To the Graduate Council:

I am submitting herewith a dissertation written by Bernard-Shaw Nwadialo entitled "Morphological, Chemical, and Mineralogical Properties of Soils and the Effects of Acid Sulfate Weathering in the Copper Basin of Tennessee." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Plant and Soil Science.

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MORPHOLOGICAL, CHEMICAL, AND MINERALOGICAL PROPERTIES OF SOILS AND THE EFFECTS OF ACID SULFATE WEATHERING IN THE COPPER BASIN OF TENNESSEE

A Dissertation

Presented for the

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ABSTRACT

The mining and smelting operations in the Copper Basin of Tennessee have left the region almost devoid of woody vegetation. The soils have been exposed to large doses of SO_2 and H_2SO_4 which could influence the weathering of the graywacke, mica schist and phyllite parent material. A study was undertaken to evaluate the effects of increased soil acidity and acid sulfate weathering on the morphological, chemical and mineralogical properties of the soils.

Five pedons were located inside the Basin to represent sites near the old and new smelters. Two pedons were located upwind from the smelter sites outside the Basin to represent soils less affected by past smelting operations. Exchangeable bases were extracted with dilute unbuffered silver thiourea (Ag-TU) containing 0.01 M Ag^+.

No differences in morphological characteristics were observed between soils inside and outside the Basin. The upland soils are all red (2.5YR 4/6) in color with a clayey argillic horizon. The soils inside the Basin are acid throughout the profile while the soils outside the Basin have an acid epipedon and slightly acid subsoil. All the soils have very low effective cation exchange capacity (ECEC) (<12.0 meq/100 g clay) and qualify as low activity clay (LAC) soils. Sulfate-sulfur is concentrated in the argillic horizons and, at this time, tends to be more concentrated in the Basin soils.

Vermiculite, hydroxy-interlayered vermiculite (HIV), mica, mica-vermiculite, kaolinite, gibbsite, and quartz are the dominant minerals in all soils. Gibbsite is the most dominant mineral beneath the argillic

horizon in upland soils outside the Basin with minute quantities of kaolinite. On the other hand, kaolinite is the most dominant mineral beneath the argillic horizon in all the Basin soils including the toe-slope soil outside the Basin.

There is chemical evidence to support differences in pH, Fe_2O_3, and SO_4 content between soils inside and outside the Basin. However, these are not manifested to a great degree in the present system. It is possible that regional influences due to removal of plant cover may have had a greater impact than the acid sulfate weathering.

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Base Saturation(BS)--The extent to which the adsorption complex of a soil is saturated with alkali or alkaline earth cations expressed as a percentage of the cation exchange capacity.

Buried Soil--A soil that is covered by a surface mantle of new material that is 50 cm or more thick or a mantle between 30 cm and 50 cm if the thickness of this mantle is at least half that of the diagnostic horizons that are preserved in the buried soil.

Cation Exchange Capacity (CEC)--The sum of exchangeable cations that a soil can adsorb at a specific pH. It is usually expressed in milliequivalents per 100 grams of soil.

Complex ion--Combination of a central ion with one or more ligands.

Effective Cation Exchange Capacity (ECEC)--The sum of exchangeable cations plus exchangeable H and Al as determined at the pH of the soil.

Exchangeable acidity--The titratable H plus Al that can be replaced from the adsorption complex.

Exchangeable basic cations--The exchangeable alkali or alkaline earth cations adsorbed by a soil.

Hydroxy-interlayered vermiculite (HIV)--Vermiculite with hydroxy-aluminum interlayer. It is characterized by the gradual collapse of the 14 Å peak to 10 Å with stage heating at 110°C, 300°C and 550°C.

The 10 Å peak is usually represented by a broad peak between 10 and 11 Å.

Lithic Material--A continuous, coherent underlying material beneath soil which makes hand digging with a spade impractical. It has a hardness of 3 or more on the Mohs scale.

Low Activity Clay (LAC)--Clays with a high proportion of constant surface potential having a ECEC $\leq$ 12 meq/100 g clay.

Paralithic Material--Similar to lithic except that the hardness is less than 3 on the Mohs scale.

Sulfate-sulfur (SO_4-S)--That fraction of total sulfur which is extracted by phosphate solution. It comprises soluble plus adsorbed sulfate.

Vermiculite--A clay mineral with 0.6 to 0.9 charge per unit formula. It is characterized by a 14 Å peak which collapses to 10 Å on potassium saturation.

CHAPTER I

INTRODUCTION

Historical Background

Mining activity in Polk County in extreme southeastern Tennessee dates to the discovery of copper in the Ducktown mining district in 1843 (Emmons and Laney, 1926, Safford, 1869) when a prospector looking for gold found native copper in a stream draining from the southwest end of the Burra Burra lode. Copper production started in 1847. During that same year, an iron furnace was built to produce iron ore from gossan. This failed because of the high copper content. The Hiwassee mine opened in 1850, and by 1855 all the mines in the district had been found and opened. The Civil War interrupted production between 1861 and 1865.

About 1870, the secondary chalcocite ores were nearing exhaustion and several mills were built to concentrate the underlying primary sulfide ores. The richer primary ores were mined out in 1879 and operations were stopped until 1890. The open roast process, in use at the time, required wood for fuel, and about 80 square kilometers of the Basin were stripped of trees for this purpose. When operations were suspended in 1879, the Basin region was almost totally devoid of woody vegetation. By 1890, a railroad had been constructed through Ducktown. The construction of this railroad into the Basin area made low cost wood fuel and coal fuel available from outside the Basin. New metallurgical advances led to economic exploitation of the lower grade primary ores. This was a turning point in the history of the area. The Tennessee Copper Company

was formed in 1899 and by 1904, the pyritic process for copper smelting was established at Isabella furnaces, ending the open roasting of ores. The manufacture of sulfuric acid started in 1907. This ended a substantial emission of sulfur dioxide gases to the atmosphere.

The major mining company in the Basin now is the Cities Service Company which emphasizes the production of sulfuric acid and related chemicals. Only three of the original mines remain operational.

Origin of Soil Acidity in the Basin

In humid, mesic environments where rainfall exceeds evapotranspiration for much of the year, soluble basic cations are lost from the soil by intense leaching. The loss of basic cations leads to acidic topsoils and as weathering progresses, the whole soil becomes acidic. Soil acidity can also arise from crop fertilization and decomposition of plant residues and organic matter.

Highly acidic conditions can arise locally from the exposure of mine spoils containing pyrite or other sulfides. The oxidation of pyrite produces sulfuric acid (H_2SO_4) according to the simplified overall reaction:

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4$$

In the Copper Basin and other industrial sites, soil acidity can arise from acid precipitation. In the open-roast smelting of copper, sulfur dioxide was liberated into the atmosphere. When this gas was dissolved in rain water it fell to the soil as a weak sulfurous acid which was then oxidized to sulfuric acid.

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

$$2H_2SO_3 + O_2 \longrightarrow 2H_2SO_4$$

The last reaction is irreversible leading to a net gain in sulfuric acid. The oxidation of copper sulfide ores and the subsequent dissolution of sulfur dioxide may have resulted in increased soil acidity. The low soil pH may not be a serious problem to plants, but may lead to increased solubility of Al, Mn, Zn, Pb, and As, which can be very toxic to plants and animals (Alloway and Davies, 1971; Davies, 1977).

The low pH of the soils, the total destruction of vegetation, the lack of soil macro organisms, and the soil erosion caused by the mining practices may have had tremendous impacts on the morphology and mineralogy of these soils.

Objectives

The objectives of this study were:

1. To evaluate the effects of increased acidity on the physical and chemical characteristics of the soils in the Basin.

2. To ascertain the mineralogy of the soils and evaluate the effect of acid weathering on the mineralogy.

3. To explain the probable genesis of the soils from morphological and mineralogical data.

CHAPTER II

LITERATURE REVIEW

Geology of the Basin

The Southern Appalachians is a belt of folded and faulted Paleozoic sedimentary rocks which range in age from Cambrian to Carboniferous (Hadley, 1970). This belt is bordered on the southeast by another wide belt of metamorphic rocks which is called the crystalline Appalachians (Unaka's). Detailed work has shown that some of the metamorphic rocks are of late Precambrian age and that there are occurrences of metamorphosed sedimentary rocks whose lithology and stratigraphy vary from place to place.

The extensive, thick metamorphosed rocks are mostly graywacke, shale, and basalt which overlie unconformably a basement of Grenville age (Mohr, 1973). These strata consist of the Swift Run, Lynchburg, and Catoctin Formations of Central Virginia (Espenshade, 1970); the Mount Rogers and Ashe Formations of southwestern Virginia (Rankin, 1970); the Grandfather Mountain Formation of northwestern North Carolina (Bryant and Reed, 1970); and the Ocoee Series of western North Carolina, eastern Tennessee and northern Georgia (Hadley, 1970). The formation of interest in the Copper Basin is the Ocoee Series.

Ocoee Series

This sequence was named by Safford (1856, 1869) for exposures along the Ocoee river between Parksville and Ducktown. It is a thick

wedge of clastic rocks of later Precambrian age which rests unconformably on older crystalline basement rocks. Many of the rocks are coarse-grained and poorly sorted. In most areas, the top and base of the Series are not visible (King, 1964). The Ocoee Series is characterized by diverse lithologies, though some Formations include sequences which are mineralogically and texturally uniform throughout. As a result, subdivision and correlation are very difficult although recent work by King et al. (1958) has significantly increased the understanding of the Series.

King et al. (1958) divided the Ocoee Series into three major groups containing twelve named Formations. However, no single area has a complete sequence. The Ocoee is divided in ascending order into the Snowbird Group, Great Smoky Group, and the Walden Creek Group. Though correlation is difficult, the Copper Basin area is underlain by rocks which have been correlated tentatively with the Great Smoky Group as used by Hurst and Schlee (1962). They subdivided the group into four Formations which in ascending order are the Copperhill, Hughes Gap, Hothouse, and Dean Formations (Table 1). Evidence from geologic mapping data (Magee, 1968) indicates that the Copper Basin is underlain by the Copperhill Formation.

Copperhill Formation

The Copperhill Formation was named (Hurst, 1955) after the town of Copperhill at the southeast corner of Polk County, Tennessee. Hernon (1968) did not use this name in his report because the United States Geological Survey had not adopted it and because the upper part of the

Table 1. Stratigraphic nomenclature of part of the Ocoee Series in Southeastern Tennessee.[a]

Age	Series	Group	Hernon (unpublished 1968)	Hurst and Schlee (1962)
Precambrian	Ocoee	Walden Creek	Unit 3	
Precambrian	Ocoee	Great Smoky	Unit 2	Dean Formation
			Unit 1	Hothouse Formation
			Slaty Unit	Hughes Gap Formation
			Unit A	Copperhill Formation
Precambrian	Ocoee	Snowbird		

[a]Adapted from Magee (1968, p. 211).

Formation had been assigned to a new Formation. This upper part known as Unit B, or Wehutty Formation, correlates with Hernon's Slaty Unit. Hernon, uses the term "metagraywacke" to represent the Copperhill Formation.

The Copper Basin region is underlain by sandy metasediments which are well exposed in the denuded Copperhill-Ducktown area. These are part of the Copperhill Formation, which according to Hurst (1955) are made up of 60% metagraywacke, about 30% mica schist, and 10% metaconglomerate, quartzite and meta-arkose. These rocks are repetitively interbedded throughout the Formation. At places the metagraywacke and mica schist alternate rhythmically, each bed of metagraywacke grading upward to mica schist. Frequently the alternation is irregular. Metaconglomerates, quartzites and meta-arkose are common in a few places and they usually grade to metagraywacke. The schist layers are usually the thinnest of the three rock groups.

Metagraywacke is dominantly fine to coarse-grained argillaceous feldspathic sandstone that has been metamorphosed by high temperature and pressure. Clasts are present and they are usually quartz and feldspar and fine to coarse mica. Metagraywacke beds are well oxidized to slightly reduced and schistosity is visible unless weathering has been very severe. The mineralogy of metagraywacke was summarized by Hurst (1955) as consisting of 50 to 60% angular-to-subrounded quartz, with feldspar, biotite, and muscovite and with minor calcite, apatite, zircon, and chlorite. Some of the accessory minerals are garnet, epidote, tourmaline and titanite. Hernon (1968) even observed monazite.

Metaconglomerate is a slightly coarser variety of metagraywacke. It is typically composed of quartz pebbles and granules with smaller amounts of feldspar clasts.

Mica schists range from fine (which resembles phyllite) to coarse schist. They are composed primarily of quartz and muscovite in various amounts and frequently grade into an intermediate rock called graywacke schist.

Origin of the Primary Ores

The sulfide deposits consist of several sulfide replacement lenses in folded metamorphosed Precambrian schists and graywackes. The lenses are conformable with the host Ocoee metasediments. The primary ore consists of pyrrhotite, pyrite, and chalcopyrite with minor amounts of sphalerite, magnetite, quartz, and chlorite.

It is presumed (Emmons, 1909; Emmons and Laney, 1911; Magee, 1968) that the original ore formed by hydrothermal replacement in Precambrian time, but underwent moderate to high later metamorphism. Based on the presence of kyanite and staurolite, the absence of cordierite and the iron content in sphalerite, Jensen and Bateman (1979) suggested that temperatures as high as 550°C to 650°C may have existed in the region.

Magee (1968) and Hernon (1968) suggested a possible sequence of events that led to the deposition of the ore and evolution of the geology of the area. It is probable that alternating coarse and fine grained clastic sediments and muds from older Precambrian land mass were deposited during the Late Precambrian period. These sediments were mixed with calcareous layers on a continental shelf environment and were gradually

bedded due to slumping and turbidity currents. This was followed by Cambrian deposition. As a result of these events, a thickness of about 9,000 meters resulted. During the early Paleozoic, there was uplift and orogeny accompanied by regional dynamic metamorphism. In the Devonian period, there was deformation which caused hydrothermal solutions to follow channelways and replace favorable zones with sulfides. There followed another deformation in the Late Paleozoic which produced the northeast-southwest faulting and rotated the ore deposits. Between the Permian and Present, the land mass was uplifted. Subsequent geomorphic processes gave rise to the present topography.

Geomorphology

The Copper Basin is a physiographic basin with an area of about 160 square kilometers (Magee, 1968). The surrounding mountains rise to about 1250 meters while elevations within the Basin range from 450 meters to 550 meters above sea level. The area is drained by the Ocoee river (known as the Toccoa river in Georgia). The surrounding ridges are dissected in several places by minor streams and creeks such as Potato Creek, Davis Mill Creek and Brush Creek. The drainage pattern in the area follows the fault zones. Lack of vegetation has led to severely eroded landscapes.

Climate

The complex topography in the Basin is a contributing factor to substantial variations in temperatures, precipitation, air flow and in other climatic conditions within relatively short distances. The Basin

is generally characterized by a moderate climate with cool winters and quite warm, moist summers. Winter (Dec., Jan., Feb.) weather is changeable due to the frequent passage of frontal systems. These bring alternating cold and warm air masses into the area with changes in precipitation, wind directions and temperature. Winter temperatures may average about 1°C warmer in the lowlands because of the sheltering effect of the mountains and the elevation differences. Temperatures fall as low as the freezing point (0°C) about half of the winter days.

The summer (June, July, Aug.) climate is influenced by moist, warm air influx from the Gulf of Mexico. Summer daytime temperatures typically range in the low to middle thirties. Precipitation is variable from year to year and from season to season, but the highest average monthly rainfall occurs during the winter and early spring months.

For the year 1980 (Table 2) the average annual temperature for Copperhill was 13.9°C while the average precipitation was 1389 mm. Based on 29 years of records, the average annual temperature and precipitation are 13.8°C and 1454 mm., respectively. July was the hottest month in 1980 with an average temperature of 26.4°C. February was the coldest month with an average temperature of 1.3°C. Based on past records, January is usually the coldest month while July is the hottest month.

In 1980, the first freezing temperature in the Fall was on November 1, and the last freezing temperature in Spring was on April 18.

Soils

The soils in the Copper Basin have not been classified, however, a soil survey is now being made. Regional studies of soils in the

Table 2. Climatic data for Copperhill, Polk County, Tennessee. 1980.

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Total
Average Temp. C°	4.8	1.3	7.4	13.1	17.8	22.2	26.3	25.8	22.5	13.0	8.6	4.1	13.9
Normal*	3.5	4.6	8.1	13.9	18.5	22.5	24.1	23.6	20.3	14.3	8.1	4.1	13.8
Average Precipitation (mm)	156	57	391	165	138	47	47	58	135	57	120	27	1389
Normal*	137	143	161	123	97	113	169	123	96	87	106	132	1454

First Freezing Temperature in Fall 1980--November 1.

Last Freezing Temperature in Spring 1980--April 18.

*Based on 29 years records, 1941-1970.

Source: Climatological Data Annual Summary, Tennessee, 1980. National Climatic Center, Asheville, North Carolina, Volume 85, No. 13.

Piedmont and Blue Ridge provinces have been made in Georgia and North Carolina. Gibbs and Perkins (1966) investigated the properties of the Cecil and Hayesville Series and identified the Cecil Series in the Piedmont while the Hayesville Series was confined to the Southern Blue Ridge. McCracken et al. (1971) conducted a regional study of these soils and enumerated their distinguishing features. Soil properties such as gibbsite content in the solum and C horizon, clay content of the B horizon, illuviation argillans, solum thickness, effective CEC and clay mineralogy of the saprolite were used to recognize these soils.

Moderate to unusually high amounts of gibbsite have been reported in upland soils of the higher Piedmont and Blue Ridge (Bryant and Dixon, 1963; Cate and McCracken, 1972). The soils in the Piedmont lowlands do not exhibit these high gibbsite contents. One explanation for this phenomenon is rapid percolation and drainage of the upland soils (Cate and McCracken, 1972; Gibbs and Perkins, 1966; McCracken et al., 1971). Differences in parent material (McCracken et al., 1971) or the slope aspect (Losche et al., 1970) could result in different mineral suites.

The upland soils in the Copper Basin are red in color. Past mining and smelting practices may have altered the soils to such an extent that they may differ from similar soils on similar landscapes in the neighboring states.

Weathering of Minerals Under Acidic Conditions

The processes of soil development involve weathering of primary and secondary minerals and the transportation and redistribution of the organic and inorganic products. Weathering is the most important process

in soil formation and the extent of soil development is usually reflected in certain soil properties such as a finer texture (Brewer and Walker, 1969), stronger structure (Campbell, 1971), horizonation and solum development, presence of cutans, and increased soil color (Cowie, 1968; Dickson and Crocker, 1954; Foss and Rust, 1962; Gamble et al., 1970; Ruhe, 1956). Soil development is also reflected in the clay mineralogy and, at times, in the total clay content (Ahmad et al., 1977).

Weathering precedes soil formation in solid rocks, accompanies it in soft rocks and proceeds both below and within the solum. Jackson and Sherman (1953) made a distinction between geochemical and pedochemical weathering. Geochemical weathering takes place beneath the soil solum while pedochemical weathering takes place within the soil. Water plays a major role in both processes. Graham (1941) reported that acidified water influences the rate of weathering and soil development. Jackson and Sherman (1953) reported that increasing acidity accelerates the rate of weathering by a very rapid removal of the metallic cations by the exchange material. They reported that the removal of the metallic cations occurs at the same time that H^+ is furnished for hydroxylation of the weathering product.

Correns (1963) investigated chemical weathering by heating powders of K-feldspar, albite, leucite, muscovite, tremolite, olivine, and volcanic glass with pure water and with dilute solutions of sulfuric acid, carbonic acid, and hydrochloric acid. He concluded that the course of decomposition depends on water flow rate, grain size, temperature, and pH of the solutions. Tan (1980) experimented on the decomposition of soil minerals by humic acids and found that while there was very little

decomposition of microcline, biotite or muscovite at pH 7.0, there was rapid decomposition at pH 2.5.

Loughnan (1969) reviewed the breakdown and alteration of various rocks in different environments. He reported that acidic conditions give rise to high amounts of sesquioxides and 1:1 clay minerals and concluded that there are three simultaneous processes in rock weathering: 1) breakdown of parent mineral structure with the release of cations and silica, 2) the removal in solution of the released constituents, and 3) the reconstitution of the residue to form new minerals which are metastable or stable in the new environment.

The new minerals formed during weathering are stable only between certain concentration limits of soluble silica, cations, and H^+. If the cations are leached away, as often happens in leaching environments, the secondary minerals weather further to more stable states. Pedochemical weathering involves the alteration and transformations of the clay minerals previously formed in soils. Research has been conducted on the weathering of clays in acid solutions (Brindley and Youell, 1951; Gastuche, 1963; Kerr et al., 1956; Miller, 1965, 1968; Osthaus, 1954, 1956.) These investigations involved the determination of the type of clay mineral formed, and dealt mainly with the mica to vermiculite transformation. Barnhisel and Rotromel (1974) worked with mixed clay mineral systems and found that both kaolinite and mica disappeared at the same rate regardless of acid concentration even though the mica released more Al^{3+} than kaolinite.

Several soil weathering studies have been made in the Southeastern United States (Bryant and Dixon, 1964; Caldwell and Pourzad, 1974;

Carlisle and Zelazny, 1974; Fiskell and Carlisle, 1963; Glenn and Nash, 1964; Rich, 1958), and in other parts of the world (Eswaran and deConnick, 1971; Kapoor, 1972; Ojanuga, 1973). In the warm tropical and subtropical regions and regions of moderate temperature and intensive leaching, 1:1 clay minerals are dominant with some hydroxy-interlayered vermiculite (in surface horizons) in acid soils.

The genesis of soils in acid environments involves aluminum; consequently, the behavior of aluminum in soils must be known before the genetic processes in soils can be understood.

Fate of Weathering Products

Ions released during weathering are either removed from the soil system in leaching water or they may recombine with other ions to form a variety of crystalline and amorphous compounds. Some of the important ions released during acid weathering are Al^{3+}, Fe^{2+}, and Si^{4+}. Aluminum and silicon are abundant constituents of rock minerals. Aluminum has a tendency to hydrolyze in solution, and at any pH above 3.5, various combinations of aluminum with hydroxide ions occur (Hem and Roberson, 1967).

a) Hydrolysis of Aluminum in Aqueous Solution. Various workers have studied the solubility and dissolution of aluminum in water (Brosset, 1952; Fripiat et al., 1965; Gayer et al., 1958; Hem and Roberson, 1967; Raupach, 1963a, 1963b). These studies indicate that when the pH of a solution containing Al^{3+} ions is raised, dissolved species consisting of Al^{3+} and OH^- are present. If the supply of OH^- is sufficient, a precipitate of the composition $Al(OH)_3$ is produced. McLean (1976) described

the process as the sixfold coordination of Al with oxygen in (OH_2^+) groups thus $Al(OH_2)_6$ or $Al.6H_2O^{3+}$ and the sequential dissociation of H^+ ions as more base is added.

In earlier investigations, the association of Al and H_2O was assumed to be a mono-nuclear process occurring in steps:

$$Al^{3+} + H_2O \longrightarrow Al(OH)^{2+} + H^+ \quad [1]$$

$$Al(OH)^{2+} + H_2O \longrightarrow Al(OH)_2^+ + H^+ \quad [2]$$

$$Al(OH)_2^+ + H_2O \longrightarrow Al(OH)_3 + H^+ \quad [3]$$

$$Al(OH)_3 + H_2O \longrightarrow Al(OH)_4^- + H^+ \quad [4]$$

$$Al(OH)_4^- + H_2O \longrightarrow Al(OH)_5^{2-} + H^+ \quad [5]$$

$$Al(OH)_5^{2-} + H_2O \longrightarrow Al(OH)_6^{3-} + H^+ \quad [6]$$

The thermodynamic equilibrium constant for reaction [1] has been determined (Sillén and Martell, 1964, 1971) and most investigators agree that

$$pK = pAl(OH)^{2+} + pH - pAl = 5.0 \quad [7]$$

Some investigators feel that this reaction does not exist or that other hydrolytic species must be considered. Frink and Peech (1963) showed that at low basicities, the first stage reaction appears to be satisfactory in calculating the equilibrium constant.

In recent years polynuclear complexes have been proposed. These polymers have more than one metal atom in the simplest possible representation and the ratio of hydroxide ions to aluminum ions in the complex needs not be integral. Brosset (1952) first proposed the polynuclear complex theory. His experimental data were later re-interpreted (Brosset et al., 1954) as indicating either a single complex or a series of complexes. Several investigators (Hem and Roberson, 1967; Hsu and Bates,

1964; Schoen and Roberson, 1970; Smith and Hem, 1972) soon followed with the polynuclear theory. In none of these experiments is the composition of the solid phase or the nature of the various metastable polynuclear species known with certainty. For an example, the solubility product of gibbsite which is the thermodynamically stable phase of $Al(OH)_3$ has been measured and found to correspond to pK_{sp} = 33.5 (Frink and Peech, 1962); pK_{sp} = 34.0 (Kittrick, 1966) for solutions aged for four years, and pK_{sp} = 31.8 (Frink and Sawhney, 1967) for supersaturated solutions. Brosset et al. (1954) showed that either a single species $Al_6(OH)_{15}^{3+}$ or an infinite series of complexes is precipitated during potentiometric titrations.

These uncertainties abound in studies involving soil solutions. Hsu (1977) reported that because of these uncertainties, some workers insist that their results could be interpreted by assuming that only monomeric species are the hydrolysis products. Raupach (1963b) concluded that the hydrolysis products in the acidic range were monomeric species even though the $pAl(OH)_3$ was found to decrease with increasing pH (Lindsay et al., 1959). Frink and Peech (1963) considered the polymers to be metastable forms which would become an $Al(OH)_3$ phase with time. Frink (1972) questioned the use of polymeric species in preference to monomeric species in describing Al^{3+} activity in acid soils. Recently, Richburg and Adams (1970) suggested that the apparent increase in the solubility of $Al(OH)_3$ with increasing soil pH is due to the inappropriate choice of the monomeric hydrolysis reaction. They reported that the inclusion of the polymer species $Al_6(OH)_{15}^{3+}$, in the reaction products resulted in the calculated $pAl(OH)_3$ being only slightly pH dependent in the pH range 4.2 - 5.6.

The various theories on aluminum and hydroxide reactions under acidic conditions arose because of the slowness of the reaction, concentration of reagents, kinds of anions present, and the procedures used for solution preparation. Those workers who dissolved aluminum salts in water found the monomeric species while those who used a base to adjust the pH found polynuclear species (Hsu, 1977). These theories are not conflicting but complementary. Dalal (1975) has shown that the $pAl(OH)_3$ is independent of solution pH in the range 4.0 to 6.3 when $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_6(OH)_{15}^{3+}$, and $Al(OH)_3^0$ were considered as the hydrolysis products. He found that the predominant species in the pH range $\leq$ 4.5 was Al^{3+}, while $Al(OH)_3^0$ was dominant in the pH range 4.5 to 6.3. Rhodes and Lindsay (1978) working with soils of the humid tropics found that Al^{3+} activity was pH dependent but the $Al(OH)_3$ ion product was constant.

These results indicate that the solubility of aluminum in acid soils appears to be controlled by the solubility of gibbsite. At higher pH, soils appear to be supersaturated with respect to gibbsite and may contain the soluble forms of $Al(OH)_3$ or even soluble polynuclear species. There may also be soluble complexes of aluminum with phosphate, sulfate, fluoride and organic matter.

b) Formation of secondary minerals.

1. Clays

The Al^{3+} ions released during the weathering of primary minerals play a role in the formation of clays and other secondary minerals.

Keller (1967) outlined the processes which lead to clay formation. One such process is the crystallization of clay minerals from solution. The occurrence of euhedral crystals of clay minerals such as authigenic kaolinite or mica in cavities in sedimentary rocks supports this theory. Crystallization involves the recombination of Al and Si and the building of octahedral and tetrahedral sheets.

Progress in the synthesis of low temperature kaolinite has shown that crystallization of kaolinite involves the ordering of the octahedral sheet, ordering of the tetrahedral sheet, and the adjustment of these layers to each other during condensation (De Kimpe et al., 1961, 1964). In these experiments, it was found that the octahedral sheet was easiest to stabilize at low pH. At low pH, Al was in sixfold coordination and kaolinite was formed from silica-alumina gels. Above pH 5.5, Al was in fourfold coordination.

Clay minerals may also form by the replacement of one solid geologic substance by another. This is a special case of crystallization from solution. One compound is capable of replacing another if the chemical system in which the two interact is such that saturation point is reached for one but not for the other, that is, the system is supersaturated with one and undersaturated with the other (Keller, 1967).

Millot (1970) recognized three processes which account for the genesis of clay minerals: inheritance, transformation, and neoformation. These three processes can occur in soils. The end product depends on the silica-alumina ratio, which is influenced by the soil environment (Millot, 1970). Under very acid conditions kaolinite is

usually the most abundant mineral in highly leached environments. Fiskell and Perkins (1970) working with some Ultisols from the Southeast United States found that kaolinite was the dominant mineral. Dixon (1977, p. 373) considered this kaolinite to be inherited from acid sediments. Other workers in the tropics and subtropics (Bryant and Dixon, 1964; Caldwell and Pourzad, 1974; Carlisle and Zelazny, 1974; Eswaran and De Coninck, 1971; Glenn and Nash, 1964; Ojanuga, 1973) have found that kaolinite is the dominant clay mineral. In these acid environments, the clay minerals that form depend on drainage conditions. Under relatively good drainage, the solubility and stability of SiO_2 and Al_2O_3 in solution allow neoformation of clays of the kaolinite type in which the SiO_2/Al_2O_3 ratio is equal to 2.

Elgawhary and Lindsay (1972) and Millot (1970, p. 335) have shown that silica solubility is gradual and is pH independent below pH 8.0. This finding emphasizes the relevance of the quantity of silica as opposed to its solubility. It is now known that the quantity of silica left in solution in relation to that of alumina determines the mineral formed (Millot, 1970). When the SiO_2/Al_2O_3 ratio is zero, gibbsite is formed; when it is 0 - 2, kaolinite is formed; when greater than 2, smectites are formed (Millot, 1970).

Vermiculites have also been reported in various soils of the world. They are usually alteration products of mica or chlorite. Hoda and Hood (1972) used $MgSO_4$ to artificially alter trioctahedral mica to vermiculite and hydrobiotite. Kapoor (1972) found that vermiculite was concentrated in the surface soil horizons while chlorite was concentrated in the B horizons. In acid dissolution of mica or chlorite (Brydon and Ross,

1966; Ross, 1967, 1968, 1969) Fe, Mg and Al are released, and the loss of these together with interlayer K leads to the formation of vermiculite.

Under intensive weathering conditions, vermiculites acquire a hydroxy-Al interlayer (Rich, 1958). Hydroxy-interlayered vermiculites (HIV) were identified in acid uplands while vermiculites were identified in adjacent alluvial lowlands (Lietzke et al., 1975). The interlayering is common in surface soils with low pH and gives way to vermiculite in the subsoil (Lietzke and Mortland, 1973). The presence of HIV in acid soils is now recognized and is presumed to be the dominant mineral in many surface soils which were previously thought to be dominated by kaolinite.

2. Gibbsite

The minerals present in a soil are usually indicative of the weathering stage of that soil. Some minerals such as quartz, zircon and titanium are used as index minerals in soil weathering studies. Jackson and Sherman (1953) suggested a weathering sequence for clay-sized materials and in that sequence, gibbsite is one of the minerals characteristic of highly weathered tropical soils.

However, gibbsite has occasionally been reported among the weathering products of granitic rocks in temperate humid climates (Ball, 1964; Basham, 1974; Green and Eden, 1971; Torrent and Benayas, 1977; Wilke and Schwertmann, 1977; Wilson, 1970a; Wilson and Bown, 1976). In the Southeastern United States, gibbsite has been reported in many soils of the Piedmont (Bryant and Dixon, 1964; Cate and McCracken, 1972; Glenn and Nash, 1964).

The origin of $Al(OH)_3$ in soils has been well investigated (Mead, 1915; Harrison, 1934; Gordon and Tracey, 1952). These early papers suggested that gibbsite could be formed directly from primary minerals. Most of these studies revealed the tendency of gibbsite to form from mafic minerals while kaolinite formed from felsic rocks. Fox (1932) and Harder (1952) described bauxite deposits which formed on every type of common rock that contained aluminum. This indicated that the parent material is not critical for gibbsite formation if excess aluminum is present.

Mead (1915) attributed the formation of bauxite in Arkansas to subaerial weathering which resulted in the gradual desilication of the nepheline syenite with kaolinite as an intermediate product. Harrison (1934) concluded that there was no intermediate stage in the formation of gibbsite and that gibbsite formed directly from basic and intermediate igneous rocks. Gordon, Tracey and Ellis (1958) working on the origin of the Arkansas bauxite found that gibbsite or kaolinite could be formed from the nepheline syenite depending on the nature of the environment. Other workers (Allen, 1952; Bates, 1962) in advancing the intermediate theory, described the abundance of kaolinite and gibbsite and their inverse relationship in soils. Sherman et al. (1967) and Young and Stephen (1965) in supporting direct formation found that microscopic gibbsite replaced feldspar while preserving the outline and original cleavage of the parent crystal. Keller (1958) postulated that the formation of gibbsite and kaolinite was a precipitation reaction and was controlled by soil pH and the concentration of silicon and aluminum in solution. Many workers have examined the origin of gibbsite from a

thermodynamic perspective. Gardner (1970, 1972) predicted on the basis of theoretical thermodynamic considerations that gibbsite would form from kaolinite and potash feldspar only where pH is above 4.3, quartz is absent, and the initial concentration of total dissolved silica in the infiltrating water is less than $10^{-4.6}$ M. Lodding (1972) countered by pointing out that feldspars had altered to gibbsite in the presence of quartz in the Pensauken formation. Other occurrences of gibbsite have been attributed to a number of causes ranging from paleoclimate and intense leaching to the presence of organic acids (Green and Eden, 1971; Torrent and Benayas, 1977).

The formation of gibbsite can be very rapid when there is incongruent weathering of silicate minerals and intense leaching of soluble components. The separation of aluminum and silicon and the leaching of silicon leads to the formation of gibbsite. This has been confirmed (Rai and Lindsay, 1975) by stability diagrams. These thermodynamic studies show that gibbsite is stable relative to other clay minerals at low silica activity and a pH of 4.2 or more.

c) Reactions of aluminum in the presence of anions. The precipitation of $Al(OH)_3$ in acidic environments could be accompanied by other precipitates depending on the anions present in solution. Fluoride complexes of aluminum are quite stable and may form when both Al and F are present in soil solution. Hem (1968) has shown that fluoride complexes will predominate in most natural waters below pH 6.6 in the presence of as little as 10^{-5} M fluoride. Complexes of aluminum with phosphate may be possible and Bohn and Peech (1969) suggested that they could be important in strongly acid soils (pH $\leq$ 4.2).

Sulfate complexes with aluminum are possible in acid sulfate soils and soils affected by acid sulfate weathering. After Ensminger (1954) reported that alumina adsorbed more sulfate than did iron oxides while bauxite and kaolinite were intermediate in adsorption capacity, there have been extensive studies to elucidate the relationship of soil properties to chemical reactions and other phenomena involving sulfate ions (Chao et al., 1962, 1963, 1964, 1965). These studies revealed that soils adsorbed sulfate from equilibrium solutions but lost the sulfate when successively leached with water. The studies also showed that in well-developed soils with iron and aluminum oxides and hydroxides, aluminum and amorphous material adsorbed the most sulfate.

The retention of sulfates by acid soils was attributed to a pH dependent mechanism which involves hydroxyl and sulfate ion exchange between these oxides and soil solution (Chao et al., 1965; Rajan, 1978, 1979). Adams and Rawajfih (1977) and Wolt and Adams (1979) reported that sulfate retention may be a consequence of the insolubility of the hydroxide-sulfate complexes in acid soils. Others have reported the precipitation of aluminum sulfate during neutralization reactions involving aluminum salts and bases (Hsu and Bates, 1964). Singh (1969) and Singh and Brydon (1969) identified a crystalline basic aluminum sulfate, basaluminite, with formula $Al_4(OH)_{10}SO_4 \cdot 5H_2O$ and $pK_{sp} = 117.3$, as a metastable phase formed during the neutralization of aluminum sulfate solutions. Adams and Hajek (1978) precipitated aluminum as a basic aluminum sulfate in conjunction with $Al(OH)_3$ with as little as 0.01 M $SO_4^=$ in the reacting solution. They reported that increasing the sulfate concentration in the reacting solution increased the relative amounts

of basaluminite, while increasing the solution pH lowered the amount of basaluminite. Furthermore, the presence of 0.01 M K^+ ions in the ageing solution transformed the basaluminite into crystalline alunite. These results indicate that either one or both of these minerals should form in acid soils when sulfate is present. More recently, Wolt (1981) suggested that alunite may be forming as a weathering product of K-mica in acid-sulfate environments or that it may be a transformation product of basaluminite in the presence of K^+ ions.

Review of Cation Exchange Capacity Method

The cation exchange capacity (CEC) of soils has been used in the classification of Oxisols and in the definition of low activity clays which comprise most Oxisols and many Ultisols. Base saturation has been used in the classification of Mollisols, Alfisols, and Ultisols.

