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GEOCHEMICAL AND MINERALOGICAL CHARACTERIZATION OF SURFICIAL RESIDUUM FORMED FROM LOWER KNOX GROUP DOLOSTONE, WEST CHESTNUT RIDGE, OAK RIDGE, TENNESSEE

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Anne S. Crafts

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ABSTRACT

The nature and properties of the residuum developed on top of the Copper Ridge and Chepultepec Formations of the Knox Group at West Chestnut Ridge, Oak Ridge, Tennessee were investigated. Physical, mineralogical, and geochemical analyses of both the residuum and selected Lower Knox Group bedrock samples were used to characterize the weathering behavior of siliceous and argillaceous dolostones.

Lower Knox Group lithologies at West Chestnut Ridge are dominated by cherty dolostones with fewer beds of limestone, shale, and sandstone. The bedrock has weathered to form an overlying mantle of clay- and chert-rich residuum and soils that thicken to 30 meters or more on ridge tops. Samples were available from seven cores at various depths over an interval of one to 30 meters. Minerals in the residuum include illite, quartz, kaolinite, hydroxy-interlayered vermiculite, mixed-layer clays, amorphous iron-, manganese-, and aluminum-oxides and oxyhydroxides, as well as gibbsite, hematite, goethite, feldspars, dolomite, and calcite.

Mineralogical and chemical analyses for the residuum suggest a discontinuity at a depth of 15 meters in the two most complete cores (9 and 16) overlying the Copper Ridge Formation. Above approximately 15 meters, the residuum is more extensively leached, while at greater depths the composition of the residuum more closely reflects the

character of the original parent bedrock. Based on chemical analyses, two zones identified in the residuum can be shown to be independent populations using the t-test: (1) an upper, more thoroughly leached zone generally free of detrital feldspars and carbonates; and (2) a lower zone of accumulation in which traces of feldspars and carbonates are still present.

Chemical compositions of available bedrock samples were compared with chemical compositions of the residuum to obtain an approximation of the extent of the changes that took place during the weathering process. Upon examination of the data, several elements (such as K, Na, Ti, and Mn) appear to have been enriched during the weathering process; however, when the relative weight percentages are compared, it is apparent that these elements have been removed from the system. Only Fe, Al, and perhaps P have been concentrated in the system. These elements appear to have been leached from the upper zones and concentrated in the lower zone of accumulation. Ca is the most mobile element and was almost completely removed by groundwater. Mg is also mobile, but some Mg was retained in clay minerals. For purposes of comparison, SiO_2 is assumed to have been neither added to nor removed from the system. It was retained in the residuum in the form of relatively insoluble quartz (mostly in the sand and silt fractions), chert fragments (in the gravel, sand and silt fractions), and in clay minerals.

Ionic adsorption capacities (CEC's and AEC's) of clay minerals are dependent on many factors such as the clay mineral species present, the pH of the weathering environment (pH values indicate the soils and residuum at West Chestnut Ridge are acidic), the amount of clay surface areas (estimated from grain size analyses), and the amount of amorphous oxides, oxyhydroxides, and organics. Correlation coefficients indicate there are direct, dependent relationships between CEC's and pH (in distilled water), and CEC's and percentages of the clay-size fractions.

In the event radionuclides are buried at the West Chestnut Ridge site in the future, the soils and residuum could come in contact with the waste leachate. As a result, this study is important for the understanding of the weathering behavior of the residuum overlying the siliceous and argillaceous dolostones of the Lower Knox Group. This information will provide a basis for the interpretation of future hydrologic and chemical investigations of the site.

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CHAPTER I

INTRODUCTION

Purpose

The purpose of this study was to characterize the weathering behavior of the residuum overlying the Lower Knox Group dolostones at West Chestnut Ridge on the Oak Ridge National Laboratory Reservation, Oak Ridge, Tennessee. This was accomplished by analysing selected physical, mineralogical, and geochemical characteristics of bulk residuum samples. Processes involving solution, leaching, redistribution of elements, and precipitation of secondary minerals are especially important and were investigated.

The residuum is important because it can act as a filter for both dissolved and particulate species. Some stratigraphic horizons in the residuum contain karst features, fracture zones, and cavities that have continued to develop since the Middle Ordovician when the Knox was first exposed to weathering. Such features could act as passageways for infiltrating materials from both the surface and at depth (Lee et al., 1984).

In addition to the purpose outlined above, this study was intended to explain the weathering behavior of siliceous dolostones in a warm, humid environment (such as is present

at West Chestnut Ridge) by comparing the physical, mineralogical, and chemical analyses of the residuum with chemical analyses of equivalent Lower Knox Group bedrock.

Background

Three locations for a Central Waste Disposal Facility were considered at West Chestnut Ridge (Ketelle and Huff, 1984; Lee et al., 1984) (Figure 1). The present investigation began as a study of Knox Group residuum from cores taken at West Chestnut Ridge in preparation for the use of one or more sites for low-level radioactive waste disposal. Since the research was begun, a decision was reached not to use the site for disposal of radioactive wastes. Even so, the results of this study are important and can help to explain the weathering behavior of siliceous and argillaceous dolostones such as those found in the Lower Knox Group.

Previous Work

Stockdale (1951) studied the geologic conditions at the Oak Ridge National Laboratory area relevant to the disposal of radioactive wastes. The Knox Group at West Chestnut Ridge was mapped by Bridge and Rodgers (1956), Carroll (1961), McMaster (1962 and 1963), and others.

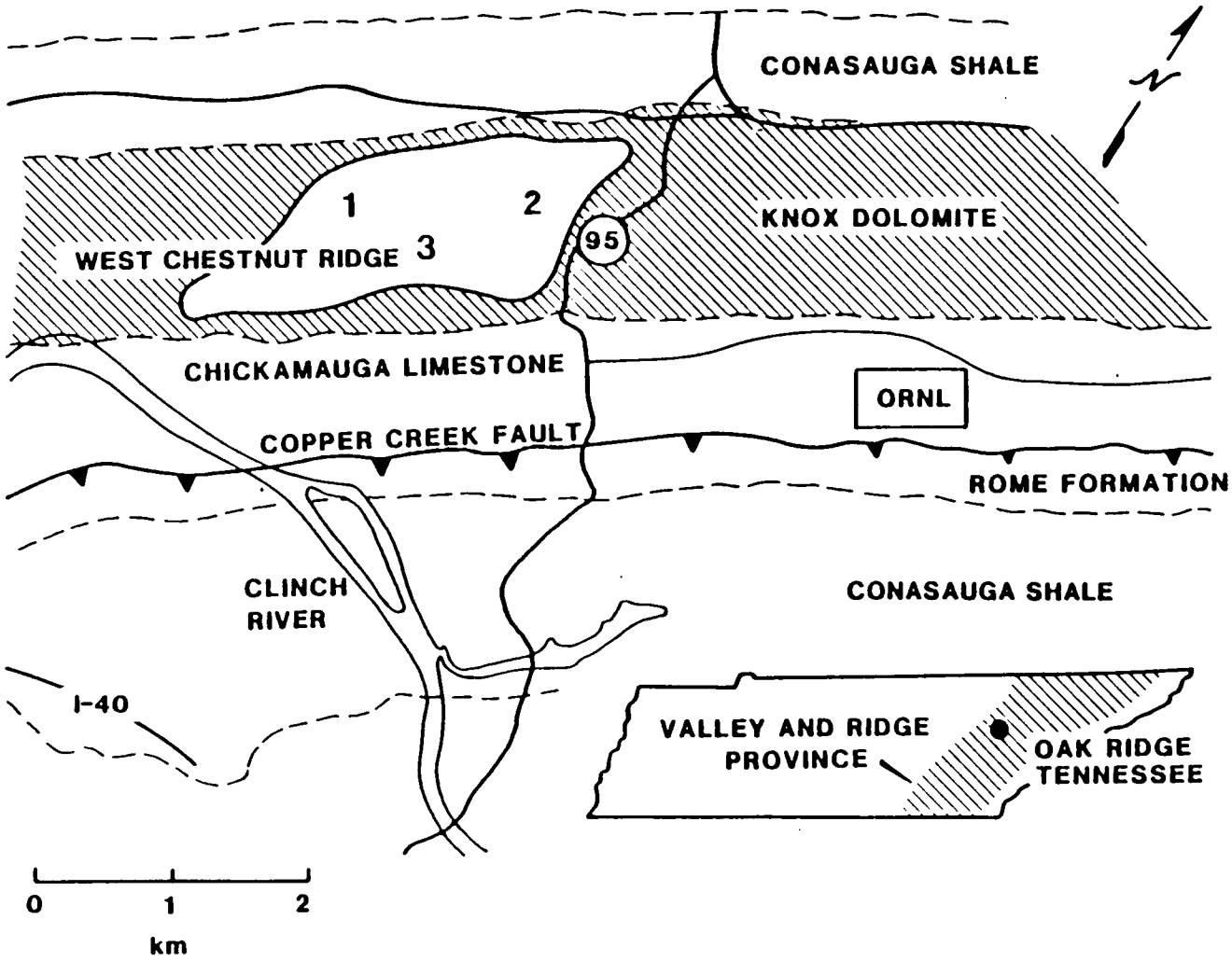


Figure 1. Three locations (1, 2, and 3) considered for construction of a Central Waste Disposal Facility at the West Chestnut Ridge Site (outlined area) (modified from Kopp and Lee, 1986).

Ketelle (1982) reported on the preliminary site characterization of West Chestnut Ridge prior to the decision for it to be chosen as a possible waste disposal site. He described the topography, geology, and hydrogeology of the site, especially noting the karst features and their effects on the hydrologic system. Lee et al. (1983a) studied the use of DOE site selection criteria for screening low-level waste disposal sites on the Oak Ridge Reservation. Ketelle and Huff prepared a more detailed site characterization of West Chestnut Ridge in 1984. They investigated the subsurface with geohydrologic testing including groundwater fluctuation monitoring, and surface water discharge and precipitation monitoring. Seeley and Kelmers (1984) performed geochemical analyses to characterize the groundwater for radionuclide sorption and concentration limits. Woodward-Clyde Consultants (1984) characterized the subsurface and evaluated the geohydrologic conditions from drilling, geophysical, soil and rock strength, and permeability tests.

The mineralogy of West Chestnut Ridge soils and residuum was characterized by Lee et al. (1984). They also measured cation exchange capacities and soil pH values, and noted that the the residuum and soils have a low buffering capacity. In other words, the mineralogical and chemical equilibria which exist could easily be altered if extreme chemical conditions (such as radioactive waste with low or

high pH) were introduced into the environment. Monger (1986) characterized the upper residuum and soils at West Chestnut Ridge both mineralogically and chemically. His samples are from seven cores within the uppermost seven to eight meters below the surface. Some of the results of his analyses will be discussed in this study.

Others have studied the mechanism of weathering of carbonate rocks in geological processes. However, most of these studies deal with weathering and solutional processes at the surface (in the soils) but not at depth. Miller (1972) studied the weathering products of carbonate bedrock, and their relationships to the soils at three localities in East Tennessee. He found that illite is the only clay mineral present in the original Knox Group bedrock. This suggests that the other clay minerals he observed in the soils, such as kaolinite and hydroxy-interlayered vermiculite (HIV), are formed in situ during the weathering process. He concluded that these minerals are either alteration products of primary minerals, or they precipitated from solutions as secondary minerals. Miller also reported higher concentrations of HIV (in the uppermost soil layers) that decrease with depth with a corresponding increase in illite content. Boul et al. (1973) found that illite in the upper residuum represents unweathered material. Lower pH (acidic conditions) results in instability and the subsequent disappearance of illite as it

is converted to HIV in the soils. Ebens and Connor (1980) statistically analysed geochemical data of loess and carbonate residuum (surficial material only) in Missouri. They discovered chemical heterogeneities in the residuum (mainly composed of iron-rich quartz and clay minerals) that are entirely dependent on the chemistry of the underlying carbonate bedrock formations.

None of these studies mentioned above provides mineralogical and chemical analyses of both the residuum and equivalent bedrock. The report by Lee et al. (1984) at West Chestnut Ridge includes analyses of six residuum samples and 20 soil samples, and has served as a starting point for this investigation.

CHAPTER II

GEOLOGIC SETTING

Stratigraphy/Structure

The Upper Cambrian-Lower Ordovician Knox Group in East Tennessee comprises approximately 1,000 meters of strata (Rodgers, 1953; Oder and Ricketts, 1961; Milici, 1973; Walker and Byerly, 1985). Table 1 lists some of the more important changes made in Knox Group nomenclature since the Knox was named by Safford in 1869. Until 1969, most field and mining geologists followed the usage of Rodgers (1953) in which the Knox Group was subdivided into the Copper Ridge Dolomite (Upper Cambrian age), Chepultepec Dolomite, Longview Dolomite, Kingsport Formation, and Mascot Dolomite (all of Lower Ordovician age). Where the contact between the Kingsport and Mascot cannot be clearly established, the formations may be combined and called the Newala Formation. In 1969, Harris proposed a revised Knox Group nomenclature for the area north of Knoxville. He dropped the term Longview and revised the contacts between the Chepultepec, Kingsport, and Mascot Dolomites (Table 1). However, Harris' proposed stratigraphic relationships are primarily applicable to the area north of Knoxville (Milici, 1973).

Table 1. Knox Group stratigraphic nomenclature in Tennessee (after Scales and Kopp 1985).

<table>
<tr><th rowspan="2">AGE</th><th colspan="5">WESTERN FACIES</th><th>EASTERN FACIES</th></tr>
<tr><th>Safford (1869)</th><th>Ulrich (1911)</th><th>Rodgers (1953)</th><th>Brokaw (1966)</th><th>Harris (1969)</th><th>Rodgers (1953)</th></tr>
<tr><td rowspan="4">Lower Ordovician</td><td rowspan="5">Knox Dolomite</td><td rowspan="2">Upper Knox Dolomite</td><td>Mascot Dolomite*</td><td>Mascot Dolomite</td><td rowspan="2">Mascot Dolomite</td><td rowspan="4">Jonesboro Limestone</td></tr>
<tr><td>Kingsport Fm.*</td><td>Kingsport Lmst.</td></tr>
<tr><td rowspan="3">Copper Ridge Chert</td><td>Longview Dolomite</td><td>Longview Dolomite</td><td rowspan="2">Kingsport Fm.</td></tr>
<tr><td>Chepultepec Dolomite</td><td>Chepultepec Dolomite</td><td>Chepultepec Dolomite</td></tr>
<tr><td rowspan="2">Upper Cambrian</td><td rowspan="2">Copper Ridge Dolomite</td><td>Conococheague Lmst.</td><td rowspan="2">Copper Ridge Dolomite</td><td rowspan="2">Conococheague Limestone</td></tr>
<tr><td>Copper Ridge Dolomite</td></tr>
</table>

* Where the Kingsport and Mascot Formations cannot be readily separated they may be classed together as the Newala Formation (Rodgers, 1953).

Whether or not the Longview exists at the West Chestnut Ridge site may be an academic question since all of the samples used in this study came from the Upper Cambrian Copper Ridge and the Lower Ordovician Chepultepec Dolomites. However, according to Ketelle and Huff (1984) and Lee et al. (1984), West Chestnut Ridge is underlain by the Copper Ridge, Chepultepec, Longview, and Newala Formations.

West Chestnut Ridge is located within the Valley and Ridge physiographic province. The study area is within the Whiteoak Mountain Allocthon and is bounded by two major northeast-southwest trending thrust faults, the Copper Creek thrust fault to the southeast and the Whiteoak Mountain thrust fault to the northwest (Figure 2). The strike and dip of the strata are approximately 57 degrees northeast and 35 degrees southeast, respectively (Ketelle et al., 1984).

Site Description

Lower Knox Group dolostones at West Chestnut Ridge are dominated by cherty dolostones with fewer beds of limestone, shale, and sandstone (Table 2) (Milici, 1973; Ketelle and Huff, 1984). The bedrock has weathered to form an overlying mantle of clay-rich residuum and soils that thickens to 30 meters or more on ridge tops. The residuum and soils consist of clay minerals (the dominant ones include koalinite and illite), iron-, manganese-, and aluminum-

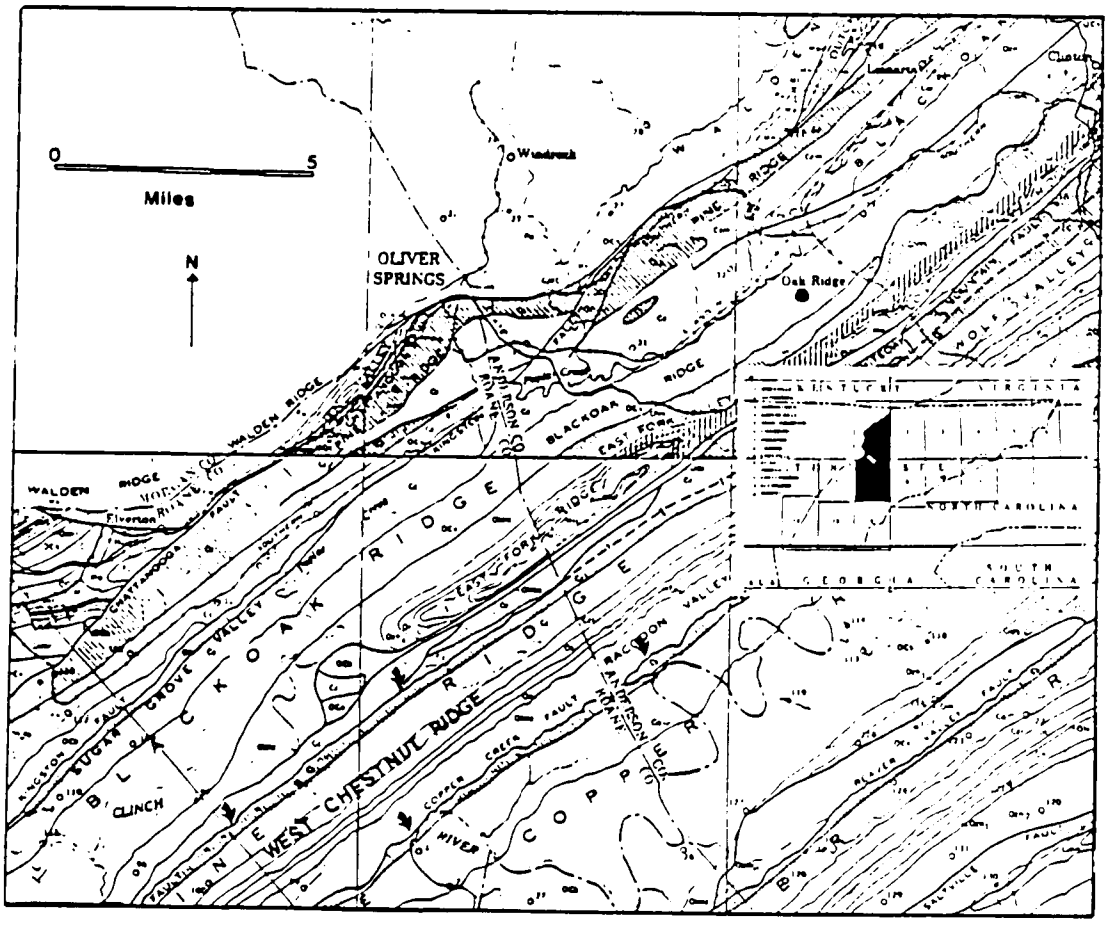


Figure 2. Location of West Chestnut Ridge and its relationship to major thrust faults. The city of Oak Ridge, Tennessee is indicated by the black dot (●). Major thrust faults are indicated by the arrows (➘).

Table 2. Stratigraphic column of bedrock formations at West Chestnut Ridge illustrating the characteristic lithologies (modified from Milici, 1973; and Ketelle and Huff, 1984).

AGE	NAME		ESTIMATED THICKNESS	CHARACTERISTIC LITHOLOGIES
MID. ORD.	CHICKAMAUGA GROUP	MOSHEIM MEMBER		
LOWER ORDOVICIAN	KNOX GROUP	NEWALA FORMATION	275m (900ft)	Dolomite, finely crystalline, grey; "recrystalline" dolomite, medium- to coarse-crystalline, medium-grey; limestone, aphanitic, grey; with collapse breccias and some chert.
		LONGVIEW DOLOMITE	15m (50ft)	Dolomite, fine- to medium-crystalline, light grey; with limestone, aphanitic, grey, some "recrystalline;" with abundant chert.
		CHEPULTEPEC DOLOMITE	215m (700ft)	Dolomite, fine-crystalline, light-grey; with prominent calcareous sandstone at base; cherty.
UPPER CAMBRIAN		COPPER RIDGE DOLOMITE	350m (1150ft)	Dolomite, medium- to coarse-crystalline, dark-grey, asphaltic, thick-bedded; with stromatolite bioherms, thin sandstones lower part; upper part is light- to medium-grey dolomite and generally not as thick-bedded.
	CONASAUGA GROUP	MAYNARDVILLE LIMESTONE		

oxides and oxyhydroxides, and microcrystalline quartz (as chert fragments). The residuum and soils developed in an environment of moderately warm temperatures (2-24°C) and relatively high annual rainfall (120 cm) (Lee et al., 1984).

CHAPTER III

SAMPLING AND ANALYTICAL TECHNIQUES

Sampling

Residuum

Samples were taken in the residuum and soils above the Upper Copper Ridge and Lower Chepultepec Formations by Woodward-Clyde Consultants in 1984 (Figure 3). They drilled boreholes to "equipment refusal" (e.g., the equipment ran into solid rock), or to a depth of 30 meters (whichever was less) (Woodward-Clyde Consultants, 1984). Intervals between samples range from a few centimeters to several meters. Samples were taken with Shelby Tubes, or "cores," (three inch by three foot long steel tubes driven into the ground with an impact device) that retained the actual cored material in the tubes. In addition, split barrel tubes were used for sampling, and three inch by five inch long sections of residuum were removed from the tubes and placed in sealed jars at the site.

The residuum in Shelby and split barrel tubes was made available by personnel at the Oak Ridge National Laboratory (ORNL). The residuum was photographed prior to removing it from the tubes (or cores). The cores were previously

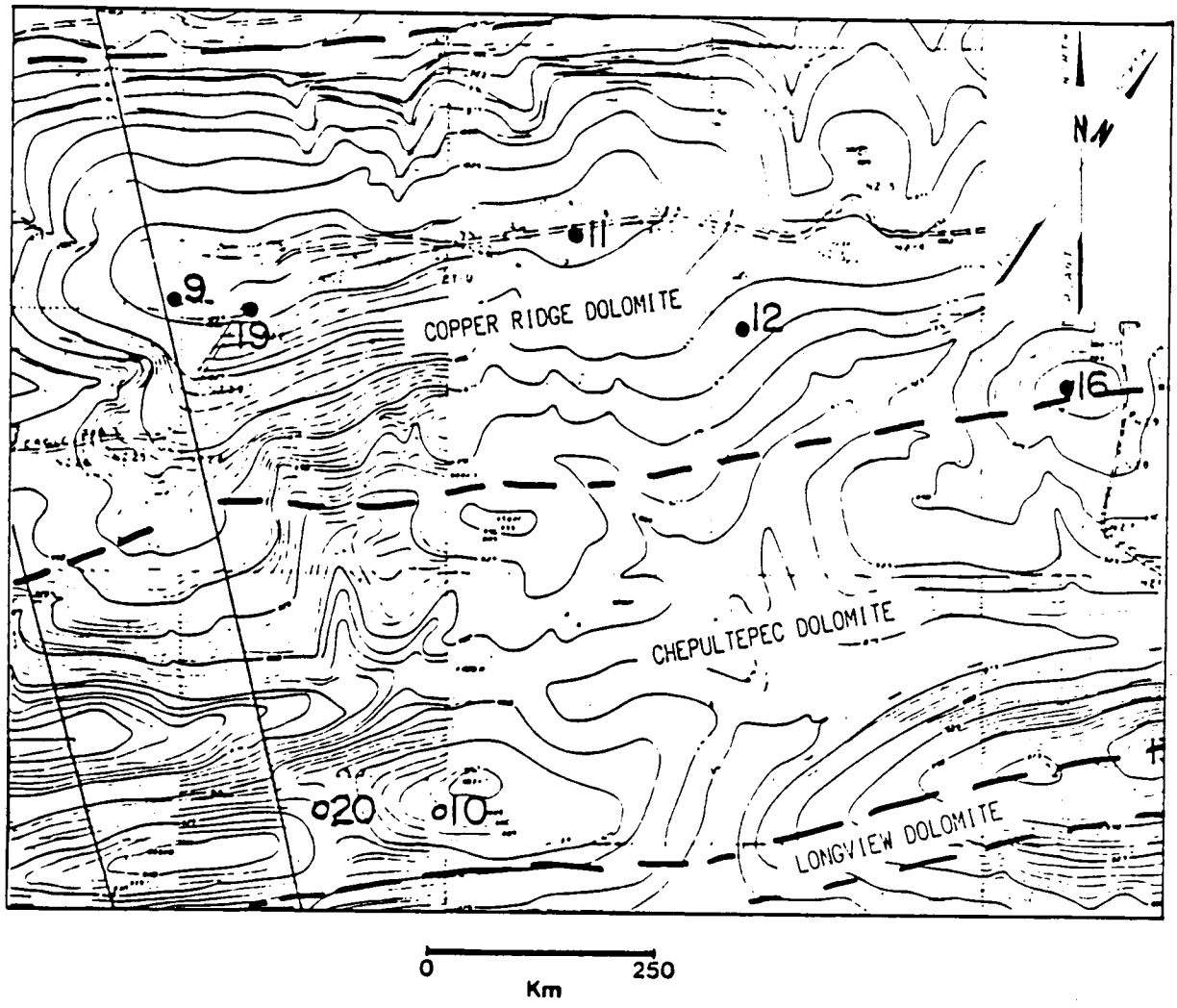


Figure 3. Topographic map of the West Chestnut Ridge site showing locations of seven cores available for the study (after Woodward-Clyde Consultants, 1984). ● = Cores drilled into <u>in situ</u> weathered residuum.

O = Cores drilled into sinkholes.

numbered by Woodward-Clyde Consultants as 9, 10, 11, 12, 16, 19, and 20. The residuum in each core was divided into samples based on changes in color, lithologies, and abundance of the gravel-size fraction. The residuum from each split barrel tube (which had been stored in jars) was considered to be a separate sample. A total of 112 samples were chosen.

Samples in this study were numbered on the basis of three criteria: (1) the borehole (location) from which the core (Shelby Tube) or split barrel came; (2) the number of the core or split barrel assigned by Woodward-Clyde Consultants (numbers increase with depth); and (3) the sample number assigned for this study (numbers also increase with depth). Sample numbers with capital letters indicate split barrel samples. Conversely, sample numbers from Shelby Tubes have no letters. For example, sample 9-10A-17 is from borehole (location) 9, it is the tenth sample (from a split barrel), and it is the seventeenth sample taken in that set of samples (for an example see Figure 4).

