550 (70)	10-70 (20)	10-20	14-20	10-15	5-21
Sc	5	15-38			<10-15 (5)	<10-20 (8)	21-24	5-8	5-10	16-53
Sr	150	50-1000	350		60-1000 (380)	50-1000 (430)	289-485	211-397	36-66	67-264
Ti	4400	1000-10000	3500	< 1.0	1000->12000	3000->12000	6610-9850	3260-4820	2875-4510	7460-10730
V	150	20-500	<100	0.5	20-300 (120)	25-300 (150)	123-195	69-96	38-68	335-690
Zn	80	10-300	80	± 30	6-30 (11)	6-22 (5)	-	66-80	-	87-204
Zr	220	60-2000			70- >1000 (700)	100->1000 (700)	321-465	446-1048	352-860	48-611

explained in terms of the soil type, parent rock composition, and conditions of formation which apply specifically to each soil; similarities in behavior are discernible only in a general way for Soils Groups and Soils Series.

In the remainder of this subsection, each minor element will be treated briefly according to 1) the principles governing its behavior in magmas and in weathering and soils (references: Goldschmidt (1954); Rankama and Sahama (1950), and 2) its behavior in the four soil profiles in relation to these principles.

Barium: Ba^{++} (r = 1.43 A) preferentially associated with K^+ (1.33 A) in magmas and is therefore concentrated in K-feldspars and micas. During weathering, Ba release is controlled by the extent to which these igneous minerals survive. Ba is soluble in bicarbonate solutions. Ba can be precipitated as the insoluble sulphate, fixed in exchange positions on clays (it is more readily adsorbed than Sr), and in special cases concentrated with Mn (in nodules,etc.). Most secondary soil minerals are low in K; hence the association of Ba with K becomes less definite and is affected by their relative solubilities and fixation properties.

Ba is lost, along with K, in the weathering of G and K suites but is enriched in N and S. In Suites G, K, and N the leaching of Ba is proportionately less than of K. This is largely the result of preferential adsorption of Ba over K, as indicated by the up-profile decrease in K/Ba ratio and by the larger relative amounts of Ba removable by leaching. Much of the Ba associates with the clays. Ba probably also shows a relative enrichment by retention in the micas (which have higher Ba/K ratios than orthoclase) which survive in Suite K (and G?) more readily than the K-feldspars. The increases in Ba and Mn and decrease in K in S-TBS substantiates the known associations of these elements. However, the C.I. values for K, Ba, and Mn all increase in the Mn-concretions from S-3. The association between Ba and Mn is again indicated in Suite N by the comparable increases in their D.I. values in contrast to a decrease for K.

Chromium: Cr^{+++} (0.64 A) can replace Fe^{+++} or Al^{+++} in igneous minerals and is therefore found in the spinels, pyroxenes, amphiboles, and micas. The spinels (magnetite, chromite, ilmenite, etc.) are relatively insoluble, effecting an enrichment of Cr^{+++}, whereas these other minerals will more readily release their Cr^{+++}. Upon weathering, part of the Cr^{+++} is usually oxidized to the soluble chromate ion $(CrO_4)^{--}$ in which Cr assumes the sexivalent oxidation state and some of the remainder of the Cr^{+++} may be affixed to clay minerals. The fraction converted to CrO_4^{--} increases with higher pH and more positive E_h conditions. Cr in weathering commonly follows Al (concentrated in bauxite deposits) and is somewhat similar to V in behavior. Cr, V, and Pb often associate together in the organocolloid fraction of the soil.

In Suite G, the loss of Cr with more intense weathering cannot be adequately explained, inasmuch as this element should be dominantly in the magnetite which proportionately increased during weathering. Neither a high pH nor E_h, capable of CrO_4^{--} formation, prevails in this soil. In Suites K and N the upward increase in Cr reflects relative enrichment in the less soluble magnetite and mica. In both soils a sharp rise of Cr in the top A horizon is believed to be caused by enrichment within organic matter. The rise in Fe/Cr ratio in the B horizons in all four soils demonstrates the greater solubility of Cr as oxidation increases the amount of Fe^{+++} collecting in mid-profile. Both Cr and Mn enrich up-profile in Suite S but not in the same manner. The low Cr content of the Mn-concretion corresponds with observations by others of an antipathy between Cr and Mn. Organic matter may again be responsible for Cr behavior in the upper part of this soil.

Cobalt: The ionic radius of Co^{+++} (0.82 A) allows it to substitute for Fe^{++} (0.83 A) and to a lesser degree for Mg^{++} (0.78 A). In weathering, Co^{++} can oxidize to Co^{+++} which roughly follows the behavior of Fe^{+++} in soils. Cobalt is moderately soluble in bicarbonate solutions but is readily precipitated along with the colloidal hydroxides of Fe and Mn. Co^{++} can concentrate in the hydrolyzates by adsorption. Co also concentrates in the oxidates (e.g.: sedimentary iron ores) to the degree that the ratio Co/Ni may exceed 1.0, much higher than the usual 0.4 to 0.6 in igneous rocks and most soils. Co also may strongly enrich in Mn nodules to form asbolan (cobalt wad) in which the Co/Ni ratio exceeds 2.5.

In Suites G, K, and N the amounts and variations of Co are both small. In all four soils, Co increases relative to Fe as weathering progresses. The much higher proportion of Co to Fe available by leaching indicates its greater solubility and/or fixation in exchange positions. D.I. values in the soils K, N, and S show Co to enrich more extensively than Fe or Mg. The depletion of Co and Mg and enrichment of Fe and Ni in Suite G suggest that, in this soil, most of the Co was originally associated with augite and not magnetite. The Ni/Co ratios decrease with more intense weathering in the basic soils G and S and increase in the acid soils K and N. This is unusual, considering that residual Ni deposits due to weathering form almost exclusively from basic parent material. Only in Suite S does the Co/Ni ratio exceed 1.0; this soil is most like an oxidate iron deposit. The pinkish-orange masses in the Mn-concretions are excellent examples of asbolan.

Copper: Cu occurs primarily in the chalcophile or sulfide phases in igneous rocks. Cu^{++} (0.83 A) can replace Fe^{++} or Mg^{++} in spinels and pyroxenes. The behavior of Cu in weathering depends largely on redox conditions. Organic matter, limited rainfall, and poor drainage favor Cu^{+} which forms insoluble Cu_2O (cuprite) whereas higher pH and E_h leads to Cu^{++} which is more easily removed in solution. Fixation by clays retains some of this element in both valence states. Cu is known to concentrate by forming compounds such as $CuMn_2O_5$ in Mn-nodules.

Despite semiarid conditions promoting Cu^{+} retention, the copper in Suite G is partially leached away. In this suite Cu closely follows Mg; both elements are largely in the augite. In Suites K and N (and possibly S) the Mg/Cu ratio drops sharply with stronger weathering due to the fixation of Cu in exchange positions on the clays. The rather small variation of Fe/Cu implies that these two elements may associate in some way. The tendency for this ratio to increase in mid-profile can be explained as evidence of precipitation of Fe versus greater solubility of Cu as oxidation increases. Copper does not seem involved in manganese compounds in Suite S, for it shows only slight enrichment in the S-3 concretion relative to a larger enrichment in the total soil. No distinct relation between organic matter and Cu is noted in any of the profiles.

Gallium: Ga^{+++} (0.62 A) can substitute for Al^{+++} (0.57 A) with which it closely associates in igneous minerals. During weathering this association continues but the Al/Ga ratio usually increases due to greater solubility of Ga (in neutral or weakly alkaline solutions). Ga is enriched, along with Al, in the hydrolyzates. An association with Fe^{+++} and Mn^{++++} has also been established; however, the Ga content in Mn nodules is usually low. An affinity for organic matter has been noted.

A strong coherence between Al and Ga is found in all four soils (Al/Ga gave the highest positive correlation coefficient). This pattern of profile variation diverges only in Suite N, in which Ga is leached from the most weathered horizons and concentrated in the topsoil whereas Al regularly decreases toward the A horizons. The ratio Al/Ga varies only slightly in all four soils. Only in Suite S does the value of Al/Ga increase noticeably with advanced weathering; this suggests that this observed increase occurs only in well-developed soils in which leaching has been active long enough to selectively remove the Ga. The very small amount of Ga available through acetic acid leaching confirms its relative insolubility in acid solutions. The enrichment of Ga in Suite G is unusual because solutions permeating this soil were likely to be alkaline. The Ga however may be associated with the montmorillonoid clays formed in this soil. There is no indication of any association of Ga with Mn in the concretion from S-3.

Manganese: The geochemistry of Mn is largely controlled by its oxidation state. In igneous minerals Mn^{++} (0.91 A) can substitute for Ca^{++} (1.06 A), Fe^{++} (0.87 A), or Mg^{++} (0.78 A). In weathering, Mn^{++} may change to the relatively insoluble Mn^{+++} or, more commonly, to Mn^{++++}. Mn^{++++} readily combines with oxygen to form the insoluble MnO_2. Mn solution is favored by a very low or very high pH and by reducing conditions. Bicarbonate solutions effectively remove Mn. The initial Fe/Mn ratio in weathering tends to be constant but as weathering continues the two elements become separated because their colloidal hydroxides are oppositely charged. The negative Mn colloids are powerful collectors of Ni, Co, Cu, Pb, Zn, V, Ti, Ca, and Ba; those elements usually enrich in Mn nodules. Mn^{+++} (0.70 A) follows Al^{+++}; Mn^{++++} (0.52 A) competes with V^{++++} (0.61 A) and Ti^{++++} (0.64 A). Precipitated $Mn(OH)_4$ in time decomposes to hydrated Mn oxides (psilomelane, etc.).

With all four soils now showing oxidation conditions and intermediate pH ranges, enrichment of Mn would be expected. However, only in Suite N is this enrichment notable; the actual amounts in this soil are low but still much greater than in the parent rock. In Suites G and K, Mn is lost whereas Fe, Ti, and V increase. This may imply that, under climatic conditions in the Rocky Mountains, Mn is more soluble than these elements and that oxidation to Mn^{++++} becomes important only with more intense weathering. Also, some of the Mn may have occurred in the plagioclases or augite and, upon destruction of these minerals, remained in the more alkaline solutions that existed in the earlier stages of weathering. The Fe/Mn ratios are not constant in any of the soils. In G and K, the ratios increase in mid-profile, due to greater solubility of Mn relative to Fe. However, Mn enrichment increases in the upper horizons of Suite K both because of the greater supply of oxygen near the surface and because of probable fixation on clays (as indicated by much higher leachability in sample K-1). The decrease in Fe/Mn in Suites N and S reflects the strong enrichment of Mn in the more weathered and oxidized upper horizons. In S, the Mn-concretion shows definite enrichment in those elements (except V) which can be adsorbed on colloidal Mn.

Nickel: Ni^{++} (0.78 A) associates with both Mg^{++} and Fe^{++} in igneous minerals. Unlike Co^{++}, Ni^{++} is not oxidized in weathering. Ni^{++} is soluble in bicarbonate solutions but is more easily reprecipitated than Mg^{++}. Ni^{++} accumulates in the hydrolyzates both by adsorption on clays and by incorporation in two-sheet hydrosilicates (garnierite, Ni-chlorites). Ni preponderates over Co in shales and many soils, both in total amount and in relative enrichment.

The affinity for hydrolyzates and the relative insolubility of Ni is demonstrated by the enrichments noted in all four soils. In none of the four soils does Ni clearly indicate whether it prefers to associate with Fe or Mg during weathering. Ni enrichment in the A horizons in the granite soils K and N is pronounced. In K the Ni associates with Fe whereas in N it associates with Mg. In both soils incorporation within and/or adsorption on clay minerals control the Ni distribution, although in Suite N the Ni increase (which does not correspond with clay size variations) may also be connected with its possible occurrence in magnetite which proportionately increases upwards. Ni enrichment in the basic-derived soils G and S is not large and may in fact represent the greater solubility of Ni in these soils which were alkaline in their early stages of weathering. Ni in Suite S is probably located in the chlorite; the nearly complete loss of this mineral in the A and B horizons may account for the upward depletion of Ni, although the loss is partly counterbalanced by retention of Ni in the Mn-concretions.

Lead: In igneous rocks, Pb^{++} (1.32 A) closely follows K^{+} (1.33) in potash feldspars and mica. Pb^{++} will also replace Ca^{++} in apatite and can complete with Sr^{++} and Ba^{++} in some minerals. Pb^{++} during weathering is readily soluble in bicarbonate solutions. Pb is usually lost in weathering but may enrich in soils with the hydrolyzate phases. Enrichment can be effected by clay adsorption, precipitation as the sulphate or sulfide, and association with organic matter.

Loss of Pb during weathering apparently occurs only in Suite S. Pb shows enrichment in the clay fraction in Suites G, K, and N. Adsorption in exchange position is probably the most important geochemical control in these soils. In addition, organic matter appears to concentrate Pb in both G and K. Except in the clays, Pb^{++} and K^{+} show no definite correlation.

Scandium: Sc^{+++} (0.83 A) follows both Fe^{++} (0.83 A) and Mg^{++} (0.78 A). Despite the larger difference in ionic radius, Sc prefers to proxy for Mg. Sc is found in the pyroxenes, amphiboles and micas. Little is known about the weathering behavior of Sc. $Sc(OH)_3$ is generally produced by hydrolysis and is a strong, relatively soluble, base. Sc associates with Fe and Mn (in the oxicates) and tends to shun $Al(OH)_3$ deposits (bauxites, etc.)

Sc behavior in the four soils cannot be conclusively tied to either Fe or Mg. Sc is lost only in Suite S. Comparison of Fe, Mg, and Sc variations in these soils shows generally a closer association of Sc with Fe in all but Suite S. In this suite Sc appears to correspond with Fe distribution in the lower profile (both Fe and Mg probably occur together with the Sc in the chlorite) and with Mg in the upper profile. However, this latter association may be coincidental, in that both elements are adsorbed in the Mn-concretions. The enrichment of Sc in the clay sizes indicates adsorption, although very little of this element is released by acetic acid leaching.

Strontium: Sr^{++} (1.13 A) substitutes primarily for Ca^{++} (1.06 A) and also for K^{+} (1.33 A) in igneous minerals. It therefore is found in the later fractions of calcic minerals and earlier fractions of potassic minerals. Sr^{++} readily passes into solution as the bicarbonate (but is less soluble than Ca) and is highly mobile during weathering. Sr undergoes moderate fixation (less than Ba) on clay minerals and may also be adsorbed by Mn colloids. Precipitation as the sulphate is unimportant in soils. Sr retains its affinity for Ca in sedimentary deposits. In mature soils, isomorphous Sr is dominantly in the illites.

In the four soils, no strong preference of Sr for either Ca or K is indicated. Ca is more soluble than Sr or K, as indicated by the higher percent leachable element values. This also implies that both Sr and K are held more tightly on clay minerals and therefore enrich by fixation. Sr fixation on clay particles is very likely in Suite N, in contrast to the extreme leaching of Ca. The reciprocal behavior of the D.I. values for Sr and K in this suite may indicate Sr to be more effectively adsorbed on the clay sizes. However, in Suites G, K, and S doubt is cast on the importance of adsorption in the clays because 1) the lowest C.I. values are found in the clay fraction, and 2) Sr values vary inversely with clay size. Because high D.I. values are found for both Sr and Ca in the silt fraction, it is suggested that the Sr variation in these three soils is mainly a function of the degree of weathering of their calcic minerals. The slight enrichment of Sr relative to Ca loss in Suite G has not been explained. No association with Mn in Suite S is indicated.