Several methods have been used to measure the CEC of soils. These are 1) the buffered, NH_4OAc, pH 7, CEC; 2) the unbuffered NH_4Cl CEC; 3) the sum of cations; and 4) the sum of bases plus KCl-extractable Al or effective CEC (ECEC). The basic principle underlying these methods is to leach a soil sample exhaustively with a solution containing a replacement or index cation. The displaced ions are then determined. The conventional methods adopted by the United States Department of Agriculture and Soil Conservation Service (USDA-SCS) are the neutral NH_4OAc and Barium chloride-Triethanolamine ($BaCl_2$-TEA) pH 8.2 (Mehlich, 1938, 1948; Peech et al., 1962).

Coleman and Thomas (1967) reported of earlier investigations which showed that the CEC measured at pH 8.2 is invariably larger than that

measured at pH 7.0, although results may be nearly the same in layer silicates where most CEC results from lattice charge. Some exchangeable ions are more easily replaced than others and the completeness of replacement of some cations depends on the particular salt solution used. Reports that the CEC of soils increased as the pH of the replacement solution increased (Pratt and Bair, 1962) soon led to the adoption and use of the ECEC method.

More recently various modifications of ECEC method have been used in tropical and subtropical regions (Gillman, 1979; Juo et al., 1976; Pleysier and Juo, 1980). This is partly due to a better understanding of the constant and variable charge theory. The highly weathered soils of these regions have a dominance of variable charge colloids and are high in Fe and Al oxides and hydroxides. The variable charge indicates that the surface properties of these colloids vary with pH and the concentration of the displacing solution (Gallez et al., 1976; Greenland, 1974; Van Raij and Peech, 1972). Parks and de Bruyn (1962) recognized that at high pH values, H^+ is released from hydroxyl groups at the surfaces of Fe and Al oxides. Juo et al. (1976) noted that the release of these H^+ does not have the same meaning as the exchangeable H^+ (or Al) ions on smectites or vermiculite surfaces which are measured with $BACl_2$-TEA. Despite these advances in the variable charge theory, different laboratories in different parts of the tropics use different methods for the estimation of ECEC. This has prompted Sombroek (1978) to advocate a uniform methodology in order to avoid soil classification problems.

Recently, the measurement of ECEC was criticized (Pleysier and Juo, 1980) because the extraction of soils with neutral normal NH_4OAc does

not represent the ionic strength of the fluid bathing the soil colloid. They suggested the use of dilute unbuffered silver thiourea solution in the extraction of the cations and the determination of exchangeable acidity in the same extract by titration with NaOH to the phenolphthalein end point.

Silver Thiourea Method

The ionic strength of the solution bathing the soil colloid is low, so a salt solution of low concentration with a metal cation that has strong affinity for soil colloids and is stable in suspension should be an adequate extractant.

Pleysier and Cremers (1973) experimented on the adsorption of silver thiourea complex in montmorillonite. Working with a mixture (0.01 N) of $NaNO_3$ and $AgNO_3$ which contains a 10:1 excess of thiourea: silver, they found that the thiourea had a remarkable effect on silver adsorption, and that the silver thiourea complex had a high adsorption energy (5 kcal/equiv.). In recognition of these properties, they recommended silver thiourea as an index cation for rapid estimation of CEC of soils.

Chhabra et al. (1975) were the first to use silver thiourea in estimating CEC. Most recently, Pleysier and Juo (1980) have used it for some tropical soils and found good correlation with the ECEC method. The low concentration of the solution, the great affinity of the complex for soil colloids, and the high adsorption energy make silver thiourea a good extractant for cations in CEC determinations. However, silver nitrate is a very expensive chemical and this may be the only drawback to this method.

CHAPTER III

MATERIALS AND METHODS

Field Methods

Soil pedons in the Copper Basin were located in three areas chosen to represent (1) the area relatively unaffected by the mining operations, (2) the area closest to the old smelter and (3) the area closest to the new smelter (Figure 1). In each area two soil pedons were located to represent the upland and lowland soil respectively. An additional pedon was located in the area closest to the old smelter to represent soils occupying the midslopes. The seven soil pedons located are:

CBCC 1A--Control (Upland)

CBCC 1C--Control (Toeslope)

CBOS 2A--Old smelter (Upland)

CBOS 2B--Old smelter (Midslope)

CBOS 2C--Old smelter (Toeslope)

CBNS 3A--New smelter (Upper toeslope)

CBNS 3C--New smelter (Toeslope)

The control site was chosen based on the presence of good vegetation and the assumption the vegetation signified a site less affected by the smelting operations.

The soil pedons were completely described according to the revised Soil Survey Manual (1981). Soil samples were collected from each horizon, bagged and transported to the laboratory. Clay skins on ped surfaces and clay flows on saprolite fragments were carefully scraped off and stored.

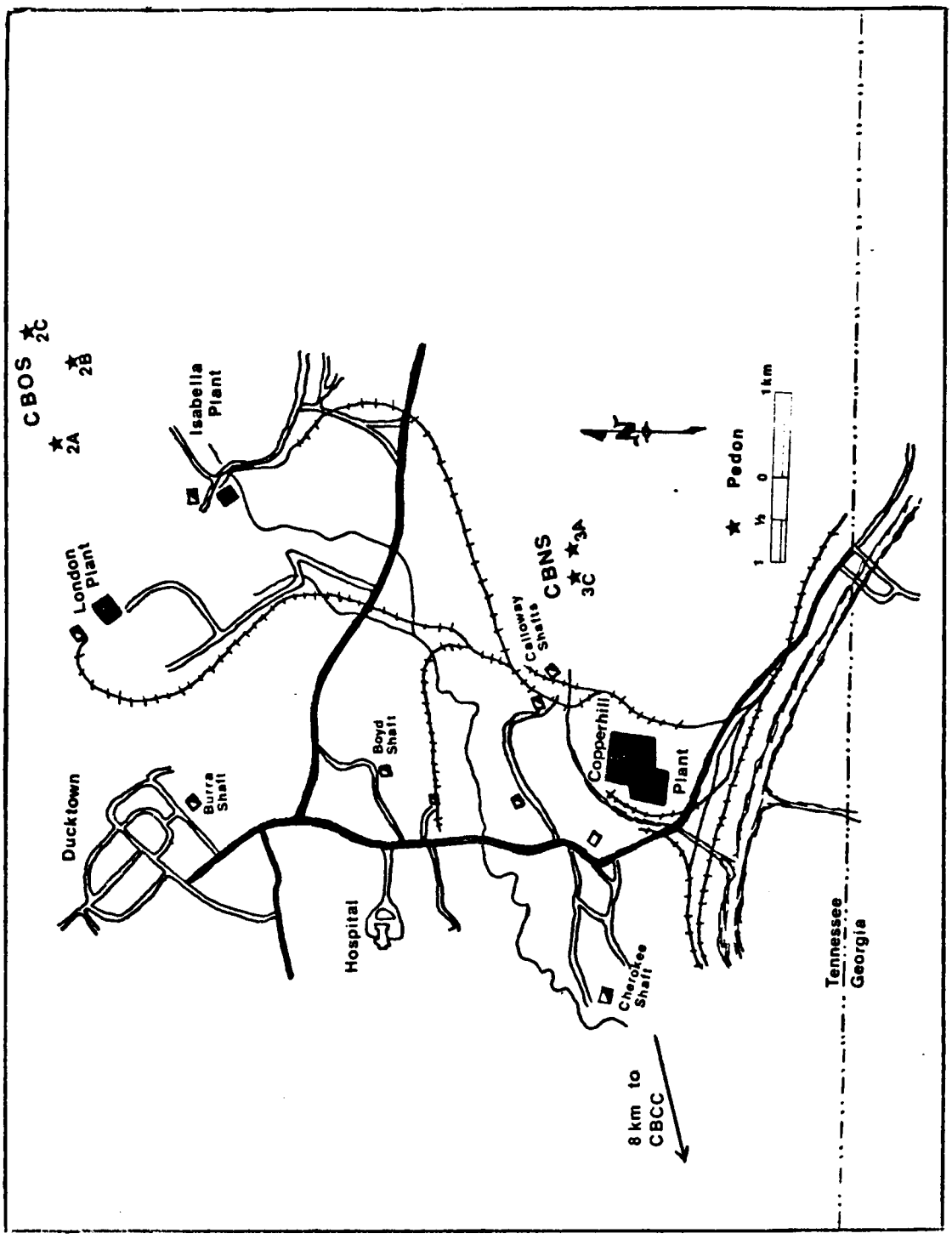

Figure 1. Location of sampling sites. Pedons 1A and 1C are about 8 kilometers southwest of Cherokee mine.

Laboratory Methods

Physical and Chemical

Physical and chemical analyses were carried out on the soil fraction <2 mm in diameter. Particle size distribution analysis was by the pipet method with prior removal of organic matter with H_2O_2. Soil pH was measured in water (1:2) and 0.01 M $CaCl_2$ (1:2) on a Fisher-Acumet pH meter using double electrodes. Exchangeable cations (Ca, Mg, K, Na) were extracted with dilute silver thiourea (AgTU) (Pleysier and Juo, 1980). Calcium and Mg in the soil extract were determined on a Perkin-Elmer Model 5000 atomic absorption spectrophotometer with the addition of lanthanum to eliminate interferences in Ca determination. Sodium and K were determined by emission. Total acidity (Al+H) was determined on the Ag-TU extract by titrating with 0.02 N NaOH to the phenolphtalein endpoint. Effective cation exchange capacity (ECEC) was estimated as the sum of the exchangeable cations plus total acidity. Exchangeable Al was extracted with 1 N KCl (McLean, 1965) and determined by atomic absorption spectrophotometry. Organic matter was determined by a modified acid dichromate digestion (Walkley-Black, 1934). Free iron was extracted by two successive extractions using the dithionite-citrate-bicarbonate (Mehra and Jackson, 1960) procedure and determined by atomic absorption spectrophotometry.

Sulfate-sulfur (SO_4-S) was determined by a modified turbidimetric procedure (Hoeft et al., 1973). In this procedure 10 g of soil was placed in a 50 ml extracting flask and 25 ml of 500 ppm $Ca(H_2PO_4)_2$ -HOAc and 0.1 g of activated charcoal (previously boiled in acetic acid,

filtered and dried) were added to the soil. The sample was shaken for 15 minutes and filtered through Whatman No. 2 filter paper (previously washed with dilute acetic acid to remove SO_4-S impurities). A 10 ml aliquot of the filtrate was transferred to a 50 ml beaker and 10 ml of $BaCl_2$-gum arabic-HOAc solution was added. The mixture was shaken for 10 minutes and the sample was transferred to a Bausch and Lomb Spectronic 20 colorimeter where transmittance was read at a wavelength of 440 nm. The SO_4-S was regressed on soil pH, clay content, Fe_2O_3, Al and BS by simple linear regression analysis.

Mineralogical

Soil fractionation was carried out using a modified Kittrick and Hope (1963) procedure. The only modification was two successive dithionite-citrate-bicarbonate extractions. Oriented clay and silt samples were mounted on ceramic tiles by suction and subjected to x-ray diffraction analysis using a Norelco-Phillips x-ray diffractometer unit with Ni-filtered CuKα radiation generated at 35 kV and 15 ma. The scanning rate was 1°2θ per minute. The samples were subjected to the following treatments before x-ray analysis: (1) Mg saturation and glycerol solvation, air dry, and (2) K saturation, air dry, and heat treatments of 110°C, 330°C, and 550°C, each for 2 hours. The treatments were applied directly on the tiles. Saprolite samples, cutans and clay flows on saprolite were crushed in a diamonite mortar, passed through a 140 mesh sieve and subjected to x-ray analysis.

A DuPont R90 Differential Scanning Calorimeter (DSC) Thermal Analyzer was used for thermal investigations of the Mg-saturated clay

and silt fractions and the non treated, non-deferrated whole soil, saprolite, and illuviation cutan samples. Sample weight was 5 mg and an empty gold pan was used as the reference material. Heating rate was 20°C per minute. Kaolinite, gibbsite and quartz were estimated by comparing their endotherm (peak) areas with those of standard curves obtained from well crystallized kaolinite (KGal) from the Department of Geology source clay mineral repository, Missouri; synthetic gibbsite Type RH-31F from Reynolds Aluminum; and quartz from quartz crystals ground to pass through a 300 mesh sieve. Mica was determined by the HF digestion procedure of Bernas (1968) followed by flame emission analysis for elemental K (10% K_2O = 100% mica). All the K was allocated to mica on the assumption that there are little or no feldspars in the soils. Vermiculite was determined on selected samples by the Alexaides and Jackson (1965) procedure.

Clay mineral identification and quantification were carried out in most pedons. In some pedons only selected horizons were chosen for mineral identification and quantification. The standard error for quantification is $\pm$ 5.0% for kaolinite.

The results of this type of quantitative analyses are subject to too many uncertainties for them to denote accurately the absolute percentages of the minerals present in soils. However, the methods are good enough for poorly crystallized minerals such as are found in soils (Dixon, 1966).

CHAPTER IV

RESULTS

Soils Outside the Basin (Upland) CBCC 1A

Morphological and Physical

The present A horizon of the upland soil is not well developed and is only about 3 cm thick. The B horizon is about 100 cm thick, its color is predominantly red (2.5YR 4/6), and the texture is clay. The lower B horizons are marked by presence of clay skins on ped faces and absence of any mottles.

The particle size distribution data are shown in Table 3. The A horizon has about 29% clay. Clay content decreases to 20% in the AB horizon and increases agin in the BA horizon. Below 30 cm there is a rapid increase in clay content to a maximum of 45% in the lower B horizons. Clay distribution with depth tends to follow a pedogenic pattern of maximum accumulation in the B horizon. The presence of clay skins in the lower B horizons indicates that some of the clay in the B horizon is illuvial clay.

The silt content is high in all horizons ranging from 35% in the Cr horizon to 58% in the AB horizon. The high silt content of the soil may be due to the initial high silt content of the mica schist and graywacke parent material. The sand content is high in the A and C horizons. Most of the sand fraction in the C horizons consists of rock fragments, very coarse and coarse sand. The very coarse and coarse sand increase with depth reaching a maximum in the C horizon. This increase may be

Table 3. Particle size distribution of Pedon CBCC 1A.

Horizon	Depth	Sand 2000-50μm	Silt 50-2μm	Clay 2μm	Very Coarse Sand	Coarse Sand	Medium Sand	Fine Sand	Very Fine Sand	Coarse Silt	Fine Silt	Silt: Sand Ratio
	cm	----------	----------	----------	----------	----------	%----------	----------	----------	----------	----------	
A	0-3	22	49	29	0	2	3	6	11	31	18	2.22
AB	3-13	22	58	20	1	1	2	6	12	30	28	2.63
BAt	13-29	20	52	28	2	1	1	5	11	28	24	2.60
Bt1	29-50	14	41	45	0	0	1	4	9	23	18	2.92
2Bt2	50-73	20	38	42	0	1	3	5	11	26	12	1.90
2Bt3	73-85	17	38	45	0	1	1	5	11	24	14	2.23
2BCt	85-115	21	38	41	0	1	1	5	14	23	15	1.80
2C	115-125	28	38	34	3	4	3	7	11	24	14	1.35
2Cr	125-155	40	35	25	6	7	6	9	12	23	12	0.87

due to less physical weathering of the quartz-mica schist at that depth. When the total silt content is expressed as a percentage of the total sand content (Table 3), it shows that there is a discontinuity at about 50 cm depth.

Chemical

The A horizon of Pedon CBCC 1A is extremely acid (pH 3.9) with moderate increase in pH with depth (Table 4). Below 50 cm there is an abrupt increase in pH from 4.7 to 5.8. This abrupt increase in pH together with the particle size distribution data indicates that there is a time discontinuity at this depth.

The time discontinuity zone is further illustrated by other chemical properties. For an example, the effective cation exchange capacity (ECEC) of the A horizon is 4.09 meq/100 g soil (Table 4). This decreases to 0.80 meq/100 g soil in the AB horizon but increases again up to 2.26 meq in the Bt1 horizon. Below this horizon the ECEC drops to 0.98 meq and decreases with depth to the 2Cr horizon. When the ECEC is expressed on clay basis it shows that this soil is a low activity clay (LAC) soil because the ECEC does not exceed 12 meq/100 g clay (Moormann, 1978) except in the A horizon.

Calcium and Mg are the dominant exchangeable basic cations throughout the profile. The distribution of Ca and Mg in the profile is similar to that of the ECEC, showing an abrupt increase in the 2Bt2 horizon. Sodium and K make up a neglible portion of the ECEC. All the exchangeable basic cations have their highest values in the A horizon. This high content of bases in the A horizon may be directly related to the organic matter content which is 9.8% (Table 4) and recycling of bases.

Table 4. Chemical properties of Pedon CBCC 1A.

Horizon	Depth	pH (1:2) H_2O	pH (1:2) $CaCl_2$	Organic Matter	Silver thiourea Exchangeable cations Ca	Mg	K	Na	(H + Al)	ECEC/ 100 g soil	ECEC/ 100 g clay	KCl Extr Al	Base Saturation	Extr SO_4	Fe_2O_3-d
	cm			%	meq/100 g								%	µg/g	%
A	0-3	3.9	3.6	9.80	0.70	0.29	0.26	0.06	2.78	4.09	14.1	3.41	32	45	2.2
AB	3-13	4.9	4.5	1.50	0.05	0.05	0.08	0.04	0.58	0.80	4.0	1.36	28	53	2.9
BAt	13-29	4.6	4.4	0.52	0.07	0.06	0.06	0.03	1.04	1.26	4.5	1.27	17	88	3.6
Bt1	29-50	4.7	4.2	0.41	0.03	0.02	0.06	0.03	2.08	2.26	5.0	1.87	6	120	6.6
2Bt2	50-73	5.8	4.8	0.13	0.25	0.42	0.05	0.03	0.23	0.98	2.3	0.16	77	48	7.1
2Bt3	73-85	5.8	5.1	0.13	0.19	0.33	0.04	0.04	0.23	0.83	1.8	0.0	72	18	7.2
2BCt	85-115	5.9	5.2	0.13	0.19	0.27	0.04	0.04	0.23	0.77	1.8	0.0	70	18	6.9
2C	115-125	5.6	4.8	0.13	0.13	0.15	0.06	0.06	0.23	0.63	1.8	0.0	64	38	5.6
2Cr	125-155	5.6	5.1	0.13	0.25	0.11	0.05	0.03	0.23	0.67	2.7	0.0	66	38	8.7

The low pH of the soils and the very low ECEC values should suggest very high extractable acidity. On the contrary, the silver-thiourea (Ag-TU) extractable acidity (H-Al) is low ranging from 2.78 meq/100 g in the A horizon to 0.23 meq/100 g in the 2Cr horizon. Base saturation (BS) is low (<35%) above the Btl horizon and increases to greater than 60% below this horizon. This may be partly due to the higher Ca and Mg contents below this horizon and the negligible amounts of acidity below this depth (Table 4).

Potassium chloride extractable Al is relatively low ranging up to 3.4 meq/100 g in the A horizon. In the lower horizons (below 50 cm) there is virtually no extractable Al. This is partly due to the high base status and the high pH (pH $\geq$ 5.6). The relationships of Al, ECEC and BS with soil depth are shown in Figure 2. The discontinuity indicated by the dashed lines is clearly illustrated by these soil properties.

The position of this pedon on the landscape suggests that the soil is well drained. This is reflected in the color of the soils and the Fe_2O_3 content. Iron oxide has a maximum accumulation in the 2Cr horizon (8.7%). The Bt horizons have moderate Fe_2O_3 contents (6.6 - 7.2%). The high contents of Fe_2O_3 in the 2Cr may suggest a translocation of Fe_2O_3 from the upper horizons, or a parent material initially high in Fe. Calcium phosphate-acetic acid extractable sulfur (SO_4-S) is highest in the Btl horizon (120 µg/g) and decreases in the lower argillic horizons. There is more SO_4-S in the upper horizons (above 50 cm) than in the lower horizons. The SO_4-S of sampled soils was regressed on soil pH, clay content, dithionite extractable Fe, KCl extractable Al and BS in order to determine if any relationships existed between SO_4-S and these soil properties. A weak and non-significant relationship (correlation

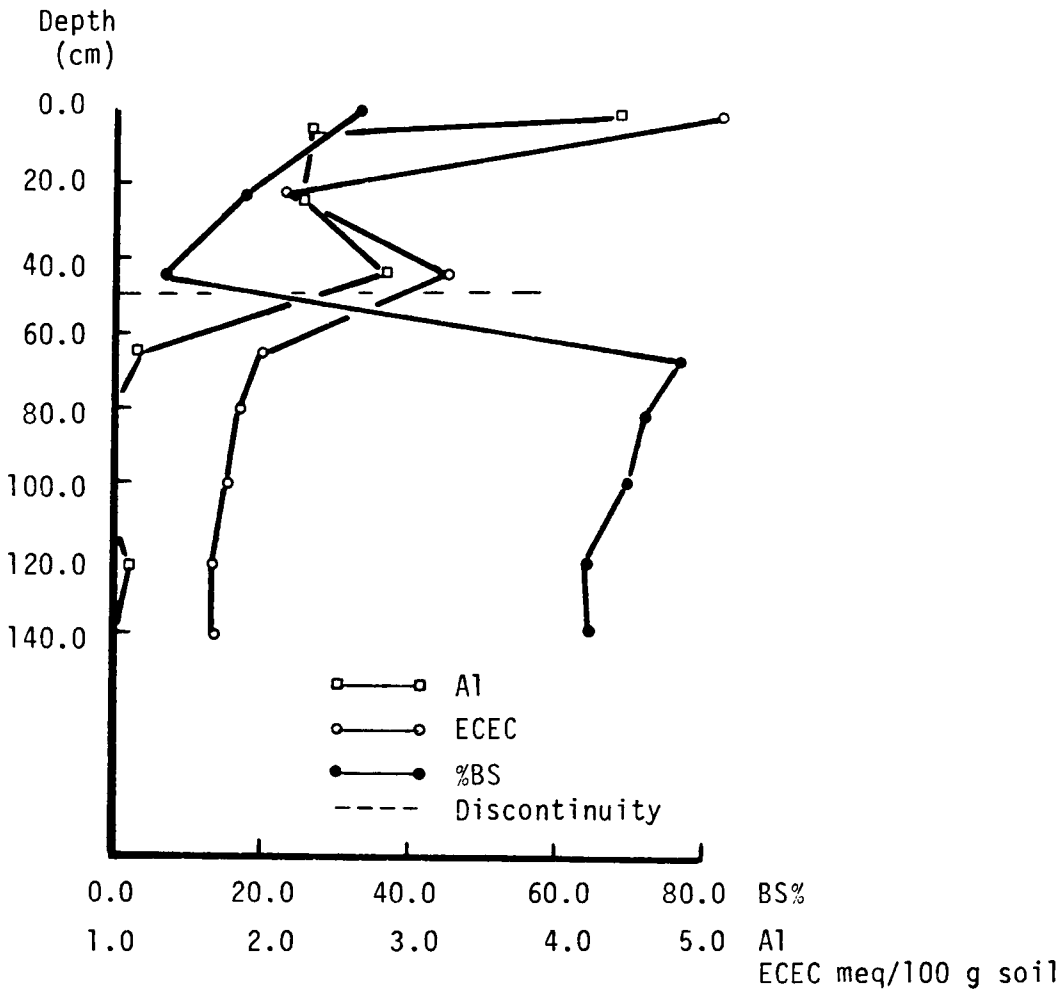

Figure 2. Depth relationships of selected chemical properties in Pedon CBCC 1A.

coefficient r = -0.56, p = 0.20) exists between SO_4-S and soil pH. No significant relationships existed between SO_4-S and the other soil properties (Table A-1, Appendix).

Mineralogical

The x-ray diffractograms of the clay fraction of selected horizons from Pedon CBCC 1A are shown in Figure 3. The fine clay and coarse clay fractions show identical patterns so only the coarse clay pattern is reported. The clay fraction of the A, Bt1 and 2Cr horizons (Figure 3) exhibit well defined diffraction maxima indicating well ordered crystalline minerals. The A horizon has peaks at 24.5 Å, 14.2 Å, 12.2 Å, 9.9 Å, 7.2 Å, 5.0 Å, 4.83 Å, 4.43 Å, 4.35 Å, 4.26 Å, 4.05 Å, 3.57 Å and 3.33 Å. The 24.5 Å peak remained unchanged after Mg and glycerol solvation. This indicates non-swelling interstratified mineral probably made up of a 10 and 14 Å spacing. The 14.2 Å peak did not show any changes with Mg and glycerol solvation. However, it became diffuse with K saturation and stage heating at 110°C, 330°C and 550°C. This gradual collapse of the 14.2 Å peak together with the non-swelling characteristic suggests the absence of montmorillonites and the presence of vermiculite with some hydroxy-Al interlayer material.

The 12.2 Å peak is the (002) reflection of the interstratified mineral (mica-vermiculite). The 9.9 Å, 5.0 Å and the 3.33 Å are the (001), (002), (003) reflections of mica. The 7.2 Å and the 3.57 Å peaks are due to kaolinite because these peaks collapsed completely after a 550°C heat treatment. Other important peaks are the 4.83 Å and the 4.35 Å. These peaks disappeared after a 330°C heat treatment and are indicative of gibbsite. The 4.26 Å peak is that of quartz. The 9.9 Å peak which

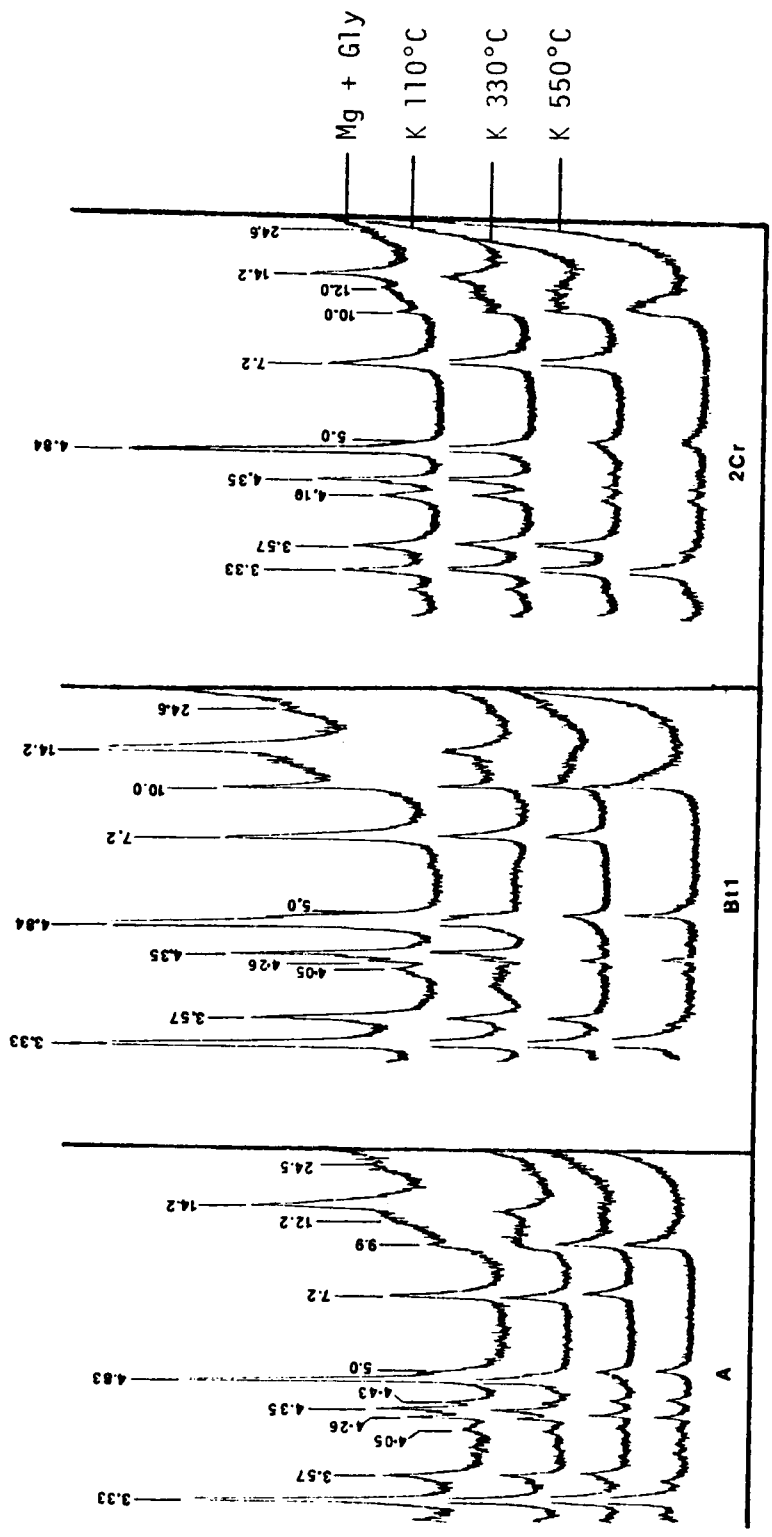

Figure 3. X-ray diffractograms of the coarse clay (2 - 0.2 μm) from Pedon CBCC 1A.

remained after the 550°C heat treatment has a shoulder on the low angle side indicating that the mica is weathering to vermiculite or is partially interlayered with Al. The 4.05 Å peak is due to feldspar.

The Bt1 and the 2Cr horizons have minerals similar to those in the A1 horizons (Figure 3). The 14.2, 10.0, 7.2, 4.84 and 3.33 Å peaks are more pronounced in the Bt1 horizon than in the A and 2Cr horizons. The 2Cr horizon has a very pronounced 4.84 Å peak. The 4.26 Å peak (quartz) is also very pronounced.

Quantitative mineralogical analysis (Table 5) of the clay fraction indicates that gibbsite and kaolinite are the dominant minerals in this pedon. Mica is found in intermediate quantities and vermiculite in minor amounts. Gibbsite increases with depth and has maximum concentration in the Cr horizon. Kaolinite increases with depth (up to 50 cm) and then decreases down in the profile. Gibbsite and kaolinite tend to have an inverse relationship starting from the 2Bt2 horizon down to the 2Cr. Mica is concentrated in the surface horizons and decreases with depth. Vermiculite is also concentrated in the A horizon but does not follow a uniform distribution with depth.

The mineralogy of the silt fraction (5 - 2 μm) as depicted by x-ray diffractograms (Figure 4) follows the same pattern as the clay fraction. The important differences to note are that (1) there is very little hydroxyl-interlayered vermiculite, (2) there is no vermiculite in the Cr horizon, (3) the kaolinite peaks are very small, (4) the mica peaks are long and symmetrical, and (5) considerable gibbsite occurs in the Cr horizon.

Table 5. Mineralogical Analysis of Pedon CBCC 1A.

		Whole Soil					Clay				
Horizon	Depth	Quartz	Gibbsite	Kaolinite	Fe_2O_3	R*	Gibbsite	Kaolinite	Mica	Quartz	Vermiculite
	cm	%					%				
A	0-3	25	5	5	2.2	0.24	15	20	18	15	11
AB	3-13	30	6	10	2.9	0.45	18	16	19	10	6
BAt	13-29	25	7	10	3.6	0.38	25	20	19	10	5
Bt1	29-50	20	15	10	6.6	0.48	32	25	14	5	6
2Bt2	50-73	20	20	11	7.1	0.65	35	22	10	0	8
2Bt3	73-85	20	20	11	7.2	0.60	37	16	10	0	8
2BCt	85-115	20	20	10	6.9	0.65	39	14	9	0	7
2C	115-125	20	17	8	5.6	0.67	36	14	9	0	9
2Cr	125-155	20	14	8	8.7	0.91	40	16	11	0	9

*(% Gibbsite + % Fe_2O_3)/ % clay

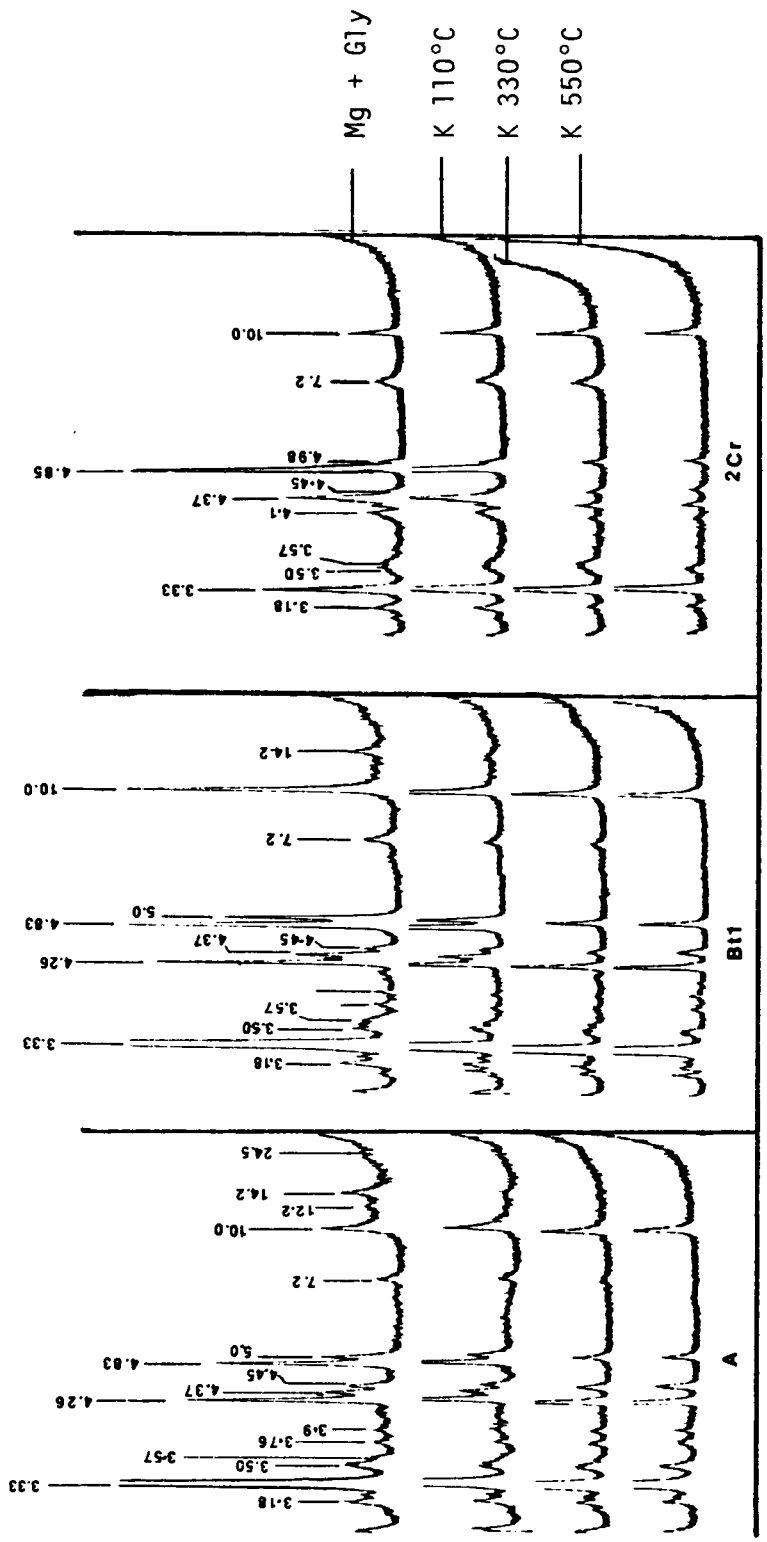

Figure 4. X-ray diffractograms of the fine silt (5 - 2 µm) from Pedon CBCC 1A.

The Differential Scanning Calorimetry (DSC) patterns (Figure 5) show that kaolinite is concentrated in the fine clay while gibbsite is concentrated in the coarse clay of the A and Bt horizons. In the 2Cr horizons, kaolinite tends to be more concentrated in the clay fraction while gibbsite is evenly concentrated in the silt and clay fractions.

Soils Outside the Basin (Footslope) CBCC 1C

Morphological and Physical

This site is distinguished by two buried soils and a younger surface capping. The lower buried soil (>111 cm) probably formed in residuum while the upper buried soil (18 - 111 cm) must have formed from rapid emplacement of mud flows. The surface capping (<18 cm) is the young soil formed from recent additions resulting from European settlement and deforestation.

The texture ranges from clay in the buried red soils to silty clay loam and gravelly clay loam in the overlying soil. A few clay skins are found on ped faces in the buried soil and indicates illuviated clay. Clay distribution with depth (Table 6) is erratic due to the buried horizons. However, the 3B'tb2 horizon has the highest clay content (56%) while the 3Cb and 3Cr have the lowest clay content (12%). Silt is high in all horizons and does not follow any trend. Sand is highest in the 3Cr horizon.