Fifty-five samples were chosen from the total 112 for analyses of their physical, mineralogical, and geochemical characteristics. These samples include 18 from core 9 and 21 from core 16. All of the residuum available from these cores was selected. Cores 9 and 16 were chosen because their samples provide the best coverage over the approximately 30 meter interval of residuum, and they

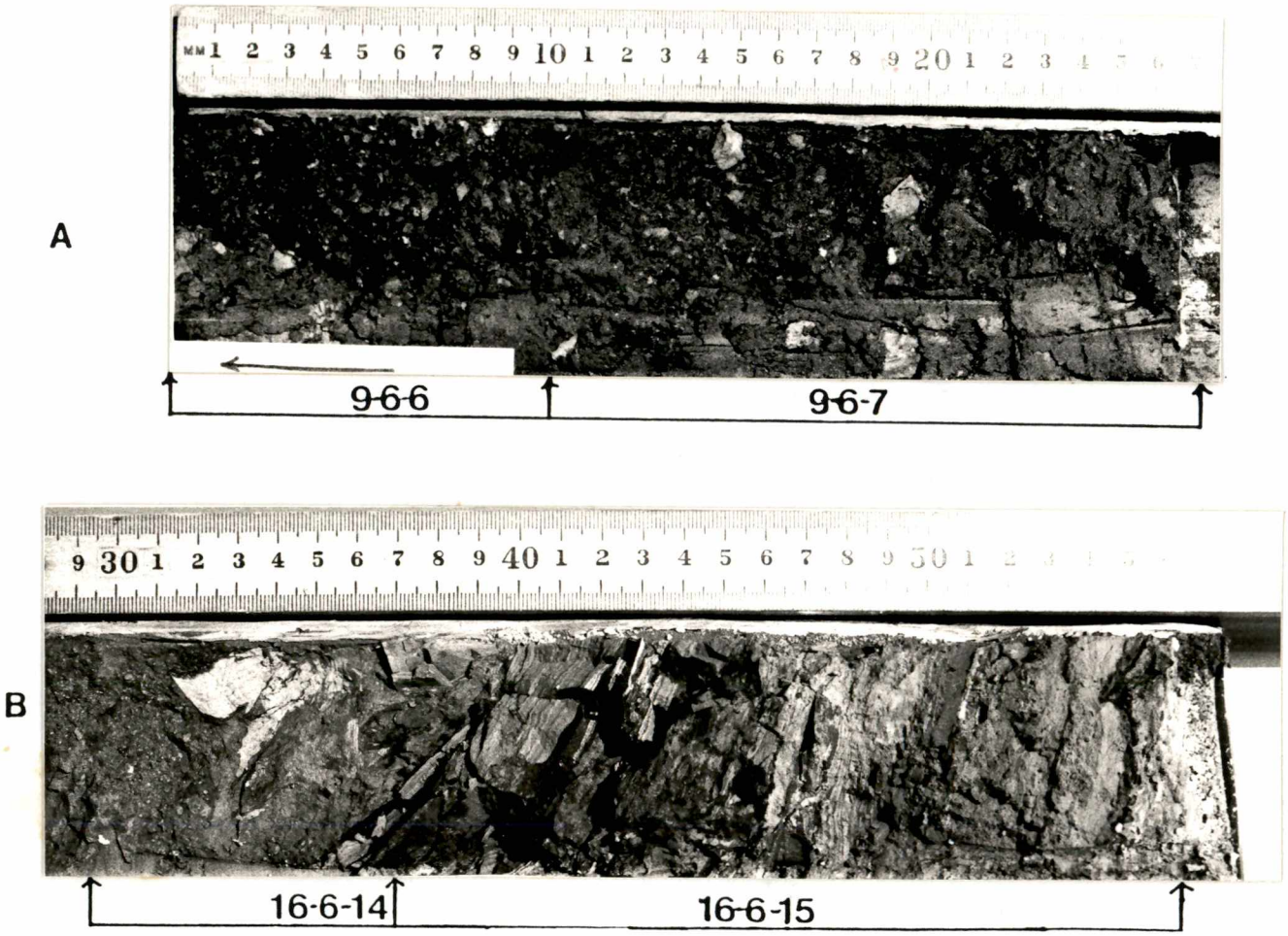


Figure 4. Examples of Shelby Tube cores from West Chestnut Ridge. (A) Core 9, samples 9-6-6 and 9-6-7, depth 16.66-16.92 meters. (B) Core 16, samples 16-6-14 and 16-6-15, depth 21.23-21.79 meters. Note irregular distribution of chert nodules and larger relict shale fragment in core 16.

illustrate in situ weathering of Knox Group bedrock (Dick Ketelle, personal communication, 1985). In situ residuum is considered in this study to include bedrock that has weathered in place and exhibits few, if any, recognizable materials that have been transported into, or through, it. Intact structures and individual beds and bedding planes have been preserved. Figure 4 illustrates an example of intact shale beds.

Additional samples chosen include three from core 11, three from core 12, three from core 10, four from core 19, and three from core 20. Samples from cores 11, 12, and 19 also represent in situ weathering of Knox Group bedrock. Cores 10 and 20 were drilled into sinkholes and contain highly leached and transported materials (Dick Ketelle, personal communication, 1985). Samples from cores 10 and 20 are much lighter in color and have no recognizable features or structures.

Bedrock

Originally, there were plans to take cores of fresh Knox Group bedrock at West Chestnut Ridge, but when the site was abandoned the drilling plans were also abandoned. Therefore, fourteen bedrock samples were collected from the Copper Ridge and Chepultepec Formations along a railroad cut near the Bull Run Steam Plant (located within the same

strike belt), approximately ten kilometers northeast of West Chestnut Ridge. This cut is the closest site at which a nearly complete section of Knox Group dolostones is exposed (Dick Ketelle, personal communication, 1985).

Analytical Techniques

Physical Analysis

Physical descriptions (wet colors, presence of clayey/sandy zones, abundance of chert, presence of Fe/Mn oxides, etc.) were completed at ORNL prior to removal of the samples from the Shelby Tubes and split barrel jars. In the lab, each air-dried residuum sample was gently crushed and passed through a 2-mm sieve. The gravel-size fraction (>2mm) was washed with deionized water and dried for morphological description. The $\leq$2mm fraction was further separated into the sand-(<2mm to >1/16mm), silt-(<1/16mm to >1/256mm), and clay-(<1/256mm) size fractions by wet-sieving and centrifugation (Jackson, 1975). The sand-size fraction was also dried for morphological investigation. Dry weight percentages were determined by preweighing five grams of the $\leq$2mm size fractions, drying it at 105°C for one hour, and reweighing it to determine weight loss due to water.

Petrographic Analysis

Fourteen bedrock samples from the Upper Copper Ridge and Lower Chepultepec Formations were collected near the Bull Run Steam Plant. The samples were made into 50x75 mm thin sections, stained with Alizarin Red S, and observed using a petrographic microscope.

X-ray Diffraction

Mineralogical analyses were performed using X-ray diffraction. Samples were run on a Norelco Diffractometer at 1° 2θ/minute, with $Cu_{K\alpha}$ radiation (λ= 1.5418A), at 35 kv and 17 ma.

Samples chosen for bulk mineralogical analyses were selected from various depths in all of the cores. The $\leq$2mm fraction was crushed using a mortar and pestle and packed into an aluminum mount. For the clay mineral analyses, five to nine grams of the $\leq$2mm fraction were suspended in ten centimeters (1000 ml) of deionized water (brought to pH 10 with sodium carbonate for purposes of deflocculation) for thirty minutes. Five centimeters (500 ml) was pipetted off, resuspended to ten centimeters (1000 ml), and allowed to settle for three hours and forty minutes (Jackson, 1950). The clay-sized particles were collected on a filter (0.2um Nuclepore) using a vacuum pump, smeared onto a frosted glass slide, and allowed to air dry prior to X-ray analysis.

Glycolation was accomplished by placing the samples in glycol-saturated vapor for 24 hours at 60° C. Heat treatment involved heating the samples at 550° C for 1 hour.

Ratios of peak heights of illite to kaolinite for the clay fractions were measured using the first-order illite (001) and second-order kaolinite (002) peaks. This ratio measures the relative amounts of one mineral to another. Error bars for each data point were calculated to assess the maximum and minium range of error for all samples. Using repeated X-ray runs of a sample, the "typical" error in the measurements of the intensities of the illite (001) and kaolinite(002) peaks was estimated to be reproducible within +/- 5 units. However, due to the nature of the calculations used to compute the error ranges, samples with I/K ratios of $\geq$1.0 have very large error ranges. The ratios become less precise and less significant as the I/K ratio increases above 1.0.

Sharpness ratios for the illite (001) and kaolinite (002) peaks were also measured. Sharpness ratios measure the degree of crystallinity of a mineral (Kubler, 1968). The sharpness ratio is defined as the peak height divided by the width at one-half the peak height. Error bars for each data point were also calculated.

X-ray Fluorescence

Bulk chemical analyses were obtained by X-ray fluorescence using an EG&G ORTEC MODEL III Tube-Excited Fluorescence Analyser, and the CLAYS and LIMDOL protocols developed in the Department of Geological Sciences. Standard calibration and mean counting errors are given in Appendix A.

The grinding and pelletizing method (Wheeler, 1979 and 1984) was used for preparation of samples for X-ray fluorescence analysis. Seven to ten grams of the $\leq$2mm fraction were dried at 105°C for one hour. Six grams of the sample were placed in a tungsten carbide mill and ground in a Shatterbox for six minutes using liquid Freon (Freon "TF") as a grinding agent. Three grams of powdered sample were placed in a stainless steel mold with boric acid added as a backing. The sample was pressed at 30,000 psi for one minute to form a pellet. Whole bedrock samples were prepared in the same manner, except that the bedrock was initially crushed to pea-size before drying, crushing, and pressing.

The data for the residuum ($\leq$2mm size fractions) were recalculated to obtain chemical compositions for the silt- and clay-size fractions, and for the original bulk samples (including all size fractions). For the two new sets of calculated data it was assumed (based on visual inspections)

that the sand- and gravel- size fractions were composed dominantly of quartz and chert grains (here considered to be 100% SiO_2). No large feldspar or carbonate grains were observed (using a binocular microscope); hence, the feldspars and carbonates detected in some samples by X-ray diffraction were thought to be exclusively in the silt- and clay-size fractions. In addition, no attempt was made to correct for minor amounts of iron and manganese oxides present in the sand- and gravel-size fractions.

Using the relative percentages of each of the size fractions, "correction factors" were calculated and multiplied by each oxide and element for all samples. The two new sets of data include: (A) the silt- and clay-size fractions; and (B) the gravel-, sand-, silt-, and clay-size fractions. Eleven of the 55 residuum samples were excluded from the recalculations in (B) because they contain siltstone and shale fragments in the sand- and gravel-size fractions, thereby invalidating the assumption that these fractions are composed of 100% SiO_2. The two new sets of recalculated chemical compositions make it possible to compare the chemical character of the bulk residuum with the parental dolostones, as well as to relate the mineralogical and chemical compositions of the combined silt- and clay-sized material. Although the recalculations may introduce some errors in the analyses, the two additional data sets

will permit more direct comparisons between the results of the mineralogical and chemical analyses.

Ionic Adsorption Capacities

Cation and anion exhange capacities (CEC's and AEC's) of the $\leq$2mm fraction were determined using X-ray fluorescence and the IONEX protocol developed in the Department of Geological Sciences. The $\leq$2 mm size fractions of eighteen near-surface samples available from the surface to a depth of approximately 14 meters were used. Standards spiked with known barium and chloride ion concentrations were used as standards for this procedure.

The procedure to measure ionic adsorption capacities (CEC's and AEC's) included placing five grams of sample in a preweighed Erhlenmeyer flask. Fifty milliliters of 0.1M $BaCl_2 \cdot H_2O$ were added to the sample. It was shaken several times and allowed to stand for 24 hours. After 24 hours, the supernatant was pipetted off (being careful not to disturb or remove any of the sample), and each sample was rinsed three times with 0.002M $BaCl_2 \cdot H_2O$ (pipetting off the supernatant each time). The samples were then reweighed to determine the volume of entrained 0.002M $BaCl_2 \cdot H_2O$. Finally, each sample was dried for one hour at 105° C, and pressed into pellets using the procedure described above.

The most widely accepted methods for the determination of ion exchange capacities are: (1) the summation method; (2) the direct displacement method; and (3) the radioactive tracer method (Rhoades, 1982). The X-ray fluorescence method used in this study is similar to the direct displacement method (McLean, 1982) in which a sample is saturated with an index cation ($BaCl_2$) and/or anion. The adsorbed index ions are displaced by another solution, and the concentration of the index ions in the leachate is measured (Rhoades, 1982). The method used in the present study did not include displacing the $BaCl_2$ with $MgSO_4$. The results obtained with X-ray fluorescence are usually larger than those obtained using the true displacement method and, thus, individual values are not directly comparable although trends are comparable.

CEC's and AEC's were determined by measuring the amount of adsorbed barium (and chlorine) in each sample using X-ray fluorescence. This method eliminates the step that includes displacing the adsorbed index ion by measuring the adsorbed index ion on the solid. Both the CEC's and AEC's were determined using the procedure outlined in Appendix B.

pH Values

For measurements of pH values of the soil samples, five milliliters of deionized water were added to five grams of sample ($\leq$2mm fraction). The mixture was shaken for approximately five seconds, and then allowed to stand for ten minutes. The supernatant pH was measured (using an X-EL Flat Surface Electrode) and defined as the soil pH in distilled water. The supernatant (salt) pH in 0.01M $CaCl_2$ was measured by adding one drop of 1M $CaCl_2$ solution to the soil/water mixture and letting the mixture stand for 30 minutes (with intermittent stirring) prior to measuring the pH.

CHAPTER IV

RESULTS

Residuum Descriptions

The 55 residuum samples chosen for the analyses (Appendix C) vary in physical composition and particle size distribution (Tables 3, 4, and 5). Generally, they comprise clays and silty to sandy clays in shades of orange-yellow (10YR7/4) to brown (5YR3/4), with abundant chert fragments and Fe/Mn oxide nodules and coatings. Some samples contain large chert fragments (>30 cm), while others have only a few small chert grains. Some weathered shale and/or siltstone fragments remained intact even after physical disaggregation. Some of the larger chert grains were probably fragmented by the coring equipment.

Gravel-Size Fraction

The dominant mineral in the gravel-size fraction is microcrystalline quartz (as chert grains and nodules). Lithologic descriptions of this fraction are given in Appendix D.

Nine types of chert fragments were recognized in this fraction: massive, chalcedonic, oolitic, porous, chalky, porcelaneous, banded, dolomoldic, and "conglomeratic"

Table 3. Physical properties of residuum for core 9.

Sample no.	Depth (m)	Color [a]	Size distribution, <2mm fraction			
			Wt.% Gravel	Wt.% Sand	Wt.% Silt	Wt.% Clay
9-1A-1	1.19	5YR4/4-3/4	7	21	60	19
9-2A-2	4.08	5YR5/6	27	9	28	63
9-4A-3	10.33	5YR5/6	20	29	36	35
9-5-4	13.41-13.54	5YR5/6	33	18	38	44
9-5-5	13.54-13.87	5YR5/6	47	13	49	37
9-6-6	16.66-16.74	5YR4/4	57	43	43	14
9-6-7	16.74-16.92	5YR4/4	28	29	49	22
9-6A-8	17.02	5YR4/4	37	24	54	22
9-7-9	19.72-19.90	5YR4/4	44	28	36	36
9-7-10	19.90-19.96	5YR4/4	60	32	25	43
9-8-11	22.39-22.58	5YR4/4	31	17	33	50
9-8-12	22.58-22.65	5YR4/4	25	14	28	58
9-8-13	22.65-22.75	5YR5/6	24	17	38	45
9-8-14	22.75-23.01	5YR5/6	12	25	67	8
9-9-15	25.62-25.74	5YR5/6	15	15	35	50
9-9-16	25.74-26.06	5YR5/6	2	17	48	35
9-10A-17	28.56	5YR4/4	13	12	62	26
9-10C-18	28.80	5YR4/4	72	20	35	45

[a] Rock Color Chart, 1980.

Table 4. Physical properties of residuum for core 16.

Sample no.	Depth (m)	Color[a]	Size distribution, <2mm fraction			
			Wt.% Gravel	Wt.% Sand	Wt.% Silt	Wt.% Clay
16-1-1	2.14-2.29	5YR5/6	46	24	33	43
16-2A-2	5.85	5YR5/6	53	42	24	34
16-3-3	9.45-9.69	10YR6/6	45	33	34	33
16-4-4	13.33-13.45	5YR4/4	47	35	32	33
16-4-5	13.45-13.69	5YR5/6	59	29	30	41
16-5-6	17.21-17.29	5YR5/6	35	23	30	47
16-5-7	17.29-17.46	5YR5/6	35	22	35	43
16-5-8	17.46-17.52	5YR5/6	6	27	33	40
16-5-9	17.52-17.58	5YR5/6	2	18	36	46
16-5-10	17.58-17.65	5YR4/4	1	26	41	33
16-6-11	21.23-21.36	5YR5/6	22	19	41	40
16-6-12	21.36-21.47	5YR4/4	2	15	34	51
16-6-13	21.47-21.54	5YR4/4	2	33	24	43
16-6-14	21.54-21.60	5YR4/4	26	44	35	21
16-6-15	21.60-21.79	10YR6/6	47	38	53	9
16-7A-16	25.39	5YR4/4	9	14	32	54
16-7B-17	25.54	5YR5/6	5	6	54	40
16-7C-18	25.73	5YR4/4	6	12	32	56
16-8A-20	29.50	5YR5/6	24	7	40	53
16-8B-21	29.69	5YR4/4	<1	4	43	53
16-8C-22	29.87	5YR4/4	<1	5	43	52

[a] Rock Color Chart, 1980.

Table 5. Physical properties of residuum for cores 10, 11, 12, 19, and 20.

Sample no.	Depth (m)	Color[a]	Size distribution, <2mm fraction		
			Wt.% Gravel	Wt.% Sand	Wt.% Silt/Clay[b]
10-2C-3	6.37	10YR7/4	17	44	56
10-4-5	10.62-10.81	10R4/6	1	12	88
10-5-7	14.49-14.63	10YR6/2	8	54	46
11-3-4	9.70-9.82	10YR7/4	8	6	94
11-5-12	17.66-17.83	10YR7/4	3	16	84
11-7B-17	25.66	5YR5/6	30	16	84
12-3D-10	7.71	10YR6/6	2	11	89
12-8B-14	22.52	10YR5/4	29	23	77
12-9B-16	25.66	10YR5/4	17	21	79
19-3-4	7.43-7.56	5YR5/6	1	15	85
19-4-7	10.49-10.64	10YR7/4	4	4	96
19-5-11	13.71-13.87	10YR5/4	19	15	85
19-6-13	16.68-16.79	5YR5/6	56	13	87
20-3-5	9.86-10.06	10YR6/2	27	30	70
20-4-9	14.08-14.33	5YR7/2	2	17	83
20-7-13	25.67-26.21	5YR5/6-4.4	2	6	94

[a] Rock Color Chart, 1980.

[b] Silt- and clay-size fractions were not separated.

(Figure 5). The "conglomeratic" cherts were formed by Fe/Mn oxides and oxyhydroxides that diffused into porous zones creating dark surface stains and chert "conglomerates" cemented with these compounds. Moneymaker (1981) noted that Fe/Mn oxide nodules formed during leaching and precipitation in soils above the Knox Group dolostones in Anderson County.

Many of the chert grains also have clay minerals that developed as surface coatings. Two or more types of chert may be present in the same fragment because of the differing degrees to which individual fragments have been weathered. Some Knox Group chert appears to have formed during the early stages of diagenesis, but much of the chert probably formed epigenetically (Harris, 1969). Some of the evidence for epigenetic chert includes silica-replaced ooids and silica- replaced dolomite rhombs.

Chert layers are abundant in many bedrock horizons and have been used by some workers (Oder, 1934; Oder and Miller, 1945; Oder and Ricketts, 1961) as marker beds in the zinc mining districts. Chert layers have also been used as guides for the recognition of individual formations where the Knox Group is deeply weathered or absent. Residual chert is one of the few remaining features that can aid in field mapping (Swingle, 1959). Swingle noted three types of cherts that distinguish the Copper Ridge Dolomite; oolitic, banded, and chertified Cryptozoa (common only in the lower third of the formation). Chert in the Chepultepec Dolomite

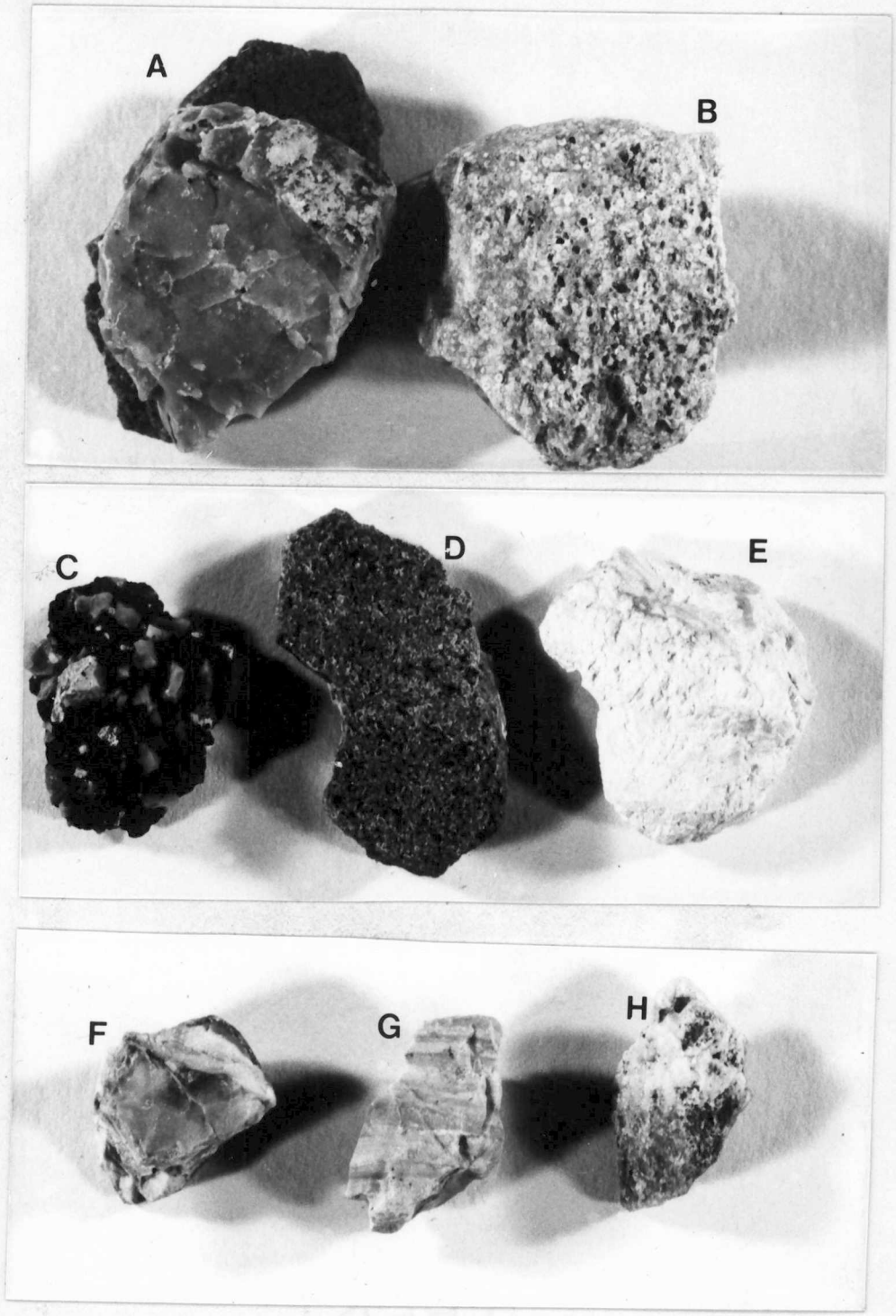


Figure 5. Typical Knox chert types. A. Massive, chalcedonic; B. Oolitic, porous; C. Conglomeratic D. Porous; E. Chalky; F Porcelanous; G. Banded; H. Dolomoldic. (Scale bar = 1 cm)

is less abundant than in the Copper Ridge. Very porous, light-colored chert in irregular masses (porous and dolomoldic) is typical of the Chepultepec, but occurs only at the base and top of the unit. Oolitic cherts occur only in the lower third of the Chepultepec (Swingle, 1959).

Originally, the intention in this study was to use the different chert types described to establish chert "marker beds" based on recognizable chert zones. However, it was not possible to do this when the cherts were described because of the absence of any recognizable similarities in the chert types from core to core.

Authigenic quartz clusters are also found in the gravel fraction. Fragments of siltstone and fine-grained sandstone in this fraction are remnants from silty and sandy beds in the original Knox lithologies.

Sand-Size Fraction

The sand-size fraction (Appendix E) is similar in composition to the gravel-size fraction, but it differs in its abundances of microcrystalline quartz (chert fragments), and Fe/Mn oxide nodules. Typically there is more quartz than chert fragments and Fe/Mn oxides. The chert in this fraction represents all of the chert types found in the gravel fraction; however, chalky, porcelaneous, and oolitic cherts are most frequently observed. Most of the quartz

grains are relatively well-rounded (smooth surfaces with no crystal faces or jagged edges) with frosted surfaces (suggesting either windblown grains or corrosion surfaces). Both clear and milky quartz grains are abundant. Authigenic quartz clusters are also present in this fraction.

Trace amounts of fine-grained magnetic particles (possibly maghemite and/or magnetite) (Kopp and Lee, 1986) were observed at various depths in all cores during physical inspection. They were identified with a binocular microscope and hand magnet, noted, but not analysed further.

Bedrock Descriptions

At the outcrop near the Bull Run Steam Plant primary porosity was not observed. However, secondary porosity can and does exist, ranging in size from small vugs and fractures to huge caverns. Secondary porosity may result from dolomitization (recrystallization), structural deformation (fault zones), solutional activity (stylolites and enlarged fractures), and collapse brecciation. Evidence for secondary porosity is especially apparent in areas of zinc mineralization (in East and Central Tennessee) where there has been extensive brecciation and mineralization during solutional activity.