Titanium: Ti^{++++} (0.64 A) in igneous minerals is found primarily with Fe^{+++} in ilmenite, magnetite, and rutile. Both Ti^{++++} and Ti^{+++} may also substitute for Al^{+++}, Fe^{+++}, and Mg^{++} in the pyroxenes, amphiboles and micas. Ionic Ti and titanates are very uncommon. Most Ti released in weathering recombines with oxygen to form rutile which occurs in clay minerals as tiny, often submicroscopic, needles. Some Ti follows Al into the lattice structure of the clay minerals. Only a very small amount of Ti is fixed on the clay minerals. In mature soils (and in sediments) some of the Ti occurs as leucoxene, a first stage alteration product from Ti-bearing resistate minerals.

The behavior of Ti in the four soils is somewhat erratic. Except for Suite N, Ti does not strongly enrich nor does it undergo any substantial depletion in the total soil. Much of the Ti in Suites G, K, and N is present in magnetite and rutile. Because these minerals concentrate as resistates, the slight increase in total Ti observed in these suites is partly explained. The positive correlation of Al with Ti in Suite K signifies incorporation of released Ti in the clay minerals formed by weathering. However, a strong positive association of Fe with Ti in the silt fraction in this suite indicates a further part of the Ti occurs in magnetite which has accumulated in that size range. The enrichment of Ti in G-2 relative to G-4 in all size fractions appears to contradict the evidence noted in the total bulk soil analyses of a depletion of most minor elements in G-2 relative to both G-1 and G-4. However, this discrepancy is reduced when the concentration changes in each fraction are adjusted according to their proportions in each sample. In G-2, Ti increase in magnetite (especially in the finer fractions) is partly offset by a reduction in rutile-leucoxene. The source mineral for Ti in Suite S is unknown. The behavior of Ti in this suite follows both Fe and Al in the silt but not in the clay, in which Ti enrichment reaches a maximum. The complete absence of detectable Ti in all leachates confirms the insoluble character and very low fixation of this element.

Vanadium: V^{+++} (0.65 A) associates with Fe^{+++} and Cr^{+++} in igneous minerals such as magnetite, chromite, amphiboles, and micas. Oxidation converts V^{+++} to V^{+++++} (0.4 A) during weathering. A high redox potential favors formation of the $(VO_4)^{---}$ ion which is soluble over a wide range of pH. $(VO_4)^{---}$ is precipitated by 1) reduction to V^{+++} by such agents as organic matter, 2) formation of Pb, Zn, Cu vanadates, 3) incorporation with Al or Fe hydroxides, or 4) formation of a basic ferric vanadate. V^{+++++} ion (as the vanadate) associates with ferruginous deposits (e.g.: laterites) and bauxitic clays (highest V content when derived from basic parents); V^{+++} associates by adsorption and lattice substitution with the hydrolyzate clays. V has a preference for organic substances and for MnO_2.

A tendency for enrichment of V in soils and for a strong association between Fe^{+++} and V (probably in the quinquivalent oxidation state) is noted in all four soils. V increases with % free iron oxide in the B horizon of these soils and probably follows Fe upon oxidation into the iron-rich cements, stains, and colloids. The Fe/V ratio varies little during weathering; a slight decrease in the ratio toward the profile top, due to a small relative decrease in V, can be noted in Suites K, N, and S. Some of the V enrichment is evidently associated with the clay fraction, especially in K and N. Less V than Fe is removable by leaching, indicating stronger fixation. A part of the V undoubtedly remains in magnetite and other resistate minerals. In the S-3 concretion, V and Mn do not show parallel associations. No indication of enrichment within organic matter is seen in any of the soils.

Zinc: Zinc is found as Zn^{++} (0.83 A) in Fe^{++} or Mg^{++} lattice sites in igneous biotites, amphiboles, or ilmenite. Most Zn occurs as the sulfide. Zn^{++} in weathering is soluble in sulphate and chloride solutions but is precipitated as the carbonate or oxide. Zn concentrates primarily by fixation on clay minerals and by incorporation in organic matter.

The Zn geochemistry in the four soils is obscured by its only partial detection in some of the soils and their size fractions. A definite tendency to enrich in the clay (and silt) fraction is evident in Suites G, K, and S. The Zn increase in these suites toward mid-profile shows its mobility during leaching from iron-bearing minerals, together with partial recapture by fixation in the B horizon colloids. Organic matter apparently has little influence in these soils.

Zirconium: Zr is present in igneous rocks largely as the stable $ZrSiO_4$ (zircon) but a small amount of Zr^{++++} (0.87 A) occurs in femic minerals. Zircon is slowly soluble during weathering; the zirconate thus formed will precipitate in (as ZrO_2 or $ZrSiO_4$) or adsorb on the hydrolyzates.

In Suites K and N, the increase in Zr is directly attributed to its survival in zircon relative to loss of other minerals. In both G and S, the presence of any appreciable zircon is doubtful, although this mineral may be present in submicroscopic sizes. The gradual loss of Zr in Suite G is not explained by the meager evidence. The absence of Zr in the leachate from G would seem to rule out loss through increased solubility. On the other hand, the strong enrichment in Suite S from a parent rock almost devoid of Zr, together with a virtual absence of zircon and a high percent leachable Zr indicates this element to be present as soluble zirconate reprecipitated from soil solutions as the oxide or silicate. The tendency in all four soils for a higher Zr content in the sand and silt fractions is certainly due to preservation of zircons of these size ranges.

CONCLUSIONS AND RECOMMENDATIONS

Specific interpretations and conclusions concerning the results presented in this thesis are summarized on pages 14-17. In this concluding section the writer presents his general evaluation of the thesis results and his proposals and recommendations for future investigations of trace element behavior in rock weathering and soil formation.

The original postulate that minor elements would serve as far more sensitive guides to chemical changes in weathering has not been supported by the results to the degree expected by the writer. As a general rule, enrichments of minor elements (expressed as Distribution Indices) range from equivalent to two-three times greater than those shown by the major elements. Depletions in the soil for both major and minor elements are generally of similar magnitudes.

After the analytical results were obtained, the writer noted erratic behavior and anomalies in some element variation trends in a series of samples (see, for examples, G-2 and K-4 analyses). This introduced an uncertainty as to whether an anomaly was caused by a real geochemical variation or by experimental errors. This question is still unanswered; however, a survey of the few studies made of major and minor element distributions in a profile (e.g.: Butler, 1954; Shimp et al, 1957) disclosed that these studies show similar anomalies, of comparable magnitudes and patterns; these anomalies are usually ignored and unexplained by the investigators. The writer has found no other published analytical work having fractions separately analyzed to which the present results can be compared to determine whether a "material balance" is the exception or the rule. The work of Joffe and Kunin (1943) shows analyses of individual fractions but does not give corresponding size percentages.

In regard to the objective of determining the trace element distribution among individual size fractions, it cannot be said conclusively that the thesis results are either typical or erroneous. The 28% interplate error indicates that element distributions (changes in concentration) among the several fractions cannot be directly compared with high confidence.

It is concluded that the character of the results (including particle size and soil chemistry analyses) given in this thesis do not differ in any abnormal way from results of other studies of a similar nature.

In addition to providing specific results and interpretations for four soil suites, this thesis has served as a "pilot" study for future detailed work. Drawing upon experience gained from the thesis investigation, the writer would like to make, for the benefit of others interested in this aspect of weathering, the following recommendations for further study:

1.) The sampling program should be designed and extended to include a wider range of soils formed from a variety of parent rocks and under all kinds of climates. Conclusions regarding geochemical behavior of the minor elements in this thesis are severely limited by the small number of profiles studied, even though these profiles were chosen from widely different parent rocks and climates. In future work, representative samples from each of the Great Soils Groups and, if possible, many of the Soils Series should receive thorough treatment. In addition, there is a need for information on the variations in concentrations encountered within a single soil type; several profiles should be sampled over a limited area to ascertain the averages and typical ranges of concentrations in a particular soil.

2.) For the rapid study of large numbers of elements simultaneously, the mutual standard method can be further improved to compete favorably with the best of the other analytical methods. Improvement over the results obtained in this thesis can be achieved by:

(a) Using a wide variety of soil and rock standards to prepare the working curves. At present, such accurately analyzed standards are not available.

(b) Correcting for the matrix effect by use of curves which show the variation of an analysis line intensity as a function of variable amounts of dominant elements.

(c) Employing a modified analytical set-up such that Al 3082 need not be used as the variable internal standard. In order to analyze for as many or more elements as in this thesis, it is suggested either to cover a wider spectrum range by photographing on two plates or to analyze independently for Al (and several other major elements) by x-ray fluorescence spectroscopy.

3.) Other analytical methods having greater accuracy may be necessary to pinpoint the location of some trace elements within the various phases in a soil. If the study can be restricted to one or several trace elements, some of the extraction (e.g., dithizone) or colorimetric methods are capable of very sensitive detection and acceptable reproducibility.

4.) Improved techniques for separating and isolating mineral, colloidal, and organic phases in the soil need to be developed before the trace element distribution within discrete phases can be ascertained. Most existing techniques, at least in the final refining stages, involve such harsh chemical treatments that elements from phases other than those being separated are often added to the extracts. The difficulty of mechanically or chemically separating discrete phases in a soil (or sedimentary) complex is at this time (in the writer's opinion) the chief limitation to the advancement of our knowledge of the geochemistry of such systems.

5.) Further work needs to be done along the lines of Roy and others at Penn State (Roy, 1955) in synthesizing clay minerals in the presence of minor elements. Preparation of synthetic clays would allow determination of 1) tolerance limits of minor elements in clay mineral structures, 2) the effect of minor elements on the stability of these minerals, 3) amount of a minor element that can be adsorbed on a "pure" clay mineral under different exchange conditions, and 4) the fraction of a fixed minor element that can be removed by leaching under controlled conditions.

6.) Whenever expedient, the individual minerals in a soil parent rock should be analyzed for their trace element content. This was not done in this thesis because of expected difficulties in obtaining homogenous mineral separates from the two fine-grained rocks.

7.) Further work needs to be done on the incipient and early stages of weathering. This can be effectively done by analyzing weathered crusts and near-surface layers of parent rock exposures in the vicinity of a soil profile.

APPENDIX A

SOIL CHEMISTRY

In cooperation with the Soils Stabilization Laboratory at M.I.T., measurements of soil moisture, soil pH, E_h (redox potential), salt content (conductivity), organic matter, free iron oxide, and the cation exchange capacities of the silt and clay fractions were made on each soil sample. The procedures followed in these measurements were those used in routine determinations at the M.I.T. Soils lab. Working methods have been developed there by Dr. R. T. Martin, in part as modifications of methods described in an unpublished manual by Dr. M. Peech of Cornell University.

I. Methods:

Soil moisture (pore and loosely held water) was measured as the loss in weight due to water evolution after a disaggregated portion (about 10 gms.) of gravel-free soil was heated at 105 - 115° C. in an oven for 12 hours. The $-H_2O$ loss is reported in percent. The soil weights used in other tests described below were adjusted to an oven-dried basis.

Soil pH is a measure of soil reaction or the degree of acidity or alkalinity of the soil. The significance of pH in relation to soil development, along with the problems in obtaining a meaningful measurement, have been summarized by Thorne and Seatz (Chemistry of the Soil, 1955, pp. 219 - 251). It should be noted here that the pH values obtained in a particular measurement will vary according to the method, instrumentation, time, and conditions selected for the measurement.

A Beckman pH meter, with calomel and glass electrodes, was calibrated before each series of pH determinations by balancing against standard buffer solutions of pH = 4 and pH = 7. Ten grams (± 0.1 g.) of air-dried soil was mixed in a 50 cc. beaker with 10 cc. distilled water and 10 cc. 0.02 M $CaCl_2$ (see Schofield and Taylor, 1955). After standing 30 minutes to reach equilibrium, the pH of each suspension was read directly on the pH meter.

The <u>redox</u> (<u>or</u> <u>oxidation-reduction</u>, <u>O/R</u>) <u>potential</u> E_h, expressed in volts, is a measure of the oxidizing or reducing ability of a system. The E_h of a soil represents the composite effect of the relative oxidation and reduction states of all solid phases (minerals, organic matter, exchangeable cations, etc.), liquid phases (pore water, etc.) and gaseous phases (free oxygen, CO_2, etc.) which make up the soil. It is further strongly influenced by the quantity, types, and relative activities of any bacteria present. The many factors which influence and vary the E_h in soils and sediments and the difficulties of obtaining representative measurements are aptly summarized by ZoBell (1946) and by Merkle (1955).

The E_h of a soil measured in the field under natural conditions may differ considerably from that measured later in the laboratory on the same samples. Dr. K. S. Spiegler of Gulf Research has pointed out to the writer that a given E_h measured in the laboratory may be only an evanescent or non-typical value if the soil system by that time is no longer poised (E_h-buffered). An estimate of the extent that this E_h reflects the field conditions can be made by determining the reducing capacity (see ZoBell, 1946, pp. 496-98) of the system.

The E_h of selected samples from each suite was measured by the standard procedure of determining (on a Leeds and Northrup potentiometric pH meter) the potential difference set up between platinum and calomel half-cells. This potential difference E was converted to E_h by the equation $E_h = 0.242 + E$, in which the term 0.242 converts the calomel half-cell voltages to that of the standard hydrogen cell to which E_h values are referred. The E_h meter was calibrated with a standard $K_3Fe(CN)_6 - K_4Fe(CN)_6$ solution having an O/R potential of +0.430 Volts (European sign convention) at 25° C. The meter read +0.417 Volts; hence a correction factor of +0.013 Volts was added to each reading. The reducing capacity of each soil was roughly estimated by observing the relative rate and degree of voltage drop to a constant value after addition of 0.025 me/cc. of $KMnO_4$ solution.

Because E_h is a function of pH, the pH of each 10 gm. sample, suspended in 120 cc. H_2O, was measured just prior to the E_h determinations. All E_h values can be reported in terms of a hypothetical equivalent at pH = 7 by applying the correction factor $E_h = 0.06$ Volt per pH unit, subtracting from E_h values for pH's less than 7 and adding for pH's greater than 7.

The pH, the initial E_h, and E_h adjusted to pH = 7 (E_{h_7}) for the selected soil samples and the parent rock from each suite are given in Table 9 on page 65.

The pH values are about 0.6 - 0.9 pH units higher than those (shown in the same table) first determined at M.I.T. This is due to the higher water: soil ratio of 6:1 in the E_h runs as compared to the 2:1 ratio in the initial runs. Most of the soils appeared to be poorly poised; hence the E_h values may not be representative of the field values.

Electroconductivity of a soil suspension is an indication of the amount of *soluble salts* present in the soil complex. The principles of measurement are discussed in the U.S.D.A. Soil Survey Manual, (1951, pp. 343-53). Conductivity was measured in the soils samples in terms of the resistance R offered by an ionic solution (from the dissolved salts) to the free passage of current through this solution. A Wheatstone bridge circuit was used to measure first resistance R' of 10 cc. of 0.02 N KCl (as standard) and then R offered by a 5 gm. soil suspension in 10 cc. distilled water. The soluble salt content, in terms of milliequivalents (me) NaCl/100 grams soil, was then calculated as: Sol. Salts $= 4.78 \frac{R'}{R} = \frac{817}{R}$ (when $R' = 171$).