Chemical

The surface soils at this site are acid (pH 4.8) and the pH tends to increase with depth (Table 7). The 3B'tb horizons have the highest

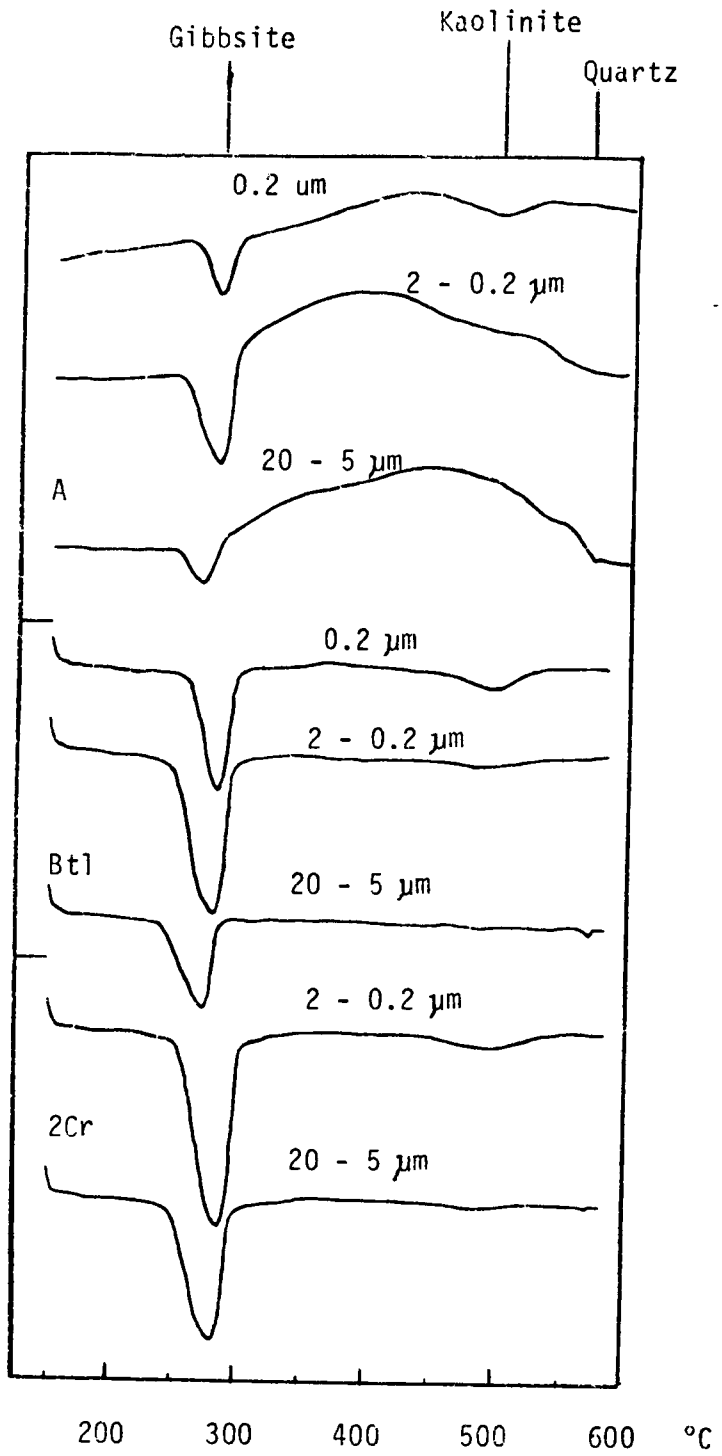

Figure 5. DSC curves of the clay and silt fractions of Pedon CBCC 1A.

Table 6. Particle size distribution of Pedon CBCC 1C.

Horizon	Depth	Sand 2000-50 um	Silt 50-2 µm	Clay <2 µm	Very Coarse Sand	Coarse Sand	Medium Sand	Fine Sand	Very Fine Sand	Coarse Silt	Fine Silt	Silt:Sand Ratio
	cm	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------
							%					
A11	0-5	24	62	14	1	2	4	8	9	33	29	2.58
A12	5-9	36	52	12	0	1	6	12	17	28	24	1.44
BA	9-18	23	57	20	0	2	4	6	11	24	33	2.47
2BAt	18-39	12	52	36	0	1	1	3	7	12	40	4.33
2Btb1	39-54	12	52	36	0	1	1	3	7	12	40	4.33
2Btb2	54-71	14	50	36	1	1	2	3	7	14	36	3.57
2BCtb	71-82	20	44	36	1	2	3	5	9	8	36	2.20
2Cb1	82-91	26	42	32	3	3	4	6	10	14	28	1.61
2Cb2	91-111	34	38	28	7	5	4	7	11	14	24	1.11
3Ab	111-115	35	33	32	9	6	5	7	8	17	16	0.94
3B'tb1	115-141	18	29	53	5	3	3	4	4	21	8	1.61
3B'tb2	141-155	25	19	56	3	3	4	7	8	11	8	0.76
3Bwb1	155-171	19	53	28	1	2	3	6	8	28	25	2.78
3Bwb2	171-181	35	45	20	5	6	6	8	9	25	20	1.28
3Cb	181-199	42	46	12	8	7	7	9	11	26	20	1.09
3Cr	199-205	48	40	12	9	9	8	10	12	28	12	0.83

Table 7. Chemical properties of Pedon CBCC 1C.

Horizon	Depth	pH (1:2) H_2O	pH (1:2) $CaCl_2$	Organic Matter	Silver thiourea Exchangeable cations Ca	Mg	K	Na	(H + Al)	ECEC/ 100 g soil	ECEC/ 100 g clay	KCl Extr Al	Base Saturation	Extr SO_4	Fe_2O_3-d
	cm			%	meq/100 g								%	µg/g	%
A11	0-5	4.8	4.5	5.58	0.36	0.20	0.15	0.04	0.58	1.33	9.50	3.47	56	28	3.6
A12	5-9	4.8	4.5	2.64	0.05	0.10	0.07	0.19	0.41	0.82	6.80	2.51	50	45	4.2
BA	9-18	5.3	4.5	1.32	0.06	0.05	0.06	0.03	0.75	0.95	4.75	2.60	21	65	4.6
2BAt	18-39	5.2	4.4	0.59	0.06	0.05	0.06	0.02	0.70	0.89	2.47	2.61	21	70	4.1
2Btb1	39-54	5.0	4.3	0.41	0.05	0.04	0.07	0.02	1.27	1.45	4.02	2.56	12	68	4.1
2Btb2	54-71	5.3	4.4	0.27	0.12	0.21	0.07	0.09	1.16	1.65	4.58	2.50	30	53	3.4
2BCtb	71-82	5.3	4.4	0.20	0.06	0.53	0.07	0.03	1.74	2.43	6.75	3.43	28	43	3.1
2Cb1	82-91	5.1	4.3	0.20	0.01	0.47	0.11	0.05	2.66	3.30	10.31	3.97	19	30	3.2
2Cb2	91-111	5.4	4.4	0.19	0.01	0.37	0.07	0.02	2.55	3.02	10.78	3.06	16	10	3.1
3Ab	111-115	5.0	4.4	0.17	0.06	0.25	0.06	0.03	1.27	1.67	5.21	1.64	24	15	4.7
3B'tb1	115-141	5.5	4.5	0.16	0.01	0.21	0.05	0.02	1.74	2.03	3.83	1.74	14	10	6.5
3B'tb2	141-155	5.6	4.6	0.09	0.01	0.17	0.05	0.02	1.39	1.64	2.92	1.38	15	10	7.6
3Bwb1	155-171	5.2	4.5	0.07	0.02	0.13	0.04	0.02	1.51	1.72	6.14	1.74	12	20	6.5
3Bwb2	171-181	5.4	4.4	0.07	0.02	0.11	0.05	0.03	1.27	1.48	7.40	1.50	14	25	5.0
3CB	181-199	5.2	4.3	0.06	0.03	0.12	0.04	0.02	1.39	1.60	13.33	1.74	13	23	4.8
3Cr	199-205	5.2	4.3	0.06	0.02	0.08	0.04	0.03	1.16	1.33	11.08	1.34	13	20	5.1

pH (5.6). Calcium and Mg make up the bulk of the exchangeable bases while Na and K contribute very little. Magnesium is concentrated mainly in the buried horizons. The ECEC is very low in all horizons. The A horizon has a ECEC of 1.33 meq/100 g soil. This drops to less than 1.0 meq in the horizons below and increases to greater than 1.0 meq in the buried horizons (Table 7). The ECEC calculated on clay basis indicates that this soil is a low activity clay (LAC) soil because it has an ECEC that is less than 12.0 meq/100 g clay in all horizons. The surface horizon has the greatest concentration of exchangeable bases primarily due to the high organic matter content (5.58%).

Silver thiourea extractable acidity (H + Al) is low in the surface horizons but increases in the buried horizons. Base saturation is high in the A horizons (50 - 56%) but drops to less than 35% in all other horizons. Potassium chloride extractable Al is moderate in most horizons. This is primarily due to the low pH ($CaCl_2$) throughout the profile. At such low pH values (4.3 - 4.5), KCl can extract some Al (Juo, 1977).

Iron oxide is relatively high in the buried horizons and its distribution follows the trend in clay distribution with depth (Table 7). The relationships of Al, ECEC and BS with soil depth indicate similar Al and ECEC distribution while BS follows an opposite trend (Figure 6).

Sulfate-S ranges in concentration from 70 ug/g in the upper argillic horizon to 10 ug/g in the buried argillic horizon (Table 7). Relationships between SO_4-S and other soil properties are presented in Table A-2, Appendix. No significant relationships exist between SO_4-S and soil pH, Fe_2O_3, Al, BS, and clay content (Table A-2, Appendix).

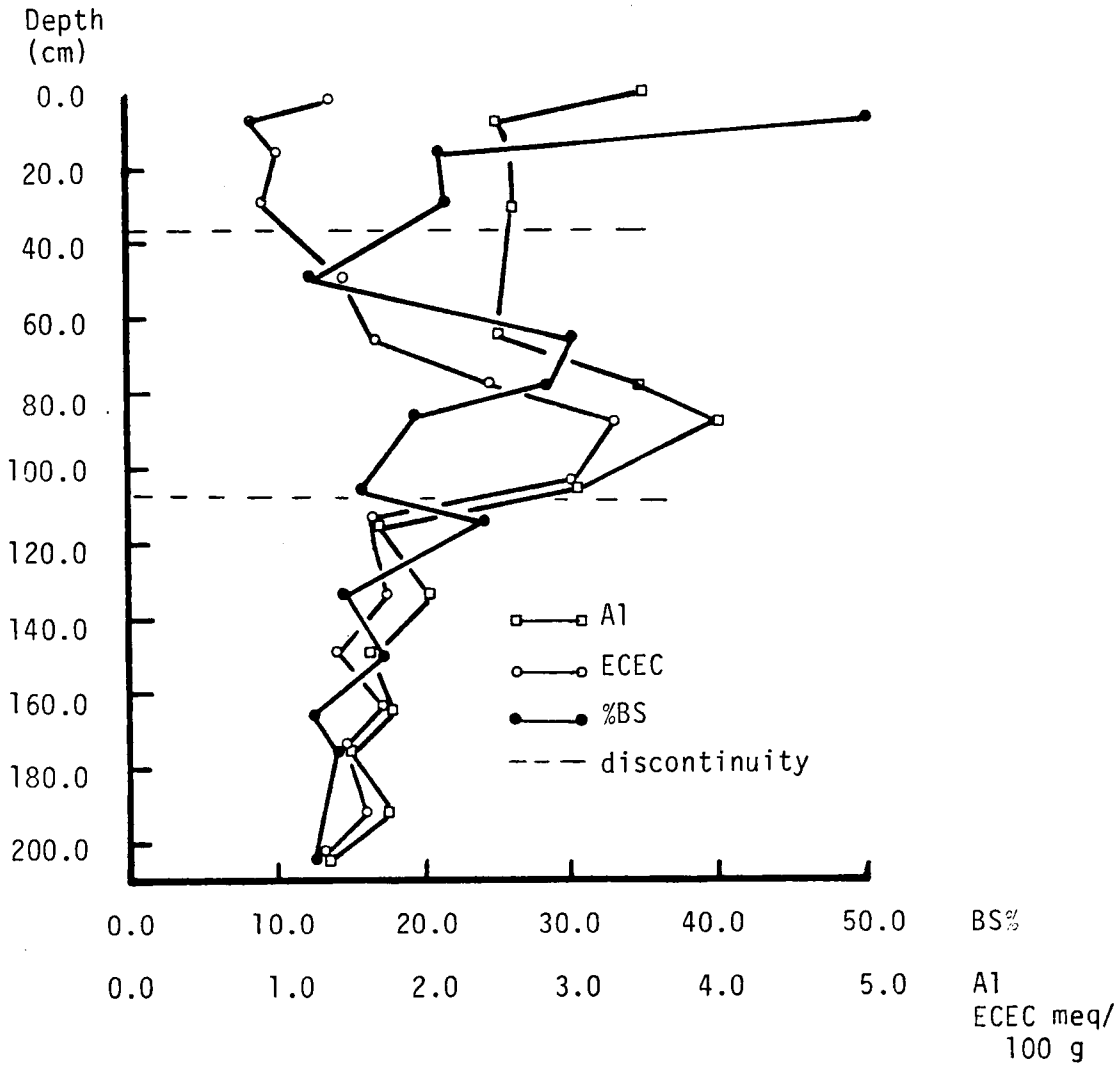

Figure 6. Depth relationships of selected chemical properties in Pedon CBCC 1C.

Mineralogical

X-ray diffractograms of the clay and silt fractions of selected horizons are presented in Figures 7 and 8, respectively. Quantitative mineralogical data are presented in Table 8. The same minerals identified in the upland soil (CBCC 1A) are found in this soil. However, HIV is found only in the A and B horizons and is absent in the C and Cr horizons. Kaolinite is the dominant mineral in this pedon and increases with depth (Figure 7). Table 8 shows that clay mica is evenly distributed in the pedon and does not show any trend with depth. Kaolinite increases with depth into the Cr horizon. Gibbsite increases with depth up to the B horizons but decreases in the C and Cr horizons. Gibbsite levels are relatively low ranging from 1.5% in the Cr to 13% in the buried argillic horizons.

The silt fraction (Figure 8) shows diffraction patterns similar to the clay fraction (Figure 7). However, the silt fraction does not contain any HIV and the silt sized mica has good diffraction maxima. Kaolinite increases with depth as indicated by increases in the 7.2 Å peak (Figure 8). The Cr is dominated by kaolinite.

The DSC patterns of this pedon (Figure 9) show the same trend observed in the upland soil with regard to kaolinite. Gibbsite, however, is found in minute quantities in this pedon and is mainly concentrated in the clay fraction.

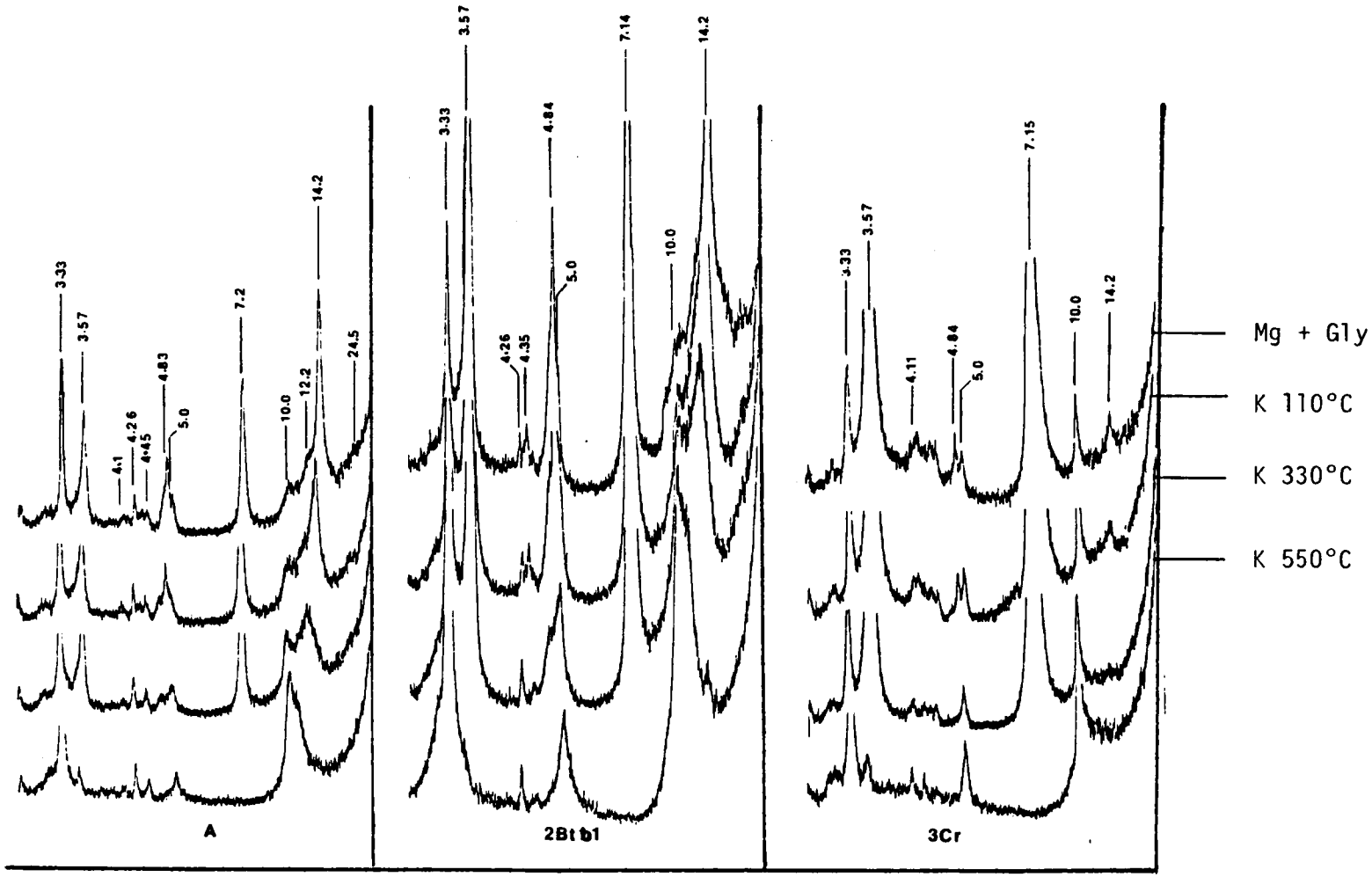

Figure 7. X-ray diffractograms of the coarse clay (2 - 0.2 µm) from Pedon CBCC 1C.

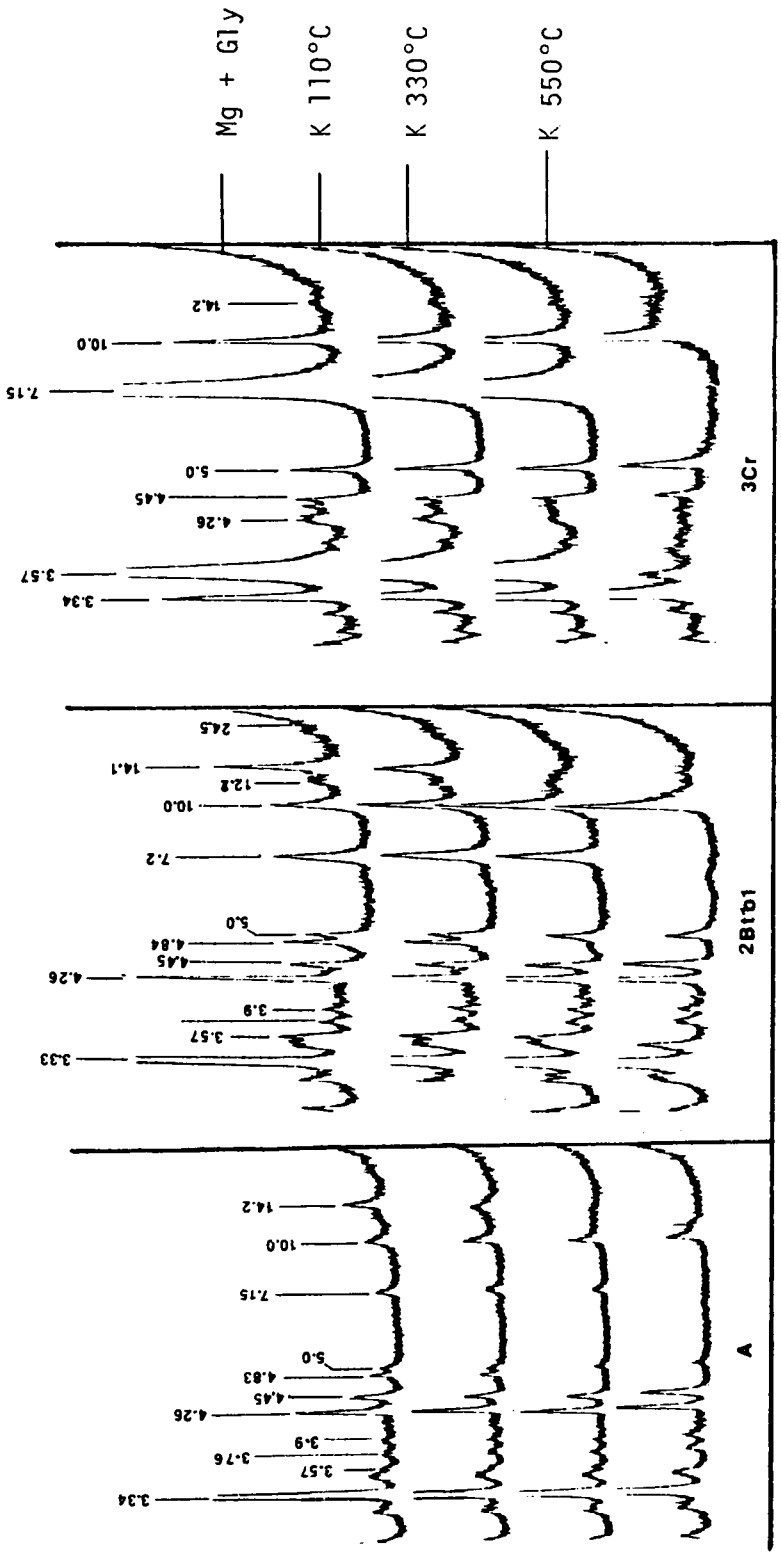

Figure 8. X-ray diffractograms of the fine silt (5 - 2 μm) from Pedon CBCC 1C.

Table 8. Mineralogical Analysis of Pedon CBCC 1C.

		Whole Soil					Clay			
Horizon	Depth	Quartz	Gibbsite	Kaolinite	Fe_2O_3	R*	Gibbsite	Kaolinite	Mica	Quartz
	cm	%					%			
A11	0-5	25	1	10	3.6	0.38	3	16	17	0
A12	5-9	25	2	6	4.2	0.55	4	16	16	0
BA	9-18	20	3	10	4.6	0.40	4	16	16	0
2BAt	18-39	20	3	10	4.1	0.21	6	15	16	0
2Btb1	39-54	25	3	13	4.1	0.21	7	20	15	0
2Btb2	54-71	25	3	13	3.4	0.20	6	20	15	0
2BCtb	71-82	25	2	12	3.1	0.14	3	23	15	0
2Cb1	82-91	30	2	12	3.2	0.16	-	-	-	-
2Cb2	91-111	35	1	13	3.1	0.17	-	-	-	-
3Ab	111-115	35	4	20	4.7	0.27	-	-	-	-
3B'tb1	115-141	20	5	29	6.5	0.22	11	50	12	0
3B'tb2	141-155	20	5	30	7.6	0.23	13	52	11	0
3Bwb1	155-171	10	0	50	6.5	0.25	-	-	-	-
3Bwb2	171-181	10	0	38	5.0	0.25	-	-	-	-
3Cb	181-199	10	0	38	4.8	0.40	2	66	11	0
3Cr	199-205	10	0	36	5.1	0.43	1	75	18	0

*(% Gibbsite + % Fe_2O_3)/ % Clay.

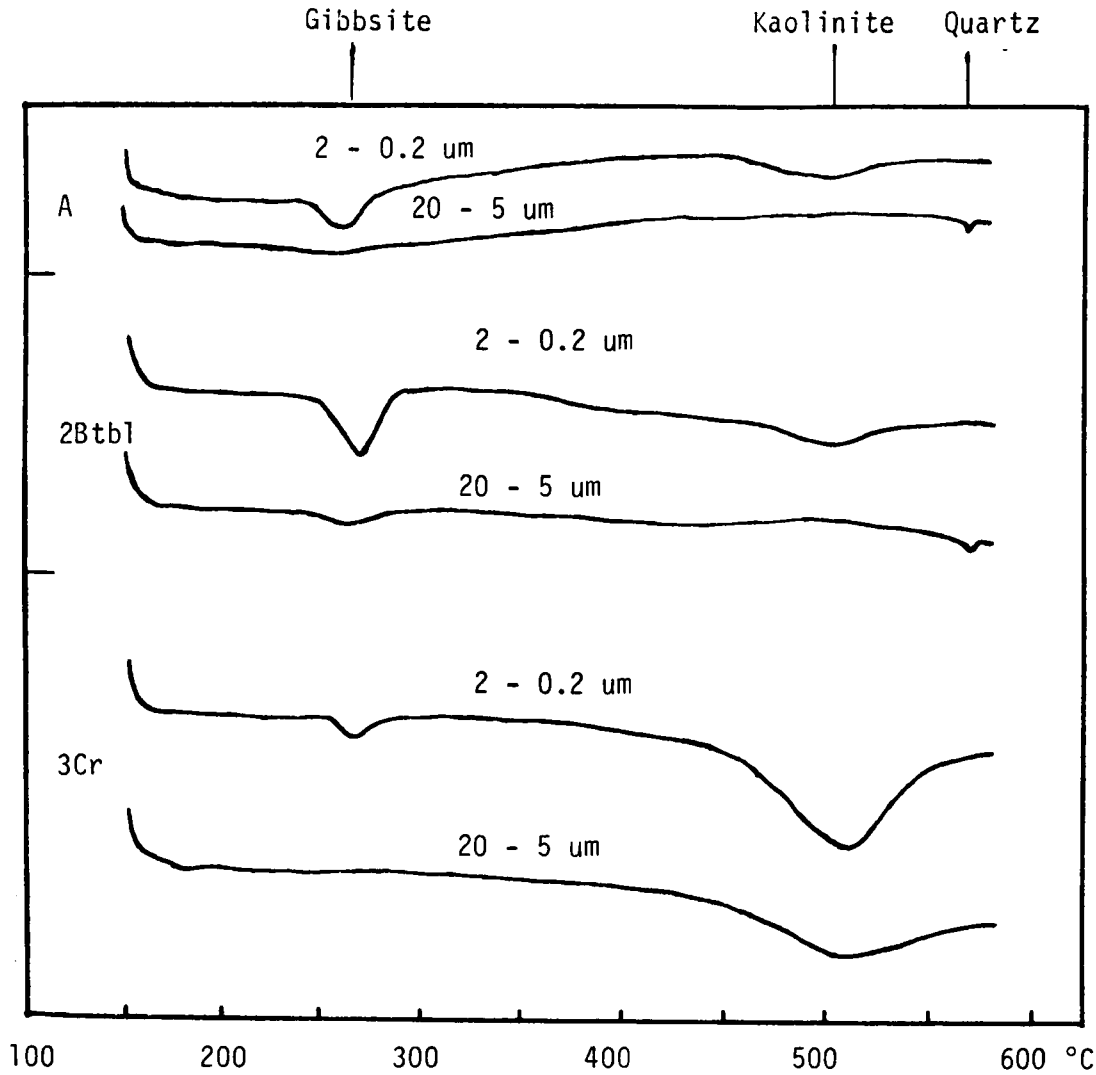

Figure 9. DSC curves of the clay and silt fractions of Pedon CBCC 1C.

Soils Inside the Basin (Upland, Old Smelter) CBOS 2A

Morphological and Physical

This upland soil has morphological and physical properties similar to that of Pedon CBCC 1A outside the Basin. This soil has been altered by change from forest to grass vegetation in the last 50 years. When compared to Pedon CBCC 1A, this pedon has no roots in the subsoil and there is no recycling of nutrients from deeper horizons. The subsoil is red (2.5YR 4/6) and clayey, the lower B horizons have clay skins on ped faces, and there is good soil development as indicated by the argillic horizon (See Pedon description). The particle size (Table 9) distribution follows a pedogenic pattern and resembles the distribution discussed in Pedon CBCC 1A. The silt:sand ratio shows a uniform parent material and the wide range in the A horizon may be attributed to wind deposited silt.

Chemical

The horizons of this pedon are acid ranging in pH from 4.0 in the A to 5.0 in the Cr (Table 10). This pedon is acid throughout in contrast to Pedon CBCC 1A which has somewhat higher pH in the lower horizons. The organic matter content is concentrated in the A horizon (5.1%) and decreases with depth. Other chemical properties such as exchangeable acidity, ECEC and extractable Al follow a pattern similar to that of Pedon CBCC 1A. Exchangeable acidity is relatively high in the A and Bt horizons (Table 10) but very low in the C and Cr horizons. Exchangeable Al is moderate to high in most horizons except the C and Cr. Base

Table 9. Particle size distribution of Pedon CBOS 2A.

Horizon	Depth	Sand 2000-50 µm	Silt 50-2 µm	Clay <2 µm	Very Coarse Sand	Coarse Sand	Medium Sand	Fine Sand	Very Fine Sand	Coarse Silt	Fine Silt	Silt:Sand Ratio
	cm	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------
							%					
A	0-7	29	55	16	1	2	4	11	11	26	29	1.89
BAt	7-14	44	28	28	2	1	4	14	23	8	20	0.63
Bt1	14-22	38	25	37	0	1	4	13	20	9	16	0.65
Bt2	22-48	29	14	57	0	1	3	9	16	6	8	0.48
Bt3	48-68	34	14	52	0	2	4	11	17	10	4	0.41
BCt	68-96	54	18	28	0	2	6	17	29	10	8	0.33
C	96-122	79	13	8	2	9	15	28	25	5	8	0.16
Cr	122+	87	5	8	2	10	16	33	26	1	4	0.05

Table 10. Chemical properties of Pedon CBOS 2A.

Horizon	Depth	pH (1:2) H_2O	pH (1:2) $CaCl_2$	Organic Matter	Silver thiourea Exchangeable cations Ca	Mg	K	Na	(H + Al)	ECEC/ 100 g Soil	ECEC/ 100 g Clay	KCl Extr Al	Base Saturation	Extr SO_4	Fe_2O_3-d
	cm			%	meq/100 g								%	µg/g	%
A	0-7	4.0	3.4	5.10	0.08	0.08	0.14	0.03	3.76	4.09	25.5	3.15	8	68	3.0
BAt	7-14	4.5	3.9	0.91	0.04	0.04	0.03	0.02	1.04	1.17	4.2	1.59	11	93	4.4
Bt1	14-22	4.3	3.8	0.50	0.02	0.03	0.06	0.01	2.08	2.20	5.9	1.99	5	115	2.5
Bt2	22-48	4.3	3.8	0.35	0.01	0.02	0.06	0.02	2.78	2.89	5.0	2.99	4	160	6.4
Bt3	48-68	4.2	3.8	0.17	0.00	0.02	0.04	0.02	1.97	2.05	3.9	2.72	4	160	7.1
BCt	68-96	4.3	3.9	0.09	0.03	0.03	0.03	0.01	1.16	1.26	4.5	1.32	8	160	5.0
C	96-122	5.0	4.3	0.06	0.40	0.30	0.05	0.03	0.23	1.01	12.6	0.45	77	95	4.4
Cr	122+	5.0	4.3	0.02	0.29	0.20	0.04	0.01	0.12	0.66	8.2	0.66	82	83	3.9

saturation follows a trend opposite to that of extractable Al and exchangeable acidity (Figure 10).

The exchangeable basic cations are very negligible in all horizons except the C and Cr horizons in the case of Ca and Mg and the A horizon in the case of K (Table 10). The ECEC indicates that this soil is a LAC soil having less than 12 meq/100 g clay ECEC in most horizons.

Iron oxide concentration is high throughout the profile ranging from 7.0% in the argillic horizon to 3.0% in the A horizon (Table 10). Manganese nodules are present in the C and Cr horizons of this pedon (See Pedon description) and may be responsible for the decrease in iron oxide content in these horizons.

Sulfate-S concentration ranges from 68 μg/g in the A horizon to 160 μg/g in the argillic horizon. No significant relationships were found between SO_4-S and soil pH, BS, and extractable Al (Table A-3, Appendix). There was a significant relationship between SO_4-S and clay content in this pedon (correlation coefficient $r = 0.79$, $p = 0.05$). A significant relationship was also found between SO_4-S and Fe_2O_3 (correlation coefficient $r = 0.76$, $p = 0.05$). These relationships suggest that SO_4-S distribution is related to the clay content of this soil and the Fe_2O_3content.

Mineralogical

X-ray diffractograms of the clay and silt fractions of selected horizons of Pedon CBOS 2A are presented in Figures 11 and 12, respectively. Basically, the same minerals identified in Pedon CBCC 1A are found in this pedon. In addition, there are conspicuous peaks at 4.43 Å in the A horizon, 8.2 Å and 4.1 Å in the Cr horizon (Figure 11). The

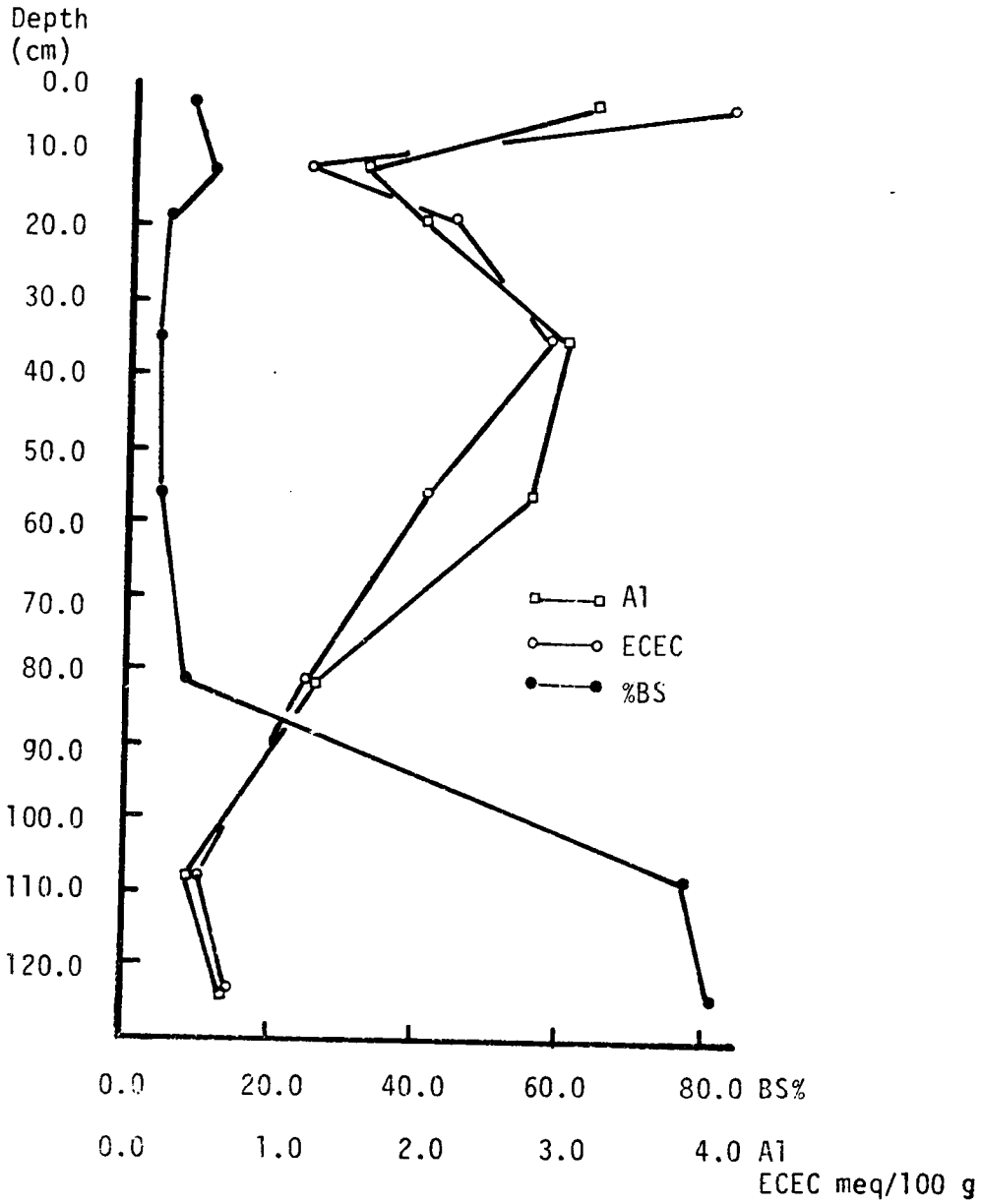

Figure 10. Depth relationships of selected chemical properties in Pedon CBOS 2A.