In hand specimen, the Knox Group dolostones are often divided into the very fine-grained types (thought to have formed more or less penecontemporaneously with deposition), and the coarser-grained types (which are generally considered to have formed by some replacement process) (Churnet et al., 1982). Three samples of polished whole rock slabs and a thin section photograph of selected Lower Knox Group dolostones (from the outcrop near the Bull Run Steam Plant) are illustrated in Figure 6. The samples are composed almost entirely of anhedral to euhedral dolomite crystals in a mud (micritic) matrix, with minor amounts of iron oxides (hematite/goethite) as coatings or stains on grains, heavy minerals (rutile, zircon, etc.), and clays filling stylolites and rimming grains. Some samples have bedded and burrow-like structures. Other samples contain fractures and/or brecciated zones filled with quartz and/or chert and heavy mineral grains. Oolites are common and have developed around pellets, heavy mineral grains, and dolomite rhombs. Intraclasts and pellets also fill faulted and brecciated zones. One sample from the Copper Ridge Dolomite contains a few subhedral K-feldspar grains. A sample from the Chepultepec Dolomite is almost entirely composed of silica-replaced ooids with fractures (in the ooids) parallel to bedding. Another sample from the Chepultepec Dolomite contains calcite-filled fractures. (Calcite was observed only in this sample.) Dolomite and chert are common

Figure 6. Typical Lower Knox lithologies in polished whole rock slabs and in thin section. A. Fine-grained dolostone. B. Medium-grained dolostone (note stylolite and chert nodule). C. Medium- to coarse-grained dolostone. D. Thin section photograph. Medium-grained dolostone (note bedding, stylolite, and small fault).

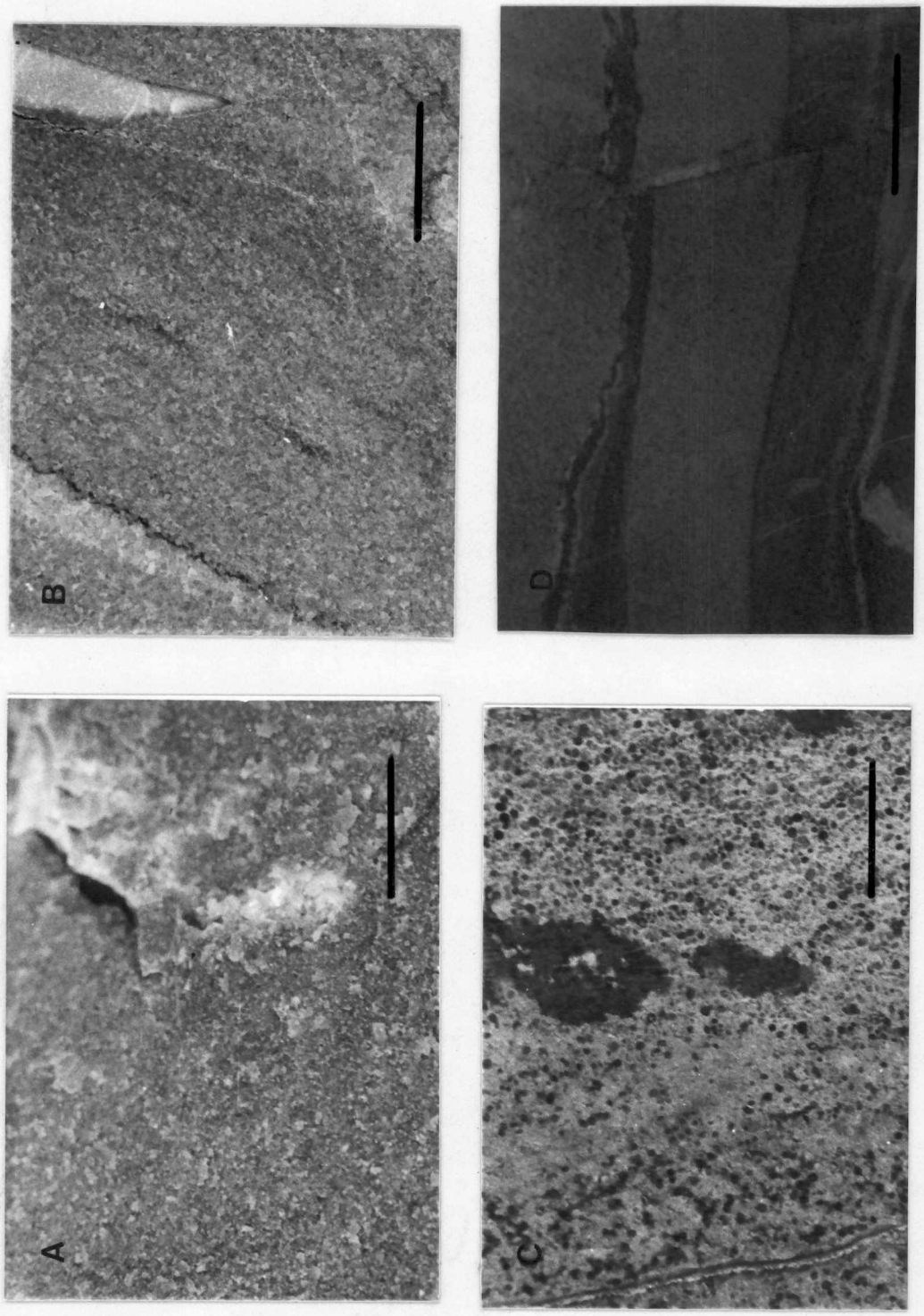


Figure 6.

replacement minerals. A coarse-grained sample from the Copper Ridge Dolomite has been almost completely replaced by chert.

Mineralogical Analyses

Bulk Mineralogy

Summaries of the minerals identified by X-ray diffraction in 33 bulk residuum samples (≤2mm fraction) are listed in Table 6. Quartz, kaolinite, and illite were readily identified in the bulk X-ray diffractograms. Numerous peaks in the X-ray patterns made it possible to tentatively indentify such minerals as gibbsite, hematite, goethite, microcline/orthoclase, dolomite, and calcite. Many peaks were obscured by overlapping (or broad) peaks of other minerals such as amorphous iron and aluminum oxides and oxyhydroxides.

Note that X-ray diffractograms for samples 9-8-14 through 9-10A-17, 16-6-15 through 16-8C-22, 10-5-7, 20-4-9, and 20-7-13 show evidence of feldspars (microcline/orthoclase) (Table 6). Dolomite and calcite also occur in samples 9-10A-17, 16-6-14, 16-6-15, and 16-7B-17 through 16-8C-22. None of the samples from relatively shallow depths (less than approximately 15 meters) show evidence of remnant feldspars or carbonates. However, it is

Table 6. Bulk (≤2mm) mineralogies of 33 selected samples from all cores.

Sample	Depth (m)	Mineralogy[a,b]	Sample	Depth (m)	Mineralogy[a,b]
9-5-5	13.54-13.87	L,H,O	10-2C-3	6.37	L,G,H,O
9-6-7	16.74-16.92	L,O	10-4-5	10.62-10.81	L,G
9-7-10	19.90-19.96	L,G,H,O	10-5-7	14.49-14.63	L,M
9-8-11	22.39-22.58	L,O			
9-8-14	22.75-23.01	L,M,G,H,O	11-3-4	9.70-9.82	L,G,H
9-9-15	25.62-25.74	L,M,O	11-5-12	17.66-17.83	L,G,H
9-9-16	25.74-26.06	L,M	11-7B-17	25.66	L,H,O
9-10A-17	28.56	L,M,O,D			
			12-3D-10	7.71	L,H,O
			12-8B-14	22.52	L
16-5-6	17.21-17.29	L,G,H,O	12-9B-16	25.66	L,H
16-6-11	21.23-21.36	L,O			
16-6-14	21.54-21.60	L,G,H,O,D,C	19-3-4	7.43-7.56	L,G,H,O
16-6-15	21.60-21.79	L,M,G,D,C	19-4-7	10.49-10.64	L,H
16-7A-16	25.39	L,M,O	19-5-11	13.71-13.87	L
16-7B-17	25.54	L,M,H,O,D	19-6-13	16.68-16.79	L,H,O
16-7C-18	25.73	L,M,H,O,D			
			20-3-5	9.86-10.06	L,G
16-8B-21	29.69	L,M,H,O,D	20-4-9	14.08-14.33	L,M
16-8C-22	29.87	L,M,H,O,D	20-7-13	25.67-26.21	L,M,H,O

[a] All samples contain quartz, kaolinite, and illite in addition to those minerals listed above.

[b] Tentative identification of the following minerals includes: L = Mixed-Layer Clays (Smectite, Vermiculite, Chlorite); M = Microcline/Orthoclase; G = Gibbsite; H = Hematite; O = Goethite; D = Dolomite; C = Calcite.

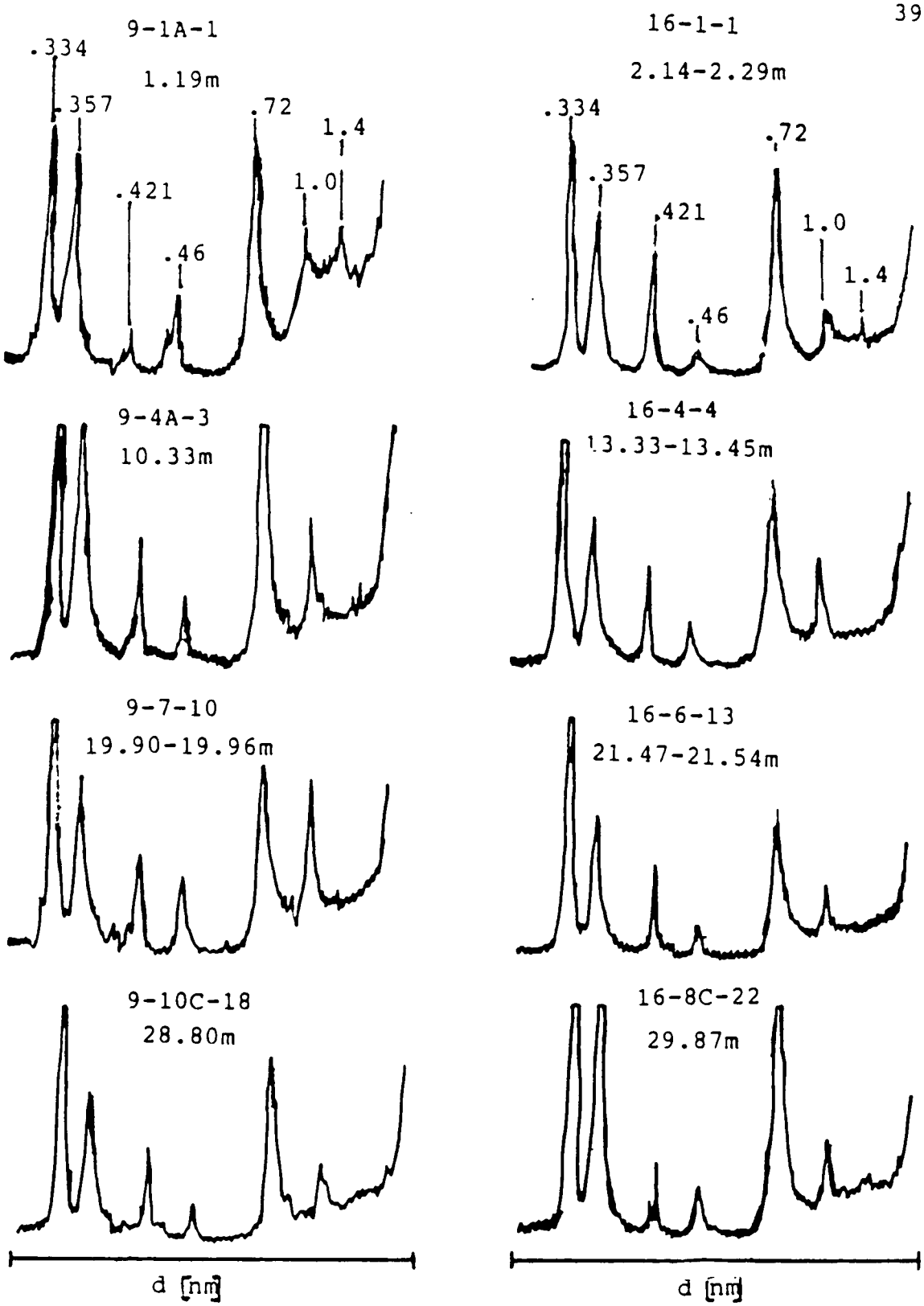


Figure 7. X-ray diffractograms of the untreated clay-size fraction of selected samples from core 9 and 16.

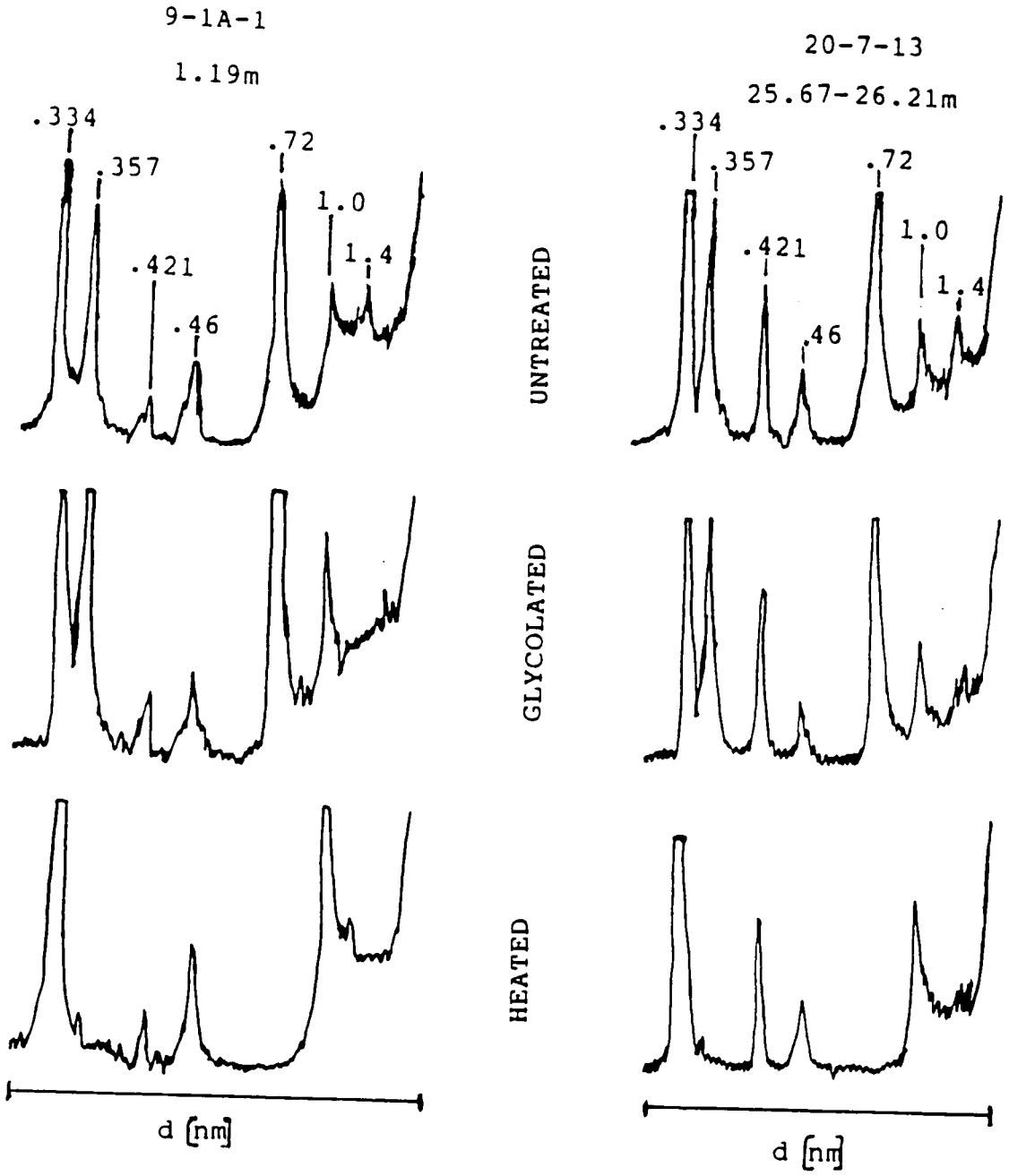


Figure 8. X-ray diffractograms of the untreated and treated clay-size fractions of selected samples.

also possible that small amounts of feldspars and/or carbonates in samples have been missed in the bulk X-ray diffractograms. Feldspars and carbonates are size related, and are often concentrated in the coarse silt-size fraction; however, this fraction was not separated in this study. Only the bulk ($\leq$2 mm) and clay-size fractions were analysed, implying that more samples may contain feldspars (and possibly carbonates) than were identified.

Clay Mineralogy

X-ray diffractograms of the untreated clay-size fraction (<2um) were run for all 55 residuum samples. The patterns reveal the presence of kaolinite (.71nm, .441nm, and .357nm), illite (1.0nm and .335nm), quartz (.421nm and .334nm), and mixed-layer clays (Figure 7). Minor amounts of hydroxy-interlayered vermiculite (HIV) occur only in near-surface samples (Lee et al., 1984).

Twenty-eight of the 55 samples were chosen for glycol and heat treatments because their untreated X-ray diffraction patterns also show evidence for minor clay minerals (e.g., smectites, vermiculites, and/or chlorites) (Figure 8).

The clay minerals were identified using methods described by Warshaw and Roy (1961) and Carroll (1970). The kaolinite peaks remained essentially unchanged with

glycolation, and collapsed upon heating. The illite peaks increased in intensity upon glycolation and heating. The untreated 1.2nm-1.5nm peaks, although somewhat obscured by "background scatter," did show the presence of smectites (which expanded from approximately 1.5nm to 1.7nm after glycolation, and collapsed to approximately 1.0nm or 1.3nm after heating). Smectites characteristically collapse to 1.0nm after heating, but the addition of a mixed-layer chlorite could account for the 1.3nm peak. Chlorites were also tentatively identified (peak position did not change after glycolation, and increased in intensity after heating). Vermiculites were not clearly identified. The best procedure for identification of vermiculites is to saturate first with KCl. Samples here were saturated with $MgCl_2$ only.

Mixed-layer clays may be either regularly or randomly interstratified (Bailey, 1982). In regular mixed-layer clays the interplanar spacings of the layers are added (e.g., a 1.0nm and a 1.25nm layer give a first order reflection at 2.25nm and a second order reflection at about 1.125nm). As a result, regular basal reflections can often be identified on X-ray diffraction patterns. On the other hand, random mixed-layer clays produce broad and/or asymmetrical peaks and hence are more difficult to identify.

Weaver (1957) studied randomly interstratified 2:1 layer clays (e.g., illite-smectite, chlorite-smectite, and illite-chlorite-smectite), and found they are common in most sedimentary rocks. Of 6,000 sedimentary specimens examined (ages ranging from Cambrian to Recent), approximately 70% contained randomly interstratified, mixed-layer clays. Mixed-layer clays usually develop from the degradation or aggradation of pre-existing clays during weathering and diagenesis. Therefore, it is often not possible to confirm the presence of discrete crystallites (random interstratifications), because overlapping and broad peaks make this part of the clay mineral identification difficult (Mills and Zwarich, 1972; Heller-Kallai and Kalman, 1972). In this study, overlapping and broad peaks in the X-ray patterns did make it difficult to clearly distinguish between individual types of mixed-layer clays (regular or random) present, or their relative amounts.

Figures 9 and 10 illustrate ratios of the peak heights of illite to kaolinite with depth for samples from cores 9 and 16. Errors are assessed in Appendix F. Note that although sample 9-1A-1 was analysed, the results for this sample were excluded from these figures and all future calculations and figures. Chemical analyses (discussed in the following section) indicate that this sample has been contaminated. Sample 9-1A-1 is from a depth of only 1.19 meters below the surface. Past farming and other

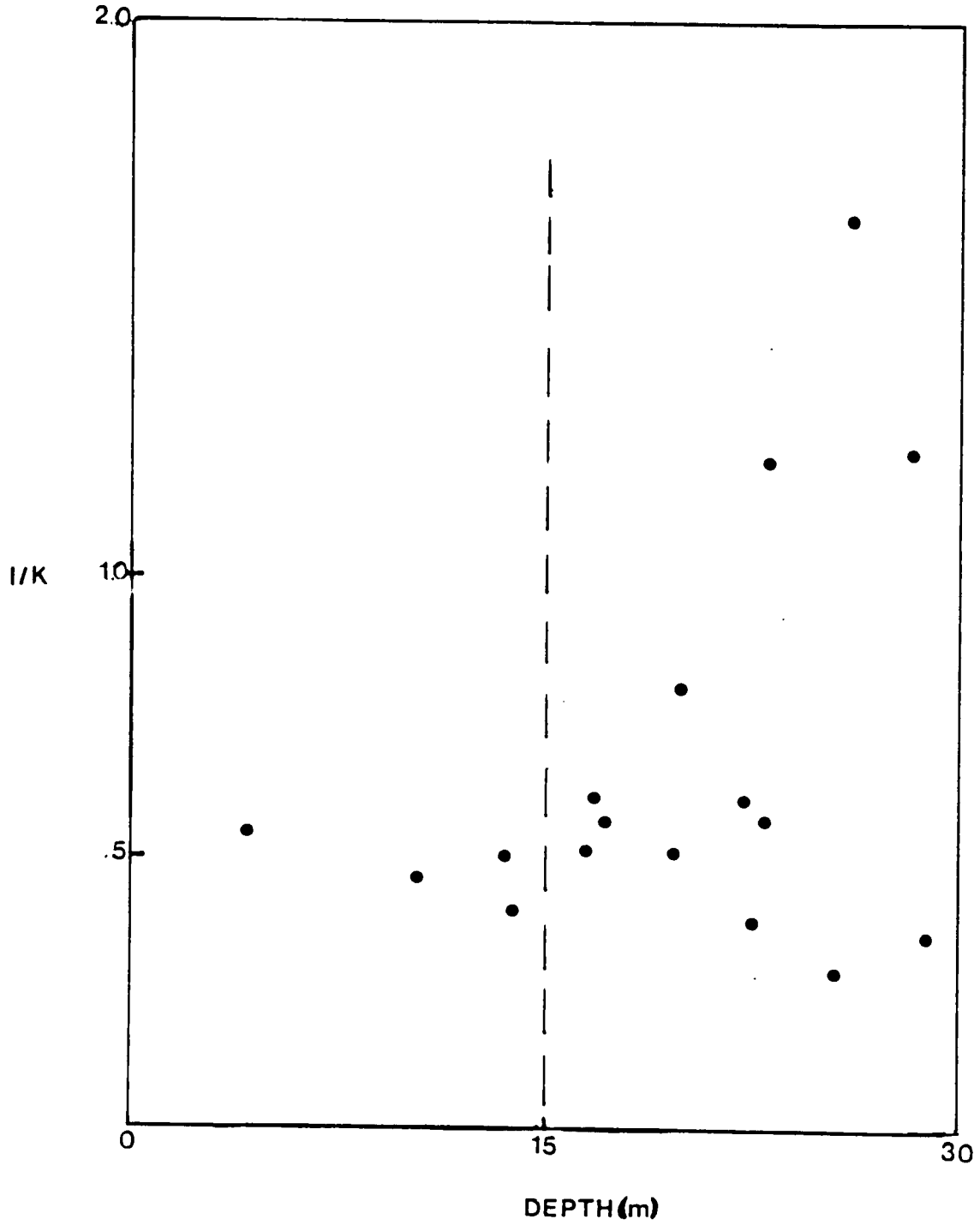


Figure 9. I/K vs. depth for samples from core 9.

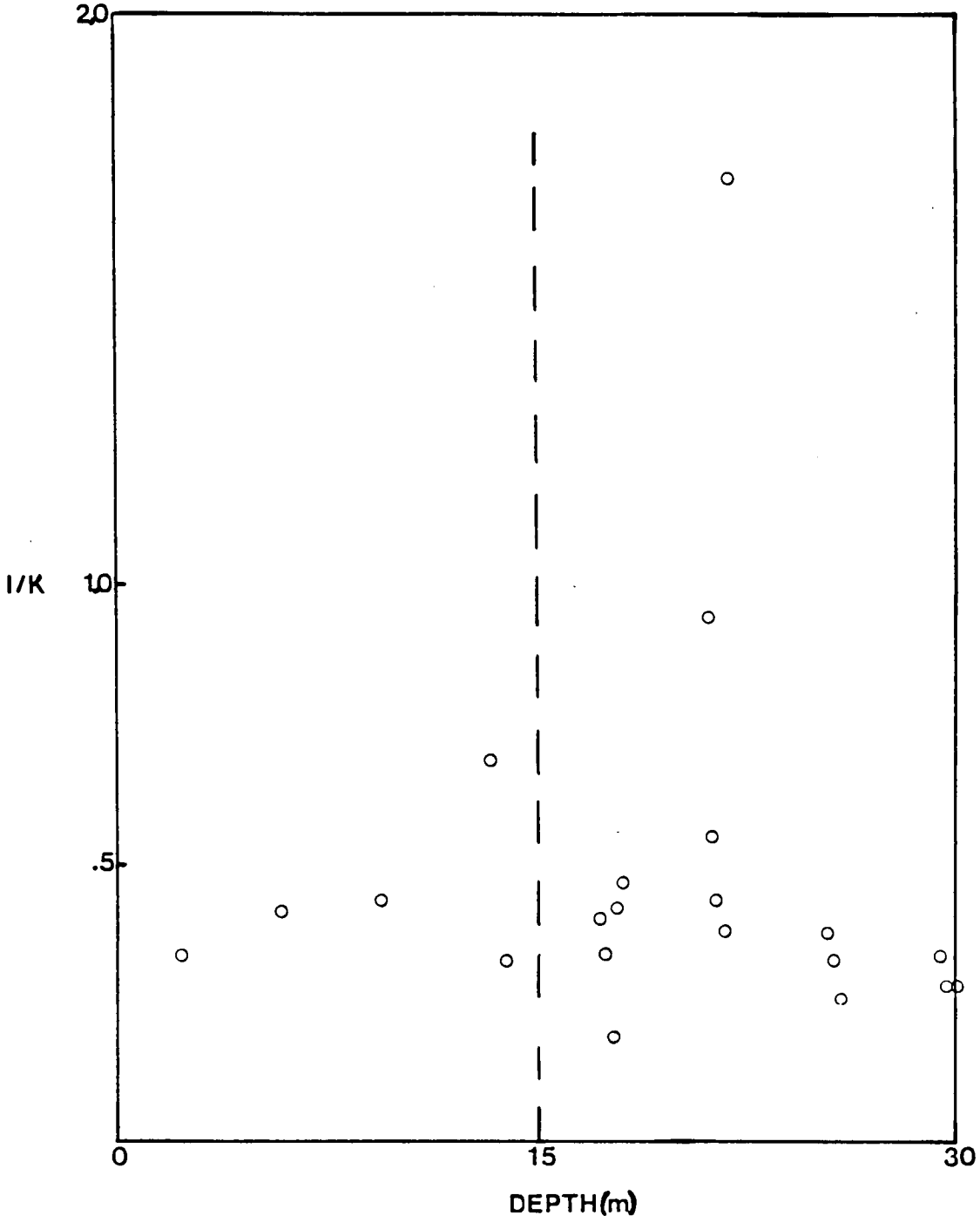


Figure 10. I/K vs. depth for samples from core 16.

anthropomorphic activities in the area have contributed to its contamination. In both Figures 9 and 10 the data points appear to scatter at depths greater than approximately 15 meters. Whereas there is a low variance between points above 15 meters, there is high variance below 15 meters.