Organic matter is present in many forms and in various degrees of decomposition in soils (see Fraser: Chemistry of the Soils, 1955, pp. 149-76). Most methods of measurement are indirect (measuring either total carbon or evolved gaseous combinations of C, H, O, and N) and give incomplete results, as all organic matter does not react or decompose to the same degree. The soil samples were analyzed for (%) organic matter by Peech's method (1947). A solution of potassium dichromate and sulfuric acid oxidized the organic matter and any unreacted dichromate was then titrated with ferrous sulphate solution (barium diphenylaminesulfonate indicator). This method accounts for about 80 - 85% of the total organic carbon in the soil.

Free iron oxide is an indirect measure of the amount of ferric hydroxide and hydrates which accumulate in the soil as cements and grain coatings and as colloidal silicate and hydroxide gels and hydrosols. This parameter is an important indicator of the degree of weathering and degree of development of the B soil horizon (zone of iron accumulation) as it indirectly defines the extent of migration of released ferrides and the relative effects of oxidation-reduction processes acting on the soil. Free iron oxides within the four soil suites were brought into solution using the extraction procedure (bleaching with sodium thiosulfate) of Mackenzie (1954) and the (%) ferric oxide was then determined colorimetrically by the use of the o-phenanthroline color reaction (Peech and English, 1944).

The exchange capacity in a complex system such as a soil is a colligative property in which the value measured is the sum of contributions from many phases. The organocolloid, ultraclay, clay, and silt fractions (in the order of decreasing capacities) are responsible for nearly all of a given exchange capacity value in a soil. The theory and significance of ion exchange and exchange capacity are thoroughly discussed by Wicklander (1955, pp. 107-48).

The cation exchange capacity (C.E.C.)[1] was determined separately on each clay and silt fraction extracted for spectrochemical analysis (see page 166). The total C.E.C. for each soil sample was then computed as the weighted sum of these fractions in proportion to their percentage size frequencies (recalculated with the sand and gravel fractions neglected). C.E.C. (expressed as milliequivalents/100 grams or me/100 g.) was determined by the ammonium acetate method of Peech (1947), with modifications. A 50 - 200 gm. sample (amount depending on the estimated exchange capacity of the soil) was treated 5 times with 1 N ammonium acetate (pH = 7), the excess salt was removed with ethanol, and adsorbed NH_4 ion was then

---

[1] Whenever possible, this abbreviation has been used in the thesis in place of cation exchange capacity.

displaced by leaching with an acid (pH = 2.3) 10% NaCl solution. The NH_4 in this solution was then determined colorimetrically after addition of Nessler's reagent.

APPENDIX B

SPECTROCHEMICAL ANALYSIS

I. Introduction:

All chemical analyses of the soil and rock samples from the four soil suites were carried out by spectrochemical methods set up and used in the Cabot Spectrographic Laboratory at M.I.T. Analyses were made for 21 elements in a total of 68 individual samples, comprised of total bulk soil, sand, silt, clay, parent rock, and leach extracts from the soil suites.

Spectrochemical analysis was chosen over other analytical methods because of 1) its rapidity in examining large groups of elements simultaneously, 2) the relatively low cost of analysis, 3) the comparative simplicity of the analytical procedures, 4) the preservation of a permanent record of the results, 5) the coherence impressed upon the data as the result of determination of all elements in the same manner, and 6) its ability to detect and measure quantitatively certain elements more efficiently than other available methods. For most of the major elements, greater accuracy and precision can be attained by classical wet chemical methods of analysis[1]. Some of the minor or trace elements also can be

---

[1] The relative merits of wet chemical and spectrochemical methods of analyzing the same elements are discussed in Fairbairn, et al. (1951).

better analyzed as individuals or in small groups by other methods (See: Yoe & Koch, 1957). However, no method developed as of 1957 has yet proved as effective for the semi-quantitative or quantitative analysis of numerous elements in a single operation as has spectrochemical analysis, in one or more of its modifications.

II. Choice of Specific Method:

At the inception of spectrochemical work in this thesis, five specific methods[1] were carefully considered as to their suitability for the analysis of soil and rock materials composed primarily if silicates. The principal requisites governing the final choice of method were 1) its adaptability to the equipment available at M.I.T., 2) rapidity, 3) cost in terms of chemicals and supplies, 4) reproducibility, 5) detection limits, and 6) its simplicity with respect to preparation of the arced samples. After considering the merits and shortcomings of each method, the mutual standard method was selected for the spectrochemical analyses of the soils.

This method, as applied to rock analysis, was developed at the Cabot Spectrographic Laboratory at M.I.T. (see Dennen and Fowler, 1955). The method therefore was particularly adaptable to the equipment in that lab, where this thesis was carried out. The method does not require sample solution, concentration of the elements, nor addition of any internal standards. It is also the fastest and least expensive of the five methods considered; six unknowns can be analyzed for 20 or more elements in 12

---

[1] The methods considered were: D.C. Spark Solution; D.C. Arc-powder-internal standard; Lithium carbonate fusion; Concentration with 8-Hydroxyquinoline; and Mutual Standard.

hours or less at an average expense (not including man-hour costs) of less than $1.00 per sample.

Prior to this thesis, the mutual standard method had been applied in (published) rock analyses only to major element determinations (Dennen and Fowler, 1955). However, the method can also be used for minor element determinations, provided these elements have lines that lie within the same wave length region as the analyzed major elements and are detectable under the conditions favorable to major element analysis.

The basic principles of the mutual standard method are described by Dennen and Fowler (1955) and were earlier discussed by Coulliette (1943); Churchill and Russell (1945, p. 25); Rosza (1947, p. 594); and Carlsson and Yu (1950, p. 276).

In this method it is assumed that 1) $\frac{I_1}{I_2} = \frac{C_1}{C_2}$, and 2) the elements analyzed for constitute essentially the entire sample, i.e., $\sum_{i=1}^{n} C_i = 100\%$, where C_i is the percent concentration of the element and n is the number of elements sought. If therefore for n elements sought: $C_1 + C_2 + C_3 + \dots C_n = 100(\%)$, then, dividing by C_1, $1 + \frac{C_2}{C_1} + \frac{C_3}{C_1} + \frac{C_4}{C_1} + \dots \frac{C_n}{C_1} = \frac{100}{C_1}$, or

$$C_1 = \frac{100}{1 + \sum_{i \neq 1}^{n} \frac{C_i}{C_1}} .$$

The concentration of any other element, such as C_3, can be found by dividing the numerator on both sides by the ratio $\frac{C_1}{C_3}$, which results in the equation:

$$C_3 = \frac{100 \cdot \frac{C_3}{C_1}}{1 + \sum_{i \neq 1}^{n} \frac{C_i}{C_1}} .$$

In practice, one element is selected as the variable internal standard. Intensity ratios of each element to this standard are determined from the spectrographic data and the corresponding concentration ratios are obtained from working curves of intensity ratios vs concentration ratios produced from standards of known composition. Details of the calculations are summarized on pages 175-177.

It is seen from the above that the only internal standard needed is self-contained. By working in ratios, many of the errors due to variations inherent in spectrographic analysis, such as those connected with sample preparation, excitation, illumination, exposure time, photographic development, and line measurement conditions are minimized according to the principle of internal standardization (Ahrens, 1950, pp. 76-95).

The mutual standard method as applied to rock powders does not normally determine such constituents as H_2O, CO_2, S, or organic matter, which may vary from 5% in igneous rocks to 20% or more in soils, shales, and carbonates. Assumption 2) on the preceding page is then invalid. In order to correct to the best estimate of actual percentages, these constituents can be independently determined.

III. Choice of Elements Sought:

It was decided at the onset of the analytical work to determine all the major elements (as oxides) normally sought in a chemical analysis. These include the oxides of Al, Si, Fe (as Fe_2O_3), Mg, Ca, Na, K, and Ti. All of these elements can be readily detected by the mutual standard method.

The bases of selection of trace elements were:

1.) Geochemical importance of the particular element.

2.) Pedological importance of the element.

3.) Availability of sensitive spectral lines within the wave length region used for the major elements.

4.) Reproducibility characteristics of the line(s) used.

Two survey plates, run under the general conditions used in the mutual standard method, were produced by arcing samples from three of the soil suites. One plate had a wave length setting between 2600 - 4100 A, the other between 2750 - 4600 A. Both plate settings contained usable lines of the 8 major elements. Each plate was scanned in detail for the most sensitive lines of 25 trace elements of geochemical interest. Certain elements were undetected in either plate and were thus eliminated from further study. Several elements of pedological importance, namely As, B, Li, and Se, could be determined spectrographically only by special techniques and were also omitted.

Those elements which produced sensitive lines, free from interference by other lines and usually with measurable densities, were: Ba, Co, Cr, Cu, Ga, Mn, Ni, Pb, Sc, Sr, V, Zn, and Zr. Tin and molybdenum, often sought in pedological studies, were undetected under the conditions used. Germanium, of recent geochemical interest, also was undetected.

The wave length region between 2750 - 4600 A contained Ba and Cr lines not detectable in the other setting as well as more sensitive Ca and Cr lines. For this reason it was selected in preference to the other setting.

This setting however required the use of Al 3082 whose line blackening for an Al_2O_3 concentration of 20% or greater approaches the maximum limit for practical use (i.e., the line blackening reaches a point where the density values plot on the non-linear toe of the photographic calibration curve). Because the Al intensity value plays a key part in the mutual standard calculations, this density difficulty appeared to be a serious source of precision and/or accuracy error. Therefore, a preliminary study was made to determine 1) the proportion of samples which produced an excessively dark Al 3082 line, 2) the precision obtainable from this line, and 3) the constancy of the ratio $\frac{\text{Al } 2652}{\text{Al } 3082}$ for various concentrations. It was concluded from the tests that 1) less than 10% of the Al 3082 lines were too dark to measure, 2) the precision of Al 3082 was comparable to the less sensitive Al 2652, and 3) the ratio of the two lines was relatively constant (within the precision limits) except for very high Al concentrations.

After the soil analyses runs had been made, it became apparent that, for high Al concentrations, composition changes of 2% or more produced corresponding density changes of less than 1 scale division on the densitometer. This borders on the limit of reproducibility of the scale readings, i.e., a repeat of any reading normally can be made to 0.5 - 1.0 scale division. A study was made of the effects of this precision uncertainty on the over-all accuracy of all element concentrations determined by mutual standard calculations and also on the use of other element lines as the variable internal standard (see Table 22 and p. 178). The conclusion is drawn that Al 3082 is usable, although not as satisfactory as Al 2652.

Table 20 lists the wave lengths of the analysis lines for each of the 21 elements determined spectrographically, together with the excitation potentials (from Ahrens, 1950), the line intensity, and the limit of detection (from Harvey, 1950, pp. 86 - 109) for most of these lines.

TABLE 20

Element	Wave Length	Excitation Potential (Volts)	Line Intensity	Detection Limit (ppm)
Silicon	2987.6			
Aluminum I	3082.2	4.00	1000	10
Iron	3196.9 (1)*	4.09	1000R	10
Iron I	3020.6 (2)			
Titanium	2956.1 (1)			
Titanium	3088.0 (2)			300
Magnesium	2779.8			
Calcium	4454.8 (1)			
Calcium	3006.9 (2)			
Sodium I	3302.3	3.74	600R	100
Potassium I	4044.1	3.05	800	1000
Barium II	4554.0	2.33	1000R	1
Cobalt I	3453.5 (1)	4.00	3000R	3
Cobalt I	3405.1 (2)	4.05	2000R	
Chromium I	4254.3	2.90	5000R	1
Copper I	3274.0	3.77	3000R	1
Gallium I	2943.6	4.30	100	10
Lead I	2833.1	4.40	500R	10
Manganese	2974.8			
Nickel I	3414.8	3.64	1000R	3
Scandium	3613.8			
Strontium I	4607.3 (1)	2.68	1000R	10
Strontium II	4077.7 (2)	3.03	400r	3
Vanadium I	3185.4	3.94	500R	3
Zinc I	3345.0	7.75	800	100
Zirconium II	3438.2	3.68	250	10

*(1) indicates line more commonly used; (2) indicates second choice

IV. Preparation of Samples for Analysis:

The soil samples from Suites G, K, and S were grouped into four categories for spectrochemical analysis: 1) parent rock, 2) total bulk soil, 3) sand, silt, and clay fractions, and 4) leach extract. Only the first two categories from Suite N were analyzed. All samples were prepared for analysis with great care in order to minimize contamination from metal, glassware, dust, etc. After initial preparation, each sample was kept in a glassine envelope until made into a spectrographic charge.

Parent rock and total bulk soil were pre-ground to pass -120 mesh before preparation as spectrographic charges. The sand, silt, and clay fractions were produced from some of the unground total bulk soil by a combination of sieving, decantation, and sedimentation procedures especially designed to insure minimal contamination. Ion exchange water was used throughout. No metal parts were ever in contact during the separations. Gravel particles were collected on a plastic screen (15 mesh) and sand particles on silk bolting cloth (200 mesh). All glassware was thoroughly rinsed by a succession of rinses using cleanser, acid, dithizone, and ion exchange water. The clay fraction, after decantation, was recovered by flocculation with a small amount of DU-559 (polydimethyl ammoethyl methacrylate, quateinized; manufactured by du Pont Co.) followed by centrifuging at 1800 rpm. The fractionation obtained was very effective between sand and silt but only moderately effective between silt and clay; hence, the analyses of the silt and clay fractions are not truly representative because some of each particle size range is included in the other.

The leach samples were obtained by a special extraction procedure devised by the writer, as follows:

10-15 gm. (accurately weighed) of -16 mesh air-dried soil was placed in a 250 cc. pyrex filter tube (60 x 2 cm.) fitted with a sintered glass filter. A wad of pyrex wool, forming a matte about 2 cm. thick, was inserted above the filter. The soil was added to the top of this filtering system until it built up a column about 5-7 cm. thick. Initially, the filter tube was closed at its bottom by a clamp attached to a 3-inch rubber tube.

About 100 cc. of purified 2.5% acetic acid was added to this closed system and allowed to remain in the soil column for 8 hours during which time the soil was thoroughly soaked. Then, with the clamp opened, the soil column was drained of the leaching solution. This natural filtration plus the wool and sintered filter produced a clear leachate. After a second soaking with 100 cc. acetic acid for 4 hours, the leachate was again collected. Two 50 cc. portions of acid were then passed successively through the <u>open</u> column at the normal rate of percolation. The column was finally washed with 75 cc. of ion exchange water. All solutions were collected, bringing the total leachate to 375 cc.

The leachate was first about 80% evaporated in a drying oven and then taken to dryness under an infrared lamp in vycor evaporating dishes. The residue (mostly acetates) was then largely converted to oxides and carbonates by charring in a bunsen flame. The percentage of leached material was calculated from the ash product as $\frac{\text{wt. ashed leachate}}{\text{wt. soil leached}} \times 100$. The samples leached and the percentage of material recovered were:

<u>Suite K</u>:	<u>Suite G</u>:	<u>Suite S</u>:
K-1: 0.58%	G-1: 1.43%	S-1: 0.34%
K-3: 0.39%	G-2: 1.95%	S-3: 0.46%
K-5: 0.14%	G-4: 1.55%	S-5: 0.92%

V. Spectrographic Conditions and Procedures:

The conditions and procedures followed in the spectrographic analyses of the soil samples are outlined in this section. Supplementary descriptions or commentary are included whenever appropriate in single-spaced indented paragraphs.

Arc Charge Preparation: 1 - 2 grams of previously prepared sample mixed, by grinding 10 minutes in an agate mortar, 1:1 by volume (using a 0.59 cc. aluminum scoop) with "special" grade carbon powder (to which palladium chloride had previously been added by another analyst as an internal standard).

Pre-arcing Treatment: Each arc charge heated to redness in a vycor dish for 5 minutes over a Tower burner to drive off water, CO_2, etc.