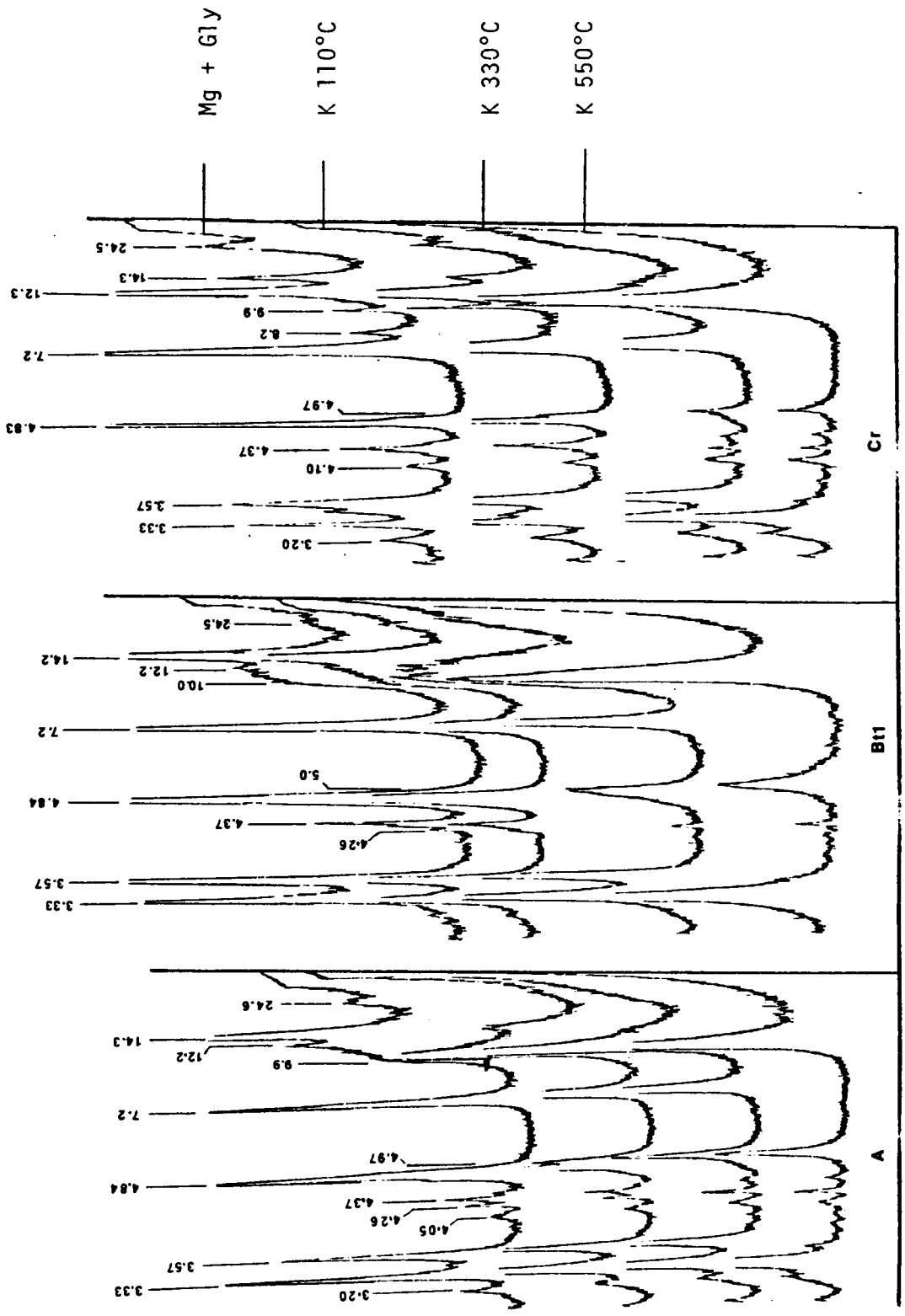

Figure 11. X-ray diffractograms of the coarse clay (2 - 0.2 µm) from Pedon CBOS 2A.

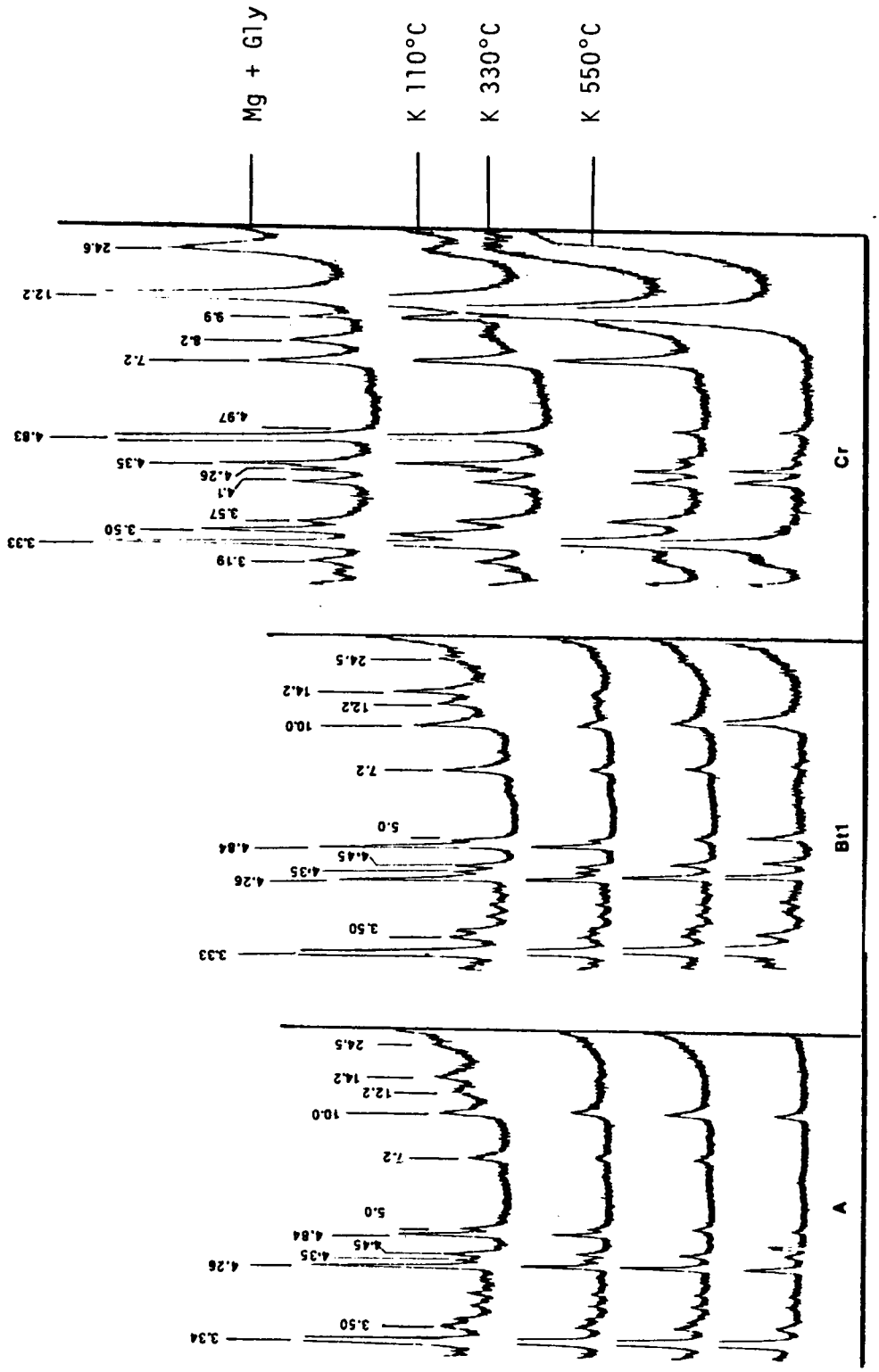

Figure 12. X-ray diffractograms of the fine silt (5 - 2 µm) from Pedon CBOS 2A.

8.2 Å peak is the (003) reflection of the 24.5 Å interstratified mineral. The 4.1 Å peak could be the (006) reflection of the interstratified mineral. However, since the 4.1 Å peak survived a 550°C heat treatment, it suggests that this peak is not due to the interstratified mineral but is due to feldspar. The 4.45 Å peak (Figure 12) is the (111) reflection of mica since it survived the 550°C heat treatment.

Interstratification is found in the A, Bt and Cr horizons of the clay and silt fractions (Figures 11 and 12). The interstratification is regular and is due to mica and vermiculite. This is confirmed by the non-expansion of the 24.5 Å peak after Mg and glycerol solvation; the asymmetry of the 10 Å peak toward the low angle side; and the broadening and attenuation of the 5.0 Å peak with heat treatments. All these suggest that mica is weathering to vermiculite.

Heat treatments confirmed the presence of HIV in the A and Bt horizons of the clay fraction (Figure 11) and its absence in the silt fraction (Figure 12). Quantitative mineralogical analysis (Table 11) shows that kaolinite and gibbsite are low in the A horizon and increase with depth. Gibbsite has its maximum concentration in the Bt horizon and decreases into the C and Cr horizons. Kaolinite, on the other hand has its maximum concentration in the Cr horizon (42%). Clay size mica is high in the A and upper argillic horizons (16 - 29%) and in the Cr horizon (18%). Vermiculite is concentrated in the A horizon (20%).

The DSC patterns (Figure 13) show that kaolinite and gibbsite are concentrated in the clay fraction of all horizons. However, in the lower argillic horizon, gibbsite is evenly distributed in the clay and silt fractions.

Table 11. Mineralogical Analysis of Pedon CBOS 2A.

Horizon	Depth	Whole Soil					Clay				
		Quartz	Gibbsite	Kaolinite	Fe_2O_3	R*	Gibbsite	Kaolinite	Mica	Quartz	Vermiculite
	cm	%					%				
A	0-7	35	3	5	3.0	0.37	14	10	18	5	20
BAt	7-14	40	5	6	4.4	0.35	19	10	20	5	7
Bt1	14-22	40	7	6	2.5	0.26	23	16	16	0	6
Bt2	22-48	20	13	10	6.4	0.35	28	23	28	0	8
Bt3	48-68	20	18	15	7.1	0.50	36	23	14	0	9
BCt	68-96	20	20	10	5.0	0.90	41	25	13	0	9
C	96-122	25	5	10	4.4	1.18	33	41	13	0	7
Cr	122+	25	1	10	3.9	0.61	18	42	18	0	7

*(% Gibbsite + % Fe_2O_3)/ % Clay.

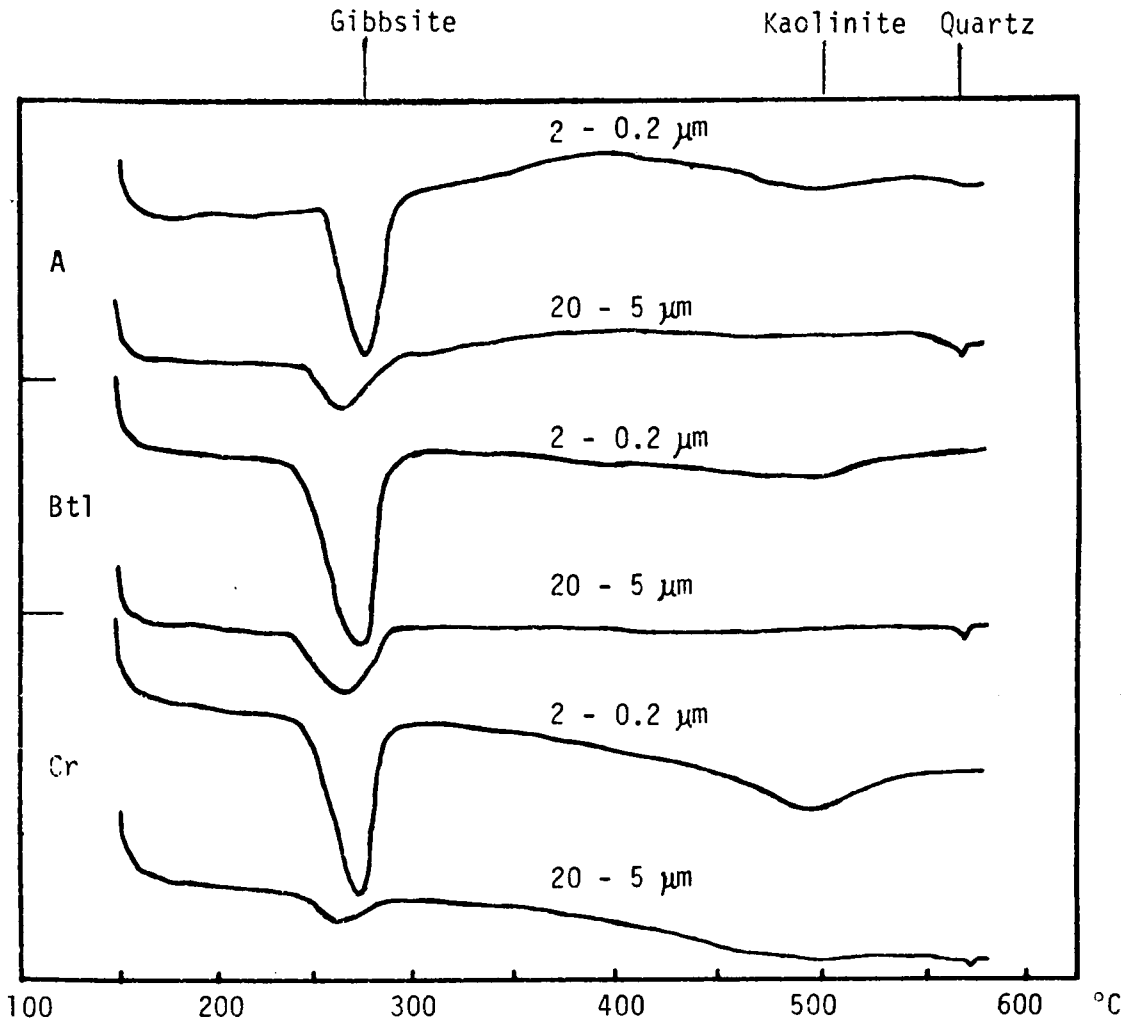

Figure 13. DSC curves of the clay and silt fractions of Pedon CBOS 2A.

These mineralogical data show that kaolinite and gibbsite distribution with depth is the exact opposite of what prevailed in Pedon CBCC 1A. Unlike Pedon CBCC 1A, kaolinite is the dominant mineral in the C horizon of Pedon CBOS 2A. While interstratified minerals (mica-vermiculite) are observed in both the clay and silt fractions of Pedon CBOS 2A, very weak interstratification is seen in the clay fraction of Pedon CBCC 1A.

Soils Inside the Basin (Midslope, Old Smelter) CBOS 2B

Morphological and Physical

This pedon is located in the midslopes close to the old smelter. It is made up of a buried older red soil overlaid by a younger soil (See Pedon description). The buried argillic horizons have a clayey texture while the young argillic horizons have clay loam texture. Clay content generally increases with depth reaching a maximum in the buried argillic horizons and subsequently it decreases with depth (Table 12). Sand content follows a reverse pattern, being lowest in the buried argillic horizons and highest in the A and Cr horizons. The ratio of silt to clay exhibits a discontinuity at about 66 cm depth. The soil horizon between 49 and 66 cm is a mixed zone of gravel concentrate and may be an old erosion surface in an argillic horizon.

Chemical

The chemical properties (Table 13) show that the surface horizons are extremely acid (pH = 3.8). Acidity decreases with depth and the pH reaches 5.3 in the Cr horizon. Organic matter is concentrated in the A horizon (4.2%) and decreases with depth. Exchangeable basic cations

Table 12. Particle size distribution of Pedon CBOS 2B.

Horizon	Depth	Sand 2000-50 μm	Silt 50-2 μm	Clay <2 μm	Very Coarse Sand	Coarse Sand	Medium Sand	Fine Sand	Very Fine Sand	Coarse Silt	Fine Silt	Silt:Sand Ratio
	cm	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------
A	0-4	47	33	20	1	2	9	17	18	17	16	0.70
Ap	4-12	48	28	24	0	3	10	17	18	7	21	0.58
Bt1	12-23	45	27	28	1	3	9	17	15	3	24	0.60
Bt2	23-49	42	30	28	1	3	8	15	15	10	20	0.71
2Bt3	49-66	46	18	36	3	4	8	15	16	1	17	0.39
2Btb1	66-92	37	19	44	1	2	6	14	14	3	16	0.51
2Btb2	92-125	31	16	53	1	1	5	12	12	0	16	0.51
2BCb	125-150	50	18	32	0	2	8	20	20	2	16	0.36
2Cb1	150-170	67	17	16	1	2	11	27	26	5	12	0.25
2Cb2	170-196	69	15	15	0	2	11	27	29	7	8	0.21
2Cr	196-230	80	12	8	3	10	18	27	22	4	8	0.15

Table 13. Chemical properties of Pedon CBOS 2B.

Horizon	Depth	pH (1:2) H_2O	pH (1:2) $CaCl_2$	Organic Matter	Silver thiourea Exchangeable cations Ca	Mg	K	Na	(H + Al)	ECEC/ 100 g Soil	ECEC/ 100 g Clay	KCl Extr Al	Base Saturation	Extr SO_4	Fe_2O_3-d
					meq/100 g								%	µg/g	%
A	0-4	3.8	3.4	4.28	0.10	0.13	0.11	0.03	4.40	4.76	23.8	3.40	8	33	2.2
Ap	4-12	4.2	3.8	1.25	0.08	0.07	0.04	0.02	1.51	1.72	7.1	2.08	12	60	1.6
Bt1	12-23	4.4	3.9	0.67	0.00	0.02	0.05	0.01	2.32	2.40	8.6	2.17	3	75	2.1
Bt2	23-49	4.5	4.0	0.41	0.01	0.01	0.05	0.01	2.20	2.28	8.1	2.47	4	93	2.4
2Bt3	49-66	4.5	4.0	0.13	0.00	0.02	0.05	0.02	2.55	2.64	7.3	3.55	3	120	3.2
2Btb1	66-92	4.5	4.0	0.13	0.01	0.02	0.05	0.02	2.66	2.76	6.3	2.74	4	150	5.4
2Btb2	92-125	4.5	4.0	0.06	0.09	0.20	0.07	0.01	2.08	2.45	4.6	2.71	15	128	6.8
2BCb	125-150	4.7	4.1	0.06	0.18	0.12	0.12	0.03	1.27	1.72	5.4	1.27	26	115	6.0
2Cb1	150-170	5.1	4.4	0.06	0.35	0.21	0.12	0.02	0.58	1.28	8.0	0.52	54	85	3.6
2Cb2	170-196	5.1	4.4	0.03	0.36	0.22	0.09	0.02	0.46	1.15	7.2	0.44	60	85	3.3
2Cr	196-230	5.3	4.6	0.03	0.28	0.12	0.23	0.05	0.35	1.03	12.8	0.11	66	28	1.2

are very low in most horizons. However, the C and Cr horizons are relatively high in basic exchangeable cations. Calcium, Mg and K make up the bulk of the exchangeable basic cations in the C horizons. The increase in basic exchangeable cations in the lower horizons is partly due to increased lateral leaching in the surface soils and the somewhat reduced vertical drainage in the whole soil. Cations may be lost from the upper horizons while the lower horizons do not lose as much as the upper horizons. The buried horizons may actually trap some of the bases leached out from the upland areas or from the colluvium capping.

Silver thiourea exchangeable acidity is relatively high in the A horizon (4.4 meq/100 g) but is very low in the C horizons (0.35 - 0.58 meq/100 g). The KCl extractable Al is relatively high in the A and Bt horizons but very low in horizons with pH>5.0 (H_2O). The ECEC is very low on a whole soil basis. When ECEC is calculated on a clay basis, most of the values are less than 12.0 meq/100 g indicating a LAC soil. Base saturation is low in all horizons (<35%) except in the C horizons where BS is high (Table 13). The ECEC and Al distribution with depth are similar while base saturation follows an opposite trend (Figure 14).

Iron oxide distribution follows a trend similar to clay distribution attaining maximum concentration (6.8%) in the 2Btb2 horizon. The 2Cr horizon has the lowest Fe_2O_3 content in the whole pedon. Compared with the Cr horizon of Pedon CBOS 2A (Table 10, page 57) this is very minute.

Sulfate-S is concentrated in the B horizons reaching its lowest value in the Cr horizon. Significant relationships exist (Table A-4, Appendix) between SO_4-S and clay content (correlation coefficient

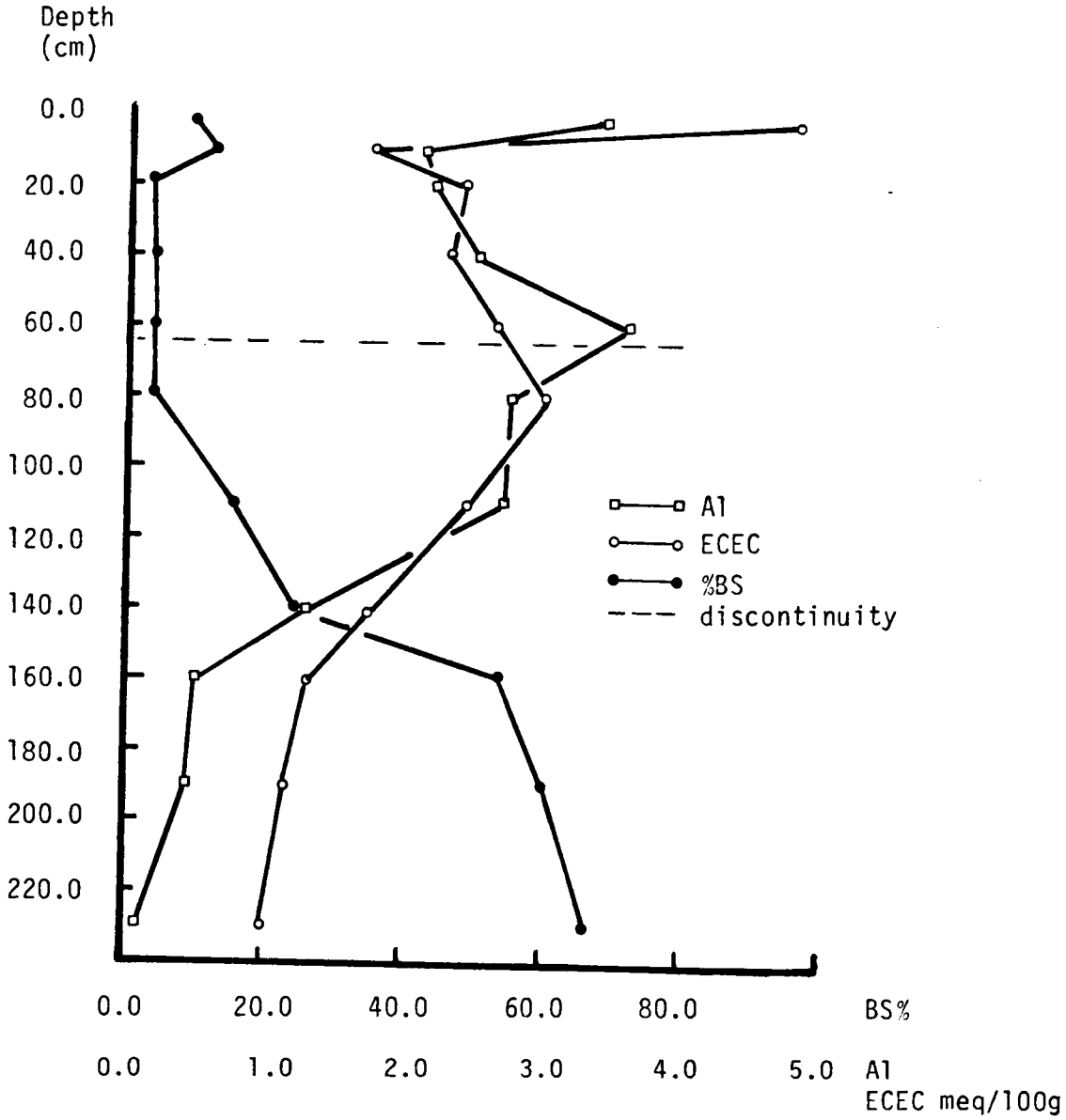

Figure 14. Depth relationships of selected chemical properties in Pedon CBOS 2B.

$r = 0.82$, $p = 0.05$) and Fe_2O_3 ($r = 0.80$, $p = 0.05$). The same significant relationships were observed in the upland soil (Pedon CBOS 2A).

Mineralogical

The x-ray diffractograms of the clay and silt fractions of selected horizons of Pedon CBOS 2B are shown in Figures 15 and 16, respectively. Figure 15 shows that this pedon has minerals similar to those found in Pedon CBOS 2A (upland soil). The Bt horizon of the upper young soil has gibbsite, kaolinite, mica, vermiculite, and mica-vermiculite as the dominant minerals. Heat treatments of the samples indicate that there is considerable HIV. The clay fraction of the saprolite has a diffuse peak at 4.45 Å which may suggest mica, or disordered kaolinite or halloysite (Figure 15). The 4.95 - 4.98 Å peak in the Bt and Cr horizons may represent the (002) reflection of mica. This peak, however, disappeared after a 550°C heat treatment in the Cr horizon and persisted in the Bt horizon. This suggests that the 4.95 Å peak in the Cr horizon is not the (002) reflection of mica.

Mineralogically, the silt fraction of this pedon resembles that of the coarse clay fraction (compare Figure 16 with Figure 15). The Cr horizon shows the same 4.45 Å peak. There are also peaks at 10.0 Å and 11.9 Å which disappeared after 110°C heat treatment. The 7.2 Å peak height is greatly reduced by the heat treatments. These facts suggest the presence of disordered kaolinite and probably halloysite in the Cr horizon of this pedon.

Quantitative mineralogical analysis of the whole soil and clay fractions (Table 14) shows that gibbsite is concentrated in the Bt

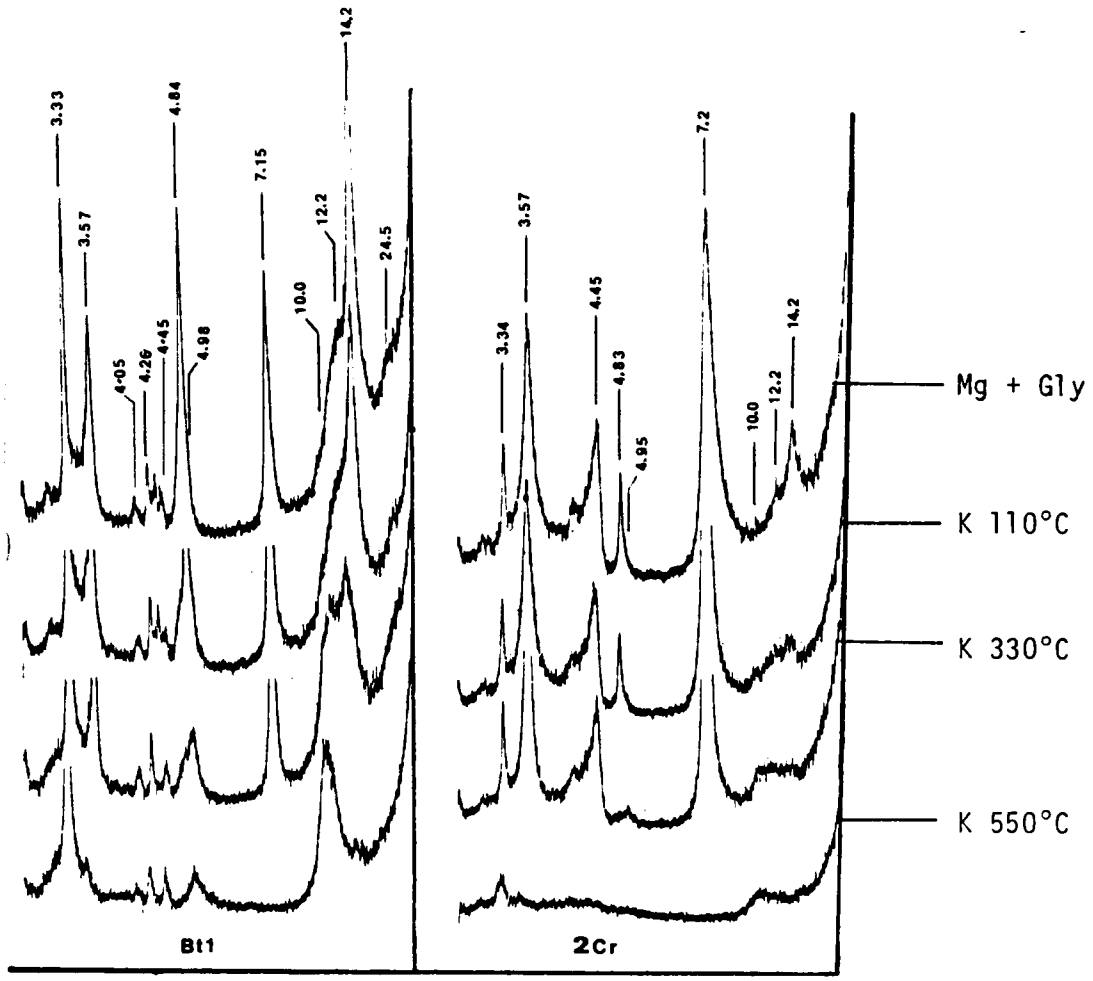

Figure 15. X-ray diffractograms of the coarse clay (2 - 0.2 µm) from Pedon CBOS 2B.

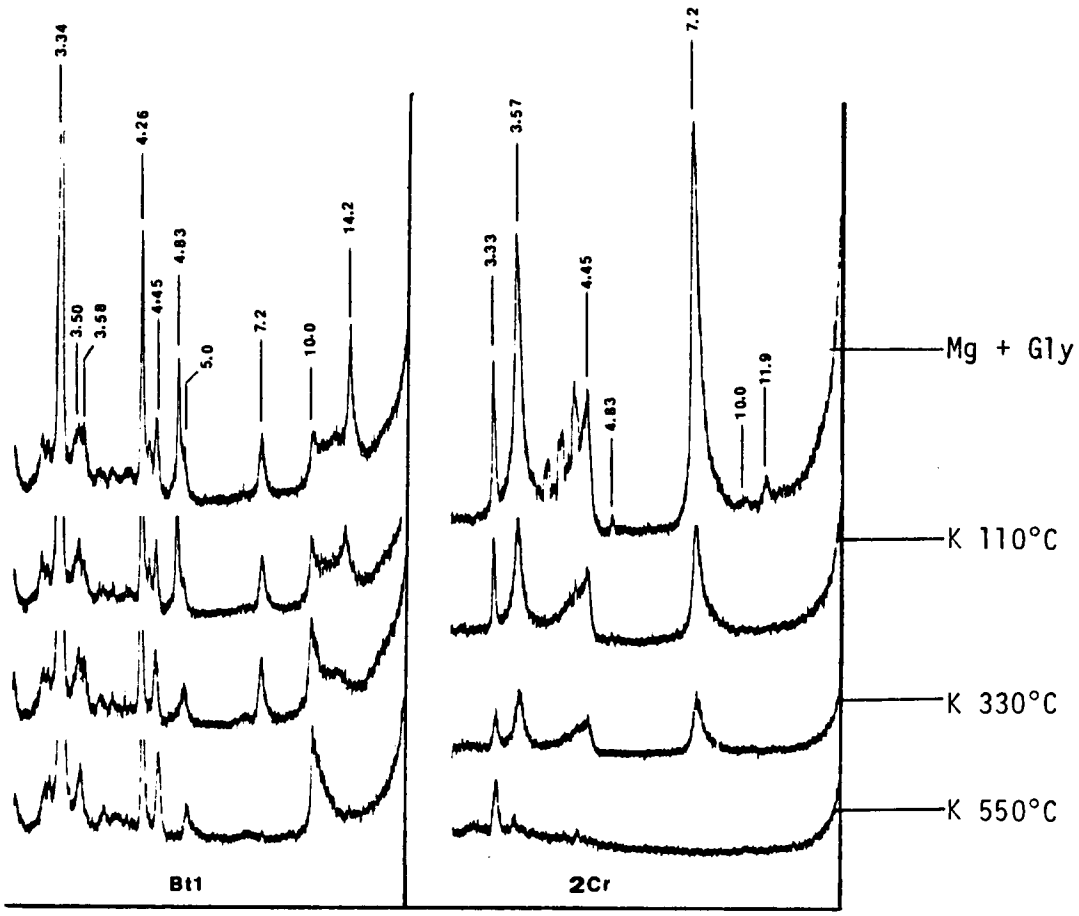

Figure 16. X-ray diffractograms of the fine silt (5 - 2 μm) from Pedon CBOS 2B.

Table 14. Mineralogical analysis of Pedon CBOS 2B.

Horizon	Depth	Whole Soil					Clay			
		Quartz	Gibbsite	Kaolinite	Fe_2O_3	R*	Gibbsite	Kaolinite	Mica	Quartz
	cm	%					%			
A	0-4	40	2	5	2.2	0.22	-	-	-	-
Ap	4-12	45	3	5	1.6	0.19	-	-	-	-
Bt1	12-23	40	4	6	2.1	0.22	14	12	22	0
Bt2	23-49	40	4	6	2.4	0.24	-	-	-	-
2Bt3	49-66	35	7	10	3.2	0.28	-	-	-	-
2Btb1	66-92	25	13	20	5.4	0.41	19	26	20	0
2Btb2	92-125	20	13	41	6.8	0.38	-	-	-	-
2BCb	125-150	15	2	46	6.0	0.25	-	-	-	-
2Cb1	150-170	30	0	40	3.6	0.26	-	-	-	-
2Cb2	170-196	30	0	40	3.3	0.20	4	78	3	0
2Cr	196-230	30	0	23	1.2	0.16	2	85	2	0

*(% Gibbsite + % Fe_2O_3)/ % Clay.

horizon while kaolinite merely increases with soil depth down to the saprolite. At this depth kaolinite accounts for about 85% of the clay minerals. Mica and gibbsite are very low in the C and Cr horizons but tend to be high in the Bt horizons. This mineral trend suggests that kaolinite and/or halloysite are dominant in the buried soil while gibbsite, mica, and kaolinite are dominant in the overlying soil.

The DSC patterns (Figure 17) further illustrate kaolinite and gibbsite distribution with soil depth. Kaolinite and gibbsite tend to be more concentrated in the fine clay fraction of the Bt1 horizon. The Cr horizon is predominantly kaolinite or halloysite in both the clay and silt fractions with small amounts of gibbsite in the clay fraction. It is very likely that disordered kaolinite is present in the Cr horizon because despite the presence of the broad band at 4.45 Å (020 reflection) the (002) reflection at 3.57 Å is more intense than the (020) reflection. This characteristic suggests the presence of kaolinite.

Soils Inside the Basin (Toeslope, Old Smelter) CBOS 2C

Morphological and Physical

This soil is found in the toeslope position in what resembles an alluvial fan. The soil is somewhat poorly drained and the subsoil shows various colorations and mottles (See Pedon description). The A horizon is very dark grayish brown to brown in color and has loam to sandy loam texture. The B horizon ranges in color from yellowish brown to red and has a range of textures.

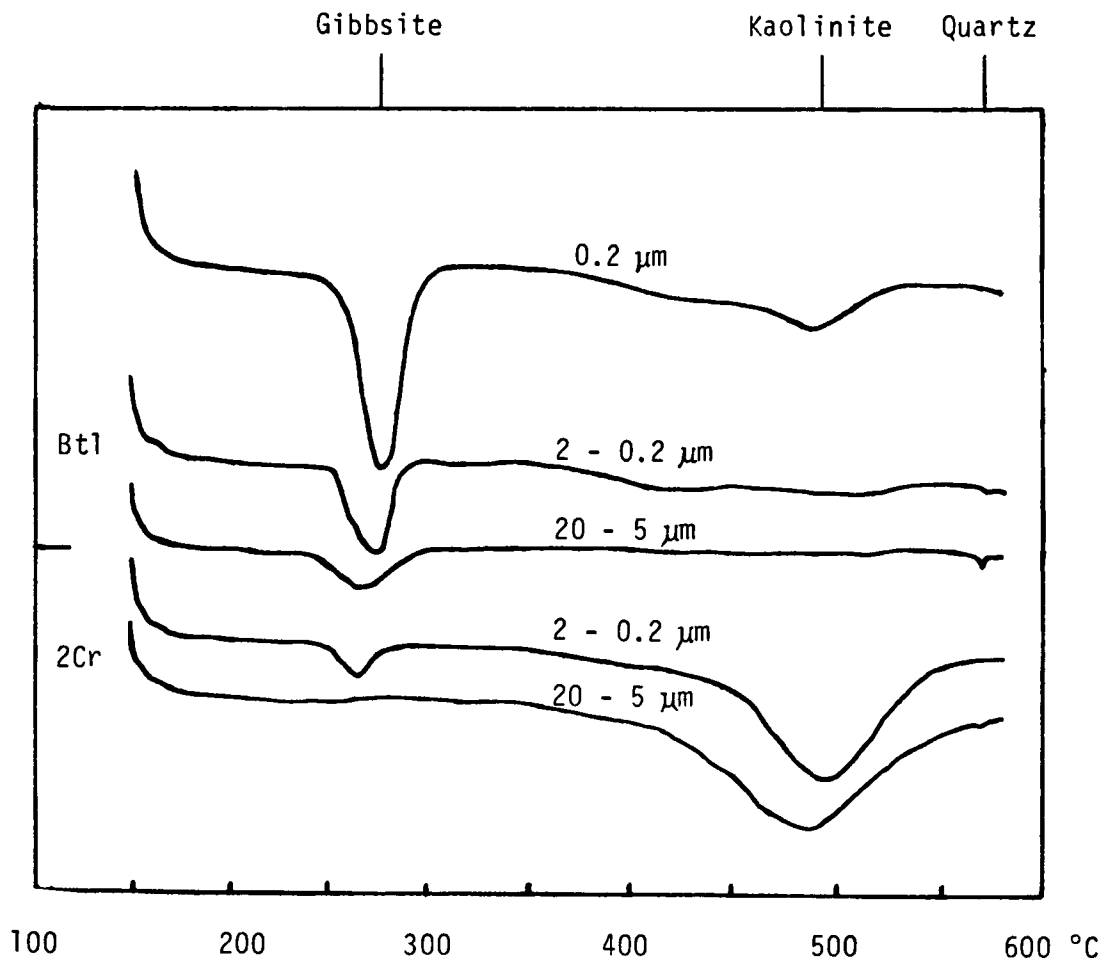

Figure 17. DSC curves of the clay and silt fractions of Pedon CBOS 2B.