Figure 11 illustrates illite/kaolinite ratios vs. depth for all of the samples from cores 9, 11, 12, 16, and 19. The data for cores 10 and 20 were not included because these samples came from above the Chepultepec Formation located on an adjacent ridge, which is not along strike with the cores above the Copper Ridge Formation. Again there appears to be greater variance of points below 15 meters.

Chemical Analyses

Residuum

X-ray fluorescence. The residuum samples were analysed for 16 oxides and elements. Results of the analyses for the 55 residuum samples (including the two sets of recalculated data) are given in Appendix G.

Figures 12 through 18 illustrate variations in chemical concentrations with depth for bulk residuum samples (recalculated for the gravel-, sand-, silt-, and clay-size fractions) from cores 9 and 16. Data from cores 10, 11, 12, 19, and 20 were omitted because there were too few samples

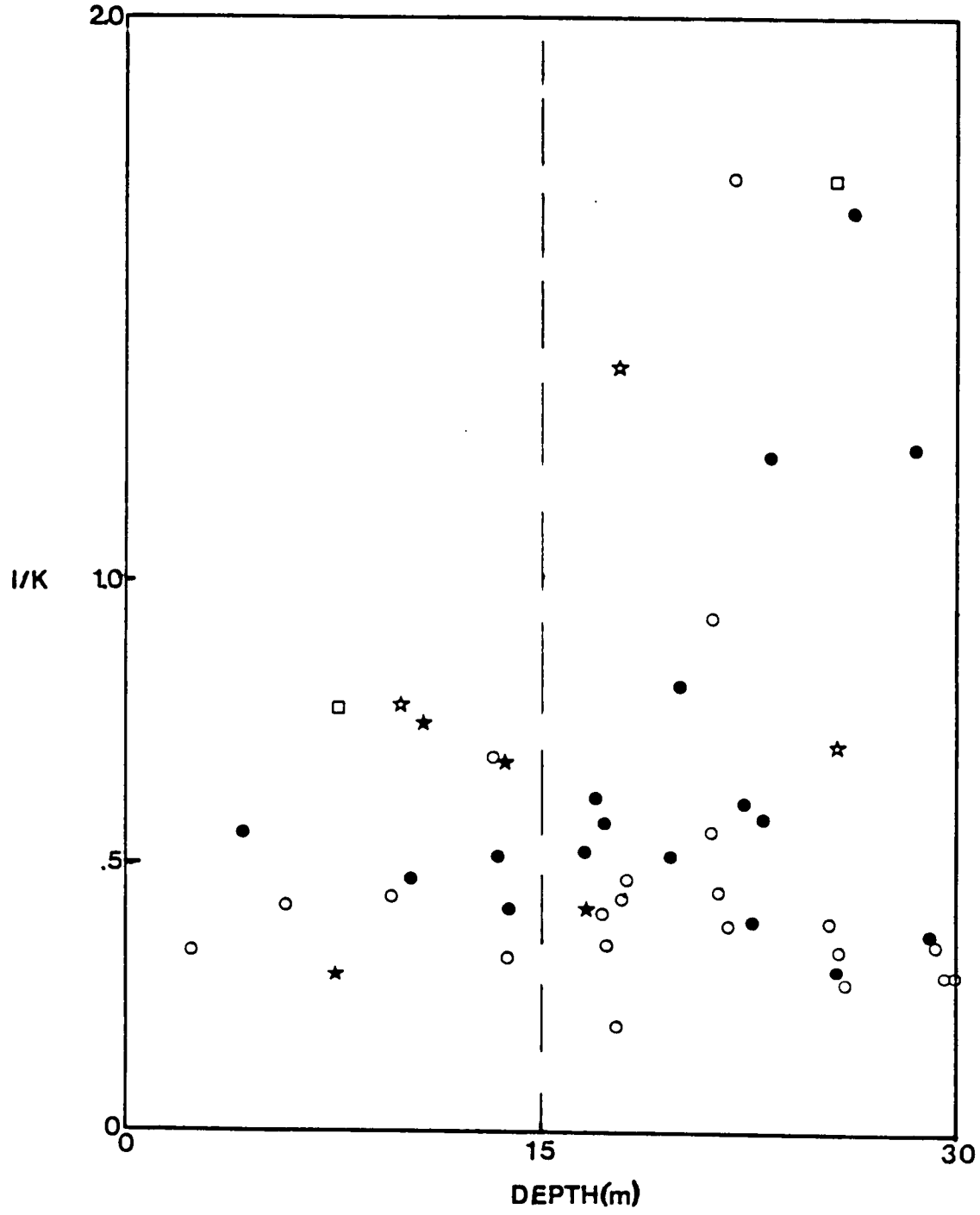


Figure 11. I/K ratio vs. depth for samples from cores 9 (●); 11 (☆); 12 (□); 16 (○); and 19 (★).

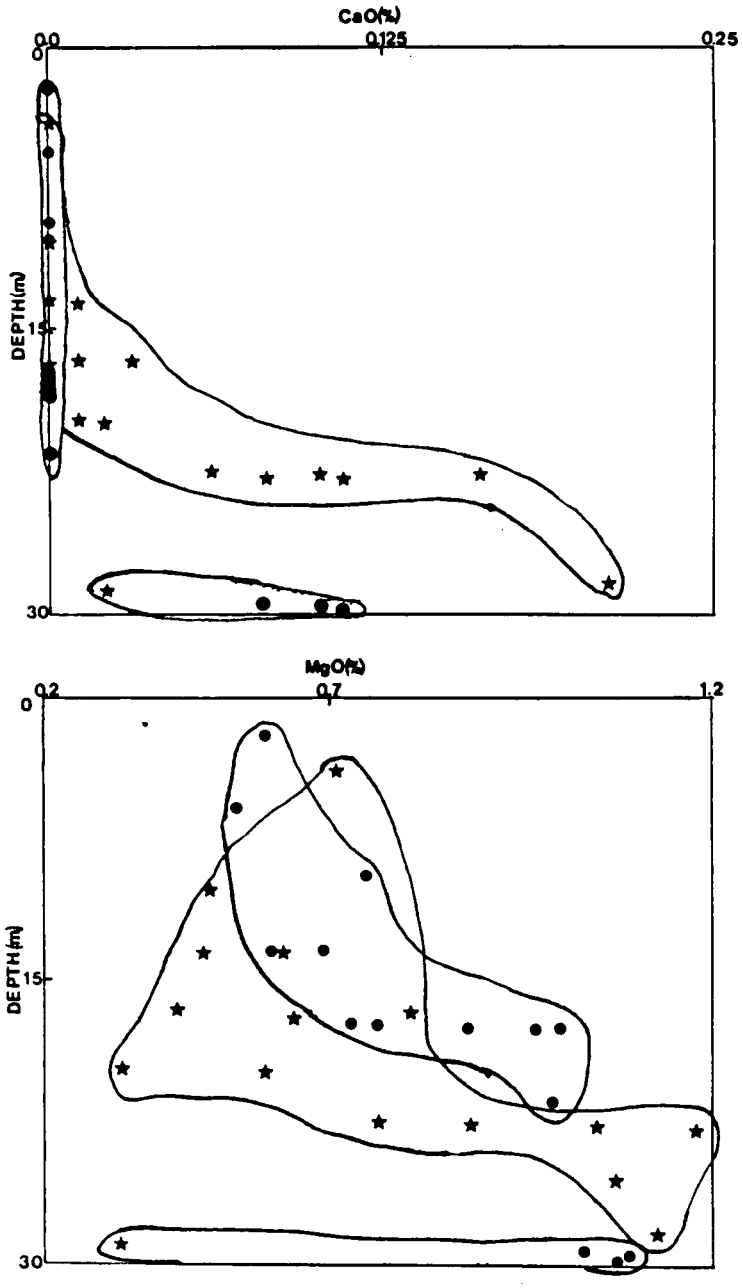


Figure 12. Concentration (CaO and MgO) vs. depth, cores 9 and 16. Concentrations represent all size fractions (gravel, sand, silt, and clay).

★ = Core 9

● = Core 16

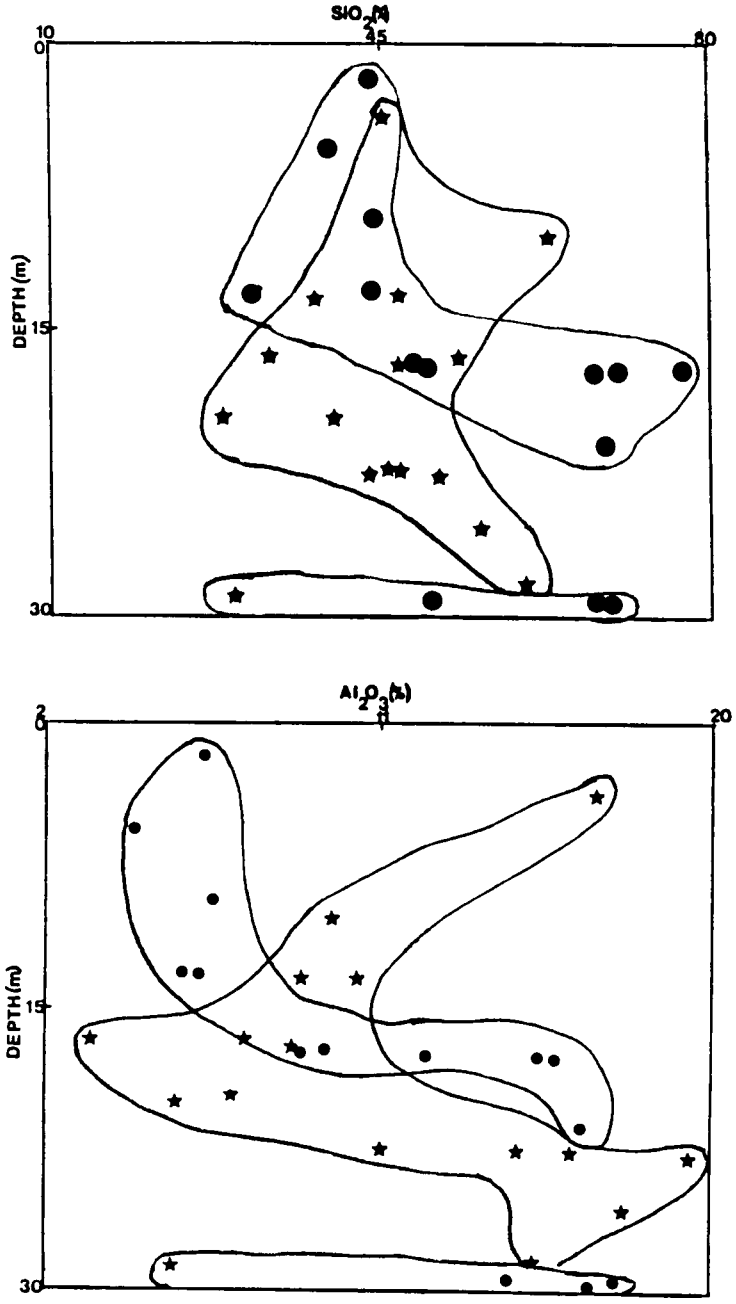


Figure 13. Concentration (SiO_2 and Al_2O_3) vs. depth, cores 9 and 16. Concentrations represent all size fractions (gravel, sand, silt, and clay).

★= Core 9

●= Core 16

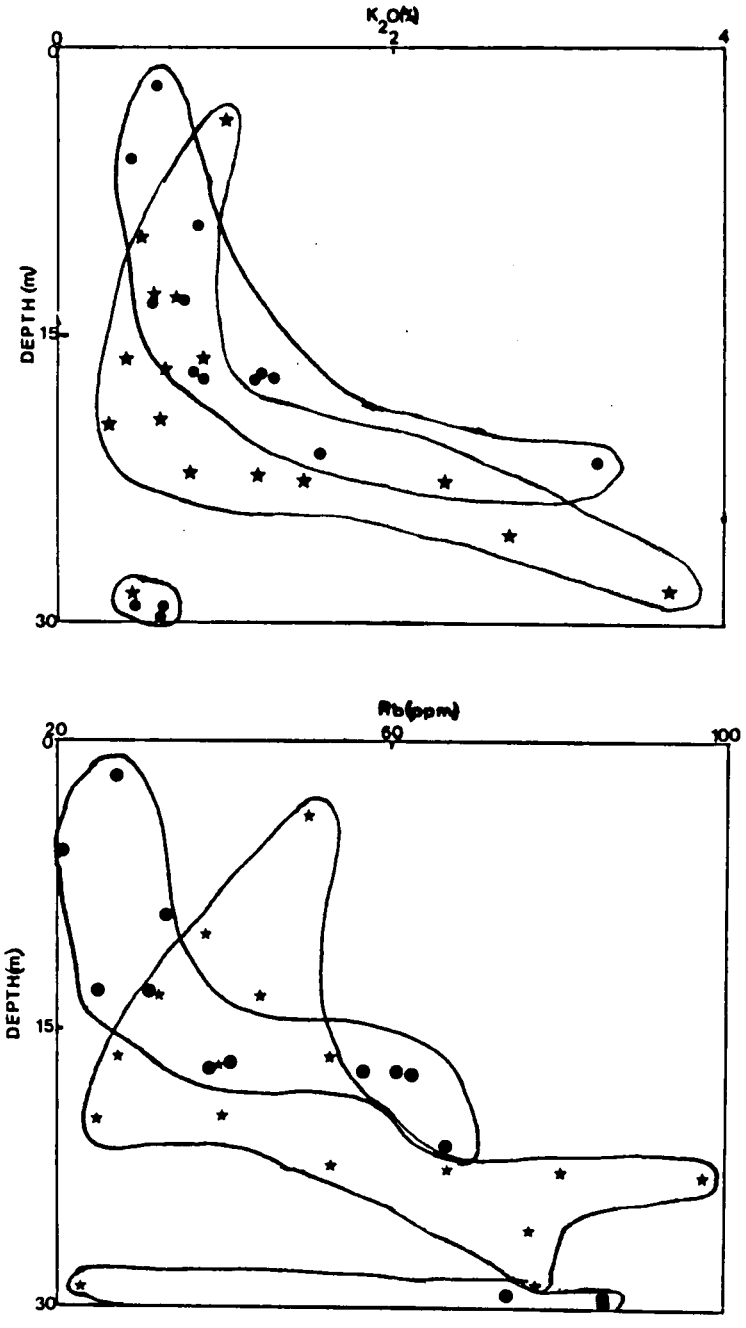


Figure 14. Concentration (K_2O and Rb) vs. depth, cores 9 and 16. Concentrations represent all size fractions (gravel, sand, silt, and clay).

★= Core 9

●= Core 16

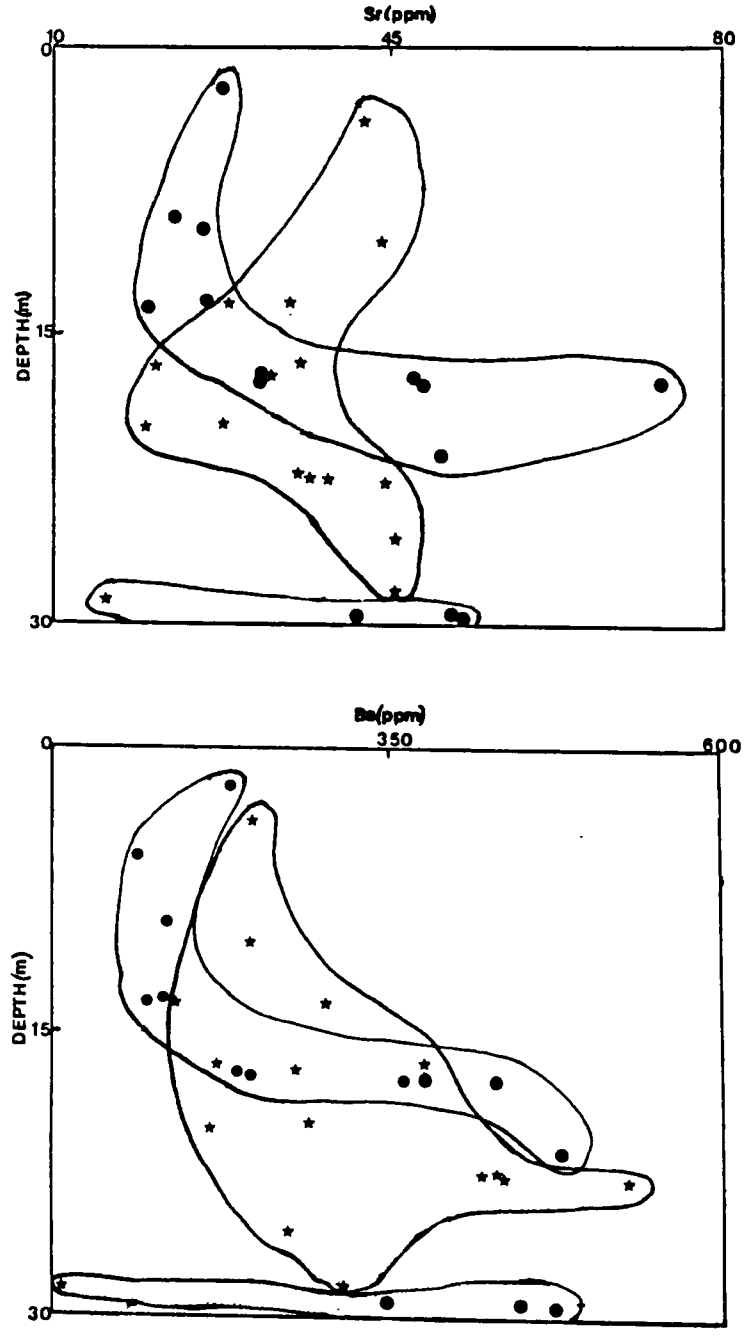


Figure 15. Concentration (Sr and Ba) vs. depth, cores 9 and 16. Concentrations represent all size fractions (gravel, sand, silt, and clay).

★ = Core 9

● = Core 16

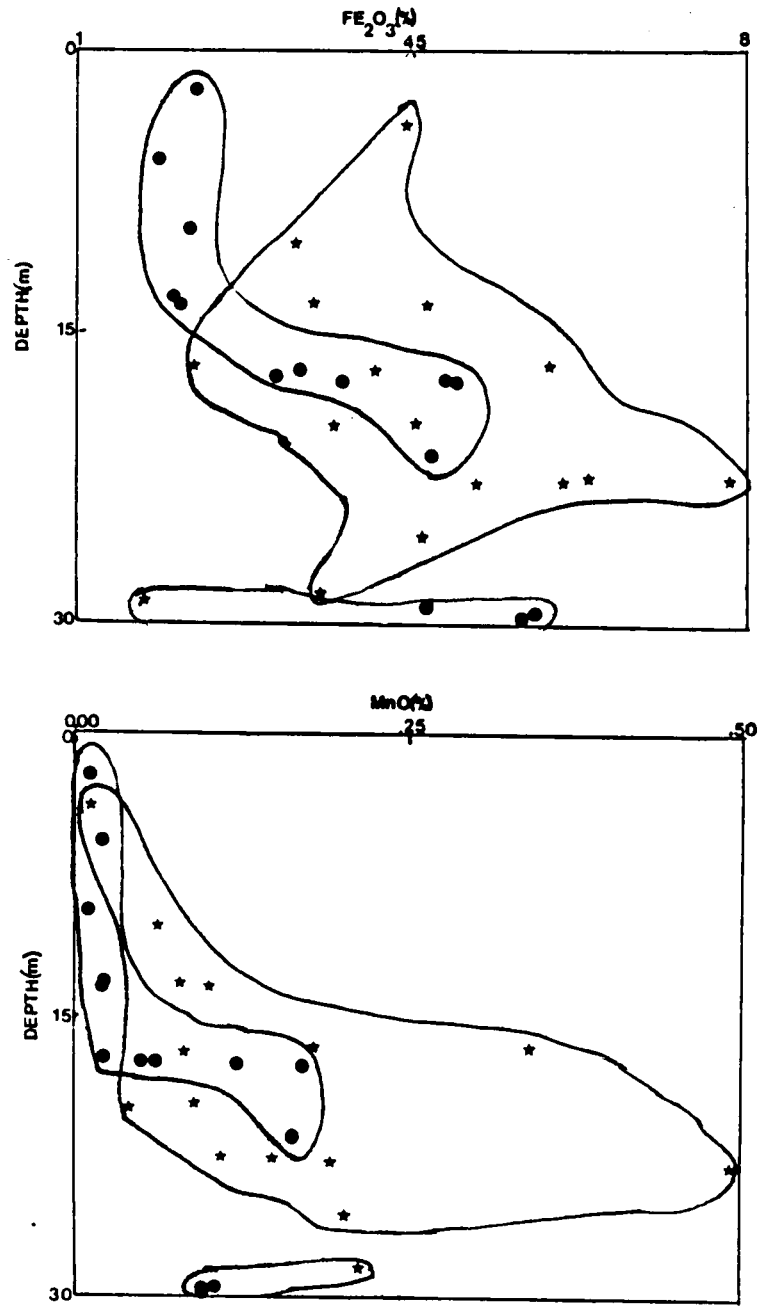


Figure 16. Concentration (Fe_2O_3 and MnO) vs. depth, cores 9 and 16. Concentrations represent all size fractions (gravel, sand, silt, and clay).

★= Core 9

●= Core 16

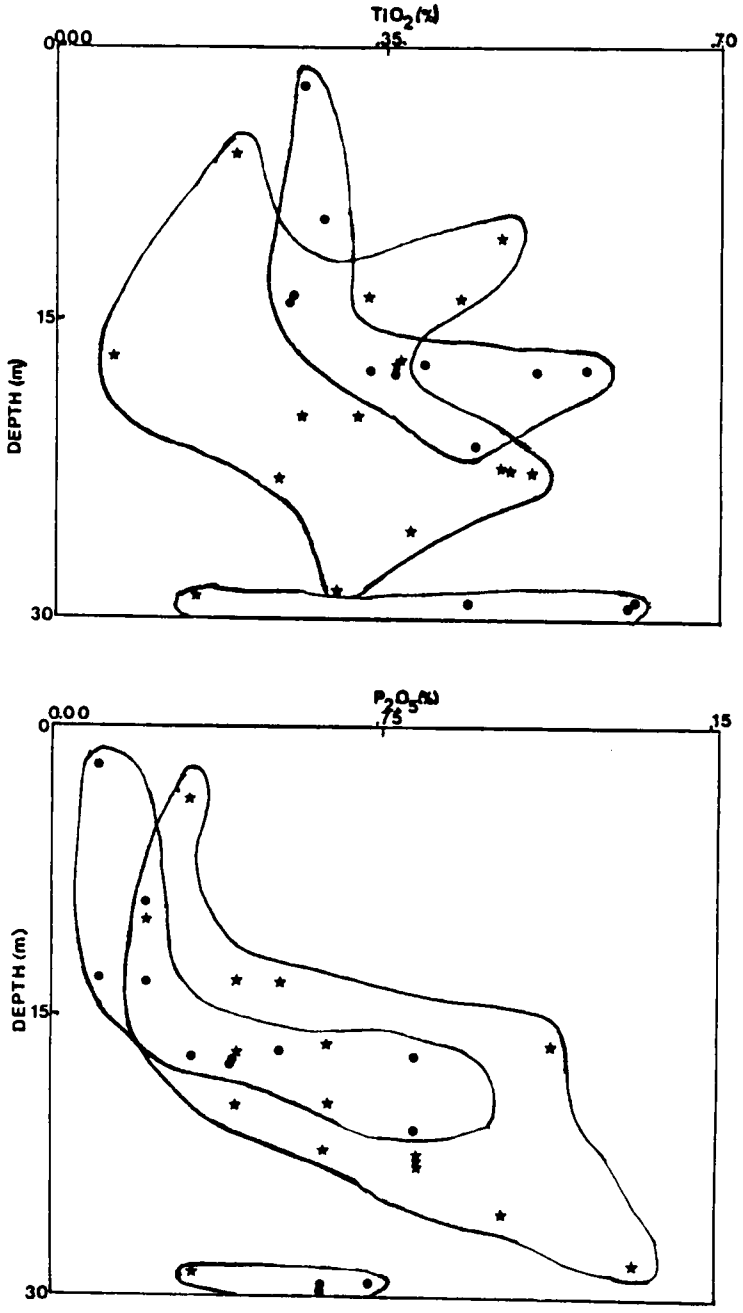


Figure 17. Concentration (TiO_2 and P_2O_5) vs. depth, cores 9 and 16. Concentrations represent all size fractions (gravel, sand, silt, and clay).

★ = Core 9

● = Core 16

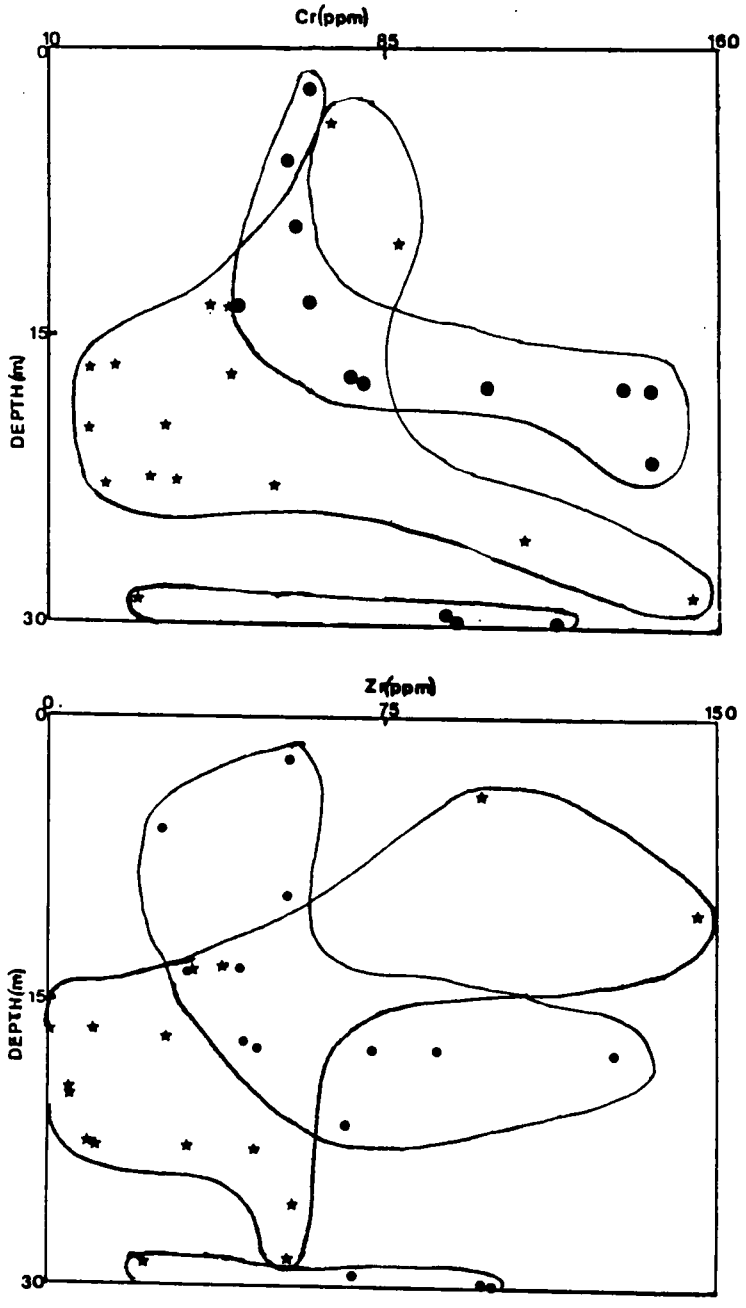


Figure 18. Concentration (Cr and Zr) vs. depth, cores 9 and 16. Concentrations represent all size fractions (gravel, sand, silt, and clay).