Electrode Cutting: All electrodes cut from National Carbon Company "Special" grade "specpure" 3/16 inch (4/57 mm.) diameter carbon rods. Charge electrode ± 0.75 inch in length, bored to a depth of 6.35 mm. and inner diameter of 2.30 mm; counter electrode (cathode) ± 4 inches in length, presharpened to a fresh point for each arcing.

Electrode Loading: Electrodes loaded following technique described by Holyk (1952); each cavity tightly packed by tamping with a plastic rod.

> Each cavity holds an average of about 0.35 to 0.42 grams of soil:carbon charge. For a series of electrodes drilled in the same way, the weight variation for repeated fillings with one sample charge is less than 5%. There is no need in the mutual standard method to weigh accurately each charge (nor to know accurately the exact amount of sample involved or the exact proportion of sample:carbon) because analysis and internal standard element values are based on ratios (i.e., are dependent on relative rather than absolute concentrations).

Spectrograph: Hilger Model $\frac{\text{E } 473.303}{47287}$ Quartz-Glass 3 meter prism; Littrow mount; variable dispersion: 6 A/mm. at 3180 A.

Power Source: 220 volt line, with ballast resistance, delivering about 50 volts at about 6 amps. across the arc gap.

Slit: Width 0.5 mm.; Height 10.5 mm.

Sectoring: Rotating (1525 rpm) 7 step sector: the step ratio based on 2^{-n} increments in relative intensity per step.

External Optics: Arc source focused on collimator lens by use of a spherical condenser (focal length: 1.5 meters) placed before slit; source to slit distance 15.5 inches; electrodes positioned by focusing through small auxiliary lens (with focal axis 30° oblique to optical bench length) on reference marks on outside of spectrograph casing.

> This optical arrangement, sometimes referred to as long focus optics, eliminates the problem of variable light intensity across the arc gap giving rise to nonuniform density of a line image on the photographic plate.

Plates: Eastman-Kodak Spectrum Analysis No. 1 glass-backed plates (4 x 10").

Excitation and Arc Control: Anode excitation; initial 10 second excitation at 3 amps., then increased to 6 amps. until arcing completed; electrodes struck by holding in direct contact for 5 seconds, then raising mechanically to a 14 mm. arc gap, periodically adjusted; arc flame stabilized by an updraft of air pulled into an overhead exhaust flue.

Exposure: 7 spectra (2 standards and 5 unknowns) recorded per plate; sample charge arced to completion according to the principle of the total energy method (Slavin, 1938); arcing continued 15 seconds after first indications of completion; each sample arced in duplicate by superimposing the spectra of two arcings in the same plate rack position, in order to produce (when long focus is used) the optimum range of line densities within which all the minor elements can be best measured.

> An exposure time of 230-245 seconds for acid rocks and soils and 240-265 seconds for basic samples was determined by a series of volatility runs (Ahrens, 1950, pp. 68-75), using an acid and a basic soil sample as charges.
>
> Arcing completion is indicated by:
>
> 1. Disappearance of distinctive colors produced by certain elements in the arc flame and subsequent dominance of the characteristic blue-white color of carbon.
>
> 2. Inception of sporadic red flame coloration due to arcing of a crust of a calcium-carbon compound formed on the electrode walls below the cavity.
>
> 3. A gradual to sharp rise in amperage to around 6.5 - 7.0 amps.
>
> In effect, the double exposure of the same sample runs is equivalent to producing a repeat analysis in duplicate, except that, instead of two separate replicates, a single photographically averaged composite of a pair of runs is obtained. Because the duplicate runs are recorded as a single exposure, it is impossible to determine the precision in the repeat pairs. The precision of the superimposed pair should be comparable (or better) to the precision obtained by using the average of two separate runs.

Photographic Development: Plates processed in Kodak D-19 developer for 270 seconds (temperature: 20° ± 2° C.); water-rinsed for 10 seconds; acid-fixed for 15 minutes; washed in cold water for 1 hour.

Analysis Line Identification: Major element lines identified from previous identifications on other plates run in the Cabot Lab; appropriate minor element lines identified by comparison with spectra obtained using a Hartmann Diaphragm (Harvey, 1950, p. 39) to produce a series of three spectral bands, each upper and lower band consisting of 15 second exposures of a spec-pure oxide of some minor element sought in the analysis and the middle band consisting of soil sample K-2 as reference.

Line Density Measurement: Line densities measured by a Jarrell-Ashe Model 200 Microphotometer-Comparator, with galvanometer deflection scale adjusted to read 0 (minimum transmission) when light entrance slit is closed and 100 (maximum transmission) when light passes through a clear portion of the plate; line density measured directly as a function of the deflection d (rather than photographic density D; see Ahrens, 1950, pp. 121-24); deflection value determined as the lowest number (read to nearest 0.1) reached on the scale when a line step image is hand traversed across the entrance slit to a photocell; background density in the vicinity of a line read as the highest transmission value attained when the entrance slit is moved off that line in the direction of the clearest proximate portion of the spectrum.

Plate Calibration: The rotating step sector method of calibration was used (Ahrens, 1950, pp. 127-29) to produce four characteristic (H & D) curves (plotted as log d versus log I, uncorrected by the Seidel function (see Ahrens, 1954, p. 11))covering photographic response in the regions: 1) 2750-2850 A, 2) 2950-3150 A, 3) 3151-3475 A, and 4) 4040-4575 A.

VI. Standardization:

Most spectrographic methods involve the preparation of working curves from standards of known composition. The working curve relates the intensity I of a given analysis line to the concentration C of the element producing that line. I versus C plots made on log-log paper are generally linear.

A standard may be either a natural material containing the analysis elements in known amounts or an artificial mixture of these elements. In either case, the more closely a standard and the unknown samples are similar in concentrations of dominant elements and in the crystal structures of the phases present (which together constitute the "matrix effect"), the greater should the precision and accuracy of the analyses based on the standard working curves. Generally, natural materials make better standards because 1) structural differences are minimized, and 2) no weighing or mixing errors result from additions.

Natural rock or soil standards having trustworthy analyses of both major and a range of minor elements are still rare as of 1958. Only two rock materials are available for use in analyzing the wide variety of elements studied in this thesis. These are the standards G-1 and W-1 analyzed in the U.S.G.S. - M.I.T. cooperative study of interlaboratory precision and accuracy (Fairbairn et al, 1951). G-1 is a granite from Westerly, Rhode Island; W-1 is a diabase from Fairfax County, Virginia.

Use of igneous rock standards for analysis of the thesis samples would be satisfactory for the parent rock and probably sand fraction analyses. However, because of the variable and often large compositional and structural differences between soils (especially the clay fraction) and igneous rocks, it was expected that the use of G-1 and W-1 would introduce a considerable matrix effect error. This has been confirmed by several reproducibility studies (see pages 181 and 191).

Despite this drawback, it was decided to use these two standards to provide two point working curves for the 21 elements sought in this thesis. A sample of each standard was arced in the same manner as unknowns on <u>each</u> plate. New working curves were thus prepared for the unknowns analyses on every plate. The advantage of obtaining a new working curve for each plate which reflects the same variations that affect the unknowns tends to offset the disadvantage of using only two points to establish each curve.

On a few plates, additional standards were run. These standards consisted of thesis soil samples analyzed by the spectrographic laboratory of the Department of Soils at Rutgers University (see page 191). The particular material used in each case was always one from the same suite as the unknown samples. In most instances, $\frac{I}{I_{Al}}$ values for the appropriate concentration ratios of these standards plotted near the G-1:W-1 working curve. In several specific instances, in the judgment of the writer, the soil standards values for certain elements provided better working curves when substituted for one of the two G-1:W-1 standards.

It was found that G-1:W-1 standards were not satisfactory for the analysis of the leach samples because of the large compositional differences between most leachates and these igneous rocks. In an attempt to improve the leach determinations, an artificial standard was prepared by mixing spec-pure or reagent grade oxides of the elements (except chlorides of sodium and potassium, recalculated than as oxides) in proportions within the expected normal range of the leachate compositions.

Table 21 gives the composition of the standards G-1 and W-1 and the artificial leachate, in terms of the percentages of the major element oxides and parts per million (ppm) of the uncombined minor elements. The data for G-1 and W-1 was taken from Ahrens (1954, page 30) except where otherwise indicated.

TABLE 21

Concentrations of Standards

Element	G-1	W-1	Artificial Leach
	%	%	%
Al_2O_3	14.40	15.10	19.50
SiO_2	72.40	52.30	11.80
Fe_2O_3 (FeO)	1.92	11.04	3.98
MgO	0.39	6.60	6.19
CaO	1.40	11.00	15.60
K_2O	5.40	0.63	23.38
Na_2O	3.25	2.00	15.55
TiO_2	0.25	1.10	0.41
	PPM	PPM	PPM
Ba	1300	270	12320
Co	2.5*	42*	1016
Cr	20	130	1322
Cu	11	110	1485
Ga	17.5	14.5	640
Mn	210	1300	2562
Ni	2.5*	92*	2035
Pb	27	7	364
Sc	3	37	465
Sr	233*	177*	2940
V	20*	220*	1960
Zn	55	90	-
Zr	200	90	-

*These values have been modified since Ahren's publication. (Dennen: personal communication)

VII. Methods of Calculation:

After density values for lines plus background were obtained, the composition of the unknown samples was calculated as follows:

1.) All lines and background densities (standards and unknowns) were converted to intensities through use of the calibration curves produced from each plate.

2.) Background intensities were subtracted from line intensities, leaving net intensities.

3.) Ratios of Na, K, and Si net intensities to Fe were computed. All other net intensities (including minors) were ratioed to Al (note that Al/Al = 1.000).

4.) Two point working curves for each element were plotted on log-log paper, using the intensity ratios of the standards versus corresponding concentration ratios (to Fe or Al).

5.) From the working curves, the concentration ratios for each (numerator) element in the unknowns was determined from the intensity ratio data for that element.

6.) The Na/Fe, K/Fe, and Si/Fe concentration ratios were multiplied by the Fe/Al concentration ratios to convert them to the base Al.

7.) All concentration ratios for a given sample were summed. The sum is assumed to represent 100% of the sample composition. Because this ignores the contribution from water (also CO_2, organic carbon, and gases, etc.), the results are on an anhydrous basis.

8.) The concentration of each element X was calculated as:

Majors

$$\text{Conc. X (\%)} = \frac{\dfrac{C_X}{C_{Al}}}{1 + \sum\limits_{X_i \neq AL}^{n} \dfrac{C_{Xi}}{C_{Al}}} \times 100$$

Minors

$$\text{Conc. X (ppm)} = \frac{\dfrac{C_X}{C_{Al}}}{1 + \sum\limits_{X_i \neq AL}^{n} \dfrac{C_{Xi}}{C_{Al}}} \times 1000000$$

9.) The sum of all major and minor element concentrations must sum up to 100% ± 0.75%, the last figure being a measure of allowable error in calculations, due to dripping of significant figures, slide rule readings, etc.

10.) Flame photometer analyses were made for K_2O and Na_2O content in total bulk samples K-2, G-2, and S-3 and clay samples K-1 and G-1 (see page 191). For these elements, this analytical procedure is generally more accurate than analysis by most spectrographic methods. For this reason it was decided to substitute flame photometer data on sodium and potassium for the spectrographic data. This was done by:

(a) Computing a factor from the ratio of the $\frac{\text{\% K or Na by flame photometer}}{\text{\% K or Na by spectrograph}}$ for the particular samples which were analyzed by the flame photometer. One set of factors will be for TBS and another set for clay samples.

(b) On the total bulk and clay sample plates, the K_2O and Na_2O values obtained spectrographically were multiplied by the appropriate factor, which thus provided an approximate proportional correction to the values produced by flame photometer analysis.

(c) On the silt and sand plates, the factor used was an average of the TBS and clay factors for that sample suite.

(d) The factor used for TBS samples was also used for parent rock samples.

(e) The concentration of Na_2O and K_2O was either reduced or increased by operations (b) or (c). If the original sum of the percentages of all analyzed elements in a given sample is X% and the revised sum (based on Na_2O and K_2O substituted values) is Y%, then in order to retain the percentages based on the original sum (100 ± 0.75%), the concentrations of all other elements were multiplied by the factor X/Y.

11.) The leach concentrations were recalculated to the actual percentages of elements leached from the total soil by multiplying each concentration by the percent of total soluble matter expressed as a fraction $\left(\frac{\%\text{ total soluble}}{100\%}\right)$ (see page 167 for these data).

APPENDIX C

REPRODUCIBILITY OF THE SPECTROCHEMICAL ANALYSES

The principal limitation of the mutual standard method is its reproducibility. Although the precision is comparable to other methods, the accuracy is usually more variable. A series of studies were conducted, both prior to the actual soil analyses and then on the analyses data obtained, to determine the precision and accuracy of the results.

I. Precision:

Several different but interrelated measures of precision were made by application of the Relative Error statistic. Relative Error (R.E.), also termed the Coefficient of Variation, is defined as:

$$\text{R.E. } (\%) = \frac{s}{\bar{x}} (100)$$

where $\bar{x}$ is the mean of a series of replicate values and s is the standard deviation from the mean.

A. Intraplate Precision:

The precision obtainable on a single plate was estimated by rerunning seven samples of K-2 TBS on one plate under identical conditions. The relative error was computed for 1) elements unratioed 2) elements ratioed to Al or Fe and 3) elements ratioed to Pd (added to the arc charge carbon as an internal standard). These R.E. values are shown in Table 22.

TABLE 22

Relative Error (%)

Analysis Line	Unratioed		$\frac{X}{Al}$	$\frac{X}{Fe}$	$\frac{X}{Pd}$
	(1)	(2)*			
Si 2987	6.0	10.2		5.2	
Al 3082	7.1	5.3	-	-	-
Fe 3196	7.2	7.3	3.9		
Ti 2956	12.4	18.2	10.2	8.1	
Mg 2778	10.4	8.9	8.8	10.7	
Ca 3006	12.6	8.6	11.0		
Ca 4454	10.9		9.6		
Na 3302	8.4	12.1		5.2	
K 4044	9.3	11.2	6.5	6.4	
Ba 4554	11.3	15.0	8.1		9.9
Co 3453	8.2	16.2	1.8		5.2
Cr 4254	10.7	13.7	8.9		10.7
Cu 3274	23.5	7.1	21.7		21.7
Ga 2943	12.5	16.1	10.9		10.9
Mn 2794	5.8	6.5	3.9		6.6
Ni 3414	11.4	9.7	10.8		13.9
Pb 2833	6.7		10.6		9.1
Sr 4077	7.1	8.6			6.9
Sr 4607	8.7				8.4
V 3185	12.4	12.0	8.6		13.2
Zr 3438	17.8	6.4			16.1
Pd 3242	7.3				

* A similar precision study of 7 samples of K-2 was run before the final spectrographic procedure was set up. The results are here included for comparison.

The average R.E. of the 8 majors is:

1.) 8.9% unratioed

2.) 7.3% ratioed to Al and Fe

The average R.E. of the 12 minors, excluding Cu which shows poor precision because of electrode impurity, is:

1.) 10.8% unratioed

2.) 7.5% ratioed to Al

3.) 10.1% ratioed to Pd

The combined average R.E. for all elements is:

1.) 9.7% unratioed

2.) 7.4% ratioed to Al

This data supports the choice of Al over Pd as the internal standard.