The particle size distribution (Table 15) does not follow any particular trend with soil depth as a result of multiple buried horizons. The sand content is high in all horizons ($\geq$ 42.0%) and compares well with the sand contents of the upland and midslope soil. The silt content of Pedon CBOS 2C is moderately high in all horizons. This is in contrast with the upland and midslope soils which have higher silt contents in the surface horizons.

Chemical

The chemical data for Pedon CBOS 2C are similar to the data from the other pedons (Table 16). The major difference is in the Fe_2O_3 content. Iron oxide percentages are generally less than 4.0% in most horizons of this pedon except in the 3Bwbl horizon which has 5.1% iron oxide.

Calcium, Mg and K are the dominant basic exchangeable cations. These cations are concentrated in the A horizon, decrease in the underlying horizons, increase again in 2Btb3 horizon and remain fairly constant in the underlying horizons (Table 16). Sodium content is negligible. Base saturation is low in the overlying soil but increases appreciably in the buried soils (>35%).

The pH is extremely acid (4.1 - 4.3) in the top horizons and this increases with soil depth. Extractable acidity and Al follow the same trend and are related to the pH. The ECEC is generally very low and the ECEC/100 g clay is also very low in most horizons (Table 16). Extractable Al and ECEC are closely related in the top soil (Figure 18) while base saturation correlates negatively with both. The trends in the subsoil and buried horizons are varied. Sulfate-S is concentrated in the buried horizons. These are the horizons with higher pH values. Significant correlation

Table 15. Particle size distribution of Pedon CBOS 2C.

Horizon	Depth	Sand 2000-50 μm	Silt 50-2 μm	Clay <2 μm	Very Coarse Sand	Coarse Sand	Medium Sand	Fine Sand	Very Fine Sand	Coarse Silt	Fine Silt	Silt:Sand Ratio
	cm	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------
							%					
A11	0-5	50	33	17	0	2	7	16	25	21	12	0.66
A12	5-16	57	27	16	1	3	8	17	28	15	12	0.47
Bw	16-35	46	38	16	1	2	6	14	23	14	24	0.82
2Btb1	35-51	42	29	29	1	2	6	13	20	5	24	0.69
2Btb2	51-73	44	32	24	1	2	6	13	22	7	25	0.72
2Btb3	73-94	42	17	41	1	2	6	13	20	5	12	0.40
2Btb4	94-105	44	20	36	1	3	6	14	20	4	16	0.45
2Cb	105-129	48	16	36	1	3	7	15	22	4	12	0.33
3BAb	129-141	46	22	32	1	2	7	16	22	6	16	0.47
3Bwb	141-157	53	27	20	1	3	9	17	23	7	20	0.50
3BCb	157-170	55	21	24	0	3	11	17	24	13	8	0.38
3Bwb1	170-195	67	21	12	0	4	15	21	27	9	12	0.31
3Bwb2	195-213	66	22	12	0	6	15	19	26	10	12	0.33
3Bwb3	213-230	64	24	12	0	4	12	18	30	8	16	0.37
3BC'b	230-248	64	28	8	1	6	11	16	30	12	16	0.43
3C	248-260	64	32	4	2	8	10	15	29	12	20	0.50

Table 16. Chemical properties of Pedon CBOS 2C.

Horizon	Depth	pH (1:2) H_2O	pH (1:2) $CaCl_2$	Organic Matter	Silver thiourea Exchangeable cations Ca	Mg	K	Na	(H + Al)	ECEC/ 100 g Soil	ECEC/ 100 g Clay	KCl Extr Al	Base Saturation	Extr SO_4	Fe_2O_3-d
	cm			%	meq/100 g								%	µg/g	%
A11	0-5	4.1	3.9	3.81	0.75	0.16	0.19	0.02	2.08	3.20	18.8	2.38	35	20	1.8
A12	5-16	4.3	4.0	1.00	0.06	0.03	0.06	0.02	1.04	1.21	7.5	1.55	14	28	1.2
Bw	16-35	4.3	4.1	0.34	0.02	0.01	0.05	0.01	1.16	1.25	7.8	1.36	7	60	1.1
2Btb1	35-51	4.3	4.0	0.29	0.00	0.01	0.09	0.01	2.32	2.43	8.3	2.83	4	75	1.8
2Btb2	51-73	4.5	4.1	0.17	0.03	0.05	0.10	0.01	2.32	2.51	10.4	2.79	8	85	1.4
2Btb3	73-94	4.9	4.4	0.10	1.16	0.46	0.22	0.01	0.70	2.55	6.2	1.00	72	78	1.7
2Btb4	94-105	5.0	4.3	0.16	0.80	0.32	0.20	0.01	0.93	2.26	6.2	1.09	58	73	1.6
2Cb	105-129	5.0	4.3	0.08	0.69	0.30	0.18	0.01	0.93	2.11	5.8	1.17	56	75	1.0
3BAb	129-141	4.9	4.2	0.06	0.51	0.28	0.19	0.02	1.27	2.27	7.0	1.50	44	88	0.9
3Bwb	141-157	4.9	4.2	0.04	0.35	0.20	0.15	0.01	1.39	2.10	10.5	1.34	34	63	0.5
3BCb	157-170	5.0	4.3	0.04	0.51	0.25	0.19	0.02	1.16	2.13	8.8	1.17	46	110	3.0
3Bwb1	170-195	4.2	4.4	0.02	0.54	0.22	0.15	0.02	0.81	1.74	14.5	0.57	53	85	5.1
3Bwb2	195-213	5.2	4.4	0.02	0.56	0.24	0.16	0.01	0.81	1.78	14.8	0.68	54	78	3.6
3Bwb3	213-230	5.1	4.4	0.02	0.47	0.19	0.17	0.01	0.93	1.77	14.7	0.86	47	80	3.5
3BC'b	230-248	4.0	4.4	0.02	0.44	0.19	0.17	0.01	1.04	1.85	23.1	0.78	44	88	3.6
3C	248-260	5.0	4.4	0.02	0.45	0.21	0.17	0.01	1.04	1.85	46.2	0.88	45	98	2.9

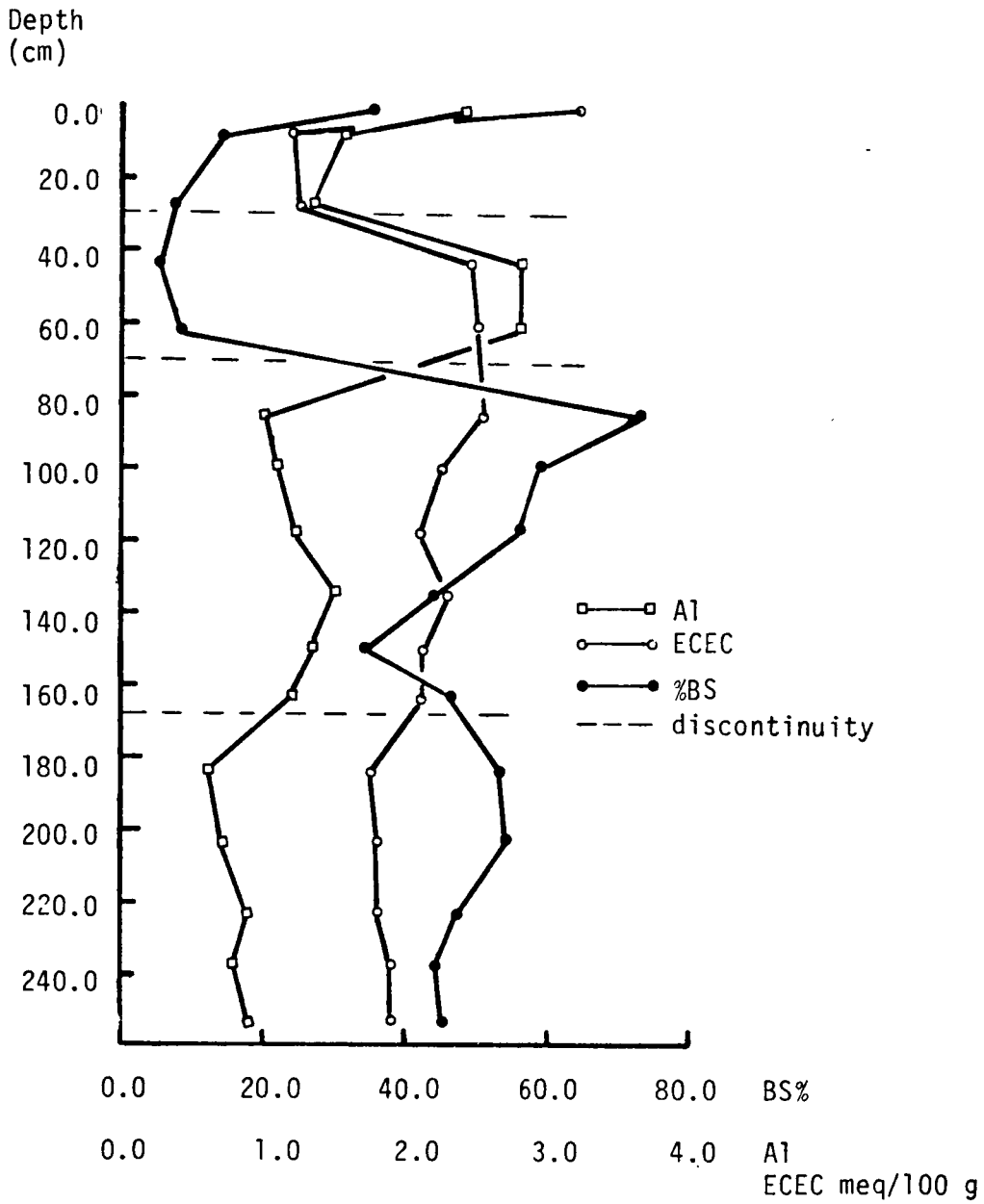

Figure 18. Depth relationships of selected chemical properties in Pedon CBOS 2C.

exists between SO_4-S and soil pH ($r = 0.69$, $p = 0.01$). The positive correlation of SO_4-S and pH may suggest a present saturation of the buried horizons with sulfate. No significant relationships are discerned between SO_4-S and clay, Fe_2O_3, Al and BS (Table A-5, Appendix).

Mineralogical

X-ray diffractograms of the clay and silt fractions of selected horizons are shown in Figures 19 and 20, respectively. The patterns are similar to previous patterns already presented except that there is no interstratification in the A and C horizons. The clay fraction of the 2Btb3 and 3C horizons have high amounts of kaolinite (Figure 19 and Table 17). Kaolinite content increases with soil depth and reaches a high of 92% in the 3BC'b horizon. Hydroxy-interlayered vermiculite is only found in the A and 2Btb3 horizons. The silt fraction (Figure 20) shows the presence of quartz, kaolinite, and mica. The C horizon has a broad peak at 4.48 Å which may indicate disordered kaolinite and/or halloysite. Gibbsite is present in both the clay and silt fractions of the A and 2Btb3 horizons in moderate amounts (≤8.0%). The gibbsite is concentrated in the upper B horizons and decreases in the lower B and C horizons. The DSC patterns (Figure 21) show that the gibbsite in the Cr horizons is in the clay fraction. Mica distribution with soil depth is irregular but the C horizon has the lowest concentration of mica (Table 17).

Two important features to note in this soil are the presence of 4.07 Å peaks in the clay and silt fractions of this pedon (Figures 19 and 20) and the asymmetry of the 500 - 525°C endothermic curves of the 3Cr horizon (Figure 21). The 4.07 Å peaks suggest the presence of feldspars

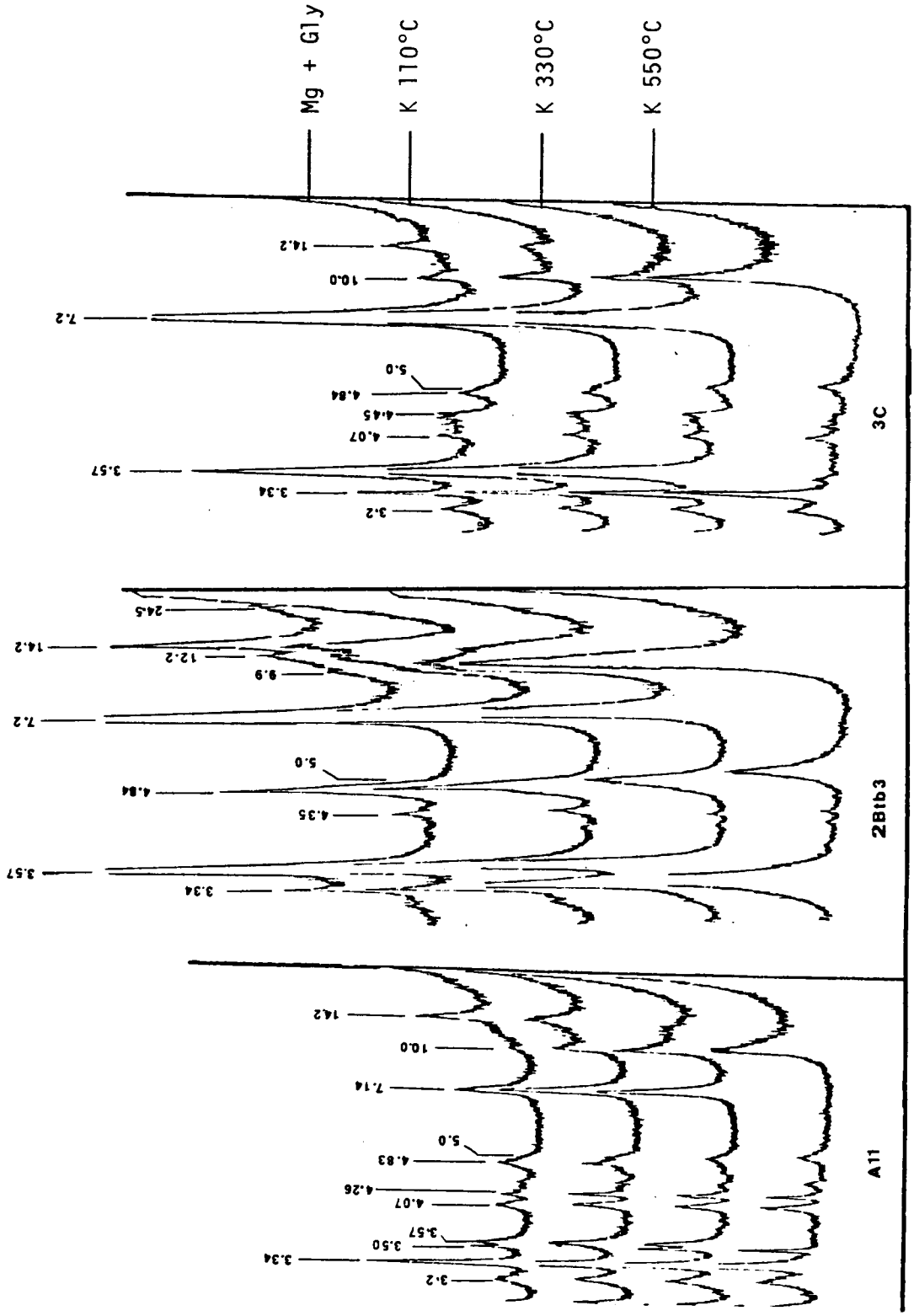

Figure 19. X-ray diffractograms of the coarse clay (2 - 0.2 µm) from Pedon CBOS 2C.

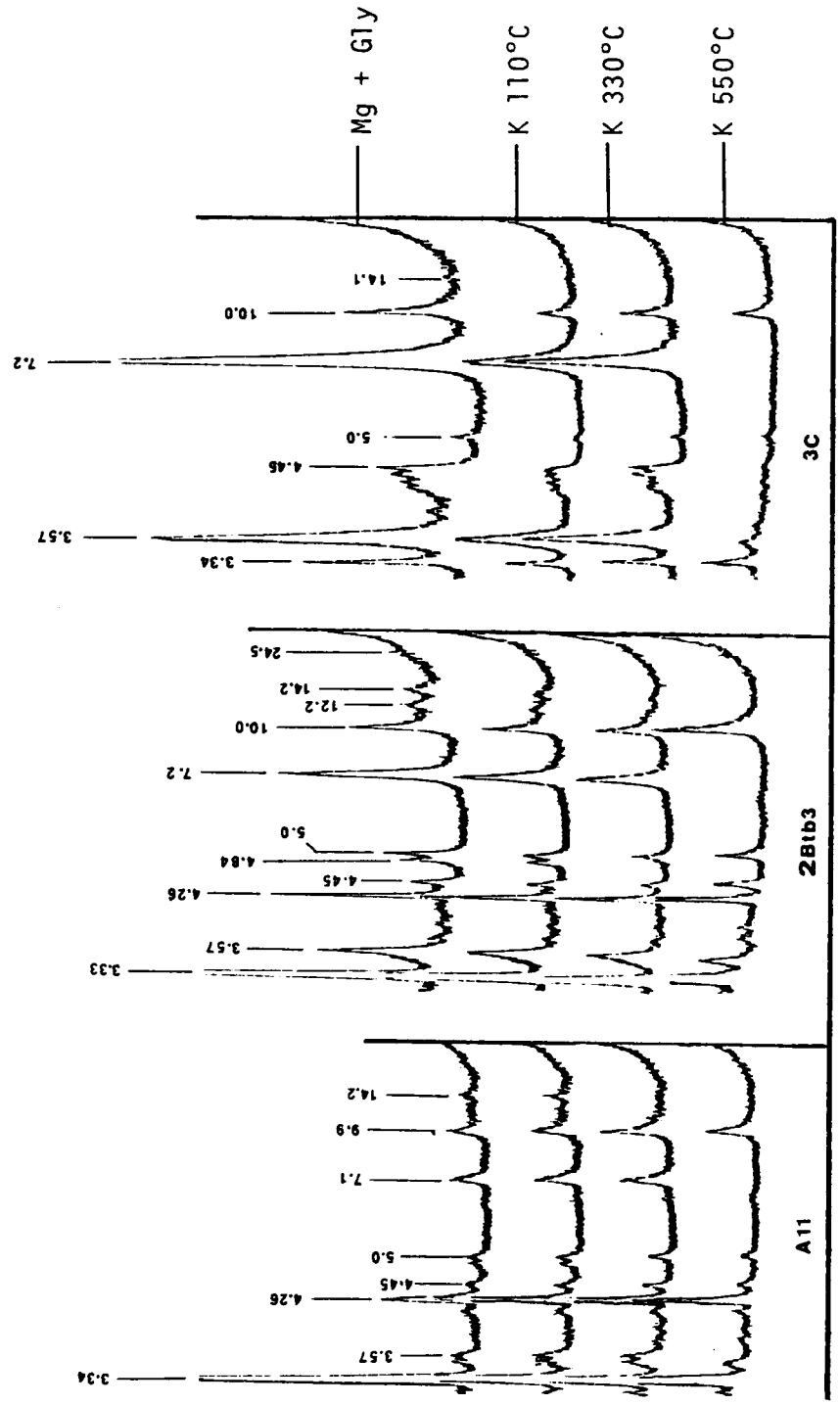

Figure 20. X-ray diffractograms of the fine silt (5 - 2 µm) from Pedon CBOS 2C.

Table 17. Mineralogical Analysis of Pedon CBOS 2C.

Horizon	Depth	Whole Soil					Clay			
		Quartz	Gibbsite	Kaolinite	Fe_2O_3	R*	Gibbsite	Kaolinite	Mica	Quartz
	cm	%					%			
A11	0-5	40	0	5	1.8	0.1	3	19	13	0
A12	5-16	40	0	5	1.2	0.1	4	20	14	0
Bw	16-35	45	0	5	1.1	0.0	3	15	17	0
2Btb1	35-51	40	1	5	1.8	0.1	3	22	14	0
2Btb2	51-73	40	1	6	1.4	0.1	-	-	-	-
2Btb3	73-94	40	3	7	1.7	0.1	7	41	21	0
2Btb4	94-105	40	3	17	1.6	0.1	-	-	-	-
2Cb	105-129	40	3	17	1.0	0.1	7	32	21	0
3BAb	129-141	30	3	18	0.9	0.1	8	53	16	0
3Bwb	141-157	35	1	23	0.5	0.0	7	46	15	0
3BCb	157-170	35	0	15	3.0	0.1	3	69	12	0
3Bwb1	170-195	35	0	20	5.1	0.4	0	87	7	0
3Bwb2	195-213	30	0	16	3.6	0.3	-	-	-	-
3Bwb3	213-230	40	0	7	3.5	0.2	-	-	-	-
3BC'b	230-248	40	0	16	3.6	0.4	0	92	6	0
3C	248-260	40	0	21	2.9	0.7	1	85	7	0

*(% Gibbsite + % Fe_2O_3)/ % Clay.

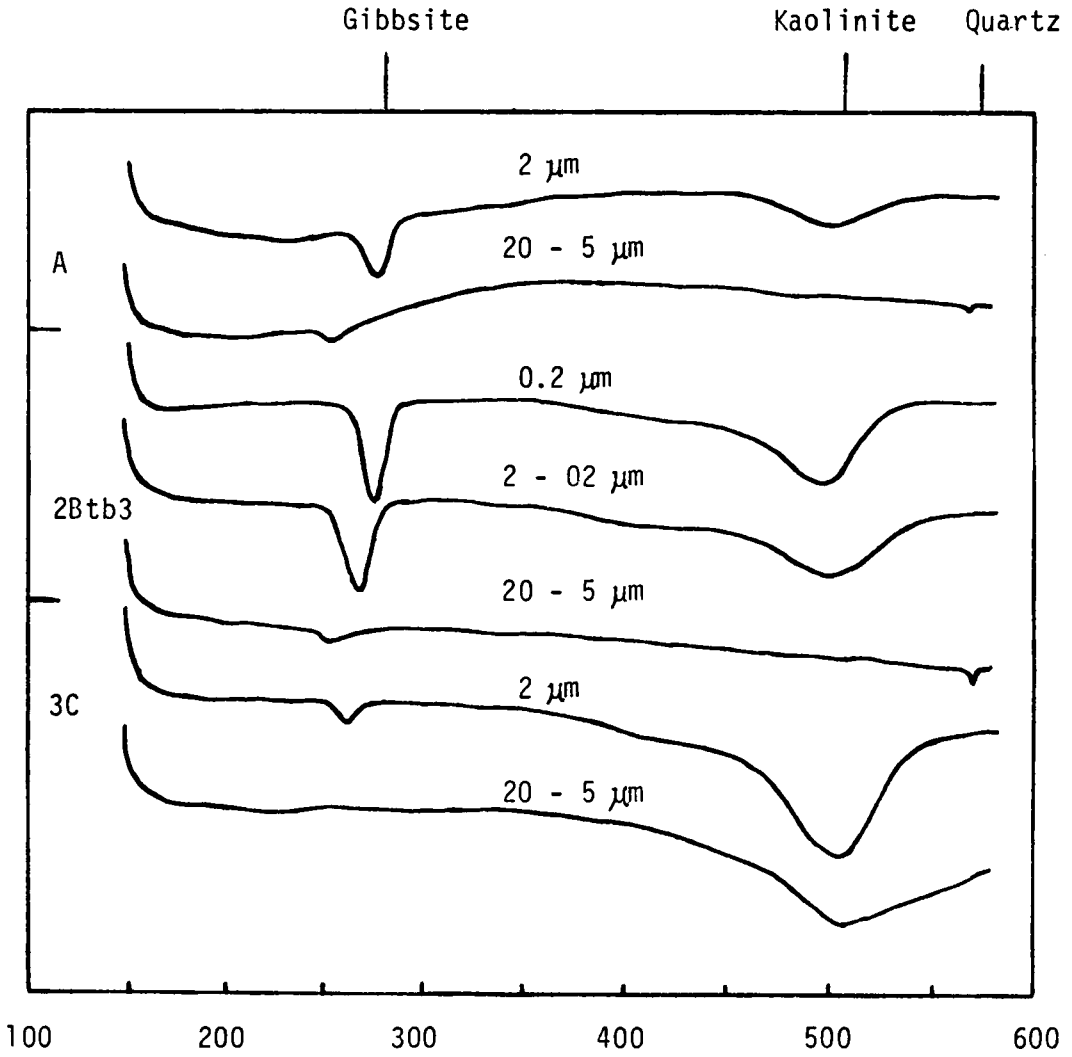

Figure 21. DSC curves of the clay and silt fractions of Pedon CBOS 2C.

while the DSC endotherm indicates disordered kaolinite. Another important feature is the % gibbsite + % Fe_2O_3/ % clay ratio (Table 17). The ratio is less than 0.20 in the control section. This indicates that the pedon does not have an oxidic mineralogy, unlike all the previous pedons reported.

Soils Inside the Basin (Upper Toeslope, New Smelter) CBNS 3A

Morphological and Physical

Pedon CBNS 3A represents the upper toeslope soil near the new smelter. This pedon and Pedon CBCC 1C are in similar geomorphic positions. The buried argillic horizons are yellowish red to reddish brown in color while the lower buried B horizons are red in color (See Pedon description). The C horizons range in color from reddish brown to red. The top recently deposited soil has a cambic B horizon below the A horizon.

Clay distribution (Table 18) with soil depth follows a pedogenic pattern, increasing in the B horizons and decreasing in the C. Clay content is generally low when compared to other pedons. Sand percentages in the lower B and C horizons are very high (>70%) and this is predominantly fine and very fine sand (Table 18). These fine sand fractions are very micaceous and contain very little quartz. Silt content is average ranging from 10 to 40%. Fine silt makes up the bulk of the silt fraction. The silt fraction is very micaceous and contains some quartz.

The silt to sand ratios show some discontinuities which are related to the depositional stages (See Pedon description).

Table 18. Particle size distribution of Pedon CBNS 3A.

Horizon	Depth	Sand 2000-50 µm	Silt 50-2 µm	Clay <2 µm	Very Coarse Sand	Coarse Sand	Medium Sand	Fine Sand	Very Fine Sand	Course Silt	Fine Silt	Silt:Sand Ratio
	cm	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------
A	0-6	49	27	24	1	4	9	17	17	11	16	0.55
Bw1	6-15	52	23	25	3	5	9	18	17	3	20	0.44
Bw2	15-34	46	33	21	1	4	7	15	19	5	28	0.71
2Ab	34-50	38	38	24	4	5	7	11	11	9	29	1.00
2Btb1	50-62	31	41	28	3	3	5	9	11	4	37	1.32
2Btb2	62-69	31	32	37	3	3	3	5	9	3	29	1.03
2Btb3	69-96	34	34	32	3	4	6	9	12	2	32	1.00
2BCb	96-132	47	25	28	4	4	7	14	18	1	24	0.53
3Bwb1	132-158	60	12	28	3	4	12	22	19	0	12	0.20
3Bwb2	158-170	58	22	20	1	3	7	19	28	6	16	0.37
3CBb	170-181	77	11	12	5	6	10	24	32	7	4	0.14
3Cb1	181-199	75	13	12	5	6	10	23	31	9	4	0.17
3Cb2	199-225	74	14	12	5	5	10	24	30	10	4	0.18
3Cb3	225-240	70	18	12	2	4	10	24	30	10	8	0.25
3Cr	240+	71	21	8	3	6	14	24	24	9	12	0.29

Chemical

Chemically the soil is characterized by low exchangeable bases, ECEC and very high BS (Table 19). The pH ranges from 4.4 in the A horizon to 5.4 in the C horizon. Organic matter is high in the top soil and decreases with depth. Extractable Al is concentrated in surface horizons and becomes negligible in lower horizons. The lower levels of Al in the lower horizons is due to the increase in pH (Table 19).

The depth relationships of extractable Al, ECEC and BS indicate that base saturation is relatively high in most horizons and follows a trend which is opposite to that of Al (Figure 22). The KCl extractable Al values in the top horizons and the upper B horizons (0 - 96 cm) are higher than the ECEC values in the same horizons. This indicates a high degree of Al saturation. Obviously 1 N KCl extracted more Al than 0.01 N Ag-TU. Iron oxide content is moderate attaining a maximum of 6.3% in the 3Bwb2 horizon (Table 19).

Sulfate-S ranges from 13 µg/g in the Bw2 horizon to 95 µg/g in the 3Bwb2 horizon. This is also the horizon of maximum Fe_2O_3 accumulation. The SO_4-S levels are low considering that this location is near the new smelter. This site, however, is an island and has not received lateral flow as the footslope site (Pedon CBOS 2C) at the old smelter has. It is possible that any sulfates which were deposited in this area must have leached out by this time such that SO_4-S distribution should merely correlate with the clay and Fe_2O_3 contents. The relationships between SO_4-S and some soil properties (Table A-6, Appendix) show that there is a significant relationship between SO_4-S and Fe_2O_3 ($r = 0.62$,

Table 19. Chemical properties of Pedon CBNS 3A.

Horizon	Depth	pH (1:2) H_2O	pH (1:2) $CaCl_2$	Organic Matter	Silver thiourea Exchangeable cations Ca	Mg	K	Na	(H + Al)	ECEC/ 100 g Soil	ECEC/ 100 g Clay	KCl Extr Al	Base Saturation	Extr SO_4	Fe_2O_3-d
	cm			%	meq/100 g								%	ug/g	%
A	0-6	4.4	3.8	5.34	0.33	0.10	0.24	0.03	1.39	2.09	8.70	2.31	33	35	3.6
Bw1	6-15	4.7	4.2	1.60	0.28	0.05	0.15	0.04	0.58	1.10	4.40	1.63	47	20	2.8
Bw2	15-34	5.4	4.8	1.83	1.35	0.16	0.17	0.03	0.23	1.94	9.23	0.42	88	13	2.8
2Ab	34-50	4.8	4.4	2.15	0.23	0.05	0.08	0.02	0.81	1.19	4.95	2.11	32	45	2.8
2Btb1	50-62	4.7	4.3	2.18	0.24	0.03	0.07	0.02	0.58	0.94	3.35	2.46	38	65	3.3
2Btb2	62-69	4.7	4.3	0.73	0.19	0.03	0.05	0.02	0.46	0.75	2.02	2.12	38	88	3.6
2Btb3	69-96	4.8	4.3	0.46	0.24	0.03	0.06	0.01	0.46	0.80	2.50	1.73	42	90	3.7
2BCb	96-132	5.3	4.9	0.16	1.01	0.19	0.09	0.02	0.17	1.48	5.28	0.41	88	73	3.3
3Bwb1	132-158	5.4	5.0	0.10	1.03	0.05	0.16	0.02	0.17	1.93	6.89	0.26	91	90	5.6
3Bwb2	158-170	5.4	5.0	0.04	0.66	0.48	0.20	0.02	0.17	1.53	7.65	0.34	88	95	6.3
3CBb	170-181	5.4	4.9	0.02	0.26	0.11	0.10	0.01	0.17	0.65	5.41	0.22	74	68	2.7
3Cb1	181-199	5.4	4.9	0.02	0.30	0.15	0.13	0.02	0.12	0.72	6.00	0.29	86	85	3.7
3Cb2	199-225	5.4	4.9	0.02	0.31	0.18	0.13	0.02	0.12	0.76	6.33	0.31	84	78	3.8
3Cb3	225-240	5.4	4.9	0.06	0.45	0.29	0.13	0.03	0.17	1.07	8.91	0.38	84	78	5.0
3Cr	240+	5.4	4.9	0.13	0.45	0.24	0.18	0.03	0.17	1.07	13.37	0.38	84	63	3.4

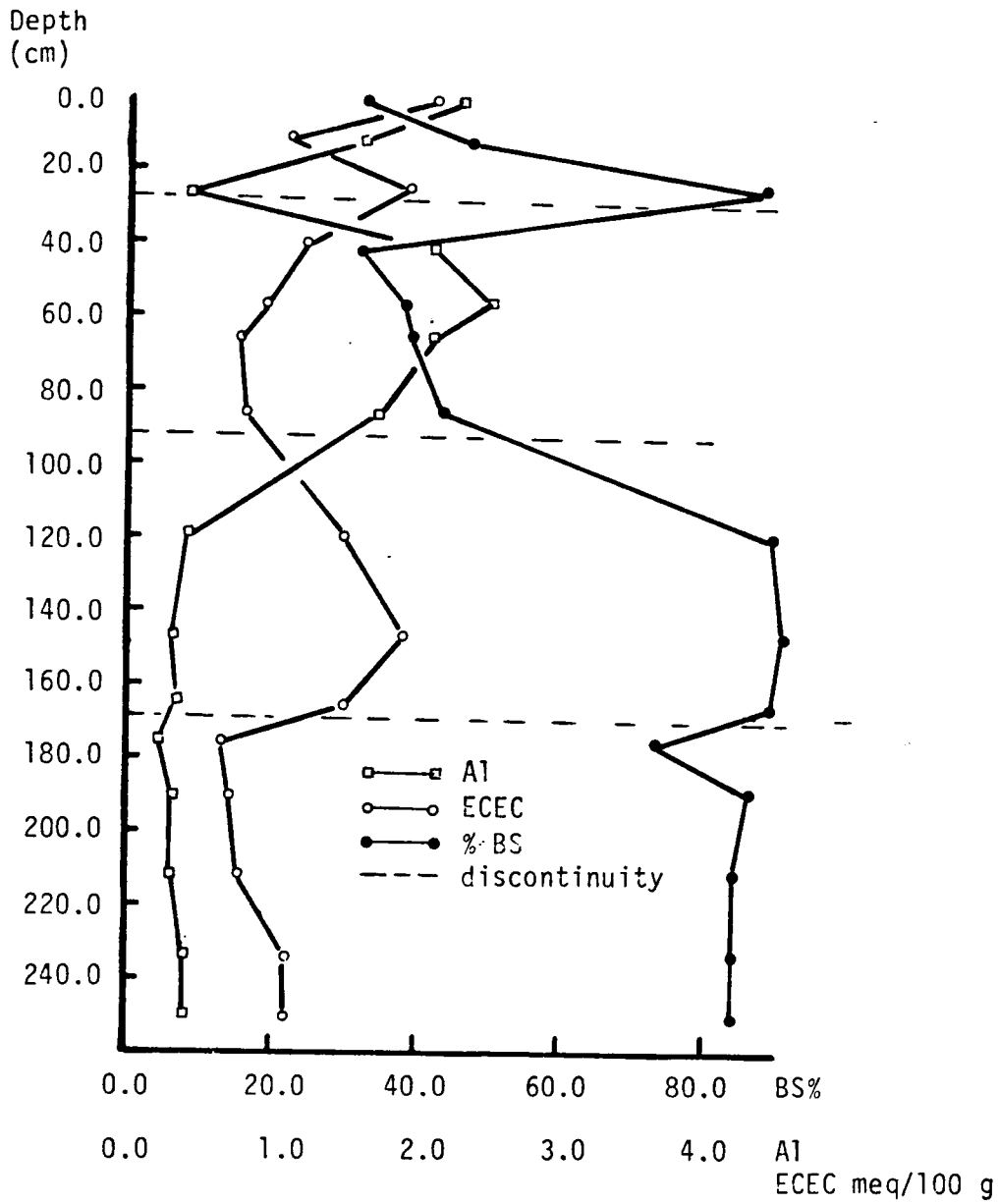

Figure 22. Depth relationships of selected chemical properties in Pedon CBNS 3A.

p = 0.05). However, no significant relationship was seen between SO_4-S and the other soil properties.

Mineralogical

The x-ray diffractograms of the clay and silt fractions (Figures 23 and 24) show regular interstratification in addition to kaolinite, gibbsite, mica, HIV and vermiculite. Interstratification (mica-vermiculite) is very pronounced in the silt fraction of the 3Cr horizon (Figure 24). The clay mineral composition of this pedon resembles that of Pedon CBOS 2A which is the upland soil near the old smelter.

Quantitative mineralogical analysis (Table 20) of the clay fraction indicates that kaolinite and gibbsite are the dominant minerals in the subsoil and reach a maximum in the 3Cb3 horizon. Mica is high in the 3Cr horizon and decreases upwards. The DSC patterns (Figure 25) show the dominance of kaolinite and gibbsite in both the silt and clay fractions and their abundance in the 3Cr horizon.