★= Core 9

●= Core 16

from each of these cores to show trends with depth. The figures illustrate concentrations vs. depth for major oxides (e.g., those with concentrations $\geq$1.0 wt.%) and minor oxides and trace elements (e.g., those with concentrations <1.0 wt.%). For purposes of discussion, both individual oxides and elements will hereafter be referred to by the element name (e.g., iron or Fe), even though the concentrations for most elements are reported for the corresponding oxide (e.g., Fe_2O_3). The data for Na were omitted in the figures because the relatively large standard error of calibration for Na (Appendix F) made it impossible to determine any trend with depth. In addition, sulfur was not included because it was detected in only two samples in the $\leq$2 mm fraction (9-9-15 = 6 ppm and 9-10A-17 = 7 ppm).

Ionic adsorption capacities and pH values. CEC and AEC values are listed in Table 7. The CEC's range from 1.42 to 19.65 meq/100 gms. The method used in the present study is similar to the displacement method, except that the final step (displacing the adsorbed Ba with Mg) was not performed. Therefore, the CEC and AEC values reported here are higher (up to two times) because total adsorbed Ba was measured.

Seeley and Kelmers (1984) noted that the AEC's for samples they studied from West Chestnut Ridge are very low. Only four of the samples in the present study have positive AEC values. The AEC values reported here are for

Table 7. CEC's, AEC's, and pH values for selected samples from all cores.

Sample	Depth (m)	CEC*	AEC*	pH[b]	Salt pH[c]
9-1A-1[d]	1.19	13.78	29.73	6.9	6.0
9-2A-2	4.08	13.64	4.68	5.9	4.3
9-4A-3	10.33	6.53	-[a]	4.3	4.3
9-5-4	13.41-13.54	8.83	-	5.0	4.2
9-5-5	13.54-13.87	8.88	-	5.0	4.2
16-1-1	2.14-2.29	6.07	-	4.9	4.0
16-2A-2	5.85	4.43	-	4.9	4.2
16-4-4	13.33-13.45	4.08	-	4.7	4.1
16-4-5	13.45-13.69	6.41	-	4.8	4.1
10-2C-3	6.37	19.65	2.86	4.9	4.4
10-4-5	10.62-10.81	10.73	51.35	5.0	4.4
11-3-4	9.70-9.82	1.42	-	4.8	4.0
12-3D-10	7.71	5.92	-	4.9	4.4
19-3-4	7.43-7.56	7.44	-	4.7	4.5
19-4-7	10.49-10.64	5.68	-	5.0	4.8
19-5-11	13.71-13.87	7.12	-	5.2	4.2
20-3-5	9.86-10.06	11.28	2.30	3.8	3.7
20-4-9	14.08-14.33	8.77	16.75	4.8	4.7

* Measured in milliequivalents per 100 grams of sample.
a Levels too low to be detected due to extremely low concentrations of chloride in original, untreated sample.
b Soil pH in distilled water.
c Soil pH in 0.01M $CaCl_2$.
d Excluded from calculations--considered to be spurious.

illustrative purposes only. They are questionable because of the possible errors due to counting statistics wen analysing for such low concentrations of chloride.

Table 7 also lists distilled water and salt pH values. These values indicate that the residuum and soil environment is acidic. This was also reported by Lee et al. (1984) and Monger (1986) at the West Chestnut Ridge site.

Bedrock

Results of the bulk chemical analyses of the 14 Knox Group bedrock samples using the LIMDOL protocol are given in Table 8. Means for each oxide and element analysed are also listed. Standard calibration and mean counting errors are listed in Appendix A.

Table 8. Bulk chemical analyses of Lower Knox Group dolomite samples.

Sample	Na_2O[a]	MgO[a]	Al_2O_3[a]	SiO_2[a]	K_2O[a]	CaO[a]	Fe_2O_3[a]	Mn[b]	P_2O_5[b]	Ti[b]	S[b]	Cl[b]	Br[b]	Sr[b]
1	0.02	21.12	0.33	1.30	0.18	29.94	0.15	137	-[c]	349	155	-	6	112
2	0.06	20.33	0.28	4.86	0.63	29.24	0.38	112	-	606	7	-	3	105
3	0.05	22.15	0.14	0.20	0.02	30.33	0.09	177	-	118	13	-	.1	124
4	-	20.78	0.38	1.19	0.11	30.32	0.15	175	69	376	112	-	2	134
5	0.14	18.73	0.41	12.39	1.07	27.95	0.72	111	-	1329	-	3741	-	159
6	0.06	21.48	0.27	3.07	0.25	29.83	0.21	137	-	342	224	-	2	170
7	0.05	20.48	0.40	4.71	0.47	29.49	0.29	121	-	481	1360	-	-	169
8	0.08	21.63	0.17	5.78	0.13	29.80	0.14	210	-	302	21	-	-	139
9	0.08	20.76	0.36	6.10	0.61	29.14	0.21	115	-	748	-	-	4	197
10	0.19	18.53	-	10.03	1.97	27.06	1.27	108	-	1080	-	997	.5	154
11	0.07	21.21	0.28	4.17	0.23	30.07	0.27	192	-	152	19	-	.8	168
12	0.04	19.73	0.41	9.44	0.38	29.14	0.28	189	-	404	1813	2756	.5	191
13	0.04	20.17	0.22	4.31	0.30	29.84	0.16	127	-	454	81	-	1	177
14	0.08	21.25	0.28	3.99	0.36	29.73	0.14	123	-	615	-	-	4	179
Mean:	0.07	20.60	0.28	5.11	0.48	29.42	0.32	145	5	525	272	535	1.8	156

NOTE: Samples 1-10 are from the Upper Copper Ridge Formation. Samples 11-14 are from the Lower Chepultepec Formation.
a Values in wt. %.
b Values in ppm.
c Not detected.

CHAPTER V

DISCUSSION

Changes Vs. Depth

Mineralogical Changes

Samples from shallower depths (9-1A-1, 10-2C-3, 16-1-1, 16-2A-2, 19-3-4, and 20-3-5) show evidence for hydroxy-interlayered vermiculite (HIV). HIV is a product of intense weathering and leaching at relatively shallow depths. Illite is the common precursor material that alters to HIV when exposed to intense weathering only a few meters below the surface (Boul et al., 1973). An $Al(OH)_x$ polymer occupies the interlayer sites of vermiculites (weathered from illites), thereby forming the HIV. The source of this aluminum is from kaolinite being destroyed during the weathering process (Rich and Obenshain, 1955; Tamura, 1957; Huang and Lee, 1969).

In his study of the soils at West Chestnut Ridge, Monger (1986) noted that the concentration of clay-size particles reaches a maximum at depths of about 3 meters. He named this the "clay bulge zone." It represents the depth at which, in an acidic environment such as is present at West Chestnut Ridge, "meteoric waters most readily

translocate and deposit clay minerals." Monger found that secondary kaolinite readily forms in this zone as the pre-existing minerals (e.g., the primary kaolinites and neoformed hydroxy-interlayered vermiculites) are dissolved by meteoric waters. Grim (1968) also noted secondary crystallization of kaolinite in acidic soils from waters containing dissolved SiO_2 and Al_2O_3. Lee et al. (1984) reported well-defined pseudo-hexagonal kaolinite within one meter of the surface at West Chestnut Ridge.

In their study of soil and residuum samples from West Chestnut Ridge, Lee et al. (1984) observed a decrease in the amount of HIV (becoming vermiculite), an increase in the amount of kaolinite, and no change in the amount of illite going from the surface towards bedrock. In the present study, the relative amounts of kaolinite and illite in the residuum are also considered.

Figures 9, 10, and 11 (pp. 44, 45, and 47) illustrate relative amounts of kaolinite and illite. Samples with low I/K ratios are relatively high in kaolinite, and samples with high I/K ratios are relatively low in kaolinite. One would expect the relative amounts of kaolinite to lessen with depth because the bulk X-ray diffractograms indicate a very small amount of original feldspars (which weather to kaolinite) in only a few samples. In addition, the amount of kaolinite originally present as clay minerals in the dolostones is also very small (S. Y. Lee, personal

communication, 1986). What is the explanation for the relatively high concentrations of kaolinite in some horizons at depth? It must be assumed that more feldspars are present at depth than were detected in the diffractograms, and/or kaolinite is precipitating at depth well below the soil horizons.

Sharpness ratios (Kubler, 1968) for illite and kaolinite were also expected to increase with depth, indicating that the minerals become more crystalline closer to bedrock. The graphs illustrate no trends with depth, but they do illustrate more variability of crystallinity below a depth of 15 meters in cores 9 and 16. However, the error bars are so large (Appendix F) that the points on the graphs are practically meaningless. As a result, further discussion has been ommited from this report.

Figures 9, 10, and 11 (pp. 44, 45, and 47) suggest a change in the character of the residuum beginning at a depth of approximately 15 meters in cores 9 and 16. The ratio of the (001) illite peak to the (002) kaolinite peak falls within 0.5 +/- 0.2 for all of the samples above 15 meters. Below 15 meters the relative intensities of the illite and kaolinite peaks are much more variable in both cores. These values range from 0.19 to 1.71. The variance (square of the standard deviation) was calculated for each set of data points in cores 9 and 16 based on a division of the residuum at 15 meters. Variances above and below 15 meters in core 9

are equal to 0.002 and 0.15, respectively. Variances above and below 15 meters in core 16 are equal to 0.018 and 0.13, respectively. In addition, detrital carbonates and feldspars are found only in samples which are from below 15 meters (Table 6). As a result, two zones can be identified in the residuum which are separated by a dashed line in Figures 9 and 10 (pp. 44 and 45). The first is an upper zone in which the variances of the ratios of illite to kaolinite are small. The second is a lower zone which contains remnant feldspars and carbonates, and in which the variances of the ratios of illite to kaolinite are larger. The boundary between these zones is not expected to be sharp, but to occur over an interval of several meters.

It should be noted that this change at approximately 15 meters depth is based on a limited number of samples from a few cores in which the residuum is at least 30 meters thick. In other cores, or where the residuum has developed on top of other carbonate formations, similar changes in the residuum might occur at different depths.

In Figures 9 and 10 (pp. 44 and 45), a high I/K ratio suggests the presence of more illite with respect to kaolinite in the clay-size fraction. If the relative amount of illite in a sample increases, the amount of K should also increase. Chemical analyses of the silt- and clay-size fractions (Appendix G) illustrate that the samples with high I/K ratios also have higher concentrations of potassium.

Those samples with larger I/K ratios and chemical compositions include 9-8-14 (3.43%), 9-9-16 (6.33%), 9-10A-17 (4.70%), 16-6-11 (2.07%), and 16-6-15 (6.65%).

Presence of a Chemical Discontinuity Between Upper and Lower Zones

Prior to considering the trends with depth for individual elements, or groups of elements, two important factors that control the chemistry of individual samples (or horizons) within the residuum should be noted. First, various mineral assemblages (including the amounts of insoluble phases present), and therefore different chemical compositions, may have been present at different horizons in the original siliceous and argillaceous dolostones. Second, individual lithologies may have weathered at different rates due to differences in the pH and Eh of the groundwater, the amount of precipitation, the extent of leaching, temperature, porosity and permeability of both the bedrock and weathered material, presence of fracture zones and solution channels, slope of the surface, and depth to bedrock. Therefore, variations in both the mineralogical and chemical character of individual horizons within the residuum are to be expected.

Each set of data points for cores 9 and 16 has been outlined in Figures 12 through 18 (pp. 48 through 54) to not only illustrate general trends with depth, but to show that changes in concentrations often occur at different depths (in both of the cores) for different elements and oxides. In addition, samples 9-10C-18, and 16-8A-20 through 16-8C-22 have been outlined as a separate group in all of the figures. These samples are aberrant, and if eliminated, stronger relationships and trends are evident.

Figure 12 (p. 48) illustrates chemical trends for Ca and Mg with depth. Both elements were present in relatively large amounts in the original carbonate bedrock. Average chemical compositions for Ca and Mg in Knox Group dolostones from East Tennessee are listed in Table 9. The chemical compositions of dolostones collected near the Bull Run Steam Plant are similar to Thorn Hill dolostones analysed by Kopp et al. (1985), Knox Group dolostones at the Coy Mine (Crattie, 1985), and Knox Group carbonates from 22 quarries in East Tennessee (Hershey and Maher, 1985). Almost all of the Ca (which ranges in concentration from 0.00% to 0.25%) has weathered out above a depth of approximately 15 meters. Some of the Mg has not completely weathered out but is retained in, presumably, the clay minerals. Below approximately 15 meters depth, both Ca and Mg increase in concentration. Concentrations for Mg range from 0.31% to 1.17% below 15 meters depth.

Table 9. Chemical compositions of selected Knox Group dolostones from East Tennessee.

Oxide	Hershey and Maher[a] (1985)	Kopp et al.[b] (1985)	Crattie[c] (1985)	This Study[d] (1986)
CaO	39.2%[e]	29.22%	30.14%	29.42%
MgO	10.2%	21.74%	19.95%	20.60%

[a] Knox carbonate bedrock samples from 22 quarries in East Tennessee. Analyses include dolomitic limestones.

[b] Xenotopic, fine-grained Lower Knox dolostones from the Thorn Hill Section, East Tennessee.

[c] Xenotopic, fine-grained Upper Knox dolostones from the Coy Mine, Mascot-Jefferson City District, East Tennessee. Samples are from mineralized and brecciated zones.

[d] Fourteen fine- to coarse-grained Lower Knox dolostones from the Bull Run Steam Plant near Oak Ridge, Tennessee.

[e] Mean values in weight percent.

Samples from cores 9 and 16 with high concentrations of Ca and Mg in the sand-, silt-, and clay-size fractions (Appendix G) correspond to samples that contain dolomite and/or calcite in the X-ray diffractograms (Table 6). These samples include 9-10A-17, 16-6-15, 16-7B-17, 16-7C-18, 16-8B-21, and 16-8B-22.

The concentrations for Al and Si show similar trends in both cores (Figure 13, p. 49). This is expected since these elements are the major constituents in clay minerals. The trend for Si is more irregular because of abundant chert-rich horizons throughout the cores. Note the change in concentration for these elements at approximately 15 meters depth. The increase in concentration for Al below 15 meters is substantial, and is due to more extensive leaching in the upper horizons and redeposition at greater depths, and physical translocation of solid particles (clays).

The trends for K, Rb, Sr, and Ba are illustrated in Figures 14 and 15 (pp. 50 and 51). Rb substitutes readily for K, and Sr substitutes for Ca in the intersilicate sites of clay minerals. These pairs of elements have similar chemical trends. The concentrations for all of these elements generally increase below 15 meters. These changes can be explained in several ways: (1) the elements are present as major, minor, and trace elements in clays (Rankhama and Sahama, 1950); (2) the elements are present in detrital or authigenic feldspars; and (3) the elements

infiltrated from the upper zones closer to the surface to concentrate (accumulate) in the lower zone(s) closer to bedrock. Samples from cores 9 and 16 with high concentrations of K (and Rb) in the sand-, silt-, and clay-size fractions (Appendix G) correspond with samples that contain feldspars in the X-ray diffractograms (Table 6). These samples include 9-8-14 through 17, 16-6-15 through 18, and 16-8B-21 and 22. If Ba were present as barite and remained inert during the weathering process, Ba should be concentrated in the upper, more highly leached zones closer to the surface. However, this is not the case.

Fe and Mn (Figure 16, p. 52) have been the most affected by oxidation during the weathering process. Both graphs illustrate a slight increase in concentration with depth. Low pH fluids infiltrated the soils and residuum and percolated downward from the upper zones, reprecipitating some of the Fe and Mn in the forms of relatively insoluble oxides and oxyhydroxides and in organic compounds in the lower zone(s) (Schwertmann and Taylor, 1977).

Ti (Figure 17, p. 53) is probably present as a minor constituent of clays, quartz, and other silicates, although it might be present in insoluble phases such as ilmenite or rutile. Cr and Zr (Figure 18, p. 54) are probably present as trace elements in clay minerals. Trace amounts of detrital zircon may also be present. As a result, the

graphs for Ti, Cr, and Zr illustrate no apparent trends with depth.

The concentration of P (Figure 17, p. 53) increases slightly with depth, but the reasons for its behavior are not clear. It is probably present as apatite (less likely monazite or zenotime).

Based on chemical (and mineralogical) analyses it is proposed that a discontinuity occurs at approximately 15 meters depth in cores 9 and 16 which separates an upper, more weathered zone, from a lower, less weathered zone (possibly a zone of accumulation). The discontinuity was chosen because there appear to be differences between the chemistries of the residuum above and below this depth. However, all of the data do not repesent well-defined divisions at 15 meters in both cores. There appear to be zones of variable thicknesses for the elements and oxides which are present at different depths in the cores. These are illustrated by the outlined data sets.

According to S. Y. Lee (personal communication, 1986), it might be possible to further divide the lower zone (below 15 meters) into two zones based on the distribution of Fe and Al (Figures 13 and 16, pp. 49 and 52). Between approximately 15 and 23 meters the concentrations of Fe and Al increase, resulting in a "bulge," or zone of accumulation of Fe- and Al-minerals (e.g., geothite, gibbsite, hematite, etc.). Below approximately 23 meters the concentrations for

Fe and Al decrease. However, in this study, the samples will be divided into the two major zones (< and > 15 meters) mentioned above.

To test this hypothesis that a discontinuity does in fact exist in cores 9 and 16, statistical analyses (t-tests) were applied. The t-test utilizes means and standard deviations to determine if two sets of data are significantly different (Bhattacharyya and Johnson, 1977); in this case, if the average concentrations for each oxide or element are significantly different. Table 10 gives means and standard deviations for residuum samples (gravel-, sand-, silt-, and clay-size fractions) from cores 9 and 16. The samples were divided into two groups including 9 samples from above and 21 samples from below the proposed discontinuity.

The results of the t-tests (Appendix H) confirm that Mg, Al, K, Ca, Fe, Mn, P, Rb, and Ba, fall into two separate populations at the 95% confidence level, and Sr at the 90% confidence level. Those elements with means and standard deviations that do not define two separate populations are Si, Ti, Cr, and Zr. (Na and S were not considered.) The concentration of Si is quite variable because of differences in abundances of the chert contents in the >2 mm size fractions. Therefore, excluding Na, S, and Si, the presence of a chemical discontinuity at a depth of 15 meters can be

Table 10. Chemical analyses for residuum samples from cores 9 and 16.

ELEMENT	UPPER RESIDUUM[a] (depth <15 meters)		LOWER RESIDUUM[b] (depth >15 meters)	
%	$\bar{X}$	$S_{\bar{X}}$	$\bar{X}$	$S_{\bar{X}}$
Na_2O	0.15	0.15	0.24	0.19
MgO	0.47	0.10	0.77	0.27
Al_2O_3	8.21	3.76	12.13	4.79
SiO_2	43.41	8.39	51.50	14.78
K_2O	0.64	0.18	1.32	0.85
CaO	0.00	0.00	0.05	0.06
Fe_2O_3	2.85	1.08	4.54	1.44
MnO	0.04	0.03	0.15	0.11
P_2O_5	0.02	0.01	0.07	0.03
TiO_2	0.34	0.15	0.38	0.14
ppm				
S	nd[c]	nd	1.2	3.49
Cr	64	13	77	48
Rb	33	9	58	22
Sr	30	9	39	13
Zr	57	40	46	36
Ba	214	46	349	110

Note: This data is recalculated and represents all size fractions (gravel, sand, silt, and clay). Samples with shale zones have been excluded.

[a] Includes 9 samples from above 15 meters.

[b] Includes 21 samples from below 15 meters.

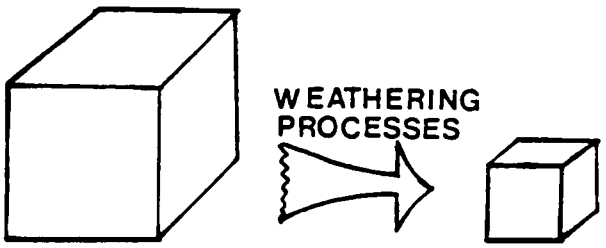
[c] nd = not detected.

demonstrated as statistically valid for 10 of the 13 major and minor oxides/elements.

Amount of Material Removed

The chemical compositions of available fresh bedrock samples were compared with the compositions of residuum samples to obtain an approximation of the extent of the chemical changes that took place during the weathering of siliceous and argillaceous Knox Group dolostones. In order to compare the elements, it was decided to select a "baseline" oxide that was assumed to be neither removed from, nor added to, the volume of rock during the weathering process.

In the comparisons which follow, it was assumed that the total amount of SiO_2 in a given volume of rock remained essentially unchanged during the weathering process. SiO_2 was chosen as the "baseline" oxide because it is present in relatively large amounts in both the original bedrock ($\bar{x}$ = 5.11%; Figure 19) and residuum ($\bar{x}$ = 43.41 ="upper" residuum and 51.50% ="lower" residuum; Table 10). In addition, SiO_2 is easy to analyse because the XRF counting statistic errors are small (Appendix A) compared to the weight percentages, and all siliceous phases in the residuum are here considered to be relatively insoluble (e.g., quartz, cherts, and clays). Some SiO_2 may have been released during the



OXIDE	1000 GMS OF BEDROCK		118 GMS OF UPPER RESIDUUM		AMOUNT RELEASED OR ADDED DURING THE WEATHERING OF 1000 GRAMS OF BEDROCK
	WT.% ($\bar{x}$)	GRAMS	WT.% ($\bar{x}$)	GRAMS	GRAMS/1000 GRAMS
CaO	29.42	294.20	0.00	0.00	-294.20
MgO	20.60	206.00	0.47	0.55	-205.45
K_2O	0.48	4.80	0.64	0.76	-4.04
Na_2O	0.07	0.70	0.15	0.18	-0.52
TiO_2	0.05	0.50	0.34	0.40	-0.10
MnO	0.015	0.15	0.04	0.05	-0.10
Fe_2O_3	0.32	3.20	2.85	3.36	+0.16
Al_2O_3	0.28	2.80	8.21	9.69	+6.89
P_2O_5	0.0005	0.005	0.02	0.0236	+0.0186
SiO_2	5.11	51.10	43.41	51.22	$\pm$0.00

Figure 19. Chemical changes associated with weathering of siliceous and argillaceous Lower Knox Group dolostones assuming the amount of SiO_2 remains relatively unchanged.

weathering of feldspars and clays, but for purposes of this comparison, the silica is assumed to have remained essentially in place. Some SiO_2 could have formed secondary chert and/or gone into newly formed clay minerals.

The average weight percentage of SiO_2 increased approximately 8.5 times during the change from bedrock ($\bar{x}$ = 5.11%) to residuum ($\bar{x}$ = 43.41%), if no appreciable amount of SiO_2 were released into the environment or added to the system from an outside source. If this assumption is reasonable, then an original quantity of average siliceous carbonate bedrock (for illustrative purposes assumed to be 1.0 kg) has weathered to form 0.118 kg of upper residuum (approximately 1/8.5 of its original mass).

Figure 19 illustrates the changes in mean composition for ten major elements for both the Knox Group dolostones and the upper zone of residuum samples. Residuum samples from the upper (<15 meters) zone were chosen for comparison because they are the most extensively weathered, and their chemical compositions are here thought to be the most dissimilar with the chemical compositions of the bedrock.

Figure 19 also illustrates the amounts (in grams) of each oxide released from, or taken into, the residuum during the weathering process. It is important to note that even though some elements (such as K, Na, Ti, and Mn) appear to have been enriched during the weathering process. When the actual masses are compared, it is clear that these elements

were depleted. Some elements (such as Fe, Al, and P) appear to have been added to, or concentrated in, the system. Of these, the change in concentration for P is minor. In the lower residuum (below 15 meters), aluminum illustrates a substantial increase in concentration (+6.89gm/1000gm). Iron illustrates a smaller increase (+0.16/1000gm). These changes in concentration are thought to be a result of leaching at the surface which causes aluminum and iron to go into solution followed by their reprecipitation and accumulation below the soil horizons. Aluminum and iron also could have been transported in the solid phase as particles, or as organic complexes. Aluminum and iron are more enriched in the lower residuum than in the upper residuum (+11.51/1000gm and +2.16/1000gm, respectively). Even though they are more concentrated in the residuum below 15 meters, they have also been retained in the upper horizons above 15 meters. As expected, Ca and Mg, originally present in the largest quantities in the dolostones, were depleted the greatest amounts.

In a study of hundreds of samples of carbonate residuum in Missouri, Ebens and Connor (1980) compared the specific gravities of residuum and carbonate bedrock. They concluded that acceptable concentration factors (in weight percent) ranged from 6 to 12 times the original carbonate rock volumes. The concentration factor of approximately 8.5

times for the siliceous and argillaceous Knox Group dolostones (in the present study) fits within their range.