B. Interplate Precision:

The precision for replicates run on more than one plate is controlled by the intraplate variables plus possible undetected plate to plate variations in the analytical setup and operational procedure and variations caused by differences in photographic development. Ideally, when all variables affecting a spectrographic run are exactly controlled, the intensity ratios of the analysis pairs, regardless of the number of single or multiple plate repeats, should remain constant and the working curves should therefore be perfectly reproducible. When separate but related sample types are run in their entirety on several individual plates, intraplate and interplate precision should be similar if the results of analyses of these types are to be compared in any way.

For the soil spectrochemical analyses, interplate precision was evaluated in three ways.

(1) Duplicate Analyses: Exact duplicates of analysis plates (normally 2 standards and 5 unknowns) consisting of K-TBS, G-TBS, K-clay and all parent rock samples were run. The two sets of analyses obtained for these samples are recorded in Table 23. The duplicates, as evaluated by a qualitative comparison, indicate good precision for K-TBS and parent rock repeats but fair to poor precision for G-TBS and K-clay.

(2) G-1:W-1 Replicates: The plate-to-plate working curves produced from G-1:W-1 data were compared statistically. Two curve variables can be readily measured, namely, the slope angle and the intensity coordinates ($\frac{I_x}{I_{Al}}$) of the mid-point between G-1 and W-1 plots.

Visual inspection of the G-1:W-1 curves of 12 selected plates showed that most of the curves underwent both a mid-point shift and a slope change from plate to plate. To evaluate quantitatively these variations, mid-point intensity ratios from 8 plates and slope angles from 12 plates for the 7 major element working curves[1] were measured. The mid-point ratios were then recalculated by a method analogous to the mutual standard method as follows:

1.) The mid-point $\frac{I_x}{I_{Al}}$ ratio for each element curve from a plate was read.

2.) Na/Fe, K/Fe, and Si/Fe ratios were converted to X/Al by multiplying with the Fe/Al intensity ratio.

3.) The sum of all majors/Al (including Al/Al = 1.000) was taken. This sum varied from plate to plate.

---

[1] No $\frac{Al}{Al}$ working curves are needed.

TABLE 23 A

Duplicate K-TBS Analyses

Element	K-1	K-1	K-2	K-2	K-3	K-3	K-5	K-5	K-7	K-7	K-7**
SiO_2	74.87	74.77	73.23	71.16	71.35	70.32	68.71	66.18	67.16	66.10	67.77
Al_2O_3	14.62	12.99	14.56	14.20	14.17	16.27	17.25	19.44	13.60	13.64	15.55
Fe_2O_3	3.73	3.84	4.31	4.40	5.10	4.68	3.46	3.90	3.68	3.34	2.80
MgO	1.02	1.04	1.03	1.71	1.21	1.63	1.03	1.74	1.01	0.75	2.33
CaO	0.78	1.03	0.64	1.15	0.77	0.58	1.41	1.84	2.21	2.19	1.69
K_2O	2.35	3.08	3.33*	3.33*	3.20	3.22	3.26	3.46	6.38	7.75	7.16
Na_2O	1.71	1.68	2.14*	2.14*	3.04	2.23	3.56	2.60	4.11	5.41	3.92
TiO_2	0.60	0.57	0.56	0.68	0.56	0.52	0.57	0.48	0.52	0.55	-
Ba	1830	1745	1682	2150	2830	2395	3020	2840			
Co	7	7	6	8	6	7	4	6			
Cr	20	28	18	30	7	12	10	10			
Cu	11	24	10	14	7	8	10	11			
Ga	16	20	16	23	15	23	16	26			
Ni	13	16	12	15	8	17	4	9			
Mn	600	555	456	630	434	476	570	434			
Pb	12	21	9	23	12	23	12	28			
Sc	10	7	10	9	9	5	5	9			
Sr	183	245	179	329	428	365	570	486			
V	86	60	80	66	127	89	118	87			
Zr	500	1460	656	1540	883	1458	386	802			

* Identical flame photometer values; K-2 taken as reference in recalculating spectrographic values to flame photometer values.

**Represents results of modal analysis of K-7 made by the writer; average composition of the minerals present (data from Dana) used in computing the chemical analysis.

TABLE 23 B

Duplicate G-TBS Analyses

Element	G-1	G-1	G-2	G-2	G-3	G-3	G-4	G-4	G-9	G-9	G-9**
SiO_2	49.90	59.81	59.80	60.16	62.81	64.28	57.12	57.79	48.60	50.56	52.59
Al_2O_3	21.77	16.65	20.19	19.80	16.54	14.45	17.43	15.75	17.30	14.14	17.91
Fe_2O_3	11.40	11.27	8.42	9.85	8.43	9.87	9.49	10.73	9.50	8.95	9.80
MgO	2.18	2.08	1.71	2.11	2.15	2.55	3.14	3.07	5.00	4.70	4.24
CaO	7.76	4.29	4.73	3.09	5.95	4.54	6.79	5.58	10.35	11.00	7.24
K_2O	3.34	3.07	2.70*	2.70*	1.98	2.02	3.64	3.88	4.25	5.45	3.83
Na_2O	1.86	1.37	1.22*	1.22*	1.12	1.00	1.27	2.02	3.77	4.01	2.93
TiO_2	1.24	1.27	0.79	0.92	0.72	0.85	0.81	1.08	1.19	0.85	0.84
Ba	932	1470	1020	963	-	-	912	1380	1002	1453	-
Co	24	9	15	8	16	17	15	19	23	19	-
Cr	74	20	26	14	61	24	60	24	95	129	-
Cu	30	53	17	50	25	58	35	65	83	93	-
Ga	30	13	25	18	21	12	23	14	11	24	-
Mn	1168	1260	1508	750	1345	1150	1650	1495	1505	2085	-
Ni	22	10	16	6	18	9	24	16	6	35	-
Pb	35	24	6	14	10	-	13	12	10	15	-
Sc	39	28	30	29	28	25	30	26	12	28	-
Sr	366	445	238	408	370	480	450	540	408	729	-
V	249	218	162	174	167	185	188	218	159	207	-
Zr	241	411	261	453	258	362	363	518	362	552	-

* Identical flame photometer values; G-2 taken as reference in recalculating spectrographic values to flame photometer values.

**Represents chemical analysis of Table Mountain basalt (same lava flow but different horizon) reported in Waldschmidt (1939).

TABLE 23 C

Duplicate K-Clay Analyses

Element	K-1	K-1[1]	K-2	K-2[1]	K-3	K-3[1]	K-4	K-4[1]	K-5	K-5[1]
SiO_2	71.20	71.86	70.90	71.53	66.10	69.93	62.60	68.86	65.70	71.26
Al_2O_3	15.48	13.56	17.80	13.74	23.20	15.44	23.18	15.53	22.28	15.99
Fe_2O_3	5.18	8.27	3.88	8.91	3.60	8.69	4.18	8.54	3.63	6.80
CaO	0.67	0.39	1.31	0.63	0.72	0.41	2.23	0.75	1.05	0.48
MgO	3.26	2.14	2.45	2.04	2.76	2.19	4.06	2.76	3.76	2.24
K_2O	1.92	2.73	1.62	2.31	0.72	2.18	1.88	2.71	1.71	2.35
Na_2O	1.72	0.38	1.56	0.37	2.56	0.40	1.34	0.39	1.47	0.37
TiO_2	0.51	0.42	0.44	0.50	0.42	0.73	0.38	0.59	0.49	0.50

Minors not calculated for the first K-samples.

Duplicate Parent Rock Analyses

Element	N-9	N-9[1]	Av. N-9	N-9*	S-7	S-7[1]
SiO_2	81.25	80.00	80.83	77.02	48.50	49.10
Al_2O_3	11.30	11.50	11.45	12.26	19.70	20.23
Fe_2O_3	0.47	1.82	1.15	1.02	12.20	15.75
MgO	0.12	0.17	0.14	0.12	7.58	5.57
CaO	0.37	0.60	0.49	0.98	7.33	4.90
K_2O	2.83	2.32	2.58	4.59	0.96	1.70
Na_2O	2.94	3.68	3.36	3.85	2.69	1.15
TiO_2	-	-	-	0.08	1.08	1.03

Minors not calculated for the first parent rock samples.

*Represents chemical analysis of Graniteville Quarry Granite reported by Tolman & Goldich (1935).

[1] These samples constitute the final reported values.

4.) Each intensity ratio was divided by this sum. This was the revised mid-point value. (The resulting values for all major elements should always add to 1.000).

The means, standard deviations, and relative errors of these measurements are stated in Table 24 below:

TABLE 24

	$\frac{Si}{Al}$	$\frac{Fe}{Al}$	$\frac{Mg}{Al}$	$\frac{Ca}{Al}$	$\frac{Na}{Al}$	$\frac{K}{Al}$	$\frac{Ti}{Al}$	Average
Slope Angle:								
Mean	43°	43°	48°	38°	44°	36°	48°	43°
Stand. Dev.	2.24°	3.50°	7.75°	6.71°	4.82°	3.60°	8.30°	5.27°
R. E. (%)	5.2	8.1	16.1	17.6	10.9	10.0	17.2	12.3
Mid-point:								
Mean	.405	.064	.131	.223	.093	.083		
Stand. Dev.	.050	.018	.037	.080	.033	.022		
R. E. (%)	12.5	28.9	28.3	35.8	35.8	26.3	29.1	28.0

A direct comparison between intraplate and interplate values of intensity ratio precision must be made cautiously because the first is based on ratios of a single point (also, unadjusted to a sum) whereas the second is based on ratios of the mid-point between two such single points. However, the 28.0% relative error for interplate mid-point shifts is significantly larger than the 7.4% intraplate error. This increase in R.E. can be interpreted as due to non-compensated errors related to several variables (see page 194).

(3) Concentration Indices: The definition, method of calculation, and interpretation of concentration indices are discussed on pages 90-98. Theoretically, the sum of the concentration indices of all size fractions (gravel, sand, silt, and clay) in a soil, as analyzed separately, should total 1.000. Any deviation from 1.000 is partly a measure of the effects of precision error and partly a reflection of other contributing errors.

Concentration index sums for all size fractions can be computed for six samples: G-2, G-4, K-2, K-5, S-1, and S-4. Table 25 lists these sums for 17 elements, together with 1) mean, standard deviation, and relative error of the combined sums of these elements in each sample (horizontal column) and 2) the mean, standard deviation, and relative error of the sum from the 6 samples of the concentration indices for each element.

The average of the mean $\bar{x}$ for the 6 samples is 1.045 and the corresponding R.E. is 28.95%. The averages of the means and R.E.'s of the individual elements, when Ga and Ni are excluded, are 1.016 and 25.75%, respectively. This R.E. value breaks down to 18.63% for the eight majors and 33.94% for the seven minors.

II. Accuracy:

Accuracy is here defined as the degree of agreement between two sets of compared values, one set of which is assumed to be the optimum estimate of the true value.

The accuracy of the thesis analyses was tested by a comparison of these analyses to several independent analyses of several of the soil samples made by other analysts, using both spectrochemical and wet chemical methods. In addition, mutual standard analyses of several igneous rocks of known composition

TABLE 25

Statistical Treatment of Distribution Ratio Data

Sample	Si	Al	Fe	Mg	Ca	Na	K	Ti	Ba	Cr	Mn	Sc	Sr	V	Zr	Av.	s	R.E.
G-2	.976	.874	1.155	1.286	1.623	1.306	1.722	1.212	.916	1.374	1.461	.622	.894	1.109	1.464	1.143	.287	25.0
G-4	.970	1.014	.973	1.320	1.115	1.359	.787	.737	1.258	1.073	.753	.547	.983	.696	1.130	1.031	.274	26.6
K-2	.997	.897	1.358	1.096	1.210	1.070	.832	.911	.727	.654	1.149	.701	1.139	.859	.296	.961	.198	20.6
K-5	1.012	.720	1.786	1.437	1.238	1.048	1.099	1.154	.903	.748	1.112	.851	.967	.807	.582	1.075	.274	25.4
S-1	1.103	.922	.656	1.291	1.311	.954	1.193	.744	.949	.418	1.250	1.428	1.539	.412	.709	1.022	.342	34.1
S-4	.995	1.092	.940	.970	1.976	.944	1.237	.804	.739	.544	1.748	.525	.928	.830	1.484	1.058	.415	39.1
Av.	1.010	.921	1.143	1.231	1.410	1.111	.978	.930	.915	.802	1.244	.780	1.075	.786	.945	1.045		28.9
s	.049	.126	.384	.169	.324	.181	.224	.204	.207	.352	.342	.338	.244	.203	.489			
R.E.	4.8	13.7	33.5	13.7	22.9	16.3	22.9	21.9	22.6	43.8	27.4	43.4	22.7	25.8	51.6			

Av. of horizontal av. column = 1.016

Av. R.E. of 8 majors = 18.6

Av. R.E. of 7 minors = 33.9

Av. R.E. of 15 elements = 25.7

were made by the writer by the exact procedure used on the soil samples. The results of these analyses are presented below. The percent bias between thesis and cross-check analyses is included in each tabulation.

A. Chemical versus Spectrochemical Analyses of Selected Rocks:

Dennen and Fowler (1955) analyzed spectrographically several igneous rocks previously chemically analyzed by Larsen and Gonyer as a means of checking the mutual standard method. Three of these same rocks were reanalyzed on the same spectrograph with, however, the technique modifications adapted to this thesis. A fourth rock, a clay called "Argosite", was also included in these runs. The results for 8 major elements in these four samples, along with the Dennen and Fowler results for comparison, are given in Table 26 on the following page. Algebraic signs indicate the direction of the spectrographic bias: + if greater and - if less than the chemical analysis.

The relative degree of accuracy between the mutual standard analyses of Dennen and Fowler and the thesis analyses is given by the comparison of the average of the percent bias of each:

	Dennen & Fowler	Short
RA 106	28.1%	37.5%
EL 38-28	9.4%	10.4%
RA 135	10.0%	14.8%
Av. of 3:	15.8%	20.9%

The average of the percent bias for the Argosite sample is 111.8% with TiO_2 and 49.4% without TiO_2. This sharp loss of accuracy is a reflection of a larger contrast in matrix composition between Argosite and G-1:W-1 than

TABLE 26

Larsen & Gonyor - Dennen - Short Analyses

	Chem.	(1) Spec.	% Bias	(2) Spec.	% Bias	Chem.	(1) Spec.	% Bias	(2) Spec.	% Bias
			RA 106					EL 38-28		
SiO_2	74.68	74.90	+0.3	77.45	+3.8	62.28	60.30	-3.2	64.20	+3.1
TiO_2	0.15	0.11	-26.7	0.49	+160	0.72	0.72	0.0	0.81	+12.5
Al_2O_3	13.80	13.62	-1.3	12.84	-6.9	16.68	17.70	+6.1	14.78	-11.4
Fe_2O_3	2.04	2.52	+23.5	1.73	-15.2	6.66	7.10	+6.6	6.94	+4.2
MgO	0.21	0.48	+128	0.36	+71.5	2.33	2.66	+14.2	2.69	+15.4
CaO	2.26	2.38	+5.3	2.31	+2.2	5.72	5.68	-0.7	5.76	+0.7
Na_2O	4.10	3.40	-17.1	3.02	-26.4	3.50	3.82	+9.2	2.98	-14.8
K_2O	2.01	2.45	+21.9	2.29	+13.9	1.49	2.02	+35.6	1.80	+20.8
	99.82	100.27		100.47		99.45	100.07		99.96	
			RA 135					Argosite		
SiO_2	72.58	73.10	+0.7	74.10	+2.1	67.11	-	-	63.30	-5.7
TiO_2	0.30	0.31	+3.3	0.41	+36.7	0.09	-	-	0.56	+500
Al_2O_3	14.12	13.55	-4.2	12.69	-10.1	22.16	-	-	21.40	-3.4
Fe_2O_3	3.27	4.20	+28.4	2.69	-17.7	4.03	-	-	5.03	-24.8
MgO	0.70	0.74	+5.7	0.80	+14.3	2.45	-	-	3.64	+48.5
CaO	2.44	2.17	-12.4	2.69	+10.3	0.75	-	-	1.56	+108
Na_2O	3.91	3.59	-8.9	3.40	-13.0	2.90	-	-	3.02	+4.1
K_2O	2.84	2.44	-16.4	3.25	+14.4	0.45	-	-	1.35	+200
	100.46	100.10		100.03		99.94			99.86	

(1) Analyses by Dennen and Fowler.
(2) Analyses by Short.