Soils Inside the Basin (Low Toeslope, New Smelter) CBNS 3C

Morphological and Physical

Pedon CBNS 3C resembles an inverted profile. The Bt3 horizon was originally the A and Bt1 horizons of the upland soil washed downslope. The Bt2 horizon was the mid-argillic horizon of the upland soil while the Bt1 was mid to lower argillic horizon of the upland soil. These horizons which have been washed downslope are red in color and overlie buried A and C horizons which have formed in alluvium.

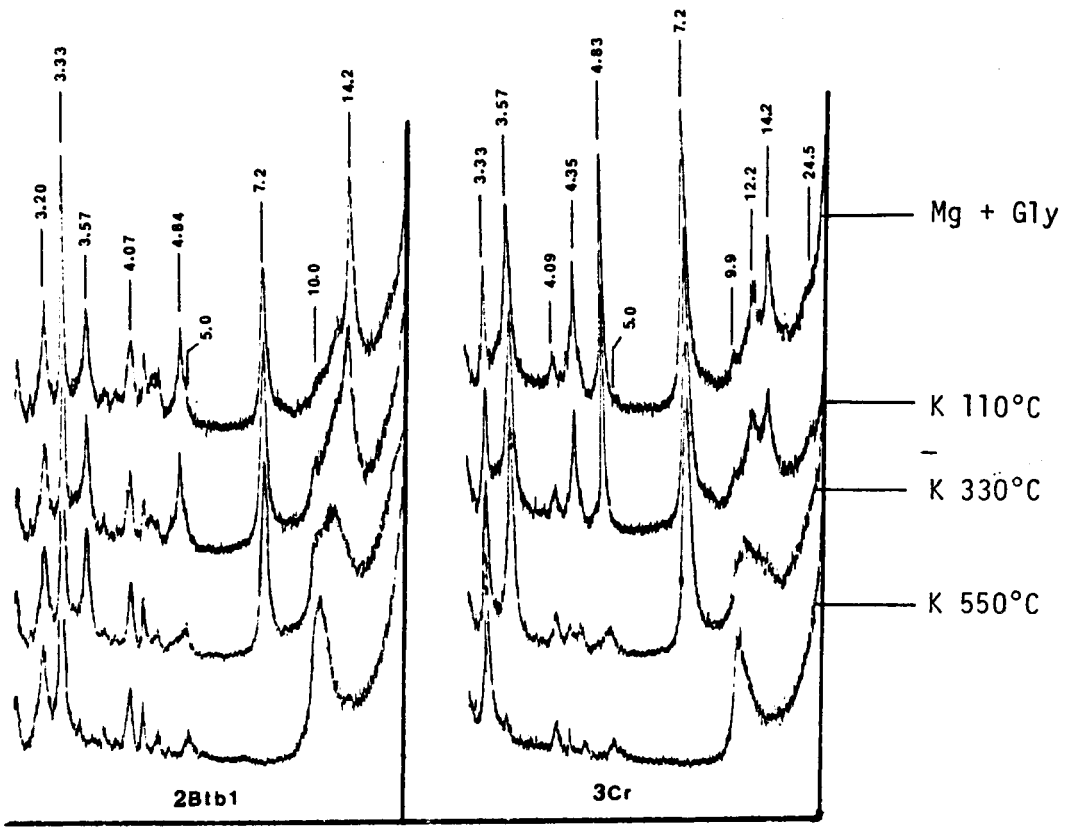

Figure 23. X-ray diffractograms of the coarse clay (2 - 0.2 μm) from Pedon CBNS 3A.

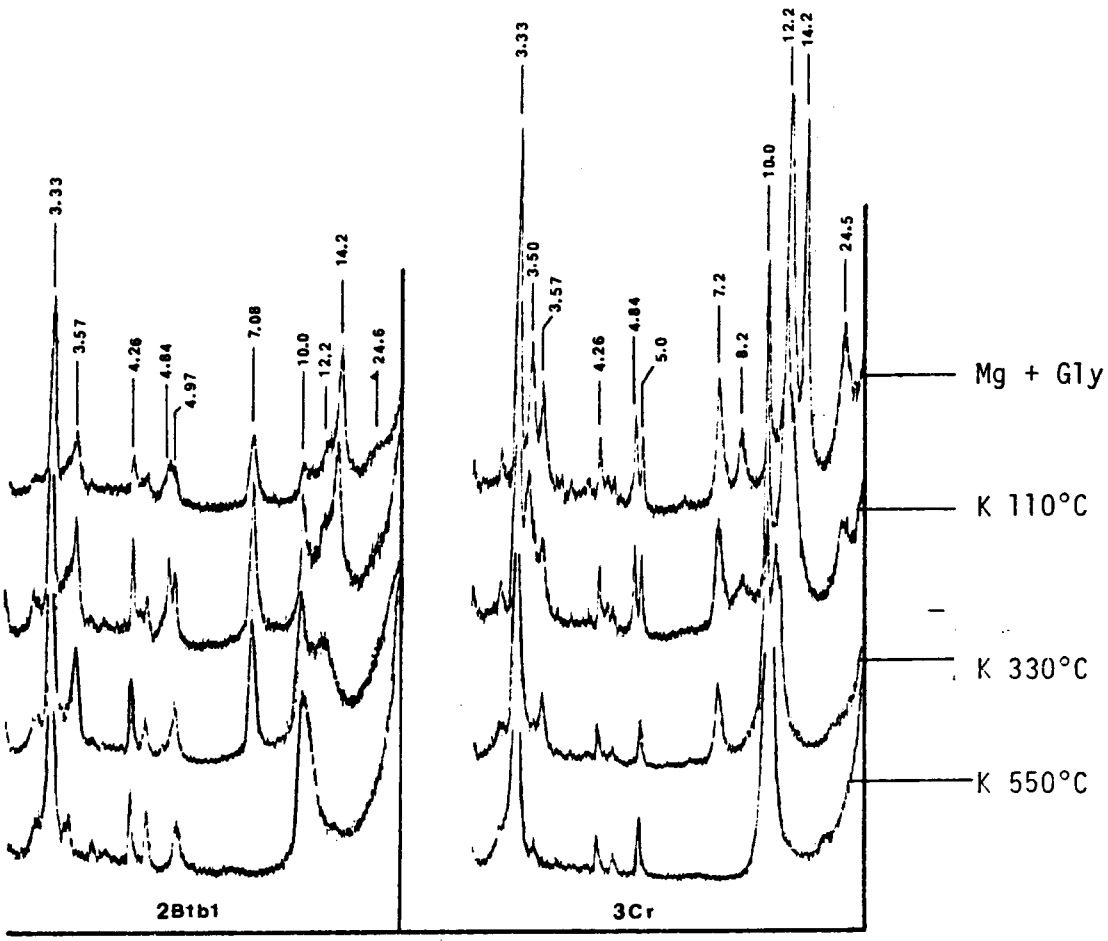

Figure 24. X-ray diffractograms of the fine silt (5 - 2 um) from Pedon CBNS 3A.

Table 20. Mineralogical analysis of Pedon CBNS 3A.

Horizon	Depth	Whole Soil					Clay			
		Quartz	Gibbsite	Kaolinite	Fe_2O_3	R*	Gibbsite	Kaolinite	Mica	Quartz
	cm	%					%			
A	0-6	35	1	5	3.6	0.1	-	-	-	-
Bw1	6-15	35	1	12	2.8	0.1	-	-	-	-
Bw2	15-34	35	1	8	2.8	0.2	-	-	-	-
2AB	34-50	35	1	8	2.8	0.1	-	-	-	-
2Btb1	50-62	30	2	8	3.3	0.1	8	12	16	0
2Btb2	62-69	25	3	8	3.6	0.1	-	-	-	-
2Btb3	69-96	25	3	8	3.7	0.2	-	-	-	-
2BCb	96-132	25	3	20	3.3	0.2	-	-	-	-
3Bwb1	132-158	20	3	19	5.6	0.3	17	32	13	0
3Bwb2	158-170	25	6	10	6.3	0.6	-	-	-	-
3CBb	170-181	30	6	10	2.7	0.7	-	-	-	-
3Cb1	181-199	30	4	10	3.7	0.6	-	-	-	-
3Cb2	199-225	30	3	13	3.8	0.5	-	-	-	-
3Cb3	225-240	25	3	13	5.0	0.6	30	54	12	0
3Cr	240+	20	2	10	3.4	0.6	24	46	18	0

*(% Gibbsite + % Fe_2O_3)/ % Clay.

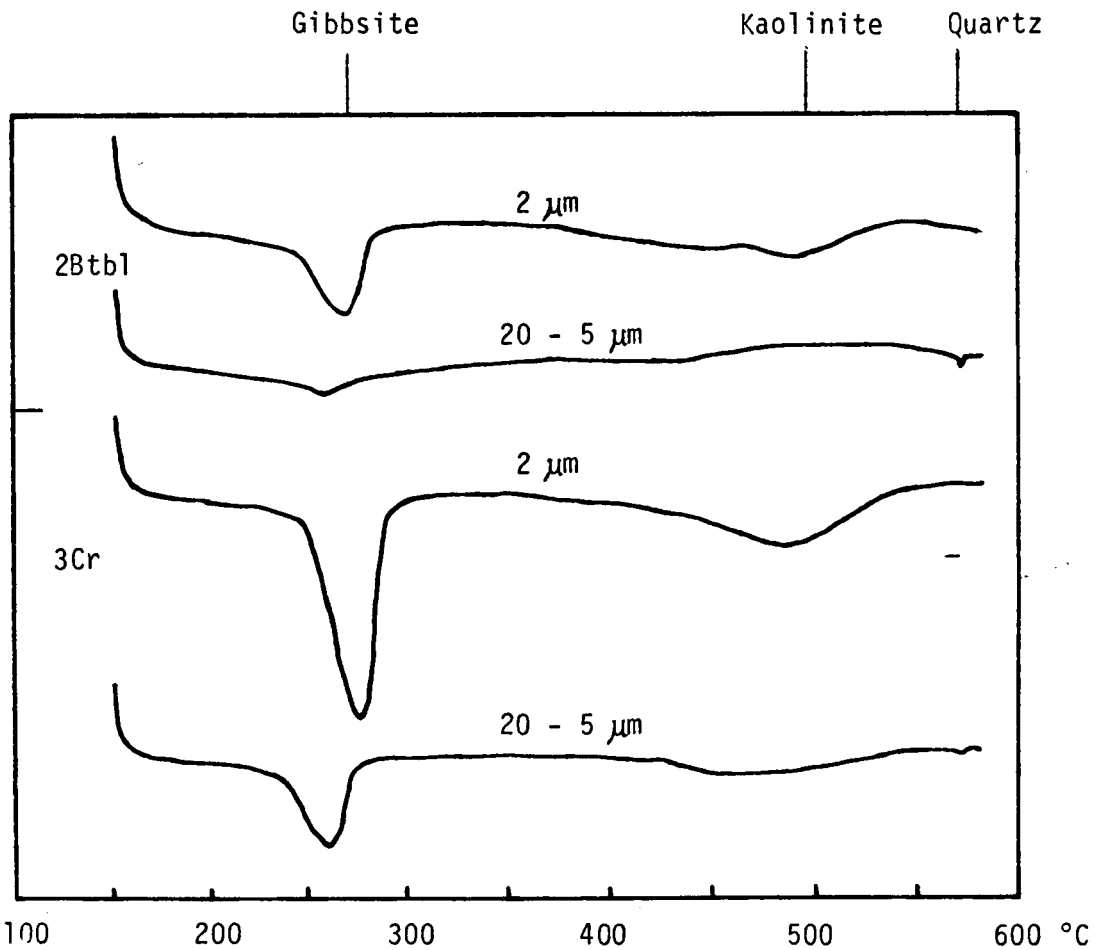

Figure 25. DSC curves of the clay and silt fractions of Pedon CBNS 3A.

The particle size distribution (Table 21) shows that the B horizons found at the soil surface have high clay content (24 - 41%) while the Ab and Cb horizons have an average of 12% clay. Sand content is high ($\geq$ 66%) in the buried horizons and silt content is low in these buried horizons. The silt:sand ratio shows a discontinuity at 31 cm depth (Table 21) marking the beginning of the buried horizons. Very fine sand and fine sand make up a large proportion of the sand fraction in all horizons (Table 21.)

Chemical

Table 22 shows that the pH is extremely acid ($\leq$ 4.6) in all horizons. Organic matter content is moderate in the surface horizons and increases in the buried horizons. Exchangeable basic cations are very low (< 0.20 meq/100 g) and K seems to be the dominant cation. Calcium, Mg, K, and Na occur in negligible amounts although K reaches a high of 0.1 meq/100 g in the surface horizon. Base saturation is very low while KCl extractable Al and extractable acidity are relatively high (Table 22). The ECEC values are very low both on whole soil and clay basis.

Figure 26 shows that extractable Al and ECEC have a similar trend in this soil. Base saturation has an opposite trend in the surface horizons but becomes irregular in the buried soil. Iron oxide content is high in the surface horizons (Table 22) and decreases with depth in the buried horizons.

Sulfate-S concentration is high in most of the horizons but tends to be more concentrated in the surface horizons. This site should receive much lateral movement of sulfate. The SO_4-S is significantly correlated with most of the soil properties (Table A-7, Appendix). The

Table 21. Particle size distribution of Pedon CBNS 3C.

Horizon	Depth	Sand 2000-50 um	Silt 50-2 μm	Clay <2 μm	Very Coarse Sand	Coarse Sand	Medium Sand	Fine Sand	Very Fine Sand	Coarse Silt	Fine Silt	Silt:Sand Ratio
	cm	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------
							%					
Bt1	0-18	9	50	41	0	0	0	0	9	13	37	5.5
Bt2	18-23	58	18	24	3	5	10	19	21	6	12	0.31
Bt3	23-31	14	45	41	0	0	1	3	10	12	33	3.21
2Ab	31-38	69	19	12	2	4	10	23	31	11	8	0.27
2Cb1	38-43	70	18	12	2	5	10	22	31	14	4	0.25
2Cb2	43-61	66	22	12	5	6	10	19	26	18	4	0.33
2Cb3	61-69	73	15	12	3	6	10	22	30	11	4	0.20

Table 22. Chemical properties of Pedon CBNS 3C.

Horizon	Depth	pH (1:2) H_2O	pH (1:2) $CaCl_2$	Organic Matter	Silver thiourea Exchangeable cations Ca	Mg	K	Na	(H + Al)	ECEC/ 100 g Soil	ECEC/ 100 g Clay	KCl Extr Al	Base Saturation	Extr SO_4	Fe_2O_3-d
	cm			%	meq/100 g								%	µg/g	%
Bt1	0-18	4.4	3.9	1.76	0.00	0.02	0.10	0.02	3.18	3.32	8.09	4.58	4	125	6.9
Bt2	18-23	4.4	4.0	1.04	0.01	0.02	0.04	0.04	1.91	2.02	8.41	2.18	5	135	3.6
Bt3	23-31	4.4	4.0	2.38	0.00	0.03	0.06	0.02	3.01	3.12	7.60	4.12	4	160	6.4
2Ab	31-38	4.5	4.1	4.07	0.06	0.05	0.07	0.02	1.16	1.36	11.33	1.74	15	93	1.5
2Cb1	38-43	4.4	4.1	1.86	0.07	0.02	0.02	0.01	0.93	1.05	8.75	1.50	11	113	1.5
2Cb2	43-61	4.5	4.3	2.21	0.07	0.02	0.02	0.01	1.04	1.16	9.66	2.13	10	90	1.2
2Cb3	61-69	4.6	4.3	2.38	0.11	0.03	0.04	0.02	0.87	1.07	8.91	1.89	18	63	0.8

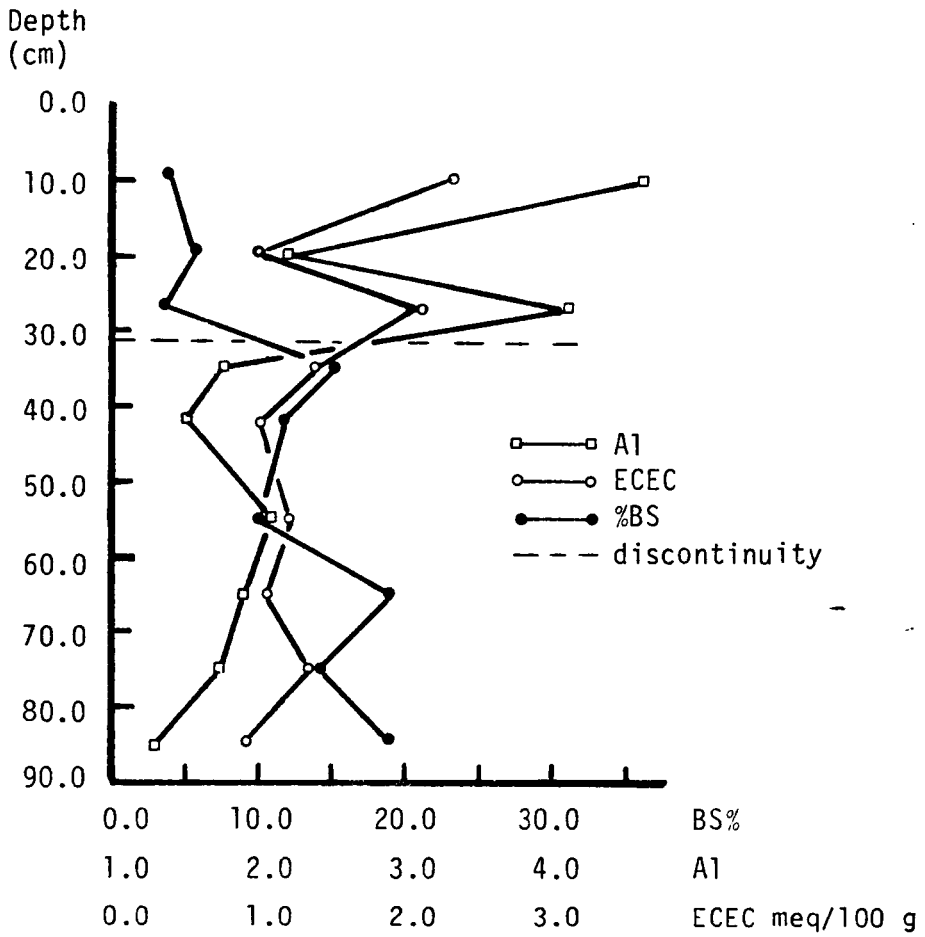

Figure 26. Depth relationships of selected chemical properties in Pedon CBNS 3C.

only exception is the relationship between SO_4-S and Al. The correlation is weak ($r = 0.62$, $p = 0.20$) and only significant at the 80% level.

Mineralogical

The x-ray diffractograms of the clay fraction of Pedon CBNS 3C indicate that kaolinite, gibbsite, mica, HIV and vermiculite are the major minerals present (Figure 27). Both the 2Ab and 2Cb3 horizons have a strong 14.2 Å peak which collapses gradually on heat treatment. At 550°C, it collapses completely to 10 Å with a shoulder on the low angle side. This suggests that the mica is weathering to vermiculite.

The silt fraction (Figure 28) shows some interstratification both in the 2Ab and 2Cb3 horizons. In addition to other minerals, this pedon has a peak at 7.2 Å which remained after 550°C heat treatment. This might suggest the presence of chlorite. However, the 14 Å entirely disappears instead of increasing in intensity as chlorite would behave when heated to 550°C. It is most likely that the 7.2 Å is due to kaolinite. Sometimes a heat treatment of 600°C may be required to destroy kaolinite.

Quantitative mineralogical analysis (Table 23) of the whole soil and clay fractions shows that kaolinite and gibbsite are dominant in the surface soil and decrease with depth. Mica is dominant in the buried horizons and decreases towards the surface. The DSC patterns (Figure 29) show that both kaolinite and gibbsite are concentrated in the clay fraction while quartz is concentrated in the silt fraction.

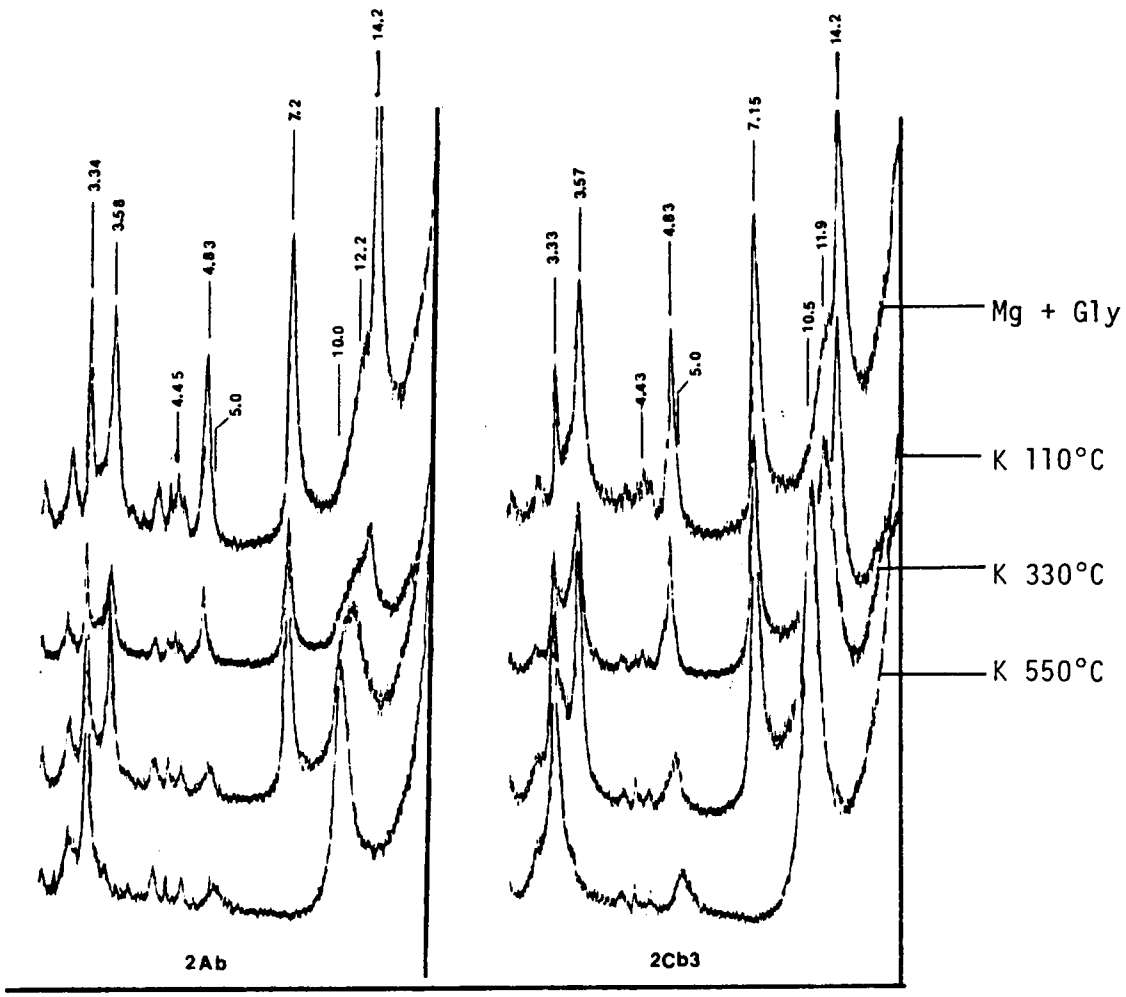

Figure 27. X-ray diffractograms of the coarse clay (2 - 0.2 μm) from Pedon CBNS 3C.

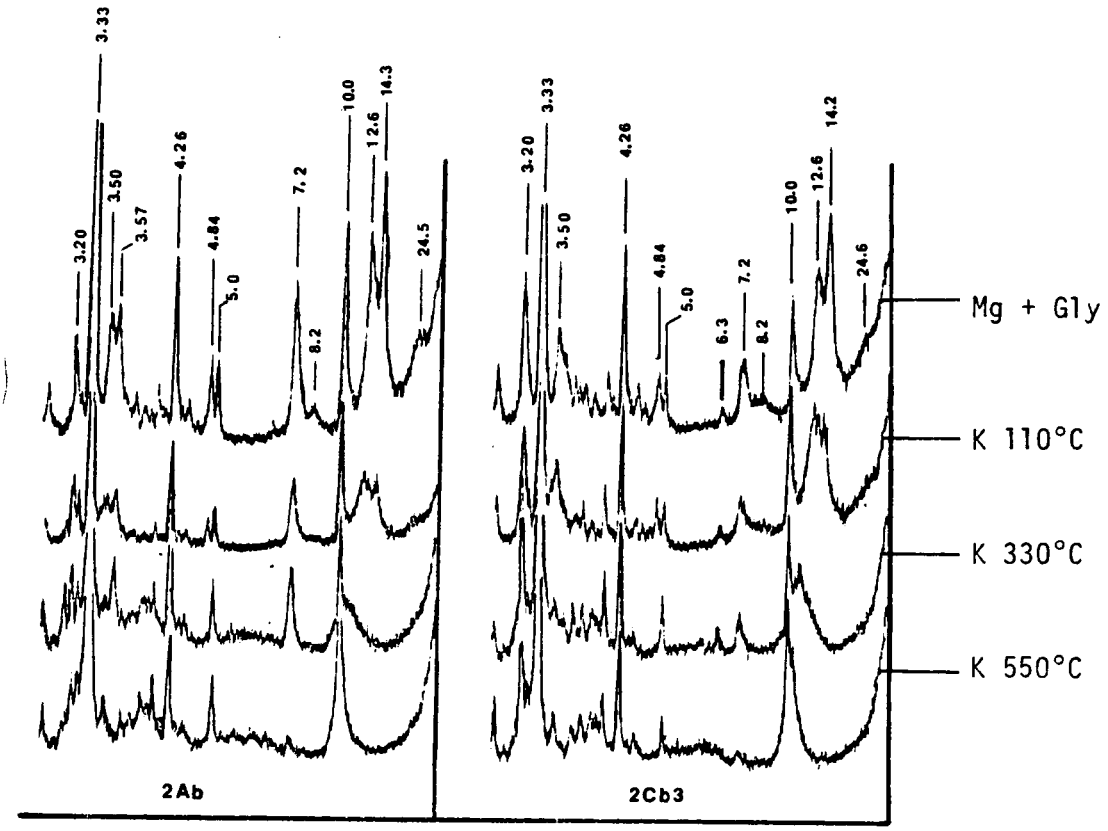

Figure 28. X-ray diffractograms of the fine silt (5 - 2 μm) from Pedon CBNS 3C.

Table 23. Mineralogical Analysis of Pedon CBNS 3C.

Horizon	Depth	Whole Soil					Clay			
		Quartz	Gibbsite	Kaolinite	Fe_2O_3	R*	Gibbsite	Kaolinite	Mica	Quartz
	cm	%					%			
Bt1	0-18	5	8	43	6.9	0.3	13	33	13	0
Bt2	18-23	20	4	18	3.6	0.3	-	-	-	-
Bt3	23-31	10	5	29	6.4	0.2	-	-	-	-
2Ab	31-38	35	0	5	1.5	0.1	8	19	17	0
2Cb1	38-43	35	0	5	1.5	0.1	5	12	17	0
2Cb2	43-61	35	0	5	1.2	0.1	-	-	-	-
2Cb3	61-69	30	0	5	0.8	0.1	6	15	16	0

*(% Gibbsite + % Fe_2O_3)/ % Clay.

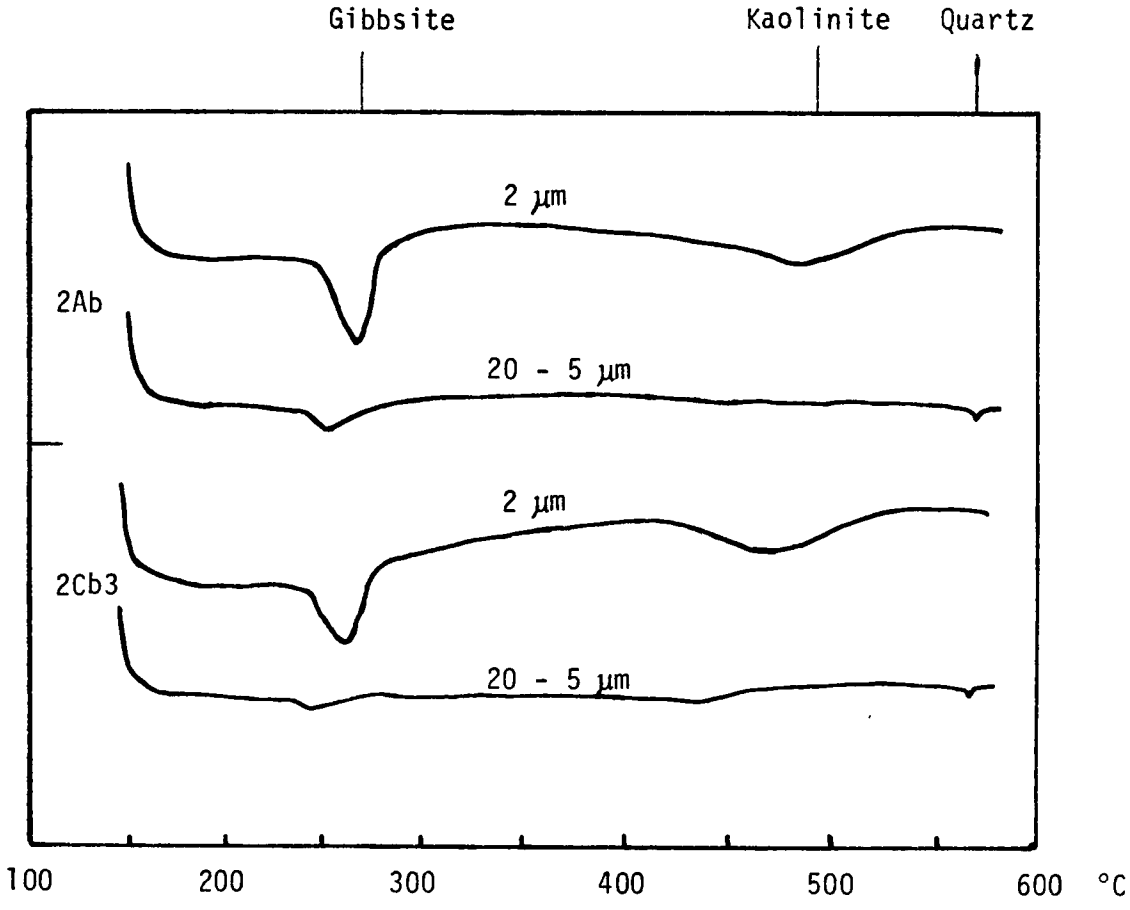

Figure 29. DSC curves of the clay and silt fractions of Pedon CBNS 3C.

CHAPTER V

DISCUSSION

Soil-Geomorphic Relationships

The major differences in soil properties used in separating soils are largely due to variations and interactions of the soil-forming factors. In the Copper Basin and adjoining areas, the terrain is mountainous such that the soils are found in toposequences or topo-litho-sequences. Any major differences in soil properties in this area, in the absence of anthropogenic influences, should be mainly due to differences in parent material and the positions of the soils in relation to other soils (geomorphic position). The soils inside and outside the Basin can be compared on the basis of their geomorphic positions. However, it should be emphasized that significant differences in soil properties can be found in soils on the same geomorphic surface (Lepsch et al., 1977). This is because weathering on any fairly level surface is not uniform and the weathering front can be found at various depths below the soil surface due to jointing and rock features which influence the penetration of the agents of weathering.

The upland soil (CBCC 1A) outside the Basin has a moderately deep solum (155 cm). Soil development in this pedon is advanced as indicated by the argillic horizon. This pedon has extremely acid (pH = 3.9) surface horizons while the subsoil is moderately acid (pH = 5.8). The higher pH levels in the subsoil of this pedon could be attributed to the older buried soil which acts as a sink for the leached cations from the

younger surface horizons. The vegetation at this site is mixed hardwood (forest) and one can assume that the low pH of the surface horizons and the high organic matter content are due to this forest vegetation.

The upland soils inside the Basin have an extremely acid reaction (pH = 4.0 - 5.0) throughout their profile. The vegetation inside the Basin is mainly grass which accounts for the lower organic matter content of the A horizons of these soils. The extreme acidity of these upland soils inside the Basin is primarily due to past SO_2 pollution and the influence of SO_4-S in addition to the inability of the grasses to recycle nutrients from deeper horizons. The major differences between the upland soils inside and outside the Basin are in the organic matter content of the A horizon and soil reaction. Other morphologic properties such as the color of the profile, thickness of the A horizon, and drainage class are similar in both sites.

The midslope soils inside the Basin (CBOS 2B, CBNS 3A) are characterized by thick colluvium. The colluvium and the underlying mica schist and graywacke give rise to soils with slightly different properties from upland summit soils. The major differences are in the depth of the solum and the frequent discontinuities.

The toeslope soils outside the Basin (CBCC 1C) and inside the Basin (CBOS 2C, CBNS 3C) have similar physical and morphological characteristics. Present geomorphic erosional processes have separated some toeslopes from the uplands. In such instances, these toeslopes may have different characteristics from those which are still connected to the uplands. Generally, all the toeslopes are characterized by buried

horizons and a relatively deep solum (except Pedon CBCC 3C). The thick solum is primarily due to colluvium which has been moved downslope.

The upland soils differ from the toeslope soils with regard to soil color, depth of solum, and drainage conditions. Soil acidity also increased from toeslope to upland except in soils near the new smelter (CBNS 3A, CBNS 3C). At this site, the low toeslope soil is more acid (pH = 4.4 - 4.6) than the upper toeslope soil (pH = 4.4 - 5.4) primarily because this low toeslope soil seems to have been affected most by the SO_4-S. The upland soils generally have more Fe_2O_3 than the toeslope soils. The Fe_2O_3 content follows a pedogenic pattern attaining maximum accumulation in the argillic horizons and decreasing in the saprolite. This trend is not easy to identify due to the discontinuities. However, in the upland summit soils, the pedon inside the Basin shows this pedogenic trend while the pedon outside the Basin (CBCC 1A) has maximum Fe_2O_3 concentration in the saprolite. Since both soils are well drained, it is possible that the SO_4-S inside the Basin is responsible for the low Fe_2O_3 in the saprolite. It is suggested that the SO_4-S reacted with the Fe_2O_3 at the saprolite-rock interface. Senkayi et al. (1981) found that a similar reaction took place when lignite overburden was leached with H_2SO_4. On the other hand, the high Fe_2O_3 content in the saprolite of Pedon CBCC 1A may be due to a parent material higher in Fe.

The sequences of minerals found in a toposequence could reflect the environmental conditions that exist. The upland soils with good drainage should be dominated by gibbsite while the lowland soils should be dominated by kaolinite and smectites (Hsu, 1977). This is essentially

true for the soils outside the Basin. However, all the soils inside the Basin are dominated by kaolinite. The gibbsite content of the upland soil (CBOS 2A) is moderately high but decreases appreciably in the lower B and Cr horizons. The low Fe_2O_3 and gibbsite may indicate sluggish drainage which leads to the accumulation of SiO_2 and reduction of Fe.

Soil Acidity and the Effects of SO_4-S

Genetic interpretations can be made by studying the distribution of chemical properties within the pedons. However, the chemical properties need to be examined with the understanding that several discontinuities are present in these soils. One cannot be certain that the chemical data reflect pedogenesis in soils with discontinuities. The same thing can be said for the depth distribution of the minerals. When the soil discontinuities reflect local slope-related sediment transport, certain chemical properties due to environmental differences can be compared. One such property is the SO_4-S content of the soils and its effect on the soils.

The present concentration of SO_4-S differs between the soils inside and outside the Basin. The SO_4-S tends to be concentrated in the argillic horizons and the experimental results show that the argillic horizons of the Basin soils contain between 65 and 160 μg S/g soil while those outside the Basin contain 6 to 77 μg S/g soil. The higher amounts of SO_4-S in the Basin and the lack of basic exchangeable cations seem to be responsible for the present low pH of the Basin soils although sulfide mineral oxidation in the parent rock could contribute. The difference in soil pH is reflected in the Basin soils which are extremely acid

(pH = 3.8 - 5.4) throughout the profile while the soils outside the Basin have an acid topsoil (pH = 3.9 - 4.8) and a moderately acid subsoil (pH = 5.4 - 5.9).

The formation of alunite is thermodynamically favorable in acid environments containing SO_4 and in the presence of clay minerals. Adams and Hajek (1978) reported that a SO_4 concentration of 0.01 M in the presence of 0.01 M K led to the precipitation of alunite [$KAl_3(OH)_6(SO_4)_2$]. Alunite was not detected in any of these soils in the present study. This does not mean that alunite may not have formed in the early stages of the open smelting operations when the soils were exposed to large doses of SO_4. Even if alunite is present in these soils now, it may not be crystalline enough to be detected by x-ray procedures. This study did not include any soil solution studies so that the activities of K and SO_4 could not be determined. However, Wolt (1981) working in the same general sampling sites, found the K and SO_4 activities were much lower than 0.01 M.