A "mass balance" problem exists with the transformation of a siliceous dolostone to a clay-rich residuum (such as is present at West Chestnut Ridge). How does one begin with a dolostone with a mean concentration for Al_2O_3 equal to 0.28%, and end up with mean concentrations for Al_2O_3 in the residuum which ranges from 8.21% (upper residuum) to 12.13% (in the lower residuum)? If Al had been chosen (instead of SiO_2) as the arbitrary baseline oxide, then the equivalent volume of rock required to weather would have been 30 to 45 times the present amount of residuum. However, even if Al was used as the baseline oxide (it was not because it was considered to be more soluble and mobile than SiO_2 in this environment), how does one account for all of the Al in this clay-rich residuum? The concentration values for the residuum (Table 10, p. 70) were calculated from samples weathered from carbonate bedrock. Samples without chert fragments (weathered from shaley beds) were excluded from the calculations. The concentrations in Table 10 represent residuum weathered from carbonate bedrock. However, the original carbonate bedrock has argillaceous beds interspersed in the dolostones. As a result, the concentrations for the residuum represent minimum concentration values for Al. If the concentrations for Al from the shaley beds had also been figured into the

calculations, the concentrations for Al would be higher, but not high enough to account for all of the aluminum present in the residuum.

Two possible explanations for the abundance of aluminum (in clay minerals) in the residuum are given. The first explanation is that much more of the original siliceous and argillaceous caronate bedrock weathered than was originally considered (8.5 times for SiO_2, or 45 times for Al_2O_3). According to S. Y. Lee (personal communication, 1986), the amount of original clay minerals (illite only) in three bedrock samples (dissolved in buffered acetic acid) from the Copper Ridge Dolomite taken at the West Chestnut site (in late 1986) is very small. If very small amounts of original clays were present in the original bedrock, much larger bedrock volumes must have weathered. The second explanation is that the Al has been transported into the environment to form residual clay minerals. It is possible that the residuum reflects a variety of different parental materials. The residuum could have weathered not only from the Lower Knox Group, but also from part of the overlying Middle Ordovician Chickamauga Group. There is no simple explanation for this mass balance problem, but it could possibly be better explained by one of the explanations given here.

Groundwater Composition

The groundwater compositions (in ppm) of seven elements are listed in Table 11. The data represent groundwater samples from both the residuum and bedrock. As expected, Ca and Mg are the major cations in the groundwater. K is present in relatively high concentrations, but the reasons for its high values are not known. K may be leached from illite or potassium feldspars. Al, Si, Fe, and Na are additional major cations in the groundwater at West Chestnut Ridge.

The chemical formula of dolomite is $CaMg(CO_3)_2$. The molar ratio of Ca to Mg in dolomite is 1:1. Using the concentrations of Ca and Mg in the residuum and bedrock groundwaters, and dividing by their respective atomic weights, the molar ratio of Ca to Mg can be calculated. In the bedrock groundwater, the molar ratio of Ca:Mg is 0.69:0.67 = 1.0, which is expected. However, in the residuum groundwater, the molar ratio of Ca:Mg is 0.60:0.43 = 1.4. A possible explanation for less Mg in the residuum groundwater is that Mg is retained by clay minerals, whereas Ca remains in solution.

Table 11. West Chestnut Ridge site groundwater quality data. Wells 9A and 9B are next to corehole 9.

Element	9A(ppm)[a] Residuum	9B(ppm)[b] Bedrock
Ca	24.2	27.5
Mg	10.4	16.4
K	17.1	17.1
Al	<0.02	<0.02
Si	2.8	3.2
Fe	<0.01	<0.01
Na	0.93	0.83

[a] Well 9A is screened in Copper Ridge Dolomite residuum.

[b] Well 9B is screened in Copper Ridge Dolomite bedrock. (From Dick Ketelle, personal communication, 1986).

CEC's and the Effect of pH

Ionic adsorption capacities (CEC's and AEC's) and pH values are important when studying the chemical behavior of the residuum. The chemical stability of the acidic environment at West Chestnut Ridge is dependent on the pH of the groundwater flowing through the residuum.

Rhoades (1982) defined cation exchange capacity as a "measure of the quantity of readily exchangeable cations neutralizing negative charge in the soil." Variable charge CEC values depend on many factors including the clay mineral species present, the pH of the soil environment, the amount of clay surface areas, and the amount of amorphous oxyhydroxides and organics (Parfitt, 1980). As the pH decreases, variable charge CEC's also decrease because the clay surfaces become more positively charged, thus inhibiting the adsorption of cations onto their surfaces. On the other hand, fixed charge CEC's are pH independent because cations are exchanged (or substituted) within intersilicate sites.

The soil pH was defined by McLean (1982) as a "measure of activity of ionized H (H^+) in the soil solution." The soil pH in distilled water is higher than the soil (salt) pH in 0.01M $CaCl_2$ solution because Ca ions effectively displace the exchangeable Al and H ions. The Al combines with the

water, in turn releasing H ions. As a result, the added H ions in solution lower the pH.

Figures 20 and 21 illustrate the relationships between CEC's and pH values in distilled water and 0.01M $CaCl_2$. Samples from cores 10 and 20 were excluded in Figures 20 and 21 because they are from sinkholes and contain highly leached materials that result in anomalous CEC values. Figure 22 illustrates CEC's vs. clay contents. CEC values are a measure of both fixed and variable charges of the clays.

Correlation coefficients and best-fit lines were calculated to determine if there is a linear relationship between CEC's and pH and CEC's and clay contents. The linear relationship between CEC's and pH for the samples in distilled water (r= .67) is good (Figure 20). The correlation coefficient is poor for pH values in 0.01M $CaCl_2$ (r= .22) (Figure 21) indicating no relationship in this figure. There is a strong linear relationship between the amount of clay-size particles present and CEC's (r = .89) (Figure 22). These figures help illustrate that fixed and variable charge CEC's are not independent, single-valued soil properties but depend on many factors.

CEC's are generally higher in the shallower samples in all of the cores (Table 7, p. 58). The reason may be due to the presence of HIV (found in the near surface samples only) which has a higher CEC. Some of the higher CEC values at

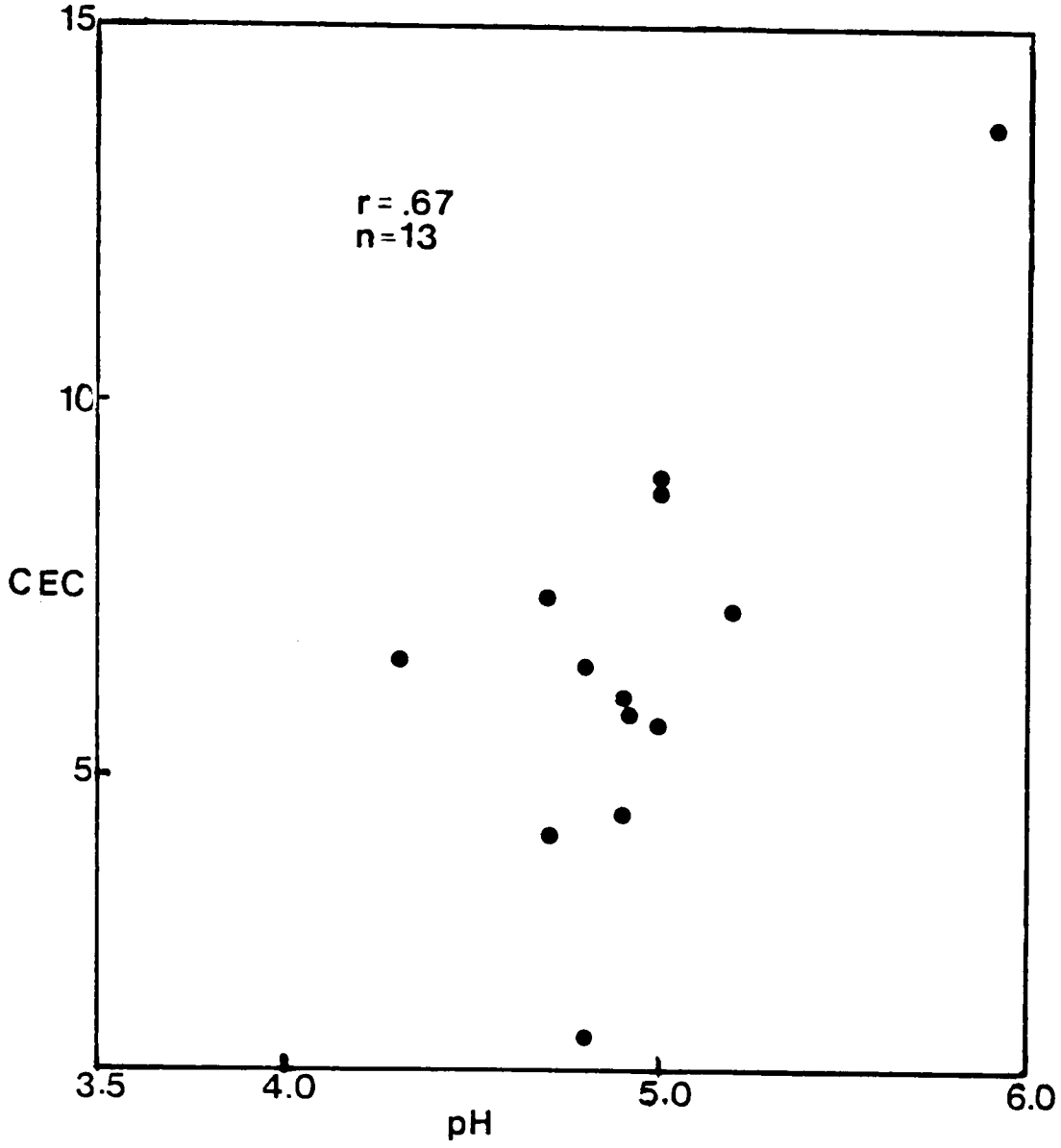


Figure 20. CEC's vs. pH (in distilled water) for samples from cores 9, 11, 12, 16, and 19. The combined sand, silt, and clay fractions were used.

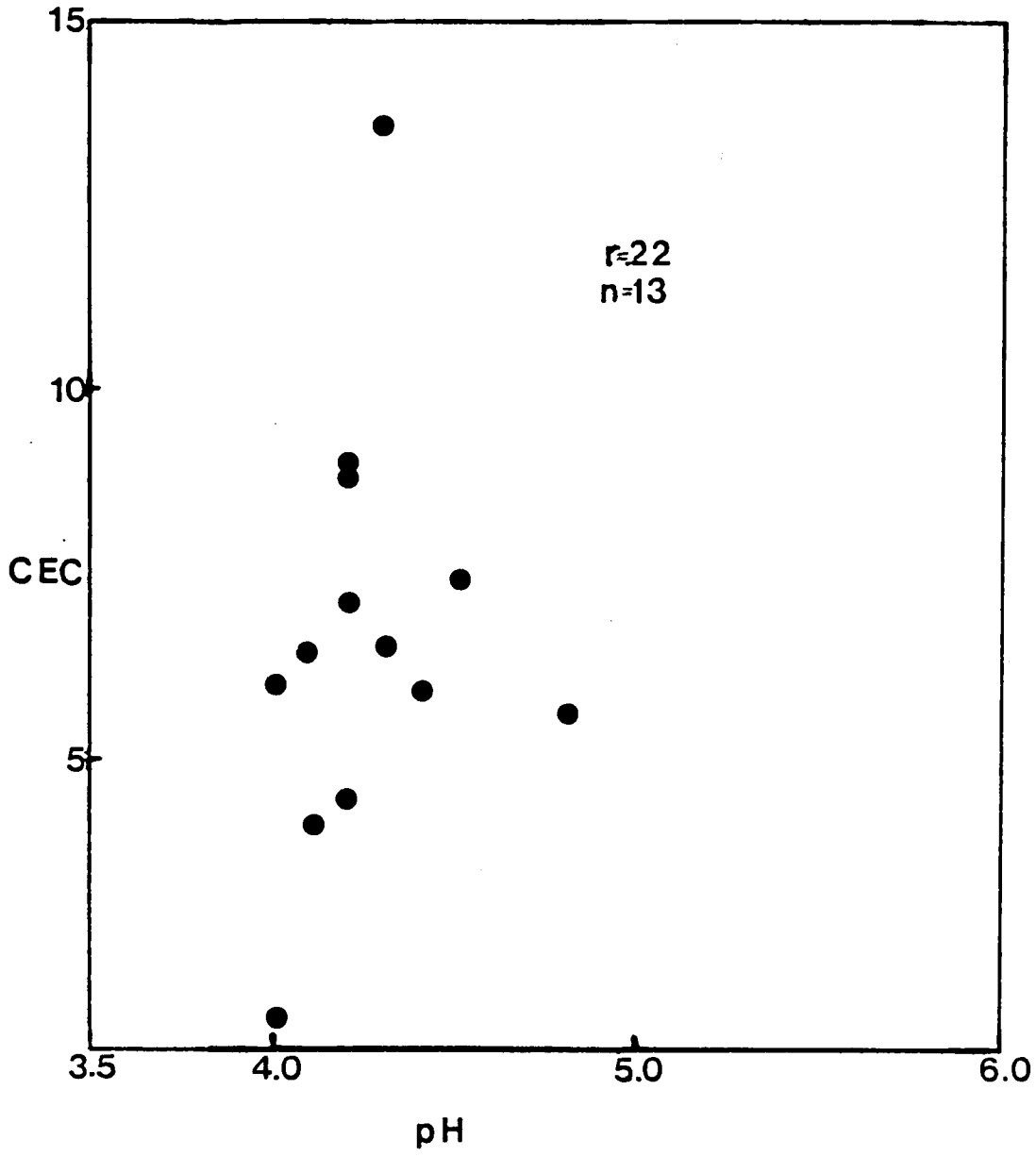


Figure 21. CEC's vs. pH (in 0.01M $CaCl_2$) for samples from cores 9, 11, 12 16, and 19. The combined sand, silt, and clay fractions were used.

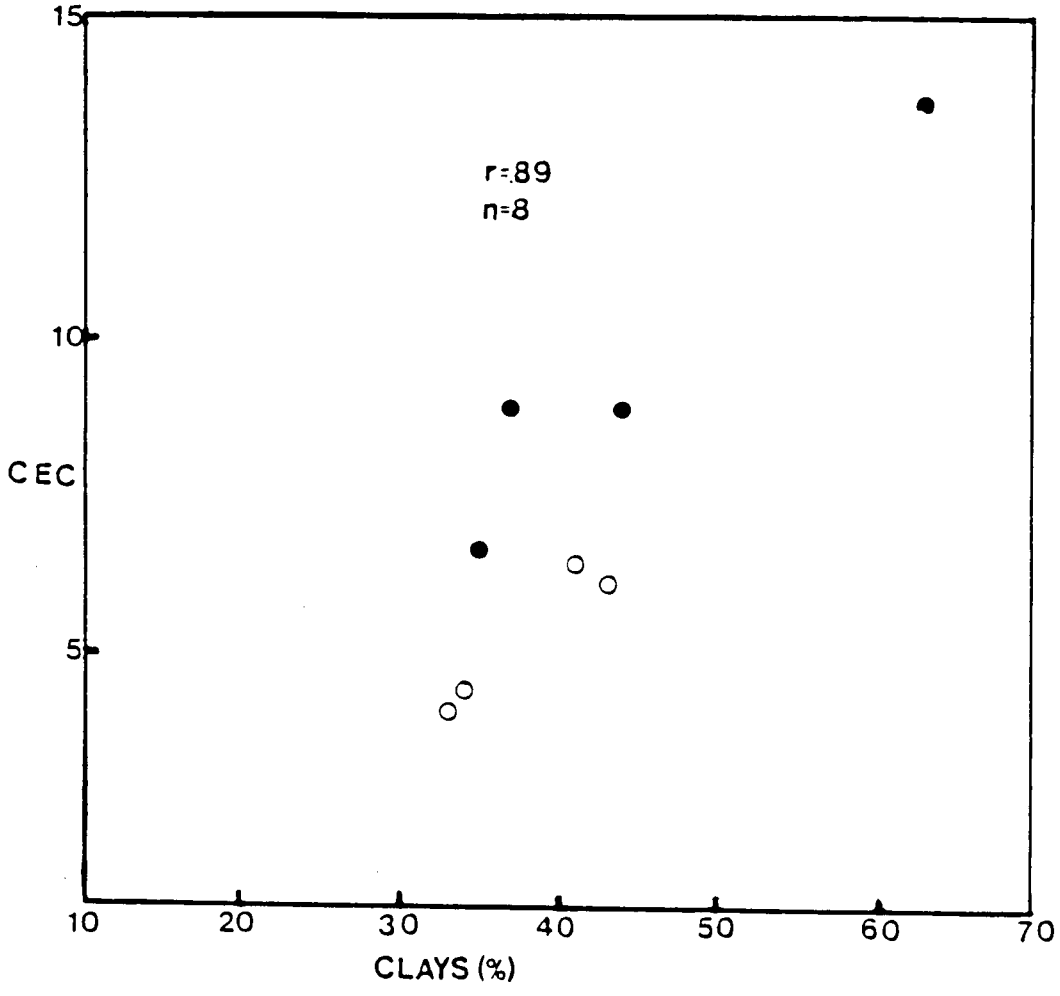


Figure 22. CEC's vs. clay contents for samples from cores 9 and 16. No other cores are included because the clay and silt fractions were not separated during physical analyses.

● = Core 9 samples.

○ = Core 16 samples.

greater depths (e.g., 9-5-4 and 5, 10-4-5, and 20-4-9) are probably due to the presence of smectites and/or vermiculites which have higher CEC's than other clay minerals such as illite and kaolinite (Grim, 1968).

Mineralogical Relationships of the Residuum to Bedrock

Figure 23 illustrates general mineralogical changes that are associated with the weathering of siliceous and argillaceous Lower Knox Group dolostones. The bedrock minerals represent the original mineralogy, taking into account the minerals that are known to be present in these dolostones and similar dolostones in East Tennessee. Although this figure is speculative, it is intended to illustrate the kinds of mineralogical changes that have occurred during the formation of the residuum. It is meant to aid in the understanding of the weathering processes at West Chestnut Ridge.

BEDROCK MINERALS	RESIDUUM MINERALS
K-Spar and Albite	K and Na are released as soluble ions, some of which go into clay minerals, especially illite and mixed-layer clays. Al and Si go into newly formed clays such as kaolinite. Some Si may go into chert fraction.
Illite Kaolinite Minor Clays: Smectite Chlorite Vermicluite	These minerals accumulate in the insoluble fraction; however, even original clays are subject to weathering. Soluble ions (K, Na, Ca, and Mg) are leached out. Amorphous Al-hydroxides and oxyhydroxides remain behind. Hydroxy-interlayered vermiculite (HIV) is present in near-surface samples as a result of intense weathering of illite, becoming vermiculite at depths below the soil horizon.
Minor Minerals: Hematite Goethite Ilmenite Rutile Apatite Chromite Zircon	Fe-bearing minerals oxidize and hydrolyze to form Fe oxyhydroxides and hydroxides such as geothite, hematite, maghemite, etc. Minor minerals such as ilmenite, rutile, apatite, zircon, etc. accumulate in the insoluble residue and/or release ions that are adsorbed by clay minerals.

Figure 23. Mineralogical changes associated with weathering of siliceous and argillaceous Lower Knox Group dolostones.

CHAPTER VI

SUMMARY AND SUGGESTIONS FOR FURTHER RESEARCH

Summary

The nature of the residuum developed on top of the Copper Ridge and Chepultepec Formations of the Knox Group at West Chestnut Ridge, Oak Ridge, Tennessee has been investigated. Physical, mineralogical, and geochemical analyses of 55 residuum and 14 Lower Knox Group bedrock samples (from 10 kilometers away) were used to characterize the weathering behavior of siliceous and argillaceous dolostones.

Lower Knox Group lithologies at the West Chestnut Ridge site are dominated by cherty dolostones with fewer beds of limestone, shale, and sandstone. The bedrock has weathered to form an overlying mantle of clay- and chert-rich residuum and soils that thicken to 30 meters or more on ridge tops.

Samples were available from seven cores (9, 10, 11, 12, 16, 19, and 20) at various depths over an interval of one to 30 meters. Minerals in the residuum include illite, kaolinite, quartz, hydroxy-interlayered vermiculite, mixed-layer clays, amorphous iron-, manganese-, and aluminum-oxides and oxyhydroxides, as well as gibbsite, hematite, goethite, feldspars, dolomite, and calcite.

Mineralogical and chemical analyses of the residuum suggest a discontinuity at a depth of approximately 15 meters in the two most complete cores (9 and 16) overlying the Copper Ridge Formation. Above approximately 15 meters, the residuum has been more extensively leached, while at depths greater than 15 meters the composition of the residuum more closely reflects the character of the original parent bedrock. Based on the chemical analyses, two zones identified in the residuum can be shown to be independent populations using the t-test: (1) an upper, more thoroughly leached zone generally free of detrital feldspars and carbonates; and (2) a lower zone of accumulation in which traces of feldspars and carbonates are still present.

Chemical compositions of available bedrock samples were compared with chemical compositions of the residuum to obtain an approximation of the extent of the changes that have taken place during the weathering process. Upon examination of the data, several elements (such as K, Na, Ti, and Mn) appear to have been enriched during the weathering process; however, when the relative weight percentages of these elements are compared, it is apparent that they have been removed from the system. Only Fe, Al, and perhaps P have been concentrated in the residuum. These elements appear to have been leached from the upper zones and concentrated in the lower zone of accumulation. Ca is the most mobile element and was almost completely removed by

solutional processes. Mg is also soluble, but some Mg was also retained in clay minerals. For purposes of comparison, SiO_2 is assumed to have been neither added to nor removed from the system. It was retained in the residuum in the form of relatively insoluble quartz (mostly in the sand- and silt-size fractions), chert fragments (in the gravel-, sand-, and silt-size fractions), and in clay minerals.

Ionic adsorption capacities (CEC's and AEC's) of clay minerals are dependent on many factors such as the clay mineral species present, the pH of the weathering environment (the soils and residuum at West Chestnut Ridge are acidic), the amount of clay surface areas (estimated from particle size distribution analyses), and the amount of amorphous oxides, oxyhydroxides, and organics. Correlation coefficients indicate there are direct, dependent relationships between CEC's and pH (in distilled water), and CEC's and percentages of the clay-size fractions.

In the event radionuclides are buried at the West Chestnut Ridge site in the future, the soils and residuum could come in contact with the waste leachate. As a result, this study is important for the understanding of the weathering behavior of the residuum overlying the siliceous and argillaceous dolostones of the Lower Knox Group. This information will provide a basis for the interpretation of future hydrologic and chemical investigations of the site.

Suggestions for Further Research

Suggestions for further research include the following. (1) Analyses of a more complete suite of samples from the surface to bedrock would better represent the weathering profile. (2) Chemical analyses of the same elements in both the residuum and roughly correlative bedrock would permit comparison of those elements for which data were not available. (3) More detailed analyses of minor and trace elements might make it possible to determine whether or not a type of "chemical stratigraphy" exists. (4) Carefully controlled dissolution of carbonate bedrock samples for analyses of the original clays present in the unweathered bedrock would make it possible to compare parental clays with those clays in the residuum.

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APPENDIXES

APPENDIX A

STANDARD CALIBRATION ERRORS FOR CLAYS AND LIMDOL PROTOCOLS

Table A1. Standard calibration and mean counting errors for CLAYS and LIMDOL protocols.

	CLAYS		LIMDOL	
Element/Oxide	Standard Error of Calibration (%)	Mean Counting Error (%)	Standard Error of Calibration (%)	Mean Counting Error (%)
Na_2O	0.24	0.083	0.02	0.012
MgO	0.16	0.027	0.21	0.170
Al_2O_3	0.21	0.044	0.17	0.052
SiO_2	0.29	0.074	0.09	0.046
P_2O_5	0.0087	0.0052	0.0172	0.0070
S	0.0094	0.0021	0.0091	0.0024
K_2O	0.05	0.01	0.02	0.005
CaO	0.07	0.015	0.31	0.050
TiO_2	0.023	0.006	0.009	0.005
Cr	0.0041	0.0006	-	-
MnO	0.0083	0.0010	0.0055	0.0013
Fe_2O_3	0.10	0.006	0.03	0.015
Ba	0.0082	0.0038	-	-
Rb	0.0010	0.0003	-	-
Sr	0.0013	0.0003	0.0013	0.0005
Zr	0.0014	0.0004	-	-
Cl	-	-	1.22548	0.02266
Br	-	-	0.00020	0.00010

APPENDIX B

EXAMPLES OF THE DETERMINATION OF CEC'S AND AEC'S

EXAMPLE OF THE DETERMINATION OF CEC'S USING SAMPLE 9-2A-2

(A) Wt.% Barium (Untreated) = 0.03398 gm

(B) Wt.% Barium (Treated) = 1.05660 gm

(C) Dehydrated Sample Wt. = 4.91 gm

(D) Wt. Entrained 0.002M $BaCl_2 \cdot H_2O$ = 15.34 gm

(E) Wt. Barium in Untreated Sample:

(4.91)(0.03398)/100 = 0.001168 gm

(F) Wt. Barium in Treated Sample:

(4.91)(1.05660)/100 = 0.051879 gm

(G) Entrained Barium:

137.34 gm Ba/1 mole Ba * 1 mole Ba/1 mole $BaCl_2$ *

0.002 mole $BaCl_2$/1000 ml sol. * 1 ml sol./1 gm sol. *

15.34 gm = 0.004214 gm

(H) Adsorbed Barium:

(0.051879 - 0.004214) - 0.001668 = 0.04600 gm Ba/4.84 gm

(I) CEC:

1 meq/68.67 gm Ba * 1000 mg Ba/1 gm Ba *

0.04600 gm Ba/4.91 gm sample * 100 = 13.64 meq/100 gm

EXAMPLE OF THE DETERMINATION OF AEC'S USING SAMPLE 20-3-5

(A) Wt.% Chlorine (Untreated) = 0.00 gm

(B) Wt.% Chlorine (Treated) = 0.15848 gm

(C) Dehydrated Sample Wt. = 4.93 gm

(D) Wt. Entrained 0.002M $BaCl_2 \cdot H_2O$ = 13.36 gm

(E) Wt. Chlorine in Untreated Sample:

(4.93)(0.00)/100 = 0.00 gm

(F) Wt. Chlorine in Treated Sample:

(4.93)(0.15848)/100 = 0.007813 gm

(G) Entrained Chlorine:

70.90 gm Cl_2/1 mole Cl2 * 2 moles Cl_2/1 mole BaCl2

* 0.002 moles $BaCl_2$/1000 ml sol. * 1 ml sol./1 gm sol.