RA 106: Granite   EL 38-28: Granite   RA 135: Andesite or Basalt   Argosite: Clay between the igneous rocks and these standards. In matrix composition, most of the soils lie between this clay and the igneous rocks, so that the accuracy in terms of percent bias should be between the above range of values (21-49%) when G-1:W-1 standards are used.

B. Penn State Analyses:

Total bulk samples G-2, K-2, N-3, and S-2 were analyzed under the direction of Mr. Erwin Strahl of the Department of Mineralogy, Pennsylvania State University. Analyses were made by combined wet chemical and x-ray fluorescence methods developed there for use in an A.E.C.-sponsered project studying uraniferous black shales. Table 27 presents the results of the analyses. The Penn State values are recalculated to an anhydrous basis.

TABLE 27

		G-2			K-2			N-3			S-2	
	P.S.U.	Short	Bias*	P.S.U.	Short	Bias*	P.S.U.	Short	Bias*	P.S.U.	Short	Bias*
SiO_2	55.90	60.16	7.6	69.90	72.19	3.3	80.40	83.40	3.7	64.00	64.65	0.3
Al_2O_3	22.60	19.80	12.4	17.10	14.38	15.9	12.75	10.22	20.1	15.70	14.78	5.7
Fe_2O_3	11.60	9.85	14.9	4.75	4.36	7.5	3.56	3.09	12.6	17.50	16.60	6.3
CaO	3.92	3.09	21.2	1.27	0.89	29.9	0.16	0.07	56.4	0.63	0.30	52.4
MgO	3.10	2.11	32.2	2.80	1.37	51.0	0.64	0.56	18.7	1.96	0.65	66.9
K_2O	2.79	2.70	3.2	3.14	3.33	6.0	2.32	1.27	45.3	0.90	1.01	12.2
Na_2O	1.56	1.22	21.6	2.95	2.15	27.1	1.02	0.86	15.6	0.21	0.22	4.8
Av:			16.3%			20.1%			24.6%			21.1%

* P.S.U. samples are reference standards in computing bias.

All of above values reported in percent.

The average percent bias for the four samples is 20.7%.

C. Rutgers Analyses:

Dr. Neil Shimp of the Department of Soils at Rutgers University analyzed Total Bulk samples K-2, G-2, and S-3 and clay samples K-1 and G-1 by spectrographic methods established by his group (Shimp, Connor, Prince, and Bear, 1957.) His analyses are based on oven-dried (105° C) weighed samples which therefore still retain some water. Comparison of his results with those obtained for this thesis (water content usually somewhat less), along with the percent bias, is made in Table 28, on the next two pages.

D. Wet Chemical Analyses:

Total Bulk Samples K-2, G-2, and S-3 and clay samples K-1 and G-1 were digested in HF - H_2SO_4. Analyses for Fe_2O_3 and TiO_2 were made according to the procedures for these elements described in Shapiro and Brannock (1952). The results are set forth in Table 29.

E. Flame Photometer Analyses:

The same digested samples from D. were analyzed for Na_2O and K_2O by Dr. E. E. Pickett of the Department of Agricultural Chemistry, University of Missouri. These results are also presented in Table 29.

TABLE 29

		K-2			G-2			S-3	
	Spec	Flame Chem.	Bias	Spec	Flame Chem.	Bias	Spec	Flame Chem.	Bias
Fe_2O_3	4.40	6.12	28.1	9.85	12.40	20.5	18.11	17.98	0.70
TiO_2	0.68	0.53	28.3	0.92	1.11	17.1	1.38	1.40	1.40
Na_2O	3.07	2.14	43.4	1.53	1.22	25.4	0.55	0.25	120.0
K_2O	2.82	3.33	15.3	1.31	2.70	51.5	0.51	1.07	52.4
		Av.:	28.7%			28.6%			38.1%

TABLE 28 A

Rutgers Analyses

Element	(1) G-2	(2) G-2*	% Bias	(1) K-2	(2) K-2*	% Bias	(1) S-3	(2) S-3*	% Bias
Al_2O_3	19.80	20.85	+8.9	14.38	13.62	-5.6	18.12	17.43	-4.0
Fe_2O_3	9.85	10.86	+9.3	4.36	4.58	+4.8	18.11	18.60	+2.6
MgO	2.11	1.92	-9.9	1.37	0.81	-69.1	0.80	0.58	-37.9
TiO_2	0.92	0.50^{x}	-	0.62	0.07^{x}	-	1.38	0.05^{x}	-
Co	8	15	+46.7	7	7	0.0	168	172	+2.3
Cr	14	17	+17.6	26	11	-136	177	182	+2.7
Cu	50	78	+35.9	12	20	+40.0	170	174	+2.3
Ga	18	20	+10.0	19	20	+5.0	13	25	+48.0
Mn	750	230	-226	553	420	-29.2	3040	3400	+10.6
Ni	6	7	+14.2	14	16	+12.5	7	456$^{\#}$	-
Pb	14	60$^{\#}$	-	15	84$^{\#}$	-	12	85$^{\#}$	-
V	174	184	+5.4	73	75	+2.7	520	534	+2.6
Zn	-	163	-	73	116$^{\#}$	-	383$^{\#}$	115	-

(1) Analyses by Short at M.I.T.

(2) Analyses under direction of Shimp at Rutgers University.

* Rutgers samples taken as reference standards in computing bias.

\- No bias was calculated for these elements and samples.

These values probably too high (Dennen: personal communication).

X These values probably too low (See page 191).

TABLE 28 B

Rutgers Analyses

Element	(1) K-1	(2) K-1*	% Bias	(1) G-1	(2) G-1*	% Bias
Al_2O_3	13.56	18.95	+28.4	10.60	20.50	+48.3
Fe_2O_3	8.87	8.20	-0.9	10.04	8.00	-25.5
MgO	2.14	1.70	-25.9	2.86	1.52	-88.1
TiO_2	0.42	0.12^x	-	1.07	0.31^x	-
Co	6	16	+62.5	22	19	-15.8
Cr	61	54	-13.0	27	19	-31.6
Cu	19	50	+62.0	83	90	+7.8
Ga	35	27	-29.6	16	23	+30.4
Mn	545	980	+44.4	1760	650	-178
Ni	31	329	-	16	22	+27.3
Pb	60	63	+4.8	240	157	-52.9
V	133	133	0.0	108	118	+8.5
Zn	109	$306^{\#}$	-	123	$282^{\#}$	-

(1) Analyses by Short at M.I.T.

(2) Analyses under direction of Shimp at Rutgers University.

* Rutgers samples taken as reference standards in computing bias.

\- No bias was calculated for these elements and samples.

\# These values probably too high (Dennen: personal communication).

x These values probably too low (See page 194).

TABLE 29 (Continued)

	K-1 Spec	K-1 Flame Chem	K-1 Bias	G-1 Spec	G-1 Flame Chem	G-1 Bias
Fe_2O_3	8.27	10.40	20.5	10.04	9.99	0.5
TiO_2	0.42	0.79	44.4	1.07	0.86	24.4
Na_2O	0.89	0.38	134.0	0.48	0.53	9.4
K_2O	3.24	2.73	18.6	1.79	2.65	32.4
	Av.:		54.4%			16.7%

The flame or wet chemical analyses values are taken as reference standards in computing the percent bias.

III. Major Sources of Error:

The three principal sources of error which affected the spectrographic precision and accuracy in the thesis analyses are listed and commented upon below:

1.) Matrix Effects: The compositional and structural differences between mineral constituents in standards and in samples leads to differences in the pattern and rate of temperature changes during a sample excitation. The ratios of relative intensities of various analyses pairs are thus altered. An element having the same actual concentration both in samples and standard may show (apparent) differences in concentration because other elements occur in different proportions in samples and standards. The matrix effect is considered to be the most serious error involved in the spectrochemical analyses of the thesis samples.

2.) Photographic Effects: Inadequate standardization of the conditions of photographic development is believed to be responsible for a large part of the 28% interplate relative error. Failure to 1) control developer temperature within 20 ± 1° C and 2) replace weakened developer with fresh often enough to retain constant developing strength led to different degrees of development among plates and consequent variation in analyses line densities. This caused no errors among elements whose densities plotted along the linear portion of the calibration curve, as their ratios would remain constant. However, very low or very high density lines would plot along different sections of the non-linear portions of the curve in various plates having different density contrasts. Because Al, the ratio element in the mutual standard method calculations, usually produced densities within the non-linear toe of the calibration curve, its density (and therefore intensity) ratio to a given element could vary even though its concentration ratio (in a standard or replicate sample) to that element remained constant.

3.) Electrode Sputtering: Loss of sample through sputtering and globule boiling in the early stages of arcing tends to remove a fraction of the late volatile elements before they are excited. The concentration of early volatilized elements will be relatively increased over the later elements.

APPENDIX D

RULES FOR INTERPRETATION OF ASSOCIATION ANALYSES

1.) A strong positive association between concentration changes in the TBS samples and changes in any one of the three size fractions indicates that the particular fraction may be largely responsible for the behavior of the element in the total soil. If one or both of the remaining fractions show a strong negative association, the importance of the particular fraction as a concentrator is emphasized.

2.) Strong similar associations between silt and clay concentration changes indicates a) the element associates about equally in phases found in both size ranges and/or b) the size separation technique was inefficient.

3.) A strong association between silt or clay concentration changes and % silt or % clay respectively indicates that the element behavior is largely controlled by the amount of silt and clay developed during weathering and further substantiates the relation between the element and the production of a weathered silt detritus or a secondary (reconstituted) clay. A positive association implies that the element enriches in the fraction as more is produced and a negative association implies a relative depletion in the fraction.

4.) A strong association between free iron oxide and any of the ferride elements in one or more size fractions implies that any such element tends to follow iron in release and migration through the profile.

5.) A strong positive association between an element concentration change in a size fraction and its appropriate C.E.C. value implies that at least some of the variation of the element in that fraction and in the soil as a whole is controlled by the exchange capacity.

APPENDIX E

THEORETICAL BACKGROUND FOR TRACE ELEMENT BEHAVIOR DURING WEATHERING

Specific theoretical treatments of the principles of trace element behavior in weathering, soil formation, and sedimentary rocks are scarce. Good general discussions of this subject are given by Mitchell (1955) and Krauskopf (1955). The treatise by A. P. Vinogradov (1950) appears to be the only detailed effort (as of 1958) to specify and develop the principles of minor element geochemistry in the field of weathering.

For a review of the theoretical aspects of weathering and soil chemistry, the interested reader should refer to Polynov (1937), Joffe (1949, Chapters IV-VI), Reiche (1945), and Keller (1955). Perhaps the best compendium of modern theories of soil chemistry is the recent monograph on the Chemistry of the Soil (Bear, editor; 1955).

Drawing upon the above as references, the writer presents on the following pages a summary of those fundamental concepts of weathering and soil geochemistry that apply to a theoretical interpretation of major and minor element behavior:

1.) Weathering at the interface between atmosphere and lithosphere can be classed into the two realms of surface and subsoil weathering. Surface weathering takes place directly between exposed lithic bodies (outcrops) and the agents of weathering. Subsoil weathering occurs both within the parent rock and the soil mantle which overlies it. The nature of the weathering process therefore depends on the presence or absence of a soil cover. In general, the direction and degree of chemical change and the initial mineral products of weathering will be similar in the early stages within the two realms of weathering. As weathering proceeds, the character, end-products, and rates of weathering will diverge and show distinct differences in the two realms. Thus, element variation within the surface zone of a highly weathered outcrop face will show both similarities and sharp differences in comparison with nearby weathering of the same material buried beneath a modifying soil cover. In this thesis, the investigation was confined to subsoil weathering.

2.) The important chemical processes and products (Keller, 1955) are:

Processes:

a) Hydrolysis
b) Solution
c) Hydration
d) Carbonation
e) Oxidation-Reduction
f) Ion Exchange
g) Chelation
h) Diffusion
i) Adsorption & Swelling
j) Colloidal Dispersion & Flocculation

Products:

a) Ions in Solution
b) Ions adsorbed by Gels
c) Ions in Exchange Positions
d) Clay Minerals
e) Colloidal Fragments of Original Silicates in which Cations are more or less removed
f) Secondary silicate and alumino-silicate structural fragments in indeterminate degrees of lattice organization ("silicate wreakage")
g) Gels and mixtures of hydrated iron, alumina, and silica
h) Zeolitic minerals

In addition, the five physical factors of soil formation (Jenny, 1941) can be mentioned here:

a) Parent Rock
b) Climate
c) Topography & Drainage
d) Organisms
e) Time

3.) A soil is a dynamic system which continually undergoes modifications involving alterations, depletions, and additions. A soil, when sampled, represents only the geochemical state at the time of sampling. The results do not indicate end-products of a process but only the sum of all preceding stages of development. Recent events and the time of year at sampling will affect the geochemical state of a soil. Annual and even diurnal fluctuations produce continual changes both in such superficial components as organic content, available and adsorbed moisture, soluble salts, and exchangeable cations and in the gross silicate composition of the soil minerals.

4.) Given sufficient time for development, the soil profile approaches or may even attain states of equilibrium with respect to the stage of both chemical and mineralogical development. The profile migrates downward in space: erosion physically removes particles from the topsoil zone; solution withdraws or relocates components within the soil; and weathering produces new soil material from the parent rock at the base. Equilibrium is not maintained to the same degree throughout the whole profile; in effect many specific equilibria can be determined for several independent systems of components and for the different chemical processes acting within a soil. During soil development, elements tend to move through and out of the profile in migrating chemical fronts[1] which seldom coincide because of differing element mobilities. A serious disturbance of the over-all soil equilibrium can result physically from wind deflation and surface wash. The topsoil may therefore exhibit noticeable discontinuities in mineralogy, composition, and particle size distribution when compared with subsoil (e.g., G-2).

5.) The present-day soil may be considerably different from its state at an earlier time. Many of the definitive characteristics of a soil are

---

[1] Chemical fronts are defined here by the writer as the surface or zone of maximum concentration of a mobile element or substance (generally in the ionic or colloidal state but not necessarily in solution or in a soil).

therefore inherited. Parts of a soil profile can persist for many thousands of years if not removed by erosive processes. During that period one or more distinct climates may have prevailed. Different climatic regimes can then be superimposed on the developing profile. Multicycle soils are the result and in areas with a low rate of erosion are the rule.

6.) Subsoil weathering requires the presence of an aqueous medium pervading both reactants and products. The amount and composition of the soil solution governs both the character and rates of change in the weathering complex. The system CO_2 - HCO_3^- - H_2O is the most important one in considering the effects of solutions on weathering.

7.) The behavior of trace elements in high-temperature magmatic processes is far better known than in the low-temperature sedimentary (weathering, transportation, deposition, diagenetic, and lithification) processes. Liquid-solid reactions are dominant in both processes.