The only pedon that showed signs of having any alunite is Pedon CBOS 2B. This is the pedon on the midslope near the old smelter. The coarse clay of the 2Cr (Figure 15, page 71) showed a 4.95 Å peak which disappeared on 550°C treatment. The horizon has very little SO_4-S (27 ug/g), the highest exchangeable K (0.23 meq/100 g), and one of the lowest total K (0.2%) contents among all the horizons in the seven profiles. The K-mica may have weathered in the presence of SO_4 to form alunite. Harvey and Vitaliano (1964) and Hemley et al. (1969) have shown that muscovite can weather to alunite in the presence of SO_4. The presence of alunite in this pedon may have to be verified by soil

solution studies since Wolt (1981) found that alunite was potentially stable in the Basin soils and may be controlling solution Al^{3+} and $SO_4^=$ activities.

Kamprath et al. (1956) found that SO_4 adsorption decreased with increasing pH. No consistent relationship was observed between SO_4 and soil pH in the present study. Diamond and Hanley (1970) also found no consistent relationship between SO_4 and soil pH. The only relationships observed in this study are in the soils inside the Basin. The upland (CBOS 2A) and midslope (CBOS 2B) pedons near the old smelter showed positive correlations between SO_4-S and Fe_2O_3 and clay (See Tables A-3 and A-4, Appendix). The toeslope pedon (CBNS 3C) near the new smelter showed correlations for pH, Fe_2O_3, BS, clay and Al (See Table A-7, Appendix). This toeslope pedon which may be partly submerged by the polluted creek at certain times of the year, may be receiving H_2SO_4 from mine tailings farther upstream.

The difficulty encountered in relating extractable-SO_4 to soil properties is due to the gross disturbed condition of the soils and the soil discontinuities. Another reason may be due to the S fraction extracted. Sulfate-sulfur is made up of soluble SO_4 and adsorbed SO_4. The SO_4 fraction in organic matter is not extracted. It is possible that total S may have better relationships with the other soil properties.

The low pH of the Basin soils has also led to the release of basic cations (Ca, Mg, K, Na) which have been leached out and lost from the soil. Senkayi et al. (1981) found such losses while Barnhisel and Rotromel (1974) found that Al, Fe, K, and Si were also released in

solution. The acidity and leaching have also led to low BS and ECEC values. The adverse effects of low pH on soils could be counteracted by an increase in weathering and the release of more cations in areas with ultrabasic rocks. This could be a compensating process in such areas. However, it has been shown from areas in New England with igneous and metamorphic rocks that there are no indications of an increase in weathering despite large amounts of acid precipitation (Johnson et al., 1972).

Silicate Mineral Weathering Sequences

X-ray diffraction and DSC analyses indicate that there are no major soil mineralogical differences between soils inside and outside the Basin. The mineral assemblages found in the pedons are HIV, mica, vermiculite, mica-vermiculite, feldspars, kaolinite, gibbsite, and quartz. The distribution of these minerals in the soil and their relationship with soil depth and landscape position vary and may indicate changes in weathering patterns.

The parent rocks from which these soils originated are a complex mix of metasedimentary rocks including quartz-mica schist, metagraywacke, phyllite, and probably feldspathic quartzites, all of which have been folded, faulted and sheared to varying degrees. Evidence from x-ray analyses of the lithic materials indicates that they all contained feldspars and mica. The feldspar peaks are at 3.20 Å amd 4.07 Å which may suggest an orthoclase feldspar. X-ray analyses of the paralithic material (Cr) showed less feldspar while mica was abundant. This may suggest that the feldspar is relatively weathered in the paralithic material. The mica in the sand fraction as seen under the petrographic microscope is

composed of muscovite and dark-colored grains which resemble biotite, but which are actually kaolinite pseudomorphs of biotite. The soil clay mica is dioctahedral mica as is evidenced by the intense (002) reflection. These facts indicate that any biotite and/or feldspar in the parent rock must have weathered to kaolinite or gibbsite in these acid environments.

The present processes of soil formation in these pedons are complex because most of the pedons have an upper younger soil overlying an older soil. This means that the older soil represents an advanced stage of weathering while weathering is less advanced in the recently deposited upper soil which contributes soluble components to the older soil below. The extreme acid conditions of the pedons further complicate the weathering patterns. However, it is apparent from the x-ray and DSC patterns that most of the kaolinite must have originated from the biotite and feldspar. This conclusion is based on the large amounts of kaolinite in the fine clay, coarse clay, and silt fractions of the pedons and the kaolinite pseudomorphs of biotite in the sand fraction. Kaolinite is found in large amounts in the Basin soils and increases with depth. Some kaolinite in the subsoil and saprolite may have also resulted from translocation in solution or as very fine particles. If this is the case, clay flows in the saprolite should be composed mainly of kaolinite. However, gibbsite was the dominant clay mineral in clay flows and coatings in the saprolite.

Kaolinite and gibbsite are the dominant minerals in all pedons. These two minerals increase with depth (Figure 30). However, in Pedon CBOS 2A the gibbsite content actually decreases sharply below the argillic

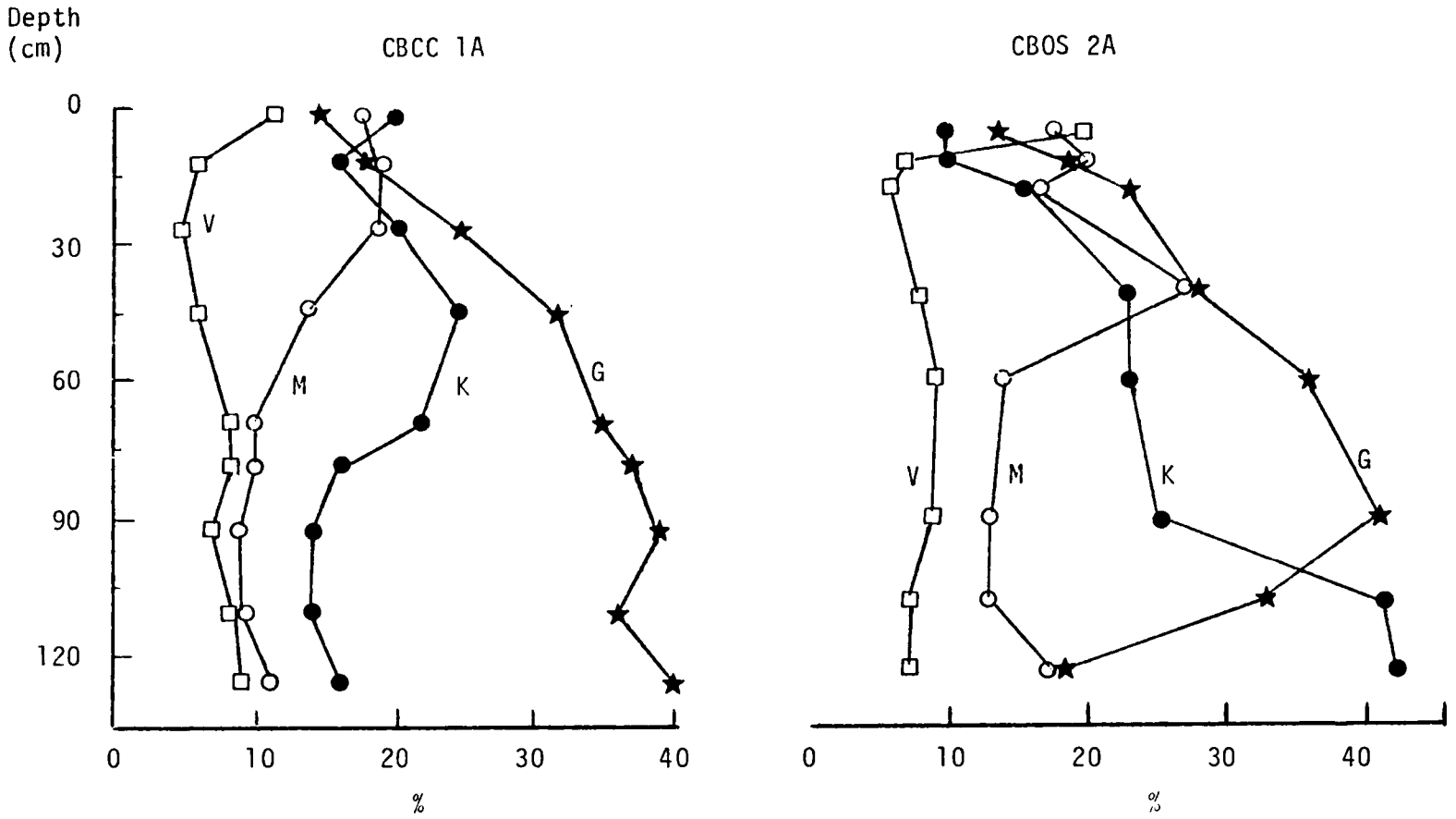

Figure 30. Depth relationships of the clay minerals in the two upland pedons. V = vermiculite; M = mica; K = kaolinite; G = gibbsite.

horizon while the kaolinite content increases down to the saprolite. On the other hand, in Pedon CBCC 1A, kaolinite content decreases below the argillic horizon while gibbsite content increases with depth down to the saprolite (Figure 30). Eswaran and Bin (1978) found that both kaolinite and gibbsite were direct transformation products of feldspar. Calvert et al. (1980) found that halloysite, amorphous aluminosilicates, and gibbsite were the direct weathering products of feldspar. The evidence from this study does not suggest a direct formation of gibbsite from feldspars, rather it suggests neoformation from solution. This is because (1) the x-ray and DSC patterns of the lithic and paralithic material did not show any gibbsite, and (2) even though the crushed saprolite showed some gibbsite, it was found that the gibbsite was in the clay flows which were lodged in cracks and fissures in the saprolite.

It is proposed here that gibbsite is formed in the upper part of the solum that formed in younger colluvial capping by the recombination of Al^{3+} and OH^- produced during the weathering of fresh feldspar and biotite in the young, rejuvenated top soil. The gibbsite formed does not persist under the extreme acid conditions in the upper solum and is translocated in solution together with Fe_2O_3 to the subsoil. Both are deposited in the subsoil and saprolite. The low gibbsite content of surface horizons is attributed to the acidity of the topsoil emanating from the organic acid from organic matter and H_2SO_4 from the open roasting operations. Of course past extreme weathering of the paleosol Bt horizons would also see the transformation of kaolinite to gibbsite and thus explain the higher gibbsite contents in these buried argillic horizons.

The change in vegetation from forest to grass vegetation in the Basin has affected clay migration and water movement in the soils. Clay seems to have accumulated more under grass vegetation than under forest vegetation. This accumulation leads to a sharp and abrupt textural contrast between the lower argillic horizon and the saprolite and thus impedes water movement. The saprolite of Pedon CBCC 1A is porous and permits rapid throughflow and loss of silica (Figure 31). This condition favors the crystallization of gibbsite. In the toeslope position (CBCC 1C) drainage is somewhat impeded in the saprolite and kaolinite is formed and stable. The upland pedon in the Basin (CBOS 2A) has a less permeable and clay-plugged saprolite which restricts throughflow (Figure 31). This is evidenced by the concentration of manganese nodules in this zone and the low levels of Fe_2O_3. The impeded throughflow favors the concentration of silica and the formation of kaolinite. The presence of SO_4-S in the soils inside the Basin may also contribute to the very low levels of gibbsite in these soils. However, all the toeslope soils both inside and outside the Basin are very low in gibbsite suggesting that percolation rate and the concentration of silica were the controlling factors in gibbsite formation and stability.

Most of the pedons have HIV in surface soils, kaolinite and gibbsite in subsoils and kaolinite and muscovite in the saprolite (Figure 30). It is suggested that muscovite is weathering to vermiculite through an interstratified mica-vermiculite stage. Under the acid conditions found in the Basin and in the presence of free Al^{3+}, any vermiculite formed from muscovite by simple transformation is readily converted to HIV in regions of low pH. This is the chloritization of vermiculite (Lietzke

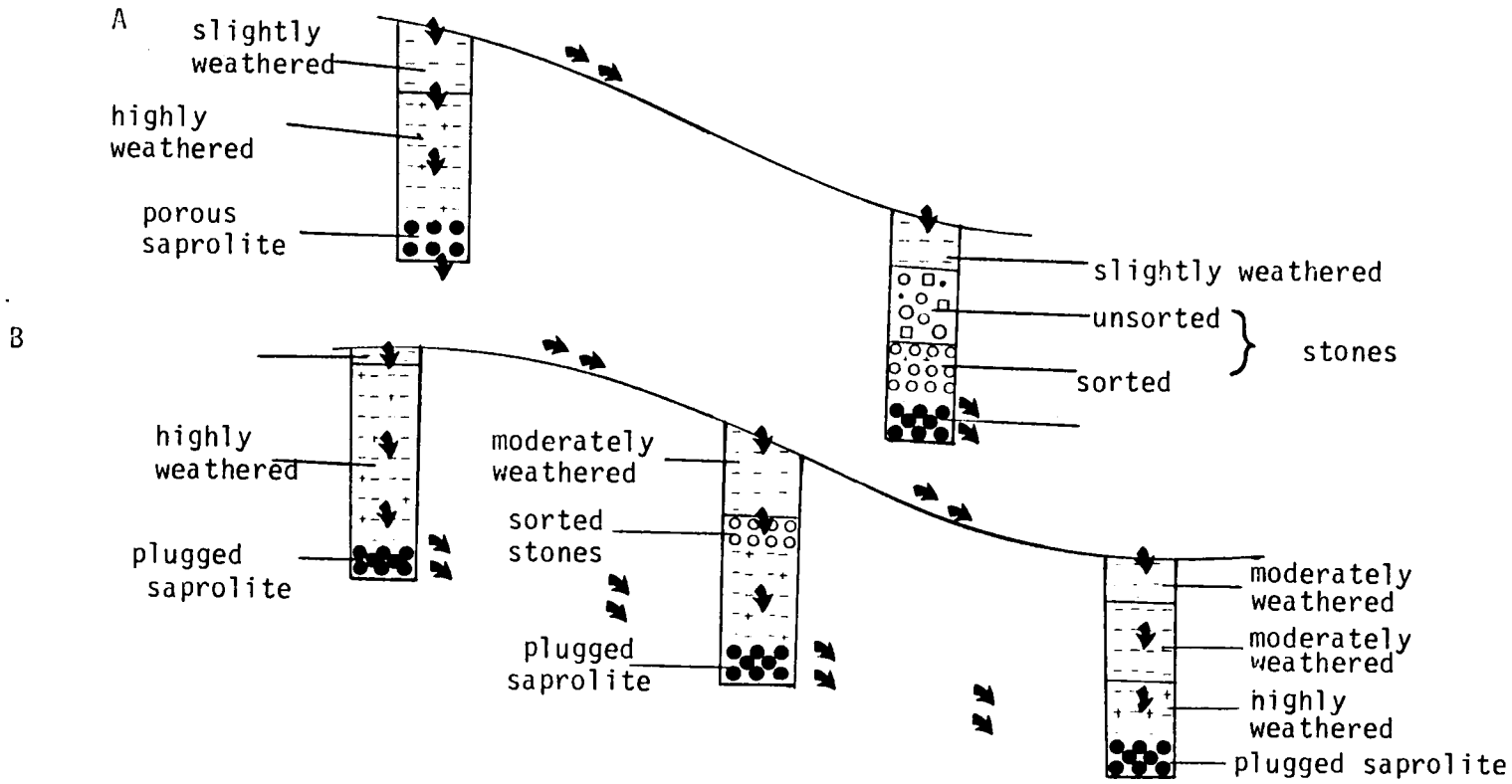

Figure 31. Schematic diagram showing water movement and drainage in sites outside the Basin (A) and inside the Basin (B). Arrows show water flow.

and Mortland, 1973). Kaolinite and gibbsite tend to concentrate in the subsoil because they are not stable in the extremely acid surface environment (Carlisle and Zelazny, 1974). Under these conditions, mica should decrease upwards in the profile and vermiculite should increase upwards since the mica is weathering to vermiculite (Kapoor, 1972). This trend is not observed in these pedons because the presence of interstratified mica-vermiculite, HIV, and buried horizons complicate the weathering sequence.

The behavior of the 24 Å peak is typical of a regular interstratification of mica-vermiculite. Many studies (Coleman et al., 1963; Wilson, 1970b) have shown that such an interstratification is derived from biotite. However, hydrobiotites are unlikely to occur in these soils because biotite was not detected, so a somewhat ordered interstratified muscovite-vermiculite mineral accounts for this 24 Å component. The regularity of the interstratification is confirmed by peaks at the low angle region (Weaver, 1956), the spacings of higher orders which are very close to exact fractions of the (001) spacing, and the closeness of the (001) spacing to the theoretical figure obtained from the sum of the (001) spacings of the two constituent phases.

Proposed Weathering Model

It is proposed from the above discussion that

1. Biotite and feldspar weather to kaolinite while the muscovite weathers to vermiculite through a mica-vermiculite interstratified phase.

2. Hydroxy-interlayered vermiculite is formed from the vermiculite in the presence of free Al^{3+} and low pH (3.8 - 4.5) in the surface horizon.

3. Gibbsite is not a direct product of weathering but rather it is a secondary mineral which is formed in the upper part of the solum and translocated to the subsoil and saprolite.

4. Gibbsite can also form in the upper subsoil as a result of desilication, and its low levels in the Basin may be a result of the presence of H_2SO_4 or imperfect drainage leading to accumulation of silica and crystallization of kaolinite.

The two upland summit soils (CBCC 1A and CBOS 2A) clearly illustrate this model (Figure 30), The absence of gibbsite in the parent rock or the partially weathered rock indicates that gibbsite is not a direct weathering product. The presence of gibbsite in saprolite clay flows supports the idea that gibbsite is translocated. The abundance of kaolinite in the fine clay and its increase with depth in the profile indicates that it is the product of advanced weathering. The feldspar identified was orthoclase feldspar which is relatively resistant to weathering. The direct formation of gibbsite from feldspar is more common in plagioclase feldspars even though Gardner (1972) mentioned that gibbsite can form from K-feldspar.

Soil Genesis and Classification

The presence of kaolinite in the silt fraction and fine clay of the saprolite suggests that kaolinite is a primary product of biotite and feldspar weathering. The abundance of muscovite mica in the silt and coarser fractions suggests that this mica is inherited and not pedogenic. It appears that most of the primary minerals in these soils are inherited from the parent material. Observations of the soils in the field show

that clay has moved within the soils. This is confirmed by the clay coatings on ped faces in the lower B horizons of the upland soils and the iron oxide distribution. If the amount of kaolinite and/or gibbsite in the clay is assumed to be directly proportional to the degree of weathering, then it is evident from the particle size distribution data that the horizons of maximum primary silicate weathering and clay mineral formation correspond with the argillic horizons and the C horizons. Thus, in situ weathering is the major source of clay. Some clay in the argillic horizons and the collapsed saprolite may also be due to illuviation and this is evidenced by the abundance of kaolinite in the fine clay fraction of the argillic horizon.

Soil development is reflected in the argillic horizons of all pedons. The presence of mottles in Pedon CBOS 2C may suggest a redistribution of mobile soil constituents. It is theorized that clay formed in situ was deposited in the microcracks and fissures of the initial material of the upland soils. This clay, which is mostly residual, gradually accumulates and affects the permeability of the soils. As soil development proceeds, loss of water-soluble mineral constituents lend permeability to the saprolite, leading to increased leaching and eluviation. The high rainfall coupled with the mesic temperature regime accelerates decomposition of organic matter and intensifies leaching. The soils are depleted of bases and this leads to acidity. The present leaching conditions favor the formation of gibbsite in these soils. This must have been the condition of the upland soils before the mining operations.

The production of H_2SO_4 in the Basin must have led to increased surface acidity of the soils. The H_2SO_4 is leached down to the saprolite

where it accelerates gibbsite dissolution. As a result, the gibbsite concentration of the C horizon is very low in Basin soils. The mining operations have also led to changes in vegetation. The grass vegetation in the Basin as opposed to forest vegetation outside the Basin can also affect the present mineralogical composition of the soils (Churchman, 1980). The soils in the midslopes are also subjected to runoff and lateral flow of water. In time it is expected that such soils would contain less clay in the upper horizons due to greater eluviation. The soils in the toeslopes receive materials from the upland soils and may be made up of an old soil overlain by colluvial or alluvial material.

All the Pedons except Pedon CBOS 2C and Pedon CBNS 3C have an oxidic mineralogy. Pedons CBOS 2C and CBNS 3C have mixed mineralogy. The chemical properties of these soils indicate that they are low activity clay soils. However, some of the soils have very high base saturation which should disqualify them as Ultisols. Base saturation computations may sometimes be meaningless when the ECEC values are very low. Another consideration is the method of the ECEC determination. Unpublished data compiled by S.W. Buol and J.R. Parades as mentioned by Lepsch et al. (1977) show that 50% BS at pH 8.3 equals 62% BS at pH 7.0. Juo et al. (1976) reported that for a given soil sample, BS at pH 8.2 was the lowest while the ECEC method gave the highest BS. The Ag-TU method extracts the cations at the pH of the soil, which in this case ranges from 3.8 to 5.9. This means that BS determined at pH 5.9 or less will be much more than BS at pH 8.2.

All the pedons are Typic Hapludults with the exception of Pedon CBNS 3C which is a Typic Udifluvent.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Summary

The open roasting of sulfides in the Copper Basin in Tennessee has certainly led to increased soil acidity. The effects of this acidity and the loss of vegetation were investigated to see whether they influenced the morphology, chemistry and mineralogy of these soils.

Five pedons were located to represent upland and toeslope soils inside the Basin and two pedons were located 8 km upwind from the smelter sites to represent soils outside the Basin. The soils outside the Basin are presumed to be less affected by the smelting and mining operations and this is reflected in the dense vegetation.

From the morphological, chemical, and mineralogical data, this study shows that there are no major morphologic differences between the soils inside and outside the Basin. Differences do exist in pH and mineralogy. Generally, all the pedons are acid (pH = 3.8 - 5.9); soils inside the Basin being more acid than soils outside the Basin. All the pedons have low ECEC, BS and exchangeable cations. The low ECEC of all pedons is attributed to the advanced weathering and leaching conditions. The SO_4-S concentration is low in all pedons and does not seem to correlate well with pH, dithionite extractable Fe, clay, BS and KCl extractable Al content of soils outside the Basin. Inside the Basin, the upland and midslope soils near the old smelter have good correlations between SO_4-S and Fe_2O_3, and SO_4-S and clay. The low toeslope soil in the new smelter

region shows very significant correlations between SO_4-S and each of the soil properties discussed. The nonsignificant correlation shown by the other pedons is attributed to the discontinuities in the soil profile and the present leaching regime.

The distribution of iron oxides in the soils and their relationship with soil depth shows that Fe_2O_3 is concentrated in the saprolite of the upland soil (CBCC 1A) but is depleted in the saprolite of Pedon CBOS 2A. If the drainage conditions are similar in both Pedons, the low Fe content of the Cr horizon of Pedon CBOS 2A may be due to H_2SO_4 produced acidity which increased the oxide solubility or it may be due to a parent material initially low in Fe.

The major difference found between the soils inside and outside the Basin is in the weathering and weathering products. In both sites, the basic mineralogical composition of the soils is the same. Hydroxy Al-interlayered vermiculite (HIV) is found in the surface soils while kaolinite and gibbsite are found in the subsoil. Mica and vermiculite are found in moderate amounts throughout the pedons. This suggests that muscovite is now weathering to vermiculite. Kaolinite and gibbsite are the dominant minerals in all pedons and increase with soil depth. Kaolinite is the dominant mineral in the lowland pedons with somewhat poorly drained soils.

The dominance of kaolinite in these Basin soils may be due to the high acidity in the subsoils and the possible formation of a complex between $Al(OH)_3$ and SO_4. Although no minerals like alunite or basaaluminite were detected in the Basin soils, it is believed that these, or other more soluble Fe and Al sulfate minerals, must have existed in

these soils during the early mining days when the soils were exposed to large doses of H_2SO_4. Alternatively kaolinite or gibbsite may be dominant in the saprolite depending on the drainage condition and porosity of the saprolite.

Conclusions

From the results of this study, it is concluded that:

1. No major differences in morphology exist between soils inside and outside the Basin.

2. All the soils in the study area are acid (pH = 3.8 - 5.9) and highly weathered. They have very low ECEC (<12.0 meq/100 g) and BS and high exchangeable acidity.

3. Mineralogically, the upper solum is similar in both areas but significant differences exist in the subsoil and saprolite.

4. Slight variations in weathering patterns between the two regions are due to the presence of SO_4-S in the Basin and to drainage conditions.

5. Even though there is chemical evidence to support differences in pH, Fe_2O_3, and SO_4-S content between soils inside and outside the Basin, these are not manifested to a great degree in the present system. It is possible that regional influences due to removal of plant cover may have had a greater impact than the SO_4-S and acid weathering.

6. With the exceptions of the lowland soils (Pedons CBOS 2C and CBNS 3C) which have mixed mineralogies, all the soils have oxidic mineralogy and are classified as Typic Hapludults. Pedon CBNS 3C is a Typic Udifluvent.

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APPENDICES

APPENDIX A

SO_4-S AND SOIL PROPERTIES

Table A-1. Regression equations ($\hat{Y}$) showing relationships between SO_4-S (Y) and soil properties (X) in Pedon CBCC 1A.

X	Y	$\hat{Y}$	r
pH	SO_4-S	190.5 - 26.6X	-0.56
Base Saturation	SO_4-S	52.0 - 0.25X	-0.29
KCl Extr. Al	SO_4-S	39.8 + 13.3X	0.48
Clay	SO_4-S	53.3 - 0.07X	-0.02
Fe_2O_3	SO_4-S	70.3 - 3.2X	-0.22

Base saturation, clay, Fe_2O_3 . . . . %

KCl Extr. Al . . . . . meq/100 g

Table A-2. Regression equations ($\hat{Y}$) showing relationships between SO_4-S (Y) and soil properties (X) in Pedon CBCC 1C.

X	Y	$\hat{Y}$	r
pH	SO_4-S	182.6 - 28.6 X	-0.30
Base saturation	SO_4-S	26.4 + 0.31 X	0.19
KCl Extr. Al	SO_4-S	10.7 + 9.7 X	0.37
Clay	SO_4-S	38.0 - 0.16 X	-0.10
Fe_2O_3	SO_4-S	66.7 - 7.16 X	-0.44

Base saturation, clay, Fe_2O_3 . . . . %

KCl Extr. Al . . . . . meq/100 g

Table A-3. Regression equations ($\hat{Y}$) showing relationships between SO_4-S (Y) and soil properties (X) in Pedon CBOS 2A.

X	Y	$\hat{Y}$	r
pH	SO_4-S	274.3 - 35.4 X	-0.34
Base saturation	SO_4-S	130.4 - 0.55 X	-0.48
KCl Extr. Al	SO_4-S	97.6 + 10.3 X	0.27
Clay	SO_4-S	68.9 + 1.63 X	0.79*
Fe_2O_3	SO_4-S	31.2 + 18.43 X	0.76*

*Significant at p = 0.05.

Base saturation, clay, Fe_2O_3 . . . . %

KCl Extr. Al . . . . . meq/100 g

Table A-4. Regression equations ($\hat{Y}$) showing relationships bewtwen SO_4-S (Y) and soil properties (X) in Pedon CBOS 2B.

X	Y	$\hat{Y}$	r
pH	SO_4-S	84.4 + 0.85 X	0.01
Base saturation	SO_4-S	101.7 - 0.58 X	-0.37
KCl Extr. Al	SO_4-S	68.3 + 10.3 X	0.32
Clay	SO_4-S	21.3 + 2.41 X	0.82*
Fe_2O_3	SO_4-S	30.1 + 16.72 X	0.80*

*Significant at p = 0.01.

Base saturation, clay, Fe_2O_3 . . . . %

KCl Extr. Al . . . . . meq/100 g

Table A-5. Regression equations ($\hat{Y}$) showing relationships between SO_4-S (Y) and soil properties (X) in Pedon CBOS 2C.

X	Y	$\hat{Y}$	r
pH	SO_4-S	-136.9 + 43.9 X	0.69*
Base saturation	SO_4-S	58.6 + 0.38 X	0.34
KCl Extr. Al	SO_4-S	72.3 + 0.13 X	0.12
Clay	SO_4-S	73.0 + 0.02 X	0.01
Fe_2O_3	SO_4-S	61.3 + 5.8 X	0.33

*Significant at p = 0.01

Base saturation, clay, Fe_2O_3 . . . . %

KCl Extr. Al . . . . . meq/100 g

Table A-6. Regression equations ($\hat{Y}$) showing relationships between SO_4-S (Y) and soil properties (X) in Pedon CBNS 3A.

X	Y	$\hat{Y}$	r
pH	SO_4-S	-57.7 + 24.2 X	0.34
Base saturation	SO_4-S	45.6 + 0.30 X	0.28
KCl Extr. Al	SO_4-S	74.6 - 8.39 X	-0.28
Clay	SO_4-S	65.1 + 0.04 X	0.01
Fe_2O_3	SO_4-S	4.54 + 16.1 X	0.64*

*Significant at p = 0.01.

Base saturation, clay, Fe_2O_3 . . . . %

KCl Extr. Al . . . . . meq/100 g

Table A-7. Regression equations ($\hat{Y}$) showing relationships between SO_4-S (Y) and soil properties (X) in Pedon CBNS 3C.

X	Y	$\hat{Y}$	r
pH	SO_4-S	1745.0 - 366.5 X	-0.89**
Base saturation	SO_4-S	161.23 - 5.21 X	-0.89**
KCl Extr. Al	SO_4-S	68.6 + 16.4 X	0.62
Clay	SO_4-S	70.3 + 1.86 X	0.79*
Fe_2O_3	SO_4-S	78.8 + 10.1 X	0.81*

*Significant at p = 0.05.

**Significant at p = 0.01.

Base saturation, clay, Fe_2O_3 . . . . %

KCl Extr. Al . . . . . meq/100 g

APPENDIX B

SULFATE-SULFUR CORRELATIONS

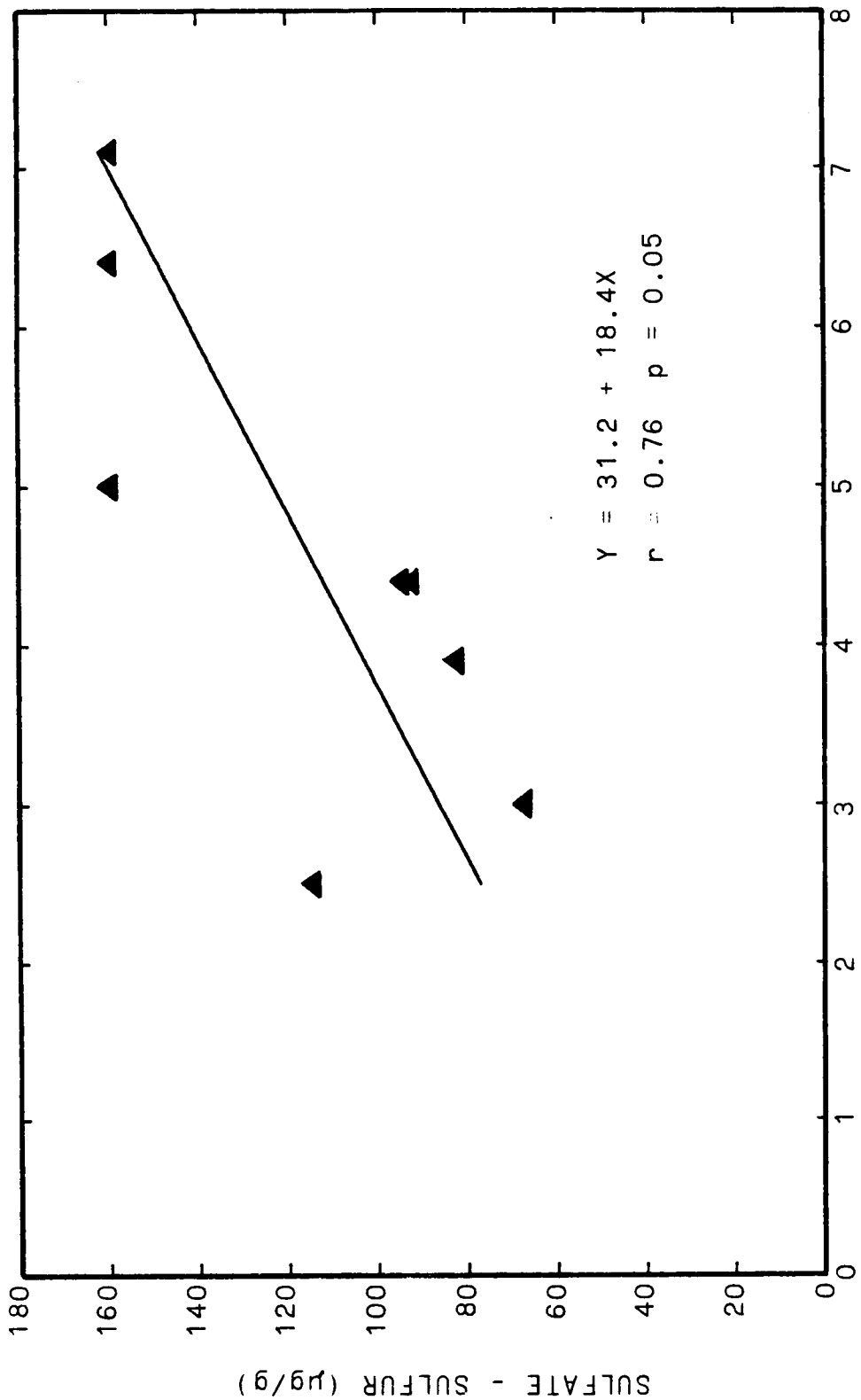

Figure A-1. Correlation between SO_4-S and Fe_2O_3 in Pedon CBOS 2A.

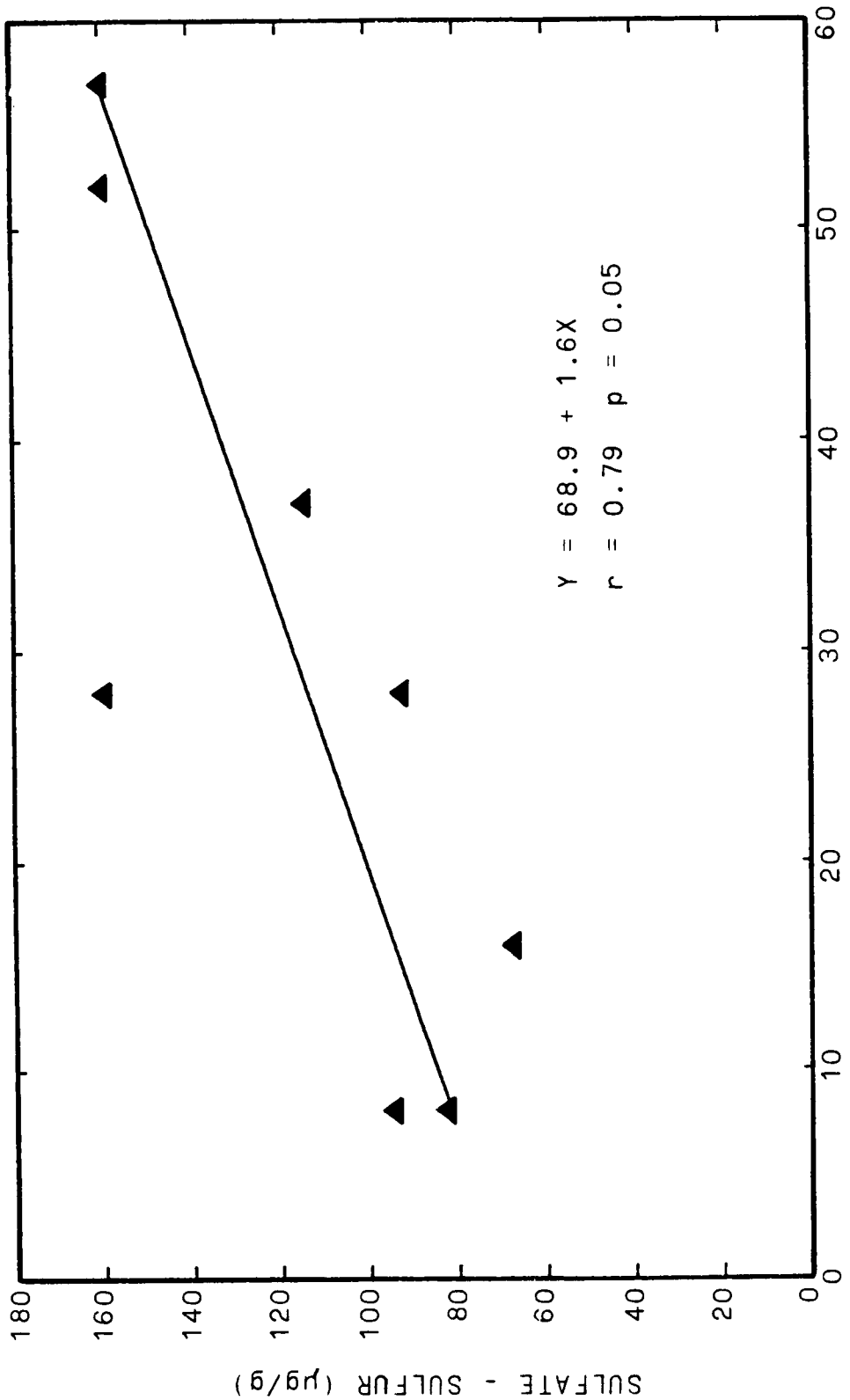

Figure A-2. Correlation between SO_4-S and clay in Pedon CBOS 2A.