* 13.36 gm = 0.0037888 gm

(H) Adsorbed Chlorine:

(0.007813 - 0.0037888) - 0.00 = 0.0040242 gm Cl_2/4.93 gm

(I) AEC:

1 meq/35.45 mg Cl_2 * 1000 mg Cl_2/1 gm Cl_2 *

0.0040242 gm Cl_2/4.93 gm sample * 100 = 2.30 meq/100 gm

APPENDIX C

ANALYSES PERFORMED (INDICATED WITH AN X)

ON THE 55 RESIDUUM SAMPLES

ANALYSES PERFORMED (INDICATED WITH AN X) ON THE 55 RESIDUUM SAMPLES

Sample	Depth (m)	Physical Descriptions	Bulk (<2mm) Mineralogical Analyses	Clay (<2um) Mineralogical Analyses		Bulk (<2mm) Chemical Analyses	Ionic Adsorption Capacities	pH Values
					Glycol/Heat			
9-1A-1	1.19	X		X	X	X	X	X
9-2A-2	4.08	X		X		X	X	X
9-4A-3	10.33	X		X		X	X	X
9-5-4	13.41-13.54	X		X		X	X	X
9-5-5	13.54-13.87	X	X	X		X	X	X
9-6-6	16.66-16.74	X		X		X		
9-6-7	16.74-16.92	X	X	X		X		
9-6A-8	17.02	X		X		X		
9-7-9	19.72-19.90	X		X		X		
9-7-10	19.90-19.96	X	X	X	X	X		
9-8-11	22.39-22.58	X	X	X		X		
9-8-12	22.58-22.65	X		X	X	X		
9-8-13	22.65-22.75	X		X	X	X		
9-8-14	22.75-23.01	X	X	X	X	X		
9-9-15	25.62-25.74	X	X	X	X	X		
9-9-16	25.74-26.06	X	X	X	X	X		
9-10A-17	28.56	X	X	X	X	X		
9-10C-18	28-80	X	X	X	X	X		
16-1-1	2.14-2.29	X		X	X	X	X	X
16 2A-2	5.85	X		X	X	X	X	X
16-3-3	9.45-9.69	X		X		X		
16-4-4	13.33-13.45	X		X		X	X	X
16-4-5	13.45-13.69	X		X		X	X	X
16-5-6	17.21-17.29	X	X	X		X		
16-5-7	17.29-17.46	X		X		X		
16-5-8	17.46-17.52	X		X		X		
16-5-9	17.52-17.58	X		X		X		
16-5-10	17.58-17.65	X		X		X		
16-6-11	21.23-21.36	X	X	X		X		
16-6-12	21.36-21.47	X		X		X		
16-6-13	21.47-21.54	X		X		X		
16-6-14	21.54-21.60	X	X	X		X		
16-6-15	21.60-21.79	X	X	X	X	X		
16-7A-16	25.39	X	X	X	X	X		
16-7B-17	25.54	X	X	X	X	X		
16-7C-18	25.73	X	X	X	X	X		
16-8A-20	29.50	X	X	X	X	X		
16-8B-21	29.69	X	X	X	X	X		
16-8C-22	29.87	X	X	X	X	X		
10-2C-3	6.37	X	X	X	X	X	X	X
10-4-5	10.62-10.81	X	X	X	X	X	X	X
10-5-7	14.49-14.63	X	X	X	X	X		
11-3-4	9.70-9.82	X	X	X		X	X	X
11-5-12	17.66-17.83	X	X	X		X		
11-7B-17	25.66	X	X	X		X		
12-3D-10	7.71	X	X	X	X	X	X	X
12-8B-14	22.52	X	X	X	X	X		
12-9B-16	25.66	X	X	X	X	X		
19-3-4	7.43-7.56	X	X	X		X	X	X
19-4-7	10.49-10.64	X	X	X		X	X	X
19-5-11	13.71-13.87	X	X	X		X	X	X
19-6-13	16.68-16.79	X	X	X	X	X		
20-3-5	9.86-10.06	X	X	X	X	X	X	X
20-4-9	14.08-14.33	X	X	X	X	X	X	X
20-7-13	25.67-26.21	X	X	X	X	X		

APPENDIX D

DESCRIPTIONS OF GRAVEL FRACTIONS FOR THE 55 RESIDUUM SAMPLES

DESCRIPTIONS OF GRAVEL FRACTIONS FROM CORE 9

Sample	Color/Size	Chert Types	Quartz Grains	Fe/Mn Nodules	Miscellaneous
9-1A-1	Light to dark grey; stained pale- to dark-orange; 2-20mm	Massive, porous, oolitic, banded.	Authigenic qtz. clusters.	Both as stains and grains.	Cherts both altered and fresh; one severely altered is releasing unaltered qtz. grns.
9-2A-2	Light grey; stained yellowish-orange; 2-28mm.	Massive, porous, oolitic.	None.	None.	Cherts mainly altered; some drusy crystals on chert surfaces; larger grns. are oolitic conglomerates altered to SiO_2.
9-4A-3	Grey to very dark orange; 2-30mm.	Massive, porous, porcelaneous, oolitic, banded.	Authigenic qtz. clusters.	Both as stains and grains.	Cherts relatively fresh; some altered; some drusy crystals on chert surfaces; altered cherts have Fe/Mn crystals.
9-5-4	Light- to Bluish-grey; stained pale orange; 2-37mm.	Massive, porous, porcelaneous, oolitic, banded, dolomoldic.	"	"	Cherts both altered and fresh; some cherts are qtz. pebble conglomerates; drusy crystals on cherts.
9-5-5	Light- to Bluish-grey; stained pale to dark orange; 2-55mm.	Massive, porous, oolitic, banded.	None	"	Cherts both altered and fresh; some drusy crystals on chert surfaces.
9-6-6	Bluish- to Light-grey; stained dark orange to black; 2-30mm.	Massive, porous, banded, dolomoldic, porcelaneous.	None.	"	Cherts both altered and fresh; some Fe/Mn oxide chert conglomerates; altered cherts have Fe/Mn oxide crystals.
9-6-7	Light Bluish grey; stained yellowish to dark orange; 2-33mm.	Massive, porous, dolomoldic.	Authigenic qtz. clusters.	"	Cherts both altered and fresh; one pyrite (?) crystal; some drusy crystals on cherts; some Fe/Mn oxide chert conglomerates.
9-6A-8	Light- to Bluish-grey; a few slightly stained grains; 2-30mm.	Massive, porous, oolitic, banded, dolomoldic.	None.	"	Cherts bothe altered and fresh; some drusy crystals on chert surfaces.
9-7-9	Light- to Bluish-grey; stained pale yellowish orange; 2-70mm.	Massive, porous, banded, dolomoldic.	Authigenic qtz. clusters.	"	Cherts both altered and fresh.
9-7-10	Light grey; stained pale yellowish to dark orange; 2-40mm.	Massive, porous, banded, dolomoldic.	"	"	Cherts mainly altered; some drusy crystals on chert surfaces.
9-8-11	Light- to Bluish-grey; stained pale yellowish to orange 2-30mm.	Massive, porous, banded, dolomoldic.	"	"	Cherts both altered and fresh; some drusy crystals on chert surfaces.
9-8-12	Light- to Bluish-grey; stained pale yellowish to orange 2-22mm.	Massive, porous, banded, dolomoldic, oolitic, porcelaneous.	"	"	Cherts both altered and fresh.
9-8-13	Light- to Bluish-grey; stained pale yellowish to orange 2-25mm.	Massive, porous, banded, dolomoldic, oolitic, porcelaneous.	"	"	Cherts both altered and fresh.
9-8-14	Light- to Bluish-grey; stained pale yellowish to orange 2-17mm.	Massive, porous, banded, dolomoldic.	"	"	Cherts both altered and fresh.
9-9-15	Light- to Bluish-grey; stained pale yellowish to orange 2-19mm.	Massive, porous, banded, dolomoldic, porcelaneous.	"	"	Cherts both altered and fresh; some drusy crystals on chert surfaces.
9-9-16	Light grey; stained pale yellowish to orange; 2-14mm.	Massive, porous, dolomoldic.	"	"	Abundant siltstone/shale chips; very few chert grains; some dark drusy crystals on chert surfaces.
9-10A-17	Light- to Bluish-grey; stained pale yellowish orange to dark orange; 2-20mm.	Massive, porous, dolomoldic.	"	"	Cherts both altered and fresh; some drusy crystals on chert surfaces; a few siltstone/shale chips.
9-10C-18	Light- to Bluish-grey; stained pale yellowish orange to dark orange; 2-32mm.	Massive, porous, banded, dolomoldic.	None.	"	Cherts mostly fresh; some are altered.

DESCRIPTIONS OF GRAVEL FRACTIONS FROM CORE 16

Sample	Color/Size	Chert Types	Quartz Grains	Fe/Mn Nodules	Miscellaneous
16-1-1	Light grey; stained pale to dark orange; 2-40mm.	Massive, porous, oolitic, banded, dolomoldic, chalky.	Authigenic qtz. clusters.	Both stains and grains.	Cherts both fresh and altered; one chert grain appears to contain bright green, smaller crystals.
16-2A-2	Light to dark grey; stained pale orange; 2-28mm.	Massive, porous, oolitic, chalky.	"	"	Cherts both fresh and altered; a few individual oolites were released from oolitic chert conglomerates.
16-3-3	Light to dark grey; stained pale to dark orange; 2-55mm.	Massive, porous, oolitic, banded, dolomoldic, chalky, porcelaneous.	"	"	Cherts both fresh and altered; some drusy crystals on chert surfaces.
16-4-4	Light to dark grey; stained pale to dark orange; 2-35mm.	Massive, porous, oolitic, banded, dolomoldic, chalky, porcelaneous.	"	"	Cherts both altered and fresh; some drusy crystals on chert surfaces.
16-4-5	Light grey; stained pale yellowish to dark orange; 2-55mm.	Massive, porous, oolitic, dolomoldic, chalky.	"	"	Cherts both fresh and altered; some drusy crystals on chert surfaces.
16-5-6	Light grey; stained pale yellowish to dark orange; 2-22mm.	Massive, porous, oolitic, dolomoldic, porcelaneous.	"	Only as stains.	Cherts both fresh and altered; some drusy crystals on chert surfaces.
16-5-7	Light to dark grey; stained dark orange; 2-65mm.	Massive, porous, oolitic, banded, dolomoldic, chalky.	"	Both stains and grains.	Cherts both altered and fresh; some drusy crystals on chert surfaces; bands of oolites in massive cherts.
16-5-8	Light to dark grey; stained dark orange; 2-15mm.	Massive, porous, oolitic, dolomoldic, porcelaneous.	"	"	Cherts both fresh and altered; a few siltstone/shale chips are present.
16-5-9	Light to dark grey; stained dark orange; 2-5mm.	Massive, porous, oolitic, dolomoldic, chalky.	"	"	Cherts mostly altered; one chert grain has bright green crystals; a few siltstone/shale chips too.
16-5-10	Light to dark grey; stained dark orange; 2-6mm.	Massive, porous, dolomoldic	"	"	Cherts mostly altered.
16-6-11	Light to dark grey; stained pale yellowish to dark orange; 2-54mm.	Massive, porous, oolitic, banded, dolomoldic, chalky.	"	"	Cherts both altered and fresh; a few siltstone/shale chips are present.
16-6-12	Light to dark grey; stained pale yellowish to dark orange; 2-17mm.	Massive, porous, oolitic, dolomoldic.	"	"	Cherts both altered and fresh; abundant siltstone/shale chips.
16-6-13	Light to dark grey; stained pale yellowish to dark orange; 2-10mm.	Massive, porous, oolitic, dolomoldic, porcelaneous.	"	"	Cherts both altered and fresh; some drusy crystals on chert surfaces.
16-6-14	Light grey to tan brown; stained dark orange; 2-27mm.	Massive, porous, oolitic, dolomoldic.	"	"	Cherts both fresh and altered abundant siltstone/shale chips.
16-6-15	Light grey to tan brown; stained dark orange; 2-35mm.	Massive, porous.	"	"	Cherts both fresh and altered; abundant siltstone/shale chips.
16-7A-16	Light grey to tan brown; stained orange; 2-25mm.	Massive, porous, oolitic, dolomoldic.	"	"	Cherts both fresh and altered; abundant siltstone/shale chips.
16-7B-17	Light grey to tan brown; stained orange; 2-16mm.	Massive, porous, oolitic, dolomoldic.	"	"	Cherts both fresh and altered; abundant siltstone/shale chips.
16-7C-18	Light grey to tan brown; stained orange;2-12mm.	Massive, porous, oolitic, dolomoldic.	"	"	Cherts both fresh and altered; abundant siltstone/shale chips.
16-8A-20	Light grey; stained pale to dark orange; 2-65mm.	Massive, porous, oolitic.	"	"	Cherts both fresh and altered; some drusy crystals on chert surfaces; a few siltstone/shale chips.
16-8B-21	Light grey; stained pale to dark orange; 2-6mm.	Porous.	None.	Only stains.	Cherts mostly altered; a few siltstone/shale chips.
16-8C-22	Light grey; stained pale to dark orange; 2-14mm.	Massive.	None.	Only stains.	Cherts both fresh and altered.

DESCRIPTIONS OF GRAVEL FRACTIONS FROM CORES 10, 11, 12, 19, AND 20

Sample	Color/Size	Chert Types	Quartz Grains	Fe/Mn Nodules	Miscellaneous
10-2C-3	Light tan to brown;	None.	None.	Only grains.	All siltstone/shale chips.
10-4-5	Reddish brown to; dark grey; 2-9mm.	Massive, dolomoldic, chalcedonic.	"	"	Some altered cherts; abundant siltstone/shale chips.
10-5-7	Light to dark grey; stained orange; 2-20mm.	Massive, porous, dolomoldic.	"	"	Cherts both altered and fresh.
11-3-4	Light to dark grey; stained light to dark orange;2-26mm.	Massive, oolitic.	Authigenic qtz. clusters.	Both as stains and grains.	Cherts both fresh and altered.
11-5-12	Light grey; stained light to dark orange 2-15mm.	Massive, dolomoldic, porcelaneous, chalcedonic.	None.	"	Cherts both altered and fresh.
11-7B-17	Light to dark grey; stained dark orange; 2-36mm.	Massive, porous, banded, dolomoldic.	Authigenic qtz. clusters.	"	Cherts both altered and fresh; some drusy crystals on chert surfaces.
12-3D-10	Light to dark grey; stained pale yellowish to orange; 2-10mm.	Massive, porous, oolitic, dolomoldic, porcelaneous, chalky, conglomeratic.	None.	"	Cherts mostly altered; abundant Fe/Mn nodules.
12-8B-14	Light to dark grey; stained light orange 2-55mm.	Massive, oolitic, dolomoldic, porcelaneous.	"	"	Cherts both altered and fresh.
12-9B-16	Light to dark grey; stained light orange 2-23mm.	Massive, oolitic, chalcedonic.	"	"	Cherts both altered and fresh.
19-3-4	Light to dark grey; stained light to dark orange; 2-13mm.	Massive, porous, oolitic, dolomoldic.	"	Only stains.	Cherts both altered and fresh; few siltstone/shale chips.
19-4-7	Dark grey; stained orange; 2-26mm.	Massive, porous.	"	Both as stains and grains.	Cherts mostly altered; abundant Fe/Mn nodules.
19-5-11	Light to dark grey; stained light to dark orange; 2-33mm.	Massive, porous, banded, dolomoldic, porcelaneous.	Authigenic qtz. clusters.	"	Cherts both altered and fresh; some drusy crystals on chert surfaces.
19-6-13	Light to dark grey; stained light to dark orange; 2-45mm.	Massive, porous, oolitic, banded, dolomoldic, porcelaneous.	"	"	Cherts both fresh and altered.
20-3-5-	Light gey to white; stained pale yellowish orange; 2-35mm.	Massive, porous, oolitic, dolomoldic, porcelaneous, chalcedonic.	"	"	Cherts mostly altered; some drusy crystals on chert surfaces.
20-4-9	Light grey to tan brown;2-16mm.	Massive, porous, oolitic, dolomoldic, porcelaneous, chalcedonic.	"	"	Cherts mostly altered; some drusy crystals on chert surfaces; a few greenish siltstone/shale chips.
20-7-13	Light grey; stained light to dark orange 2-34mm.	Massive, porous, dolomoldic porcelaneous.	None.	"	Cherts mostly altered; some drusy crystals on chert surfaces; a few greenish siltstone/shale chips.

APPENDIX E

DESCRIPTIONS OF SAND FRACTIONS FOR THE 55 RESIDUUM SAMPLES

DESCRIPTIONS OF SAND FRACTIONS FROM CORE 9.

Sample	Color	Quartz Grains	Fe/Mn Nodules	Miscellaneous
9-1A-1	Variable; light to dark brown; light to dark orange.	Rounded, subangular; frosted, clear, milky.	Few grains.	Mostly weathered; almost all siltstone grains, and conglomerates of silt, qtz., chert grains, and Fe/Mn nodules.
9-2A-2	Light to dark orange to white; few dark grains.	Angular to subangular; frosted, clear, milky.	Abundant.	Mostly weathered; mostly chert grains; some qtz; a few siltstone chips.
9-4A-3	Light orange to white; some dark grains.	Rounded to subrounded; frosted, clear, milky.	Same as above.	Relatively clean and fresh.
9-5-4	Same as above.	Rounded to angular; frosted, clear, milky.	Same as above.	Same as above.
9-5-5	Same as above.	Same as above.	Same as above.	Same as above.
9-6-6	Same as above; abundant dark grains.	Same as above.	Same as above.	Abundant weathered Fe/Mn nodules.
9-6-7	Same as above.	Same as above.	Same as above.	Same as above.
9-6A-8	Same as above.	Same as above.	Same as above.	Same as above.
9-7-9	Same as above.	Same as above.	Same as above.	Same as above.
9-7-10	Same as above.	Same as above.	Same as above.	Same as above.
9-8-11	Light to dark brown to white; abundant dark grains.	Same as above.	Same as above.	Same as above.
9-8-12	Light to dark orange light to dark brown to white; some dark grains.	Same as above.	Same as above.	Both fresh and weathered; abundant silty grains; a few qtz. and chert
9-8-13	Same as above.	Same as above.	Same as above.	Same as above with more abundant silty grains.
9-8-14	Same as above.	Same as above.	Same as above.	Abundant silty grains and Fe/Mn nodules; few chert grains.
9-9-15	Same as above.	Same as above.	Same as above.	Few silty grains; some poorly cemented.
9-9-16	Same as above.	Same as above.	Same as above.	Abundant silty grains; few chert grains and quartz.
9-10A-17	Light orange to white; some dark grains.	Same as above.	Same as above.	Relatively clean and fresh; few silty grains.
9-10C-18	Same as above.	Same as above.	Same as above.	Same as above.

DESCRIPTIONS OF SAND FRACTIONS FROM CORE 16

Sample	Color	Quartz Grains	Fe/Mn Nodules	Miscellaneous
16-1-1	Light orange to white; few dark grains.	Rounded to subrounded; frosted, clear, milky.	Few grains.	Relatively clean and fresh; some weathered; abundant quartz.
16-2A-2	Same as above.	Same as above.	Same as above.	Same as above; some cherts with oolites; more chert grains than quartz.
16-3-3	Same as above.	Same as above.	Same as above.	Relatively clean and fresh; few silty grains.
16-4-4	Same as above.	Angular to rounded; frosted, clear.	Same as above.	Relatively clean and fresh; some oolitic cherts; few silty grains.
16-4-5	Light to dark orange to white; some dark grains.	Same as above; plus milky.	Same as above.	Mostly weathered; few silty grains.
16-5-6	Same as above.	Same as above.	Same as above.	Same as above; with abundant silty grains and silty conglomerates.
16-5-7	Same as above.	Same as above.	Same as above.	Same as above.
16-5-8	Same as above.	Same as above.	Same as above.	Same as above.
16-5-9	Same as above.	Same as above.	Same as above.	Both fresh and weathered; few silty grains.
16-5-10	Same as above.	Same as above.	Same as above.	Weathered; few silty grains.
16-6-11	Same as above.	Same as above.	Same as above.	Abundant silty grains and silty conglomerates.
16-6-12	Same as above.	Same as above.	Same as above.	Same as above.
16-6-13	Light to dark orange to yellowish brown to white; few dark grains.	Rounded to subrounded; frosted, clear.	Same as above.	Both weathered and fresh; abundant Same as above.
16-6-14	Same as above.	Same as above.	Same as above.	Same as above; with more chert grains and some oolitic cherts.
16-6-15	Same as above.	Same as above.	Same as above.	Mostly silty grains and Fe/Mn nodules; few quartz and chert grains.
16-7A-16	Same as above.	Same as above.	Same as above.	Same as above; with more chert grains and some oolitic cherts.
16-7B-17	Light to dark orange some dark grains.	Same as above.	Same as above.	Abundant silty grains and silty conglomerates.
16-7C-18	Dark orange to dark brown.	Same as above.	Same as above.	Same as above.
16-8A-20	Same as above.	Same as above.	Same as above.	Same as above; but fewer silty grains; more quartz and chert grains.
16-8B-21	Light orange to white;few dark grains.	Rounded to angular; frosted, clear, milky.	Same as above.	Both deeply weathered and fresh.
16-8C-22	Same as above.	Same as above.	Same as above.	Same as above.

DESCRIPTIONS OF SAND FRACTIONS FROM CORES 10, 11, 12, 19, AND 20

Sample	Color	Quartz Grains	Fe/Mn Nodules	Miscellaneous
10-2C-3	Yellowish brown to light orange; few dark grains.	Rounded and angular; frosted, clear.	Abundant.	Weathered; few quartz grains.
10-4-5	Same as above.	Same as above; plus milky.	Same as above.	Both weathered and fresh; few quartz grains.
10-5-7	Light to dark brown to white; some dark grains.	Same as 10-2C-3.	Same as above.	Same as above.
11-3-4	Light to dark orange light yellowish to dark brown to white; some dark grains.	Same as 10-4-5.	Same as above.	Same as above; abundant chert grains.
11-5-12	Same as above.	Subrounded to angular; frosted, clear, milky.	Same as above.	Same as above.
11-78-17	Same as above.	Same as above.	Same as above.	Relatively clean and fresh; abundant quartz grains.
12-30-10	Same as above.	Rounded to angular; frosted, clear.	Same as above.	Weathered; abundant Fe/Mn oxides and chert grains.
12-88-14	Same as 11-3-4.	Subrounded to angular; frosted, clear, milky.	Same as above.	Relatively clean and fresh.
12-98-16	Light orange to yellowish brown to white.	Same as above.	Same as above.	Both fresh and altered; some oolitic cherts.
19-3-4	Light to dark orange to white; some dark grains.	Same as above.	Same as above.	Weathered and fresh; mostly silty grains.
19-4-7	Orange to yellowish brown to white; some dark grains.	Rounded to angular; frosted, clear, milky.	Same as above.	Same as above.
19-5-11	Same as above.	Same as above.	Same as above.	Weathered; abundant cherts.
19-6-13	Same as above.	Same as above.	Same as above.	Same as above.
20-3-5	White to light yellowish brown; some dark grains.	Same as above.	Same as above.	Relatively clean and fresh; some green silty grains; some oolitic cherts.
20-4-9	Same as above.	Same as above.	Same as above.	Same as above; no oolitic cherts.
20-7-13	Light orange to light brown to white; few dark grains.	Same as above.	Same as above.	Weathered and fresh; abundant quartz and chert grains; some green silty grains.

APPENDIX F

ERROR RANGES FOR I/K RATIOS AND SHARPNESS RATIOS FOR SAMPLES FROM CORES 9 AND 16

ERROR RANGES FOR I/K RATIOS AND SHARPNESS RATIOS FOR SAMPLES FROM CORES 9 AND 16

Sample	I/K Ratio	Range of Error	Length of Error Bar	Sharpness Ratio		Range of Error		Length of Error Bar	
				Illite	Kaolinite	Illite	Kaolinite	Illite	Kaolinite
9-1A-1	0.53	0.44-0.64	0.20	7.00	26.33	5.69-8.55	21.14-33.60	2.86	12.46
9-2A-2	0.54	0.45-0.64	0.19	17.20	26.67	12.67-24.00	21.43-34.00	11.33	12.57
9-4A-3	0.46	0.38-0.55	0.17	20.50	29.67	14.40-30.67	24.00-37.60	16.27	13.60
9-5-4	0.50	0.35-0.68	0.33	5.75	13.14	4.00-8.00	10.25-17.00	4.00	6.75
9-5-5	0.41	0.34-0.49	0.15	13.33	32.33	10.00-18.00	26.29-40.80	8.00	14.51
9-6-6	0.51	0.41-0.62	0.21	12.33	48.67	9.14-16.80	34.00-78.00	7.66	44.00
9-6-7	0.61	0.48-0.76	0.28	9.71	28.00	7.25-13.00	20.40-40.67	5.75	20.27
9 6A-8	0.57	0.41-0.76	0.35	13.00	18.40	8.40-20.67	13.67-25.50	12.27	11.83
9-7-9	0.51	0.39-0.65	0.34	9.67	19.00	6.86-13.60	14.86-24.80	6.74	9.94
9-7-10	0.81	0.68-0.97	0.29	14.86	21.33	11.75-19.00	16.86-27.60	7.25	10.74
9-8-11	0.60	0.44-0.80	0.36	10.80	12.86	7.33-16.00	10.00-16.67	8.67	6.67
9-8-12	0.38	0.31-0.46	0.15	12.00	31.33	8.86-16.40	25.43-39.60	7.54	14.17
9-8-13	0.57	0.49-0.66	0.17	20.80	26.00	15.67-28.50	21.50-32.00	12.83	10.50
9 8-14	1.22	1.03-1.46	0.43	18.57	9.64	15.00-23.33	8.00-11.60	8.33	3.60
9-9-15	0.29	0.20-0.40	0.20	6.33	26.00	4.00-9.60	20.00-35.00	5.60	15.00
9-9-16	1.65	1.18-2.39	1.21	19.00	3.54	13.20-28.67	3.00-4.00	15.47	1.00
9-10A-17	1.23	1.02-1.49	0.47	29.50	7.38	21.60-42.67	6.14-8.83	21.07	2.69
9-10C-18	0.36	0.24-0.50	0.26	4.75	15.14	3.11-6.86	12.00-19.33	3.75	7.33
16 1-1	0.33	0.23-0.45	0.22	5.00	20.00	3.33-7.14	15.71-26.00	3.81	10.29
16 2A-2	0.41	0.30-0.55	0.25	5.75	18.67	4.00-8.00	14.57-24.40	4.00	9.83
16-3-3	0.43	0.35-0.51	0.16	8.89	26.86	7.00-11.25	22.25-33.00	4.25	10.75
16-4-4	0.69	0.54-0.87	0.33	11.67	14.57	8.57-16.00	11.50-18.67	7.43	7.17
16-4-5	0.32	0.24-0.42	0.18	7.14	30.80	5.00-10.00	24.00-41.00	5.00	17.00
16-5-6	0.40	0.29-0.53	0.24	5.33	20.00	3.80-7.25	15.71-26.00	3.45	10.29
16-5-7	0.34	0.28-0.42	0.14	7.33	32.00	5.60-9.50	26.00-40.40	3.90	14.40
16-5-8	0.19	0.13-0.26	0.13	4.50	31.33	2.89-6.57	25.43-39.60	3.68	14.17
16-5-9	0.42	0.31-0.54	0.23	10.40	15.50	7.00-15.50	12.67-19.14	8.50	6.47
16-5-10	0.46	0.36-0.57	0.21	11.00	20.57	8.00-15.20	16.75-25.67	7.20	8.92
16-6-11	0.94	0.76-1.16	0.40	13.14	8.91	10.25-17.00	7.33-10.80	6.75	3.47
16-6-12	0.55	0.43-0.68	0.25	11.33	15.50	8.29-15.60	12.67-19.14	7.31	6.47
16 6-13	0.43	0.30-0.59	0.29	7.33	14.57	4.86-10.80	11.50-18.67	5.94	7.17
16-6-14	0.38	0.30-0.48	0.18	8.57	31.20	6.25-11.67	24.33-41.50	5.42	17.17
16-6-15	1.71	1.24-2.42	1.18	13.67	3.20	10.29-18.40	2.38-4.14	8.11	1.76
16 7A-16	0.37	0.30-0.45	0.15	8.25	29.67	6.22-10.86	24.00-37.60	4.64	13.60
16 7B-17	0.33	0.24-0.44	0.20	4.00	22.00	2.83-5.40	17.43-28.40	2.57	10.97
16 7C-18	0.26	0.15-0.33	0.18	2.36	20.00	1.33-3.60	15.00-27.50	2.27	12.50
16-8A-20	0.34	0.29-0.44	0.15	6.40	29.67	4.91-8.22	24.00-37.60	3.31	13.60
16 8B-21	0.28	0.16-0.42	0.26	2.55	16.67	1.50-3.80	12.86-22.00	2.30	9.14
16 8C-22	0.28	0.22-0.35	0.13	7.00	33.33	5.11-9.43	27.14-42.00	4.32	14.86