In igneous processes, the liquid state persists up to the last stages of magmatic activity. The number of major solid phases at a given stage is generally less than 5 and these are nearly always in equilibrium with the liquid phase. High temperatures facilitate diffusion of ions through the liquid phase and into actively crystallizing solid phases. The distribution of minor elements within these solid phases is governed by the principles of isomorphism (c.f.: Goldschmidt, 1954; Mason, 1952, pp. 75-78). These principles state that, in general, ions can freely substitute in lattice sites occupied by other ions whose ionic radii do not differ by more than 15% from the radii of the replacing ions. Substitution is also most likely between ions in the same valence state. High temperatures increase the ability of diadochical elements to tolerate differences in size and charge when substituting in lattices.

In contrast to the comparative simplicity and well established principles of trace element behavior in an igneous system, the principles which determine behavior during weathering and soil formation are both more complex and less understood. In outline summary, the factors in weathering which differ from those in magmatic crystallization are:

a) The liquid melt phase is replaced by an aqueous phase which, although not predominant volumetrically, plays a vital role in solution and diffusion processes.

b) The number of solid phases are greater (2 to 4 times) and hence the possibilities for distribution of an element among phases are multiplied.

c) Reaction rates are reduced in the lower T^o and P ranges.

d) The degree of isomorphous substitutions in newly forming phases is reduced by the lower temperatures and less active diffusion.

e) The range in stability of <u>all</u> solid phases is greater (i.e., high-temperature (metastable) and low temperature phases can coexist).

f) Equilibria among phases are far more complex and exist to varying degrees in different parts of a profile.

g) Free ions tend to hydrate and therefore develop effective ionic diameters which inhibit substitution for some of the elements with which they have diadochical similarity in igneous rocks.

h) Adsorption has a stronger influence on the location of an element among phases.

i) Non-silicate phases (carbonates, hydroxides, organic matter, etc.) can compete for some of the released elements.

j) The immediate soil system is <u>open</u>, both to additions of elements from outside sources and to departures of elements, mainly in migrating groundwater solutions.

k) Any given atom released from the parent rock may successively be incorporated by or adsorbed on many different phases before eventual removal from the system by groundwater, erosion, etc.

8.) The parent rock composition influences the behavior of a given trace element during weathering by:

a) Establishing the initial concentration of the element.

b) Determining, as the result of the different stabilities of the primary phases and the distribution of the element within these phases, the relative proportion of that element released at any stage of the weathering process.

c) Controlling, in the early stages of weathering, the pH of the soil solution.

d) Governing the initial character of the clay minerals formed.

9.) As a general rule, the mineral phases in both igneous rocks and weathering and soil products derived from them are undersaturated with respect to the amounts of minor elements that can be tolerated in these phases. Most minor elements enter crystallizing phases as "structural impurities" and the actual amounts that are accepted in any phase usually can vary considerably, depending on the initial concentrations, rates of diffusion and crystallization, temperatures, etc. The trace element content does not affect the application of the phase rule (in which the components are the major elements) either to an igneous or a weathering system. The stability of a few phases may be slightly altered by incorporation of certain trace elements but the amounts incorporated must be notably greater than normally available to natural rock systems to render these phases unstable under weathering conditions. In general, the geochemical processes and products of subsoil weathering are not substantially affected by the trace element content of either parent rock or soil; a 10- or 100-fold increase in concentration of a minor element does not noticeably change the over-all appearance of a soil (except in the rare case where it may be able to localize in a distinct phase, as does Mn and Co in the Suite S concretions) nor does it appreciably affect the chemical parameters (pH, E_h, C.E.C., etc.) which control soil formation.

10.) Although trace elements have little influence on the chemical state of a soil, they are affected by the same geochemical factors that control major element variations. These factors are:

a) Lattice substitutions in secondary phases.
b) Relative distribution of elements among all phases.
c) Relative stabilities of these phases.
d) pH and E_h conditions.
e) Solubilities of phases (ionic solution).
f) Adsorption characteristics.
g) Hydration of ions.
h) Inclusion within amorphous substances.
i) Affinities for organic matter (also biological control).

Each of these factors is discussed below in the light of its known or speculative effects on trace element behavior in subsoil weathering.

(10a) Lattice Substitutions: In igneous minerals, practically all of a given element occurs within the lattices of crystalline phases. In weathering and soil products, however, small but important amounts reside on surfaces, in amorphous phases, and in organic matter.

The principles of lattice substitution in high-temperature silicates probably apply in a closely similar way to secondary crystalline silicate phases. Thus, in clay minerals, hydrated oxides, etc., Co, Cr, Mn, Ni, Ti, and V should proxy mainly for Fe; Ni, Cu, and Sc will substitute for Mg; Ga and Ti can occur diadochically with Al; and Sr ought to be found in K and Ca positions. However, the extent of substitution within a forming crystal lattice is restricted by the oxidation and hydration states of the ions concerned and the tolerance limits (affecting lattice and bonding energies) at the prevailing thermodynamic conditions. The upper limits of tolerance (saturation) and the exact structural locations of the common minor elements in most of the secondary phases in soils or sediments have not been determined.

(10b) Relative Distribution of Elements: The distribution of many minor elements among phases in igneous rocks is known in a general way (Wager and Mitchell, 1951; Nockolds and Mitchell, 1948) for the common minerals. Thus, the relative proportion of a given minor element which can substitute within several coexisting phases can be predicted from 1) crystal chemical considerations, and 2) data showing the trend of distribution through a series of igneous differentiates. It has been possible to formulate a distribution law for trace elements (Neumann, Judson, and Vitaliano, 1954) which can be used to predict the probable element distribution among phases when the compositional and thermodynamic conditions in a magma can be specified.

In the weathering process, lack of data regarding the trace element content in individual clay minerals, colloidal phases, hydroxides and hydrated oxides, and organic matter prevents an accurate accounting of the distribution and preference of a minor element among the several phases which can compete for it. Knowledge of element distributions among phases in a natural soil system are hampered by the inability to separate these phases for study. A further complication within a soil ensues from the ability of fractions of each element content simultaneously to be fixed on particle surfaces or to remain in solution as well as to be incorporated within phase lattices.

The most promising way of determing minor element distributions lies in a systematic study of trace element behavior in synthesized clay minerals, etc. It is probable that the principle of the distribution law would apply to lattice substitutions in these phases.

At any given stage of soil development, the over-all distribution of trace elements between the primary phases surviving from the parent rock and the secondary products formed by weathering depends on the relative stabilities of all phases and on the intensity of weathering.

(10c) Relative Stabilities: Much more is known regarding phase equilibria and fields of stability of the igneous minerals than of many of the minerals which characterize soils. Such descriptive approaches to the stabilities of silicates in the high temperature ranges as Bowen's Reaction Series, the classification according to bonding or lattice energies, and the phase diagrams of simplified systems (e.g., $MgO - SiO_2 - Al_2O_3$) are well known. Mineral syntheses and application of thermodynamic theory have succeeded in providing precise stability data for some minerals.

The stabilities of these same igneous minerals relative to the environment of weathering can be predicted from both experimental and observational studies (Goldich, 1938; Keller, 1954). Far less is known regarding the conditions of stability of most of the secondary minerals (except common carbonates, sulphates, sulfides, and several hydroxides). A qualitative estimate of the most stable soil minerals to be expected at any stage of weathering can be determined from the Weathering Sequence of Clay Size Minerals developed by Jackson et al (1948).

The stabilities of mineral phases in subsoil weathering depend mainly on their major element constituents. Minor elements are released as "fellow travelers" as various phases become unstable in the changing environment and undergo destruction. In the course of weathering, the effect of minor elements on the stabilities of secondary phases is probably too small to alter or disturb the development of these phases.

(10d) pH and E_h Conditions: The hydrogen ion concentration and the redox state of a soil closely control the character and solubilities of the various ions in the system. pH and E_h also influence the nature of the colloids which are formed in the soil.

The principles by which pH and E_h govern the stability fields of free ions and influence the geochemical environment have been covered by many authors (e.g., Garrels, 1954; Mason, 1949). An excellent summary of these principles has been presented by Krauskopf (1955, pp. 430-37) specifically for the minor elements. Krauskopf shows several figures in which the stability fields of the various ionization states and combinations with H and O of Ag, As, Au, Bi, Cd, Co, Cr, Cu, Ga, Ge, Hg, In, Mn, Mo, Ni, Po, Pd, Pt, Re, Sb, Se, Sn, Te, Ti, Tl, and V have been defined at a specified temperature, pressure, and concentrations on the basis of E_h and pH. Thus, it is possible to deduce the most probable form assumed by an element at the pH and E_h which prevails at any point within the soil or weathering surface. From such information, it is further possible to predict the behavior of that fraction of the total content of any element which is directly influenced by pH and E_h. Thus, the solubility, the permissible substitutions within lattices, the exchange power, and the degree of hydration (provided these data have been established for a given element) of the element can be assessed and then related to the possible states and combinations it may assume among the soil phases. As an example: at a low pH and a low negative to low positive E_h, V exists as V^{+++} and readily enters into lattice substitution for Fe^{+++}, becomes fixed on surfaces, or remains in solution; at a higher positive E_h, V forms the less soluble VO_4^{++}; and at high pH and a negative E_h, V, in several valencies, forms stable hydroxides. The history of a minor element in the soil largely reflects both its response and the response of the major elements in the host phases to the changing pH-E_h conditions.

(10e) Solubilities: The solubilities of free metal ions of the minor elements in dilute solutions in the presence of one or several anions have been determined primarily from laboratory studies. These data have been effectively extrapolated to predict the solubilites of some of the naturally occurring carbonates, hydroxides, and sulfides of the minor elements. Studies of the solubilities of silicates (irrespective of trace element content) are limited; it is therefore difficult to predict when and under what conditions an element will be released to solution during the weathering of most phases either in the parent rock or the soil.

Once released however the expected behavior of the minor element can be specified in terms of either the relative solubilities of its ion forms (Krauskopf, 1955, pp. 438-41) or by the ionic potential concept (Cartledge, 1928; Goldschmidt, 1937). The ionic potential Φ is defined as Z/r, in which Z is the valency of the cation and r is its ionic radius (in Angstrom Units). Goldschmidt demonstrated a general relationship between Φ and the relative bond strengths of the two bonds in the structure Cation - O - H such that cationic species with 1) Φ less that 2.5 have their weaker bonds between cation and OH^- and are soluble, 2) Φ greater than 2.5 and less than 8.5 have approximately equivalent bond strengths between all components and therefore form insoluble hydroxides, and 3) Φ greater than 8.5 form strong cation - O bonds and hence exist as soluble anionic radicals. In general, a minor element will follow in solution the behavior of the major element with the closest ionic potential value, provided the two ion species are also similar in size. In a soil therefore Ca, Na, K, Fe^{++} and Ba, Sr, and Mn^{++} will be preferentially removed in solution whereas Fe^{+++}, Mg, Al, Si and most of the ferride minor elements, Ga, and Zr will concentrate as or with insoluble metal hydroxides. Because these hydroxides and some hydrated oxides are common products of weathering, the enrichment in many soils of trace elements relative to the loss of most of the major elements can be explained. The ionic potential concept does not apply directly to complex silicates; however, Φ affects the availability of trace elements to the silicates by determining which elements will remain largely in solution and which will be tied up in non-silicate precipitates. As a rule, the intermediate Φ group of trace elements are also those which associate with the hydrolysates (clay minerals, etc.); this association is the result both of co-precipitation of hydroxides with these silicates and of replacement of the dominant cations (Fe, Al, Si) in the hydrolysates.

(10f) Adsorption Characteristics: The exchange capacity ranges for most of the clay minerals, many organic compounds, and some of the colloidal and gel materials found in soils have been adequately determined. The relative replacing power of the common cations and anions is also well established. Both capacities and replacing powers can vary considerably among the different phases, depending on the ion exchange factors (Grim, 1953, pp. 144-152) that persist at any locality during development of a weathering complex. In most soils, H^+ and Ca^{++} are the common cations fixed in the upper profile; with depth Mg^{++} increases and Na^+ decreases in percentage of exchange positions occupied.

The replacing powers of the trace elements on a given colloid or clay mineral are incompletely known. A general order of difficulty of displacement (equivalent to replacing power) is $Cu > Pb > Ni > Co > Zn > Ba > Sr > Ca > Mg > K > Na$; the relative position of any ion species in this series can vary with changes in one or more of the ion exchange factors. The observation that most of the minor elements are held more strongly on surfaces than major elements helps to explain 10-fold or more increases in their concentrations in soils containing an abundance of colloidal and clay-sized particles. In gleyed (poor internal drainage) soils, the adsorbed trace element content is often abnormally high. However, except for the most advanced stages of soil weathering, the ratio of any element concentration associated with particle surfaces to its concentration within the lattice is usually less than 0.1 - 0.01.

The amounts of an element extracted by leaching have been used to estimate roughly the amounts available to plants through exchange. However, the leach fraction also includes contributions from soluble salts and cements, decomposable organic matter, and even the host silicates (whose outer structure may be poorly crystalline and have weaker bonds).

In the earlier stages of weathering, Co, Cu, Mn, Ni, and Zn are released from less stable phases containing Ca, Mg, and Fe. However, these same cations are among those most firmly held by adsorption. The sand fractions of soils therefore show impoverishment of these elements whereas the clays show corresponding enrichment.

(10g) Hydration: The effective diameter of an ion can increase by hydration in which it becomes surrounded by one or more layers of H_2O molecules. As a result, such an ion-hydrate is too large to enter most crystal lattices. The degree of hydration affects the proportion of a given ion that remains in solution. The effective hydration diameters of most of the minor elements have not been determined. Those ions with small ionic radius, large valence, and high polarizability are generally strongly hydrated.

(10h) Inclusion: A small and usually indeterminate fraction of a trace element can be incorporated without formation of any chemical bonds in amorphous phases, gels, or in lattice interstices.

(10i) Affinities for Organic Matter: From the standpoint of the original (parent rock) composition, organic matter, composed largely of elements not normally a part of the initial geochemical system, is both an additive and a diluent. Organic matter plays a vital role in soil development activities, being responsible for the concentration of certain elements, for chelating, exchange, and desorption processes, and for several decomposition mechanisms (including the supply of H^+ to the soil from plant roots; see Keller and Frederickson, 1952). The need in the life processes of most plants for certain trace elements, namely B, Co, Cu, Mn, Mo, and Zn has been demonstrated (see McMurtrey and Robinson, 1939). In addition, certain plant and animal organisms may have strong affinities for - and hence will concentrate - Cr, Pb, Se, and V. Trace elements are taken up by many microbacteria which then serve as carriers and distributors of these elements throughout the soil. Nonliving organic matter in the soil can effectively concentrate several minor elements in the reduced state which otherwise would be gradually removed from the soil as oxidized ions.

Summary: The general behavior of a minor element during weathering and soil formation, at any given stage, is the summed effect of many complexly interacting physical and chemical variables. A minor element species may exist in several chemical states and may be distributed among many phases within the total soil during the history of weathering and soil development. The exact character (both qualitative and quantitative) of behavior of most of the minor elements is simply not known or well understood at the present time. From the limited data, the few definitely established principles, and the information resulting from the thesis investigation, the writer has concluded that trace element behavior is controlled predominantly by 1) the degrees of decomposition of the primary host minerals, 2) the relative proportions of the more resistant minerals which accumulate in the soil, 3) the amounts that can be accepted in secondary mineral structures, 4) the oxidation states and relative solubilities of the released elements, and 5) the degree of leaching (and eventual removal) by natural solvents of the fraction of any element occupying exchange positions on mineral surfaces or held in readily soluble mineral or colloidal matter.