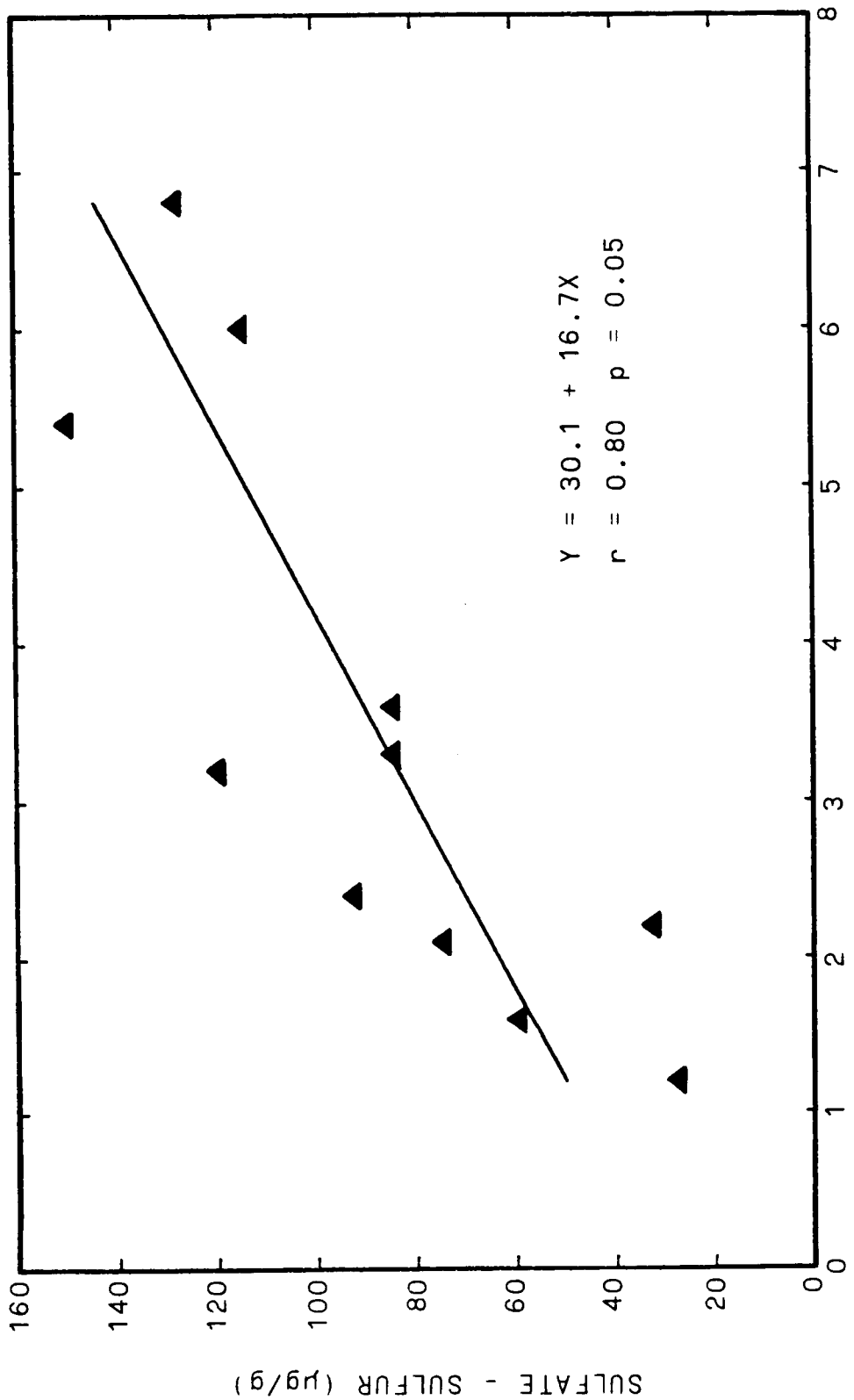

Figure A-3. Correlation between SO_4-S and Fe_2O_3 in Pedon CBOS 2B.

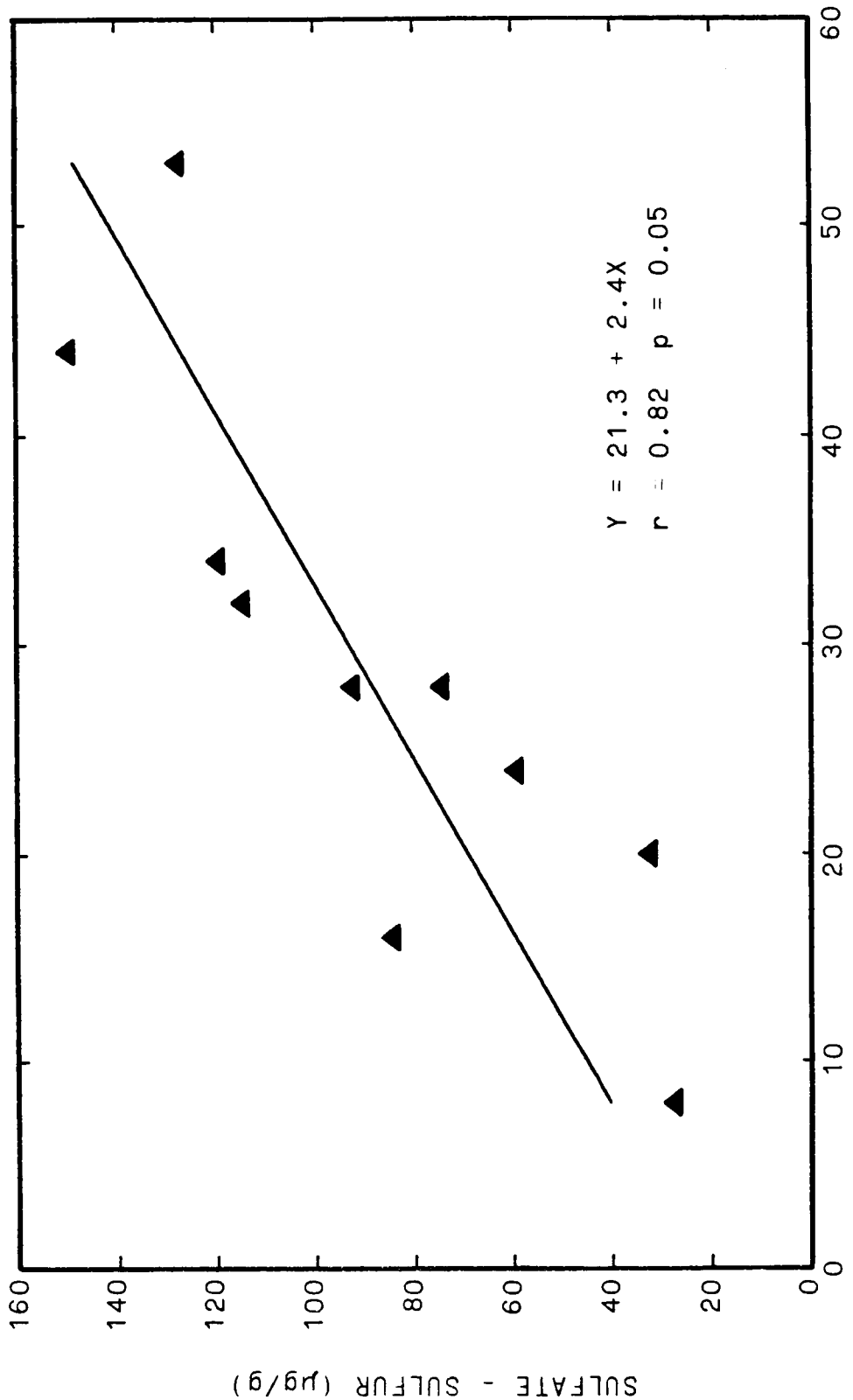

Figure A-4. Correlation between SO_4-S and clay in Pedon CBOS 2B.

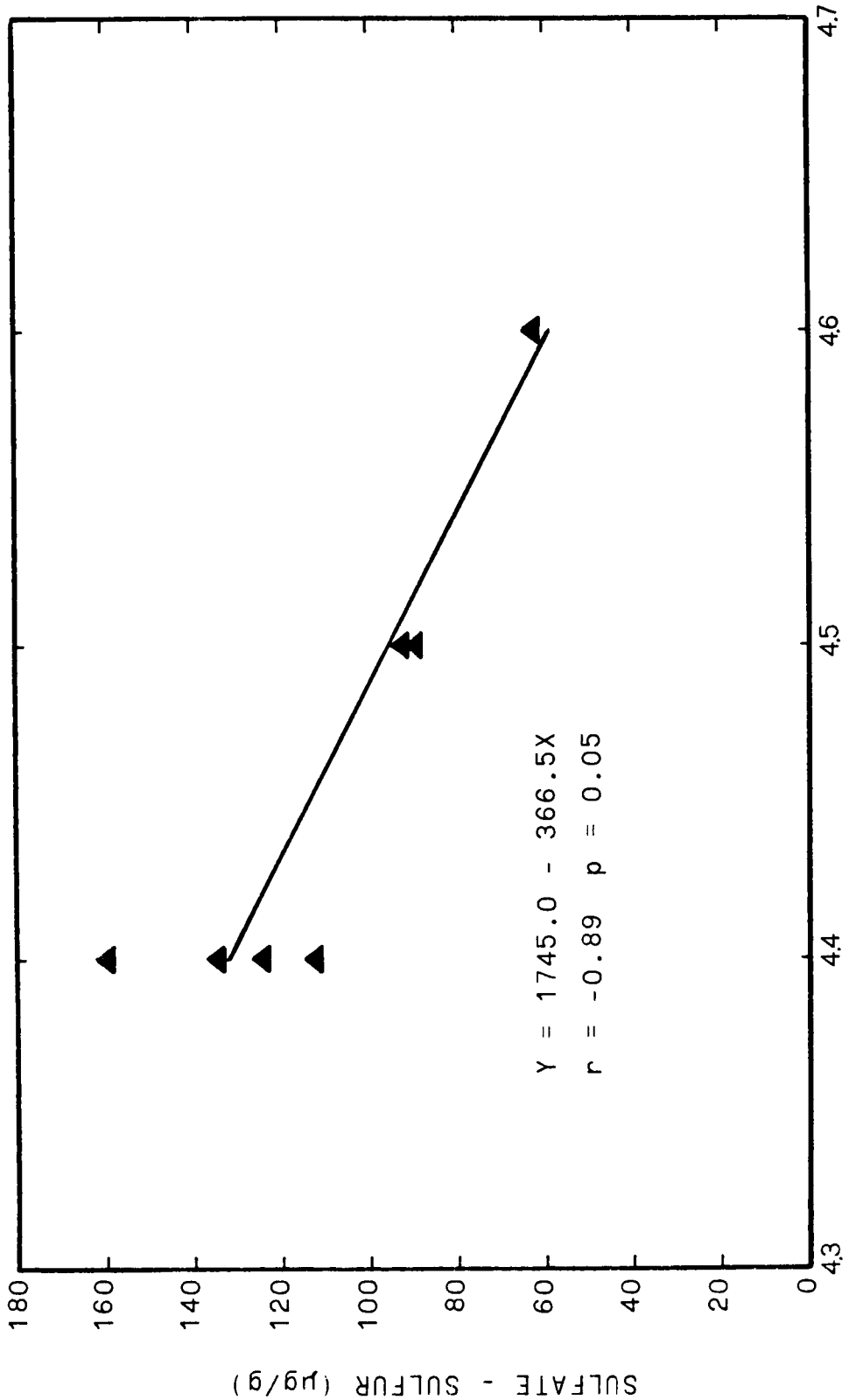

Figure A-5. Correlation between SO_4-S and pH in Pedon CBNS 3C.

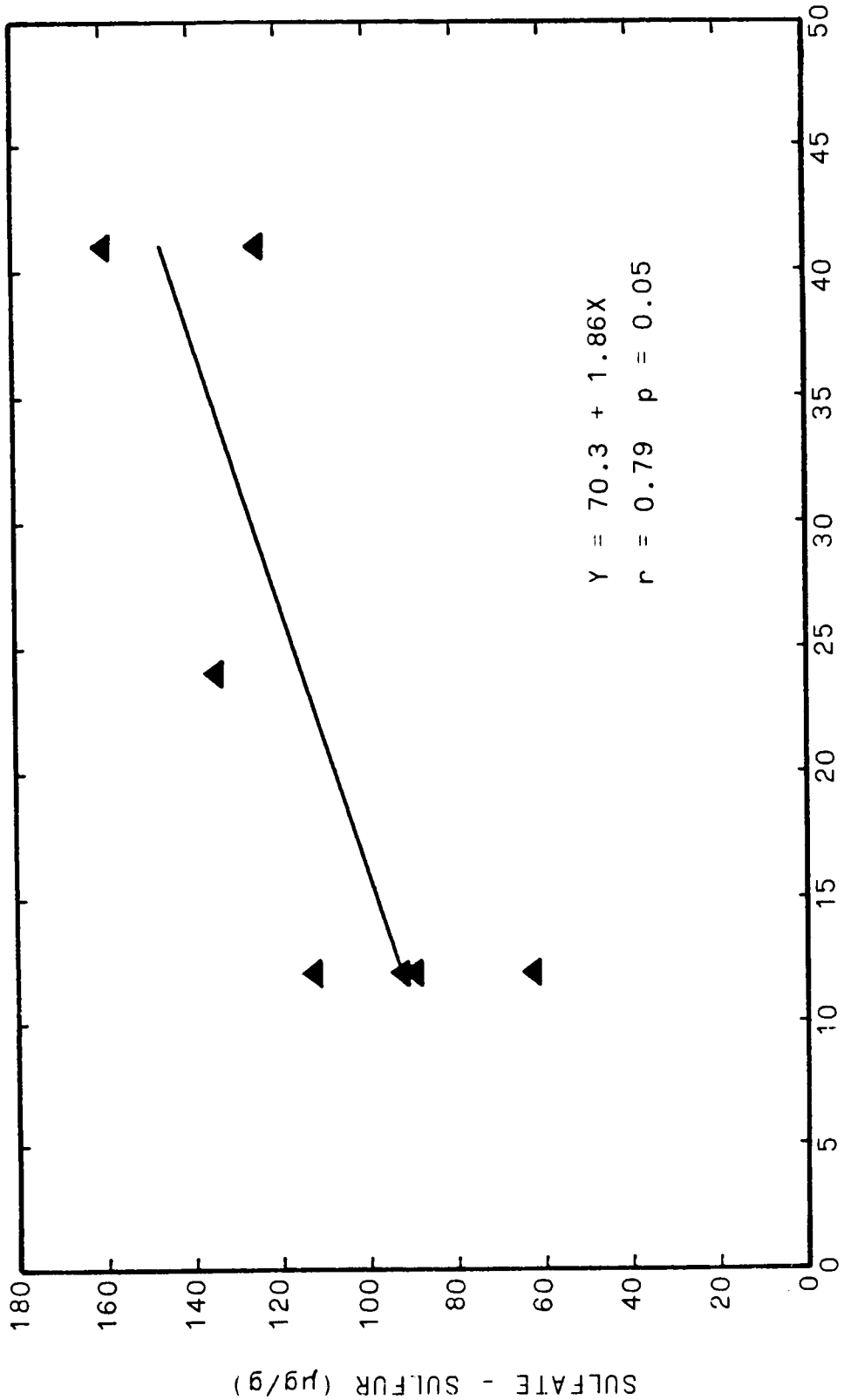

Figure A-6. Correlation between SO_4-S and clay in Pedon CBNS 3C.

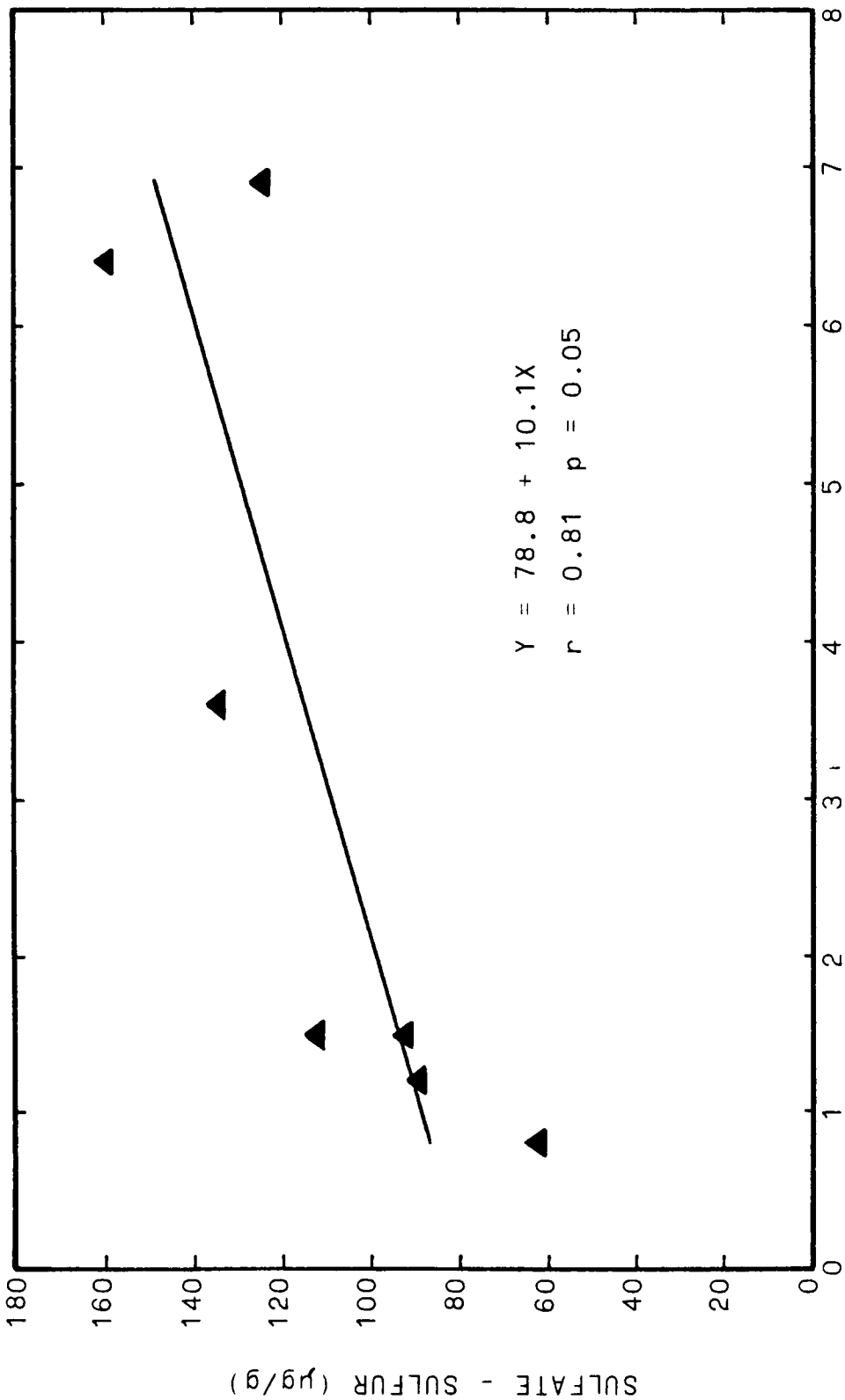

Figure A-7. Correlation between SO_4-S and Fe_2O_3 in Pedon CBNS 3C.

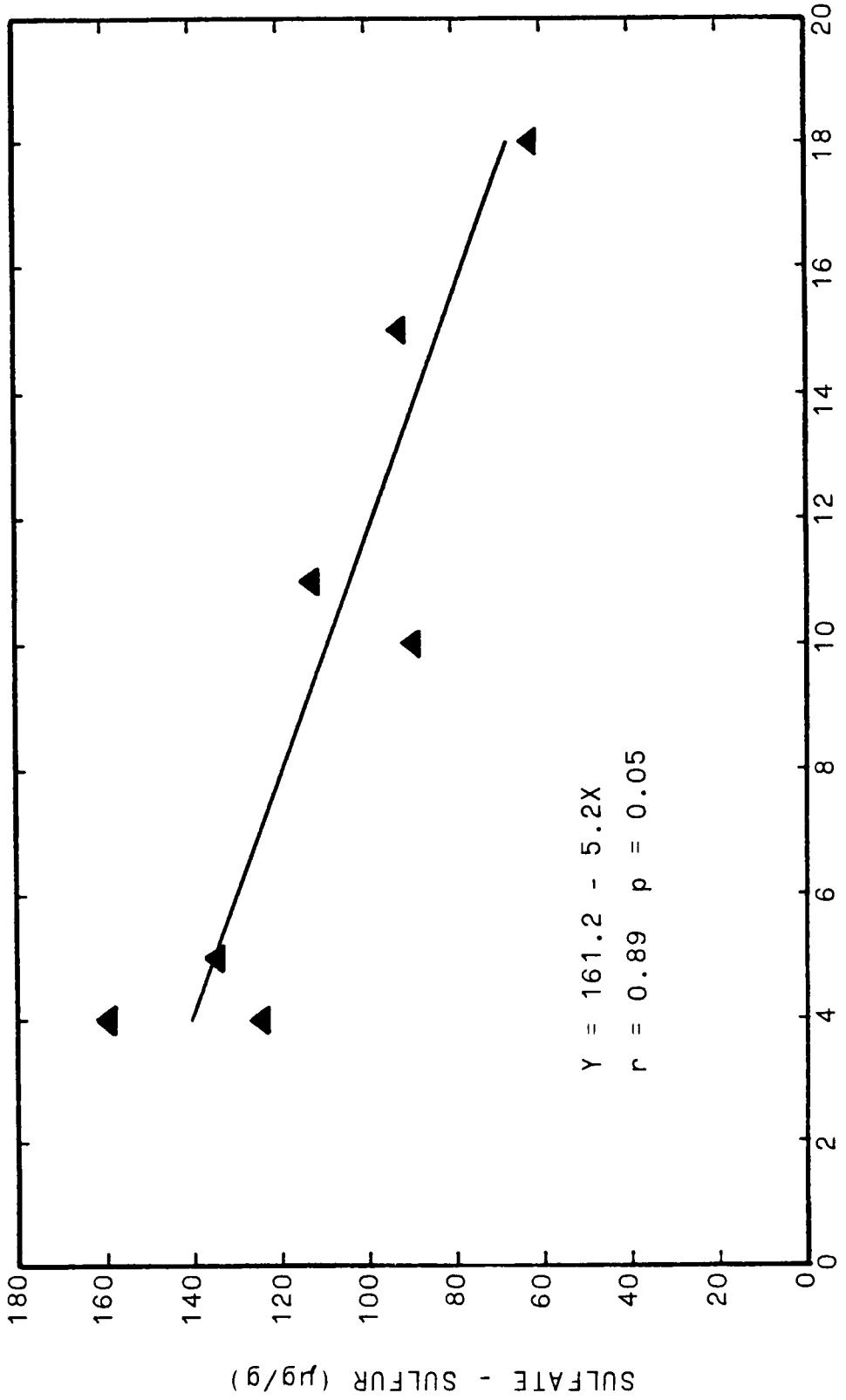

Figure A-8. Correlation between SO_4-S and BS in Pedon CBNS 3C.

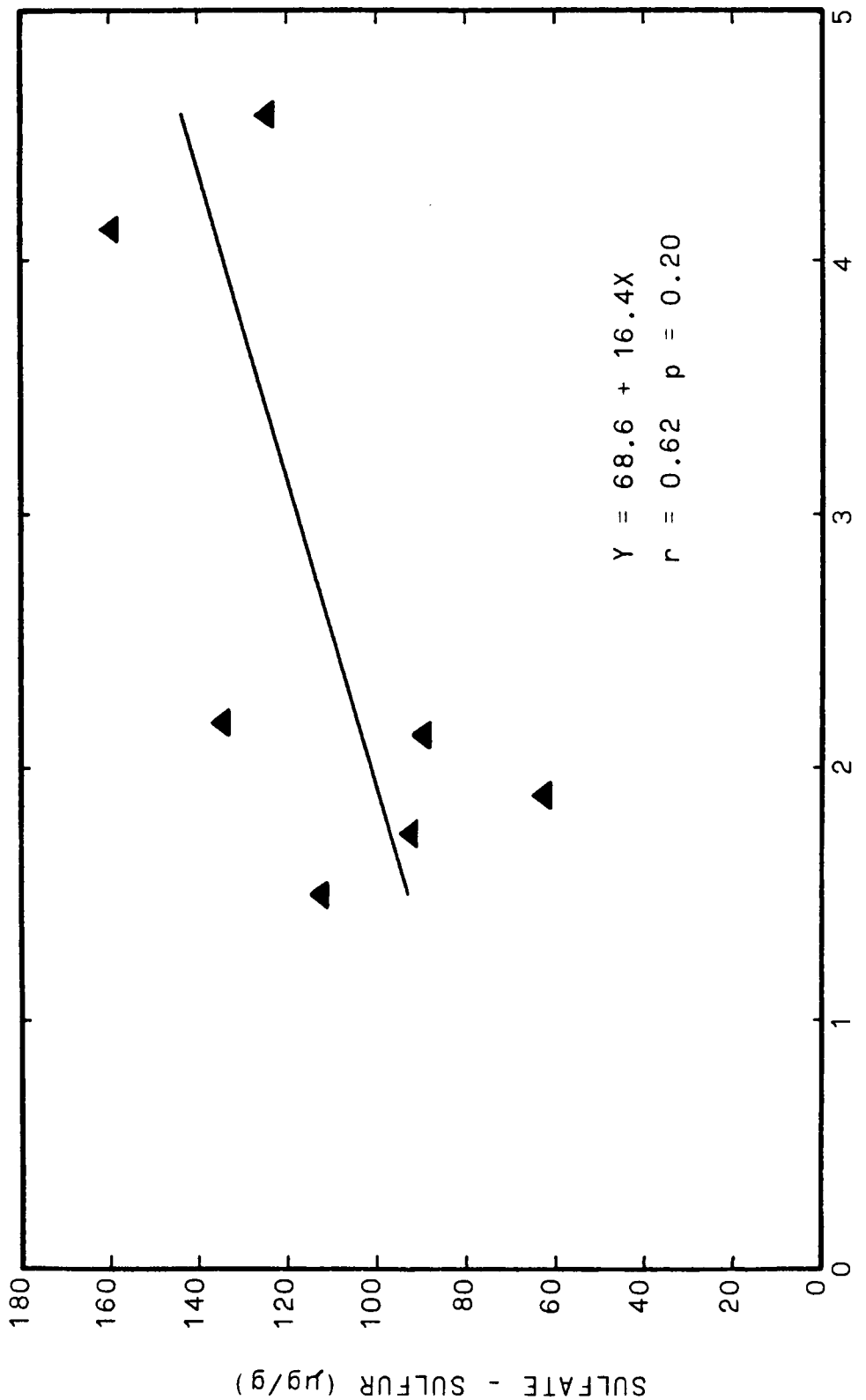

Figure A-9. Correlation between SO_4-S and KCl Exch. Al in Pedon CBNS 3C.

APPENDIX C

PEDON DESCRIPTIONS

PEDON CBCC 1A

DESCRIBED: July 7, 1980 by B.E. Nwadialo and R.D. Hammer.

LOCATION: About 7 kilometers southwest of Cherokee Mine in Grassy Creek region, Polk County, Tennessee.

PHYSIOGRAPHY: Ridgetop.

VEGETATION: Mixed hardwood.

SLOPE: 0 - 5%.

PARENT MATERIAL: Mica Schist and graywacke.

CLASSIFICATION: Typic Hapludult, clayey, oxidic, mesic.

DESCRIPTION:

A	0 to 3 cm, Very dark grayish brown (10YR 3/2) clay loam; moderate fine granular structure; dry; soft; abundant very fine and fine roots and few medium roots; non-sticky and non-plastic; extremely acid; clear smooth boundary.
AB	3 to 13 cm, Strong brown (7.5YR 5/6) silt loam; weak medium subangular blocky parting to weak medium granular structure; dry, slightly hard; few medium roots and many very fine and fine roots; non-sticky and non-plastic; very strongly acid; abrupt smooth boundary.
BAt	13 to 29 cm, Yellowish red (5YR 5/6) silty clay loam; weak medium subangular blocky structure; dry; hard; few very fine and fine roots, sticky and slightly plastic; very strongly acid; gradual wavy boundary.
Bt1	29 to 50 cm, Red (2.5YR 4/6) clay; moderate medium subangular blocky structure; dry, hard; very few fine roots, sticky and plastic, very strongly acid; diffuse wavy boundary.
2Bt2	50 to 73 cm, Red (2.5YR 4/6) clay; moderate medium to coarse subangular blocky structure; dry; very hard; few fine and very fine roots; sticky and plastic; moderately acid; gradual wavy boundary.

2Bt3	73 to 85 cm, Red (2.5YR 4/6) clay; weak medium subangular blocky structure; dry; very hard; few dark yellowish brown (10YR 4/4) clay skins on ped faces; sticky and plastic; moderately acid; abrupt smooth boundary.
2BCt	85 to 115 cm, Red (2.5YR 4/6) clay; weak, coarse subangular blocky structure; slightly hard; very few roots; many dark yellowish brown (10YR 4/4) clay skins on ped faces; slightly sticky and slightly plastic; moderately acid; diffuse irregular boundary.
2C	115 to 125 cm, Dark red (2.5YR 3/6) clay loam; massive; slightly hard; non-sticky and non-plastic; moderately acid; diffuse irregular boundary.
2Cr	125 to 155 cm, Dark red (2.5YR 3/6) weathered saprolite, massive; many mica flakes and phyllite slabs.

Notes:

The upper 29 cm contains fresh, hard phyllite coarse fragments. Below this depth, all fragments are soft and very highly weathered to the Cr horizon.

PEDON CBCC 1C

DESCRIBED: July 8, 1980 by B.E. Nwadialo and R.D. Hammer.

LOCATION: About 7 kilometers southwest of Cherokee Mine in Grassy Creek region, Polk County, Tennessee.

PHYSIOGRAPHY: Toe slope.

VEGETATION: Mixed hardwood.

SLOPE: 5 - 10%.

PARENT MATERIAL: Mica schist and graywacke.

CLASSIFICATION: Typic Hapludult, clayey, oxidic, mesic.

DESCRIPTION:

A11 — 0 to 5 cm, Dark brown (7.5YR 3/2) silt loam; weak fine granular structure; dry, soft; abundant fine and very fine roots; non-sticky and non-plastic, very strongly acid; clear wavy boundary.

A12 — 5 to 9 cm, Brown (7.5YR 4/4) silt loam; weak fine granular structure; dry, soft; abundant very fine and fine roots, few medium roots; non-sticky and non-plastic, very strongly acid; clear wavy boundary.

BA — 9 to 18 cm, Yellowish red (5YR 4/6) silt loam; weak medium subangular blocky structure parting to coarse granular structure; dry, slightly hard; few very fine and fine roots and many medium roots, slightly sticky and non-plastic; strongly acid; abrupt smooth boundary.

2BAt — 18 to 39 cm, Yellowish red (5YR 4/6) silty clay loam; weak medium subangular blocky structure; dry, slightly hard; few fine and medium roots; slightly sticky and slightly plastic; strongly acid, abrupt smooth boundary.

2Btb1 — 39 to 54 cm, Yellowish red (5YR 5/6) silty clay loam; weak medium subangular blocky structure; dry, hard; slightly sticky and slightly plastic; very strongly acid; clean wavy boundary.

2Btb2 — 54 to 71 cm, Yellowish red (5YR 5/6) silty clay loam; moderate medium subangular blocky structure; dry, slightly hard; slightly sticky and slightly plastic; strongly acid; clear wavy boundary.

2BCtb — 71 to 82 cm, Strong brown (7.5YR 5/6) silty clay loam; moderate medium subangular blocky structure; dry, slightly hard; slightly sticky and slightly plastic; strongly acid; clear wavy boundary.

2Cb1 — 82 to 91 cm, Strong brown (7.5YR 5/6) clay loam; weak medium subangular blocky structure; dry, soft; non-sticky and non-plastic; strongly acid; clear smooth boundary.

2Cb2 — 91 to 111 cm, Strong brown (7.5YR 5/6) gravelly clay loam; massive; dry, slightly hard; non-sticky and non-plastic; strongly acid; clear wavy boundary.

3Ab — 111 to 115 cm, Yellowish red (5YR 5/6) clay loam; moderate fine granular structure; dry, soft; slightly sticky and non-plastic; very strongly acid; clear wavy boundary.

3B'tb1 — 115 to 141 cm, Red (2.5YR 5/8) clay; weak medium subangular blocky structure; dry, slightly hard; sticky and plastic; common fine prominent dark yellowish brown (10YR 4/4) clay skins on ped faces; strongly acid; abrupt smooth boundary.

3B'tb2 — 141 to 155 cm, Red (2.5YR 4/6) clay; weak medium subangular blocky structure; dry, slightly hard; sticky and plastic; common fine prominent dark yellowish brown (10YR 4/4) clay skin on ped faces; moderately acid; clear wavy boundary.

3Bwb1 — 155 to 171 cm, Red (2.5YR 4/6) silty clay loam; weak medium subangular blocky structure; dry, soft; slightly sticky and slightly plastic; strongly acid; clear wavy boundary.

3Bwb2 — 171 to 181 cm, Yellowish red (5YR 5/6) loam; weak medium subangular blocky structure; dry, soft; non-sticky and non-plastic; strongly acid; clear wavy boundary.

3Cb — 181 to 199 cm, Reddish yellow (7.5YR 6/8) loam; massive; dry, sfot; non-sticky and non-plastic; strongly acid; abrupt smooth boundary.

3Cr 199 to 205 cm, Reddish yellow (7.5YR 6/8) saprolite from graywacke that crushes to loam; massive; strongly acid.

Notes:

3Ab is an intermittent horizon. There is a stone line at 95 to 105 cm, made up of unsorted gravels. Below this depth the gravels are somewhat sorted. There appears to be at least 3 depositional sequences in this soil. The lowest sequum (111 cm and below) is mostly formed in residuum and contains sorted gravel; the middle sequum (39 to 111 cm) contains unsorted gravel and was probably formed from rapid mudflow and emplacement; the upper sequum (0 to 39 cm) comprises recent additions from European settlement and deforestation and may include sediments from the upland soils.

PEDON CBOS 2A

DESCRIBED: July 9, 1980 by B.E. Nwadialo and R.D. Hammer.

LOCATION: North of old smelter. High ridge top east of London mine and northeast of Isabella mine, Copper basin, Polk County, Tennessee.

PHYSIOGRAPHY: Ridge top.

VEGETATION: Short leaf pine and grasses.

SLOPE: 0 - 5%.

PARENT MATERIAL: Mica schist, graywacke and phyllite.

CLASSIFICATION: Typic Hapludult, clayey, oxidic, mesic.

DESCRIPTION:

A — 0 to 7 cm, Brown (10YR 4/3) silt loam; moderate fine to medium granular structure; few medium and common very fine and fine roots; dry, soft; non-sticky and non-plastic; very strongly acid; clear wavy boundary.

BAt — 7 to 14 cm, Yellowish red (5YR 4/6) clay loam; moderate coarse granular structure; dry, slightly hard; few very fine and fine roots; slightly sticky and non-plastic; very strongly acid; clear wavy boundary.

Bt1 — 14 to 22 cm, Yellowish red (5YR 4/6) clay loam; weak coarse subangular blocky structure; dry, hard; very few fine and very fine roots; slighlty stick and slightly plastic; very strongly acid; clear wavy boundary.

Bt2 — 22 to 48 cm, Red (2.5YR 4/6) clay; moderate coarse subangular blocky structure; dry, hard; very few fine roots; sticky and plastic; very strongly acid; gradual wavy boundary.

Bt3 — 48 to 68 cm, Red (2.5YR 4/6) clay; moderate coarse subangular blocky structure; dry, hard; few fine and very fine roots; few dark yellowish brown (10YR 4/6) clay skins on ped faces; sticky and plastic; very strongly acid; clear wavy boundary.

BCt — 68 to 96 cm, Red (2.5YR 4/6) silty clay loam; massive; dry, hard; slightly sticky and slightly plastic; many dark yellowish brown (10YR 4/6) clay skins on ped faces; very strongly acid; clear irregular boundary.

C — 96 to 122 cm, Dark red (2.5YR 3/6) loamy sand; massive; dry, soft; non-sticky and non-plastic; few dark yellowish brown (10YR 4/4) clay skins on ped faces (upper C); many black nodules (mangans); strongly acid; abrupt irregular boundary.

Cr — > 122 cm, Dark brown (7.5YR 4/4) weathered saprolite with many mica flakes and manganese veins. Strongly acid.

PEDON CBOS 2B

DESCRIBED: July 9, 1980 by B.E. Nwadialo and R.D. Hammer.

LOCATION: North of old smelter. Side slopes about 100 meters west of road (See Figure 1).

PHYSIOGRAPHY: Mid portion of