APPENDIX G

BULK CHEMICAL ANALYSES OF THE 55 RESIDUUM SAMPLES

CHEMICAL ANALYSES OF THE <2MM (SAND, SILT, AND CLAY) FRACTIONS FOR SAMPLES FROM ALL CORES

Sample	Na_2O(%)	CaO(%)	SiO_2(%)	Al_2O_3(%)	Fe_2O_3(%)	MgO(%)	K_2O(%)
9-1A-1	0.45	1.23	57.85	19.52	6.39	1.58	4.49
9-2A-2	-[a]	-	60.90	22.91	5.99	0.86	1.34
9-4A-3	0.60	-	77.09	11.91	4.03	0.55	0.60
9-5-4	0.21	0.01	68.55	15.43	6.83	0.82	0.99
9-5-5	0.47	-	69.89	16.63	6.39	0.82	1.06
9-6-6	0.57	0.06	75.72	6.96	4.99	0.91	0.90
9-6-7	0.38	0.02	72.61	10.09	8.11	1.03	1.14
9-6A-8	0.24	-	72.37	13.50	6.43	0.81	0.95
9-7-9	0.41	0.01	70.61	12.23	8.02	0.92	1.03
9-7-10	0.47	0.05	67.67	13.52	9.03	0.77	0.69
9-8-11	0.21	0.08	65.08	15.67	9.11	1.00	1.08
9-8-12	0.06	0.10	62.10	19.43	8.04	1.11	1.54
9-8-13	0.13	0.13	56.27	21.14	10.22	1.34	1.89
9-8-14	0.63	0.13	57.01	21.85	5.83	1.33	2.60
9-9-15	0.38	0.19	64.48	20.50	5.37	1.23	3.20
9-9-16	0.57	0.21	66.29	18.04	4.29	1.24	5.23
9-10A-17	0.89	0.24	68.51	17.25	4.01	1.28	4.16
9-10C-18	0.22	0.07	64.42	18.73	5.82	1.06	1.58
16-1-1	0.38	-	79.17	11.49	4.01	0.72	1.04
16-2A-2	0.19	-	82.07	9.30	3.83	0.70	0.87
16-3-3	0.26	-	78.89	11.62	3.87	1.04	1.49
16-4-4	0.15	-	80.84	10.55	3.70	0.92	1.37
16-4-5	-	-	73.76	14.53	4.96	0.98	1.33
16-5-6	0.38	-	73.14	14.60	5.03	0.83	1.21
16-5-7	0.27	-	74.95	13.34	4.61	0.91	1.26
16-5-8	0.32	-	71.38	16.04	5.10	0.81	1.31
16-5-9	0.41	-	70.94	15.92	4.99	0.99	1.24
16-5-10	0.45	-	76.79	12.21	3.75	0.93	1.15
16-6-11	0.08	-	72.81	13.92	4.51	1.13	1.68
16-6-12	0.24	-	69.75	16.80	5.22	1.10	1.67
16-6-13	0.10	-	69.41	16.79	4.77	0.93	1.59
16-6-14	0.17	-	71.83	15.52	4.11	0.92	1.45
16-6-15	0.17	0.11	70.21	15.75	4.15	1.61	4.13
16-7A-16	0.35	0.03	67.91	17.05	5.56	1.00	2.19
16-7B-17	0.33	0.13	70.23	15.50	4.79	1.30	4.04
16-7C-18	0.26	0.11	62.62	20.24	6.54	1.13	3.03
16-8A-20	-	0.10	64.90	18.68	6.05	1.26	2.47
16-8B-21	0.20	0.10	67.75	17.39	5.82	1.05	1.98
16-8C-22	-	0.11	69.62	16.76	5.68	1.03	2.08
10-2C-3	-	-	66.01[b]	15.23	4.37	0.84	1.58
10-4-5	-	0.17	53.61	22.80	5.82	2.05	4.66
10-5-7	-	0.07	77.97	8.63	2.37	0.76	2.72
11-3-4	-	-	73.42	10.32	5.85	0.89	1.90
11-5-12	-	-	73.37	11.42	4.35	0.45	1.36
11-7B-17	-	0.02	60.33	18.87	8.34	1.26	1.63
12-3D-10	-	-	71.60	13.16	4.51	0.77	1.82
12-8B-14	-	-	75.52	8.90	3.84	0.61	1.75
12-9B-16	-	-	78.80	7.57	3.74	0.45	1.39
19-3-4	-	-	68.26	16.33	4.66	0.44	1.00
19-4-7	-	-	71.77	12.67	4.84	0.53	1.36
19-5-11	-	-	69.54	14.43	4.91	0.73	1.62
19-6-13	-	0.03	64.89	17.24	6.10	0.88	1.50
20-3-5	-	-	71.36	13.79	2.30	0.42	1.66
20-4-9	-	0.15	72.53	13.06	2.87	0.69	2.67
20-7-13	-	0.31	62.91	17.36	6.76	1.53	2.52

[a] Concentration too low to be detected by XRF.
[b] Values are averages of two XRF runs. Includes all values for cores 10, 11, 12, 19, and 20.

Note The protocol also analysed for sulfur (S), but there were only two samples containing detectable amounts. Sample 9-10A-17 contains 6ppm, and sample 9-9-15 contains 7ppm.

CHEMICAL ANALYSES OF THE <2MM (SAND, SILT, AND CLAY) FRACTIONS FOR SAMPLES FROM ALL CORES

Sample	MnO(%)	P_2O_5(%)	TiO_2(%)	Ba(ppm)	Cr(ppm)	Rb(ppm)	Sr(ppm)	Zr(ppm)
9-1A-1	0.17	0.19	0.53	439	105	123	71	117
9-2A-2	0.02	0.04	0.90	340	100	69	57	132
9-4A-3	0.08	0.02	0.58	307	110	46	55	182
9-5-4	0.14	0.07	0.62	452	73	66	51	57
9-5-5	0.15	0.08	0.61	359	85	61	52	58
9-6-6	0.79	0.13	0.11	511	43	62	47	-[a]
9-6-7	0.25	0.15	0.48	523	33	72	49	12
9-6A-8	0.13	0.07	0.55	441	79	62	50	41
9-7-9	0.16	0.11	0.56	514	63	69	49	7
9-7-10	0.11	0.09	0.63	533	45	61	47	10
9-8-11	0.16	0.09	0.66	630	47	76	50	12
9-8-12	0.20	0.10	0.62	560	51	88	51	41
9-8-13	0.25	0.11	0.64	577	29	105	48	13
9-8-14	0.56	0.09	0.26	605	68	110	50	52
9-9-15	0.23	0.12	0.43	322	136	89	53	63
9-9-16	0.21	0.15	0.35	363	142	100	52	59
9-10A-17	0.24	0.15	0.32	364	177	89	52	61
9-10C-18	0.23	0.09	0.50	374	103	80	54	74
16-1-1	0.02	0.02	0.49	432	125	50	50	99
16-2A-2	0.04	0.02	0.40	349	135	44	47	53
16-3-3	0.02	0.03	0.51	339	118	60	46	96
16-4-4	0.03	0.02	0.45	345	130	58	47	79
16-4-5	0.04	0.05	0.59	416	126	62	46	73
16-5-6	0.03	0.07	0.59	367	119	61	48	66
16-5-7	0.08	0.05	0.49	384	123	59	47	71
16-5-8	0.06	0.04	0.58	386	115	66	78	135
16-5-9	0.12	0.08	0.51	385	141	62	48	73
16-5-10	0.17	0.04	0.35	435	145	57	48	87
16-6-11	0.26	0.07	0.36	471	145	71	46	57
16-6-12	0.13	0.08	0.52	526	148	75	50	82
16-6-13	0.16	0.08	0.44	493	148	67	51	67
16-6-14	0.22	0.05	0.34	492	155	65	53	59
16-6-15	0.20	0.10	0.36	500	158	101	62	163
16-7A-16	0.15	0.09	0.47	461	120	89	58	85
16-7B-17	0.07	0.11	0.43	498	140	91	52	77
16-7C-18	0.08	0.10	0.63	486	137	97	54	91
16-8A-20	0.13	0.08	0.55	463	130	96	54	88
16-8B-21	0.09	0.07	0.61	460	102	86	52	98
16-8C-22	0.09	0.06	0.60	485	124	86	53	100
10-2C-3	0.30[b]	-	0.47	466	120	98	49	250
10-4-5	0.14	-	0.62	413	125	160	47	130
10-5-7	0.37	-	0.26	311	125	92	43	78
11-3-4	0.10	-	0.55	547	87	74	44	47
11-5-12	0.08	-	0.47	354	64	59	47	49
11-7B-17	0.13	-	0.71	634	53	91	50	70
12-3D-10	0.51	-	0.31	437	119	69	47	58
12-8B-14	0.77	-	0.20	252	90	61	46	57
12-9B-16	0.25	-	0.31	314	82	50	47	26
19-3-4	0.02	-	0.67	420	101	58	56	125
19-4-7	0.03	-	0.51	395	93	63	49	49
19-5-11	0.35	-	0.38	396	110	75	48	54
19-6-13	0.13	-	0.54	477	96	80	54	69
20-3-5	0.06	-	0.46	186	132	75	53	234
20-4-9	0.07	-	0.49	260	121	95	53	183
20-7-13	0.07	-	0.62	520	101	122	54	88

[a] Concentration too low to be detected by XRF.
[b] Values are averages of two XRF runs. Includes all values for cores 10, 11, 12, 19, and 20.

CHEMICAL ANALYSES OF THE BULK (GRAVEL, SAND, SILT, AND CLAY) AND <1/16MM (SILT AND CLAY) FRACTIONS FOR SAMPLES FROM ALL CORES

Sample	Na_2O(%)		CaO(%)		SiO_2(%)		Al_2O_3(%)		Fe_2O_3(%)		MgO(%)		K_2O(%)	
9-1A-1	0.42[a]	0.57[b]	1.14	1.55	53.87	45.70	18.15	24.60	5.94	8.05	1.47	1.99	4.18	5.66
9-2A-2	-[c]	-	-	-	44.73	56.03	16.72	24.97	4.37	6.53	0.63	0.94	0.98	1.46
9-4A-3	0.48	0.84	-	-	61.87	54.73	9.53	16.67	3.22	5.64	0.44	0.77	0.48	0.84
9-5-4	0.14	0.25	.01	0.01	46.26	56.21	10.34	18.67	4.58	8.26	0.55	0.99	0.66	1.20
9-5-5	0.25	0.54	-	-	37.51	60.80	8.81	19.12	3.39	7.35	0.43	0.94	0.56	1.22
9-6-6	0.25	0.99	0.03	0.10	33.13	43.92	2.99	12.04	2.15	8.63	0.39	1.57	0.39	1.56
9-6-7	0.27	0.54	0.01	0.03	52.56	51.55	7.26	14.23	5.84	11.44	0.74	1.45	0.82	1.61
9-6A-8	0.15	0.31	-	-	45.96	55.00	8.51	17.69	4.05	8.42	0.51	1.06	0.60	1.24
9-7-9	0.23	0.57	0.01	0.01	39.98	51.55	6.85	16.88	4.49	11.07	0.52	1.27	0.58	1.42
9-7-10	0.19	0.69	0.02	0.07	27.67	46.69	5.41	19.74	3.61	13.18	0.31	1.12	0.28	1.01
9-8-11	0.14	0.25	0.06	0.10	45.22	54.67	10.81	18.80	6.29	10.93	0.69	1.20	0.75	1.30
9-8-12	0.05	0.07	0.08	0.12	46.83	53.41	14.57	22.54	6.03	9.33	0.83	1.29	1.16	1.79
9-8-13	0.10	0.16	0.10	0.16	43.01	46.70	16.07	25.37	7.77	12.26	1.02	1.61	1.44	2.27
9-8-14	0.55	0.83	0.11	0.17	50.29	32.93	19.23	28.84	5.13	7.70	1.17	1.76	2.29	3.43
9-9-15	0.32	0.44	0.16	0.22	54.96	54.81	17.43	23.99	4.56	6.28	1.05	1.44	2.72	3.74
9-9-16	-	0.69	-	0.25	-	55.02	-	21.83	-	5.19	-	1.50	-	6.33
9-10A-17	0.77	1.01	0.21	0.27	59.73	60.97	15.01	19.49	3.49	4.53	1.11	1.45	3.62	4.70
9-10C-18	0.06	0.27	0.02	0.09	18.76	51.54	5.243	23.23	1.63	7.22	0.30	1.31	0.44	1.96
16-1-1	0.21	0.49	-	-	43.21	60.96	6.20	14.94	2.17	5.21	0.39	0.94	0.56	1.35
16-2A-2	0.09	0.32	-	-	39.10	49.24	4.37	15.62	1.80	6.43	0.33	1.18	0.41	1.46
16-3-3	0.14	0.38	-	-	43.84	53.65	6.39	17.20	2.13	5.73	0.57	1.54	0.82	2.21
16-4-4	0.08	0.23	-	-	43.32	53.35	5.59	16.14	1.96	5.66	0.49	1.41	0.73	2.10
16-4-5	-	-	-	-	30.83	53.11	5.96	20.20	2.03	6.89	0.40	1.36	0.55	1.85
16-5-6	0.25	0.49	-	-	47.89	56.32	9.49	18.98	3.27	6.54	0.54	1.08	0.79	1.57
16-5-7	0.18	0.34	-	-	49.07	59.21	8.674	16.81	3.00	5.81	0.59	1.15	0.82	1.59
16-5-8	0.30	0.44	-	-	67.16	52.11	15.08	21.97	4.79	6.99	0.76	1.11	1.23	1.79
16-5-9	0.40	0.50	-	-	69.54	58.88	15.60	19.26	4.89	6.04	0.88	1.09	1.22	1.50
16 5-10	0.45	0.61	-	-	76.03	56.82	12.09	16.48	3.71	5.06	0.92	1.26	1.14	1.55
16-6-11	-	0.10	-	-	-	58.98	-	17.12	-	5.55	-	1.39	-	2.07
16-6-12	-	0.28	-	-	-	59.29	-	19.82	-	6.16	-	1.30	-	1.97
16-6-13	0.10	0.15	-	-	68.04	46.50	16.45	25.02	4.67	7.11	0.91	1.39	1.56	2.37
16-6-14	-	0.30	-	-	-	40.94	-	27.32	-	7.23	-	1.62	-	2.55
16-6-15	-	0.27	-	0.18	-	43.53	-	25.36	-	6.68	-	2.59	-	6.65
16-7A-16	-	0.40	-	0.03	-	59.08	-	19.61	-	6.39	-	1.15	-	2.52
16-7B-17	-	0.35	-	0.14	-	66.72	-	16.43	-	5.08	-	1.38	-	4.28
16-7C-18	-	0.29	-	0.12	-	55.11	-	22.87	-	7.39	-	1.28	-	3.42
16-8A-20	-	-	0.08	0.11	49.56	60.36	14.20	19.99	4.60	6.47	0.96	1.35	1.88	2.64
16-8B-21	0.20	0.21	0.10	0.10	67.08	65.04	17.22	18.09	5.76	6.05	1.04	1.09	1.96	2.06
16-8C-22	-	-	0.11	0.12	68.93	66.14	16.59	17.60	5.62	5.96	1.02	1.08	2.06	2.18
10-2C-3	-	[d]	-		-[e]		-		-		-		-	
10 4-5	-		-		-		-		-		-		-	
10-5-7	-		0.06		71.81		7.94		2.18		0.70		2.50	
11-3-4	-		-		67.63		9.49		5.38		0.82		1.75	
11-5-12	-		-		71.20		11.08		4.22		0.44		1.32	
11-7B-17	-		0.01		42.53		13.21		5.84		0.88		1.14	
12-3D-10	-		-		70.19		12.90		4.42		0.75		1.78	
12-8B-14	-		-		53.91		6.32		2.73		0.43		1.24	
12-9B-16	-		-		65.57		6.28		3.10		0.37		1.15	
19-3-4	-		-		-		-		-		-		-	
19-4-7	-		-		68.94		12.16		4.65		0.51		1.31	
19 5-11	-		-		56.52		11.69		3.98		0.59		1.31	
19 6-13	-		0.01		29.11		7.59		2.68		0.39		0.66	
20-3-5	-		-		52.36		10.07		1.68		0.31		1.21	
20-4-9	-		0.15		71.10		12.80		2.81		0.68		2.62	
20-7-13	-		0.30		61.67		17.01		6.62		1.50		2.47	

[a] Recalculated data set #1. All size fractions (gravel, sand, silt, and clay).

[b] Recalculated data set #2. <1/16mm size fractions (silt and clay).

[c] Concentration too low to be detected by XRF.

[d] Values for the <1/16mm fractions were not calculated for samples from cores 10, 11, 12, 19, and 20.

[e] Values are averages of two XRF runs. Includes all values for cores 10, 11, 12, 19, and 20.

CHEMICAL ANALYSES OF THE BULK (GRAVEL, SAND, SILT, AND CLAY) AND <1/16MM (SILT AND CLAY) FRACTIONS FOR SAMPLES FROM ALL CORES

Sample	MnO(%)		P_2O_5(%)		TiO_2(%)		Ba(ppm)		Cr(ppm)		Rb(ppm)		Sr(ppm)		Zr(ppm)	
9-1A-1	0.16[a]	0.21[b]	0.18	0.24	0.49	0.67	408	553	98	132	114	155	66	89	109	147
9-2A-2	0.01	0.02	0.03	0.04	0.66	0.98	248	371	73	109	50	75	42	62	96	144
9-4A-3	0.06	0.11	0.02	0.03	0.46	0.81	246	430	88	154	37	64	44	77	146	255
9-5-4	0.10	0.17	0.05	0.08	0.42	0.75	303	547	49	88	44	80	34	62	38	69
9-5-5	0.08	0.17	0.04	0.09	0.32	0.70	190	413	45	98	32	70	28	60	31	67
9-6-6	0.34	1.37	0.06	0.22	0.05	0.19	220	884	18	74	27	107	20	81	-[c]	-
9-6-7	0.18	0.35	0.11	0.21	0.35	0.68	377	737	24	47	52	102	35	69	9	17
9-6A-8	0.08	0.17	0.04	0.09	0.35	0.72	278	578	50	103	39	81	32	66	26	54
9-7-9	0.09	0.22	0.06	0.15	0.31	0.77	288	709	35	87	39	95	27	68	4	10
9-7-10	0.04	0.16	0.04	0.13	0.25	0.92	213	778	18	66	24	89	19	69	4	15
9-8-11	0.11	0.19	0.06	0.11	0.46	0.79	435	756	32	56	52	91	35	60	8	14
9-8-12	0.15	0.23	0.08	0.12	0.47	0.72	420	650	38	59	66	102	38	59	31	48
9-8-13	0.19	0.30	0.08	0.13	0.49	0.77	439	692	22	35	80	126	36	58	10	16
9-8-14	0.49	0.74	0.08	0.12	0.23	0.34	532	799	60	90	97	145	44	66	46	69
9-9-15	0.20	0.27	0.10	0.14	0.37	0.50	274	377	116	159	76	104	45	62	54	74
9-9-16	-	0.25	-	0.18	-	0.42	-	439	-	172	-	121	-	63	-	71
9-10A-17	0.21	0.27	0.13	0.17	0.28	0.36	317	411	154	200	77	101	45	59	53	69
9-10C-18	0.23	0.29	0.09	0.11	0.50	0.62	105	464	29	128	22	99	15	67	21	92
16-1-1	0.01	0.03	0.01	0.03	0.26	0.64	233	562	68	163	27	65	27	65	53	129
16 2A-2	0.02	0.07	0.01	0.03	0.19	0.67	164	586	63	227	21	74	22	79	25	89
16-3-3	0.01	0.03	0.02	0.04	0.28	0.75	186	502	65	175	33	89	25	68	53	142
16-4-4	0.02	0.05	0.01	0.03	0.24	0.69	183	528	69	199	31	89	25	72	42	121
16-4-5	0.02	0.06	0.02	0.07	0.24	0.82	171	578	52	175	25	86	19	64	30	101
16-5-6	0.02	0.04	0.05	0.09	0.38	0.77	239	477	77	155	40	79	31	62	43	86
16-5-7	0.05	0.10	0.03	0.06	0.32	0.62	250	484	80	155	38	74	31	59	46	89
16-5-8	0.06	0.08	0.04	0.05	0.55	0.79	363	529	108	158	62	90	73	107	127	185
16-5-9	0.12	0.15	0.08	0.10	0.50	0.62	377	466	138	171	61	75	47	58	72	88
16-5-10	0.17	0.23	0.04	0.05	0.35	0.47	431	587	144	196	56	77	48	65	86	117
16 6-11	-	0.32	-	0.09	-	0.44	-	579	-	178	-	87	-	57	-	70
16-6-12	-	0.15	-	0.09	-	0.61	-	621	-	175	-	89	-	59	-	97
16-6-13	0.16	0.24	0.08	0.12	0.43	0.66	483	735	145	221	66	100	50	76	66	100
16-6-14	-	0.39	-	0.09	-	0.60	-	866	-	273	-	114	-	93	-	104
16-6-15	-	0.32	-	0.16	-	0.58	-	805	-	254	-	163	-	100	-	262
16-7A-16	-	0.17	-	0.10	-	0.54	-	530	-	138	-	102	-	67	-	98
16-7B-17	-	0.07	-	0.12	-	0.46	-	528	-	148	-	96	-	55	-	82
16-7C-18	-	0.09	-	0.11	-	0.71	-	549	-	155	-	110	-	61	-	103
16-8A-20	0.10	0.14	0.06	0.09	0.42	0.59	352	495	99	139	73	103	41	58	67	94
16-8B-21	0.09	0.09	0.07	0.07	0.60	0.63	455	478	101	106	85	89	51	54	97	102
16-8C-22	0.09	0.09	0.06	0.06	0.59	0.63	480	509	123	130	85	90	52	56	99	105
10-2C-3	-	[d]	-		-		-		-		-		-		-	
10-4-5	-		-		-		-		-		-		-		-	
10-5-7	0.34[e]		-		0.24		286		115		85		40		72	
1-3-4	0.09		-		0.51		503		80		68		40		43	
11-5-12	0.08		-		0.46		343		62		57		46		48	
11-7B-17	0.09		-		0.50		444		37		64		35		49	
12-3D-10	0.50		-		0.30		428		117		68		46		57	
12-8B-14	0.55		-		0.14		179		64		43		33		40	
12-9B-16	0.21		-		0.26		261		68		42		39		22	
19-3-4	-		-		-		-		-		-		-		-	
19-4-7	0.03		-		0.49		379		89		60		47		47	
19-5-11	0.28		-		0.31		321		89		61		39		44	
19-6-13	0.06		-		0.24		210		42		35		24		30	
20-3-5	0.04		-		0.34		136		96		55		39		171	
20-4-9	0.07		-		0.48		255		119		93		52		179	
20-7-13	0.07		-		0.61		510		99		120		53		86	

[a] Recalculated data set #1. All size fractions (gravel, sand, silt, and clay).

[b] Recalculated data set #2. <16mm size fractions (silt and clay).

[c] Concentration too low to be detected by XRF.

[d] Values for the <1/16mm fractions were not calculated for samples from cores 10, 11, 12, 19, and 20.

[e] Values are averages of two XRF runs. Includes all values for cores 10, 11, 12, 19, and 20.

APPENDIX H

RESULTS OF STATISTICAL TESTS (T-TESTS) OF CHEMICAL DATA FOR THE RESIDUUM USING MEANS AND STANDARD DEVIATIONS

Table H1. Results of statistical tests (t-tests) of chemical data for the residuum using the means and standard deviations.

Oxide/Element	|t|	2 Populations (95% C. L.)	2 Populations (90% C. L.)	Not 2 Populations
Na_2O	1.26			X
MgO	3.21	X		
Al_2O_3	2.18	X		
SiO_2	1.53			X
K_2O	2.35	X		
CaO	2.48	X		
Fe_2O_3	3.15	X		
MnO	2.93	X		
P_2O_5	4.85	X		
TiO_2	0.70			X
S	1.02			X
Sr	1.88		X	
Cr	0.79			X
Rb	3.27	X		
Zr	0.74			X
Ba	3.52	X		

For the 95% confidence level ($\alpha = 0.05$), $|t| = 2.045$.
For the 90% confidence level ($\alpha = 0.10$), $|t| = 1.699$.
Therefore, if the $|t|$ computed for each set of data is $\geq t$ (above), then the means are significantly different. In other words, two populations exist which are represented within a 95% or 90% degree of certainty.

VITA

In 1961, Anne Scales Crafts was born on July 4th in Wabash, Indiana. Upon graduating from Wabash High School in 1979, she attended The College of Wooster in Wooster, Ohio. She received a B. A. degree in Geology in June 1983. In September 1983, she accepted a teaching assistantship in the Department of Geological Sciences at the University of Tennessee, Knoxville, enrolling in the Master of Science program. The following year she was placed on the Oak Ridge National Laboratory--Environmental Seicnces Division/UT research program, which helped support her graduate studies during her second year. In January 1986, she accepted a position as a "geologic consultant" at the Oak Ridge National Laboratory, where she worked for ten months. In March 1987 she received the M. S. degree in Geology.

Since August 1986, she has been happily married to Greg Crafts, a fellow geologist and mechanical engineer.