BIBLIOGRAPHY

Ahrens, L.H. (1950), Spectrochemical Analysis, Addison-Wesley Press, Inc., Cambridge, Mass.

Ahrens, L.H. (1954), Quantitative Spectrochemical Analysis of Silicates, Pergamon Press Ltd., London.

Allison, R.V. and Gaddum, L.W. (1940), The Trace Element Content of some Important Soils - a comparison, Soil Sci. Soc. Florida, Proc. 2, pp. 68-91.

Brindley, G.W. and Gillery, F. H., (1956) X-ray Identification of Chlorite Species, Am. Mineralogist, vol. 41, pp. 169-186.

Butler, J. R. (1953), The Geochemistry and Mineralogy of Rock Weathering (1) The Lizard Area, Cornwall, Geochim. et Cosmochim. Acta, vol 4, pp. 157-178.

Butler, J.R. (1954), Trace Element Distribution in some Lancashire Soils, J. Soil Sci., vol. 5, pp. 156-166.

Carlsson, C.G. and Yu, J.T.M. (1950), Spectrochemical Analysis of Steelmaking Slags, Iron and Steel Inst. Jour., vol. 166, pp. 273-280.

Churchill, J.R. and Russell, R.G. (1945), Analysis of Aluminous Ores by means of Spark Spectra, Ind. and Eng. Chem. Anal. Ed., vol. 17, pp. 24-27.

Coulliette, J.H. (1943), Determination of Nickel and Chromium in Stainless Steel, Ind. and Eng. Chem. Anal. Ed., vol. 15, pp. 732-734.

Councill, R.J. (1953), A Preliminary Geological Report on the Commercial Rocks of the Volcanic-Slate Series, N. Carolina, N. Caro. Dept. of Conserv. and Develop. Info. Circ. #12.

Dennen, W.H. and Fowler, W.C., (1955), Spectrographic Analysis by use of the Mutual Standard Method, Bull. Geol. Soc. Amer., vol. 66, pp. 655-662.

Fairbairn, H.W. et al. (1951), A Cooperative Investigation of Precision and Accuracy in Chemical, Spectrochemical, and Modal Analysis of Silicate Rocks, U.S. Geol. Survey Bull 980.

Fairbairn, H.W., Ahrens, L.H, and Gorfinkle, L.G. (1953), Minor Element Content of Ontario Diabase, Geochim. et Cosmochim. Acta, vol. 3, pp. 34-46.

Fraser, G.K. (1955), Soil Organic Matter, in Chemistry of the Soil, Reinhold Publishing Corp., N.Y., pp. 149-176.

Goldich, S.S. (1938), A Study in Rock Weathering, J. Geol., vol 46, pp. 17-58.

Goldschmidt, V.M. (1937), The Principles of Distribution of Chemical Elements in Minerals and Rocks, J. Chem. Soc., pp. 655-673.

Goldschmidt, V.M. (1945), The Geochemical Background of Minor-element Distribution, Soil Sci., vol. 60.

Goldschmidt, V.M. (1954), Geochemistry, Clarendon Press, Oxford.

Gordon, M., Jr. and Murata, K.J. (1952), Minor Elements in Arkansas Bauxite, Econ. Geol., vol. 47, pp. 169-179.

Hardison, R.B. and Brinkley, L.L. (1915), Soil Survey of Davidson County, N. Carolina, U.S.D.A. Bur. Chem. & Soils. Report #17, pp. 461-495.

Harper, Scott, and Frahm (1932), Soil Survey of the Brighton Area, Colo., U.S.D.A. Bur. Chem. & Soils, Soils Series 1932 #1, p. 29.

Harvey, C.E. (1950), Spectrochemical Procedures, Applied Research Laboratories, Glendale, Calif.

Haseman, J.F. and Marshall, C.E. (1945), The Use of Heavy Minerals in Studies of the Origin and Development of Soils, Missouri Agri. Expt. Sta. Research Bull. 387.

Holyk, W. (1952), Some Aspects of Radioactivity, Ph.D. thesis, M.I.T.

Jackson, M.L. et al. (1948), Weathering Sequence of Clay Size Minerals in Soils and Sediments, J. Phys. & Colloidal Chem., vol. 52, pp. 1237-1260.

Jenny, H. (1941), Factors of Soil Formation, McGraw-Hill Publ. Co, N.Y.

Joffe, J.S. (1936), Pedology, Rutgers University Press, New Brunswick, N.J.

Joffe, J.S. and Kunin, R. (1943), Mechanical Separates and Their Fractions in the Soil Profile, 1. Variability in Chemical Composition and its Pedogenic and Agropedologic Implications, Soil Soc. Amer. Proc. vol. 7, pp. 187-193.

Keller, W.D. (1954), The Bonding Energy of Some Silicate Minerals, Am. Mineralogist, vol. 39, pp. 783-793.

Keller, W.D. (1955), The Principles of Chemical Weathering, Lucas Bros. Publ., Columbia, Mo.

Keller, W.D. and Frederickson, A.F. (1952), Role of Plants and Colloidal Acids in the Mechanism of Weathering, Am. J. Sci. vol. 250, pp. 594-608.

Kilmer, V.J. and Alexander, L.T. (1949), Methods of Making Mechanical Analyses of Soils, Soil Sci., vol. 68, pp. 15-24.

Krauskopf, K.B. (1955), Sedimentary Deposits of Rare Metals, Econ. Geol. Fiftieth Anniversary vol., pp. 411-463.

Krumbein, W.C. and Pettijohn, F.J. (1938), Manual of Sedimentary Petrography, Appleton-Century-Crofts, N.Y.

Krusekopf, De Young, Watkins, and Deardorff (1918), Soil Survey of Reynolds County, Missouri, U.S.D.A. Bur. Chem. & Soils 5331, p. 1326.

Mackenzie, R.C. (1954), Free Iron Oxide Removal from Soils, J. Soil Sci. vol. 5, pp. 167-172.

Mason, B. (1952), Principles of Geochemistry, John Wiley & Sons, N.Y.

McMurtrey, J.E. and Robinson, W.O. (1938), Neglected Soil Constituents that affect Plant and Animal Development, Yearbk. U.S.D.A., pp. 807-829.

Merkle, F.G. (1955), Oxidation-Reduction Processes in Soils, in Chemistry of the Soil, Reinhold Publishing Corp, N.Y., pp. 200-218.

Milne, I.H. and Warshaw, C.M. (1956), Methods of Preparation and Control of Clay Mineral Specimens in X-ray Diffraction Analysis, Proc. 4th Nat. Conf. on Clays & Clay Minerals, pp. 22-30.

Mitchell, R.L. (1946), Applications of Spectrographic Analysis to Soil Investigations, Analyst, vol. 71, pp. 361-368.

Mitchell, R.L. (1947), The Trace Constituents of the Soil, 1947 Cong. Pure & App. Chem. Trans. 3, pp. 157-164.

Mitchell, R.L. (1948), Trace Constituents in Soils and Plants, Research, Lond. vol. 1, pp. 159-165.

Mitchell, R.L. (1955), Trace Elements, in Chemistry of the Soil, Reinhold Publishing Corp., N.Y., pp. 253-285.

Mood, A.M. (1950), Introduction to the Theory of Statistics, McGraw Hill Publ. Co., N.Y., p. 206.

Neumann, H, Mead, J., and Vitaliano, C.J. (1954), Trace Element Variations During Fractional Crystallization as Calculated from the Distribution Law, Geochim. et. Cosmochim. Acta. vol. 6, pp. 90-99.

Nockolds, S.R. and Mitchell, R.L. (1948), The Geochemistry of some Caledonide Plutonic Rocks: a Study in the Relationship between the Major and Trace Elements of Igneous Rocks and Their Minerals, Trans. Roy. Soc. Edinburgh, vol. 61, pp. 533-575.

Osterwald, F.W. (1955), Petrology of Pre-cambrian Granites in the Northern Bighorn Mountains, Wyom., J. Geol., vol. 63, pp. 310-327.

Peech, M. (1945), Determination of Exchangeable Cations and Exchange Capacity of Soils. Rapid Micro Methods Utilizing Centrifuge and Spectro Photometer, Soil Sci., vol. 59, pp. 25-38.

Peech, M. (1947), Methods of Soil Analysis for Soil Fertility Investigations, U.S.D.A. Circ. 757, pp. 5-7.

Peech, M. and English, L. (1944), Rapid Microchemical Soils Tests, Soil Sci., vol. 57, pp. 167-195.

Pettijohn, F.J. (1949), Sedimentary Rocks, Harper & Bros., N.Y.

Polynov, B.B. (1937), The Cycle of Weathering, Th. Murby & Co., London.

Rankama, K. and Sahama, Th. G. (1950), Geochemistry, The University of Chicago Press.

Reiche, P. (1945), A Survey of Weathering Processes and Products, University of New Mexico Publ. in Geology No. 1.

Rolfe, B.N. (1954), Mineralogy of Soil Profiles: Iredell and Durham soils from the Piedmont Province of N. Carolina, Proc. 2nd Nat. Conf. on Clays and Clay Minerals, pp. 183-189.

Rozsa, J.T. (1947), Slag Control by Routine Spectrographic Analysis, Metal Progress, vol. 51, pp. 593-597.

Sandell, E.B. and Goldich, S.S. (1943), The Rarer Metallic Constituents of some American Rocks, II, J. Geol, vol. 51, p. 167.

Schofield, R.K. and Taylor, A.W. (1955), Measurement of the Activities of Bases in Soils, J. Soil Sci., vol. 5, pp. 137-146.

Shapiro, L. and Brannock, W.W. (1952), Rapid Analysis of Silicate Rocks, U.S.G.S. Circ. 165.

Shaw, D.M. (1954, 1956), Trace Elements in Pelitic Rocks; Geochemistry of Pelitic Rocks, Bull. Geol Soc. Amer., vol. 65, pp. 1151-1182; vol. 67, pp. 919-934.

Shimp, N.F., Connor, J., Prince, A.L., and Bear, F.E. (1957), Spectrochemical Analysis of Soils and Biological Materials, Soil Sci., vol. 83, pp. 51-64.

Shimp. N.F., Connor, J., and Tedrow, J.C.F. (1957), A Spectrographic Study of the Distribution of Trace Elements in some Podzolic Soils, Soil Sci., vol. 83, pp. 65-73.

Slater, C.S., Holmes, R.S., and Byers, H.G. (1937), Trace Elements in the Soils from the Erosion Experiment Stations with Supplementary Data on other Soils, U.S.D.A. Tech. Bull. 552.

Slavin, M. (1938), Quantitative Analysis based on Spectral Energy, Ind. Eng. Chem., Anal. Ed., vol. 10, p. 407.

Stuckey, W. (1928), The Pyrophyllite Deposites of N. Carolina, N. Caro. Dept. Commerce & Devel. Bull 37, p. 21.

Swaine, D.J. (1951), The Distribution of Trace Elements in Soils, Unpublished Thesis, University of Aberdeen.

Swaine, D.J. (1955), The Trace Element Content of Soils, Commonwealth Bur. Soil Sci. Tech. Comm. No. 48, Common. Agr. Bur., England.

Tolman, C. and Goldich, S.S.(1935)Granite, Pegmatite, and Replacement Veins in the Sheahan Quarry, Graniteville, Missouri, Am. Mineralogist, vol. 20, pp. 229-239.

Thorne, D.W. and Seatz, L.F. (1955), Acid, Alkaline, Alkali, and Saline Soils, in Chemistry of the Soil, Reinhold Publishing Corp, N.Y., pp. 219-252.

Thorp, J., Glassey, T.W., Dunnewald, T.J., and Parsons, B.L. (1939), Soil Survey of Sheridan County, Wyoming, U.S.D.A. Bur. Chem. and Soils, Series 1932, No. 33.

U.S.D.A. (1951), Soil Survey Manual, U.S.D.A. Handbook No. 18.

Vinogradov, A.P. (1950), The Geochemistry of Rare and Disperse Chemical Elements in Soils (in Russian), Moscow.

Wager, L.R. and Deer, W.A. (1939), The Petrology of the Skaergaard Intrusion, Kangerdlugssuag, East Greenland; Medd. Grønland, vol. 105.

Wager, L.R. and Mitchell, R.L. (1951), The Distribution of Trace Elements During Strong Fractionation of Basic Magma - A Further Study of the Skaergaard Intrusion, Geochim et Cosmochim. Acta, vol. 1, pp. 129-208.

Wager, L.R. and Mitchell, R.L. (1948), The Distribution of Cr, V, Ni, Co and Cu During the Fractional Crystallization of a Basic Magma, Int. Geol. Congr., Rpt. of 18th Sess., Great

Wager, L.R. and Mitchell, R.L. (1953), Trace Elements in a Suite of Hawaiian Lavas, Geochim. et Cosmochim. Acta, vol. 3, pp. 217-223.

Waldschmidt, W.A. (1939), The Table Mountain Lavas and Associated Igneous Rocks near Golden, Colo., Colo. Sch. Mines Quarterly, vol. 34.

Wheeler, G.V. and Burkhardt, W. (1950), Section 2: Semiquantitative Spectrochemical Analyses, in Analytical Data on Reference Clay Minerals, Am. Petr. Inst. Proj. 49: Clay Minerals Standards, Prelim. Rpt. No. 7.

Wicklander, L. (1955), Cation and Anion Exchange Phenomena, in Chemistry of the Soil, Reinhold Publishing Corp., pp. 107-148.

Wright, J.R., Levick, R., and Atkinson, H.J. (1955), Trace Element Distribution in Virgin Profiles Representing Four Great Soil Groups, Soil Sci. Soc. Amer. Proc., vol. 19, p. 340.

Yamasaki, C, Iida C., and Yokoi, H. (1955), A Spectrographic Determination of the Distribution of Trace Elements in a Granodiorite and its Weathering Products, J. Earth Sci., Nagoya Univ., vol. 3, No. 1, pp. 58-64.

Yoe, J.H. and Koch, Jr., H.J. (1957), Trace Analysis, John Wiley & Sons, N.Y.

ZoBell, C.E. (1946), Studies on Redox Potential of Marine Sediments, Bull. A.A.P.G., vol 30, pp. 477-513.

BIOGRAPHY

NICHOLAS MARTIN SHORT: Born July 18, 1927 in St. Louis, Missouri.

Education:

1) St. Louis University High School: 1941-45.
2) St. Louis University: 1947-51; B.S. in Geology 1951.
3) Colorado School of Mines: Summer 1949.
4) Washington University (St. Louis, Mo): 1951-53; teaching assistant; M.A. in Geology 1954; Thesis: The Ste. Genevieve Formation at its Type Locality.
5) Pennsylvania State University: 1953-54; research assistant and graduate work in Dept. of Mineralogy.
6) Massachusetts Institute of Technology: 1955-57; National Science Foundation Fellow 1056-57; Ph.D. in Geology 1958.

Professional Experience:

1) Service; U.S. Army: 1945-47.
2) Cartographic Survey Aid; U.S. Geol. Surv., S. Dak: Summer 1950.
3) Cartographic Photogrammetric Aid; U.S. Air Force Aero. Chart Plant, St. Louis, Mo: Summer 1951.
4) Asst. Field Geologist; Jones & Laughlin Ore Co, Ely, Minn.: Summer, 1952.
5) Instructor; Dept. Geology, University of Missouri: 1954.
6) Instructor; Dept. Geology, Washington University: Summer 1955.
7) Research Geologist; Gulf Research & Development Co., Pittsburgh, Pa, Sept. 1957 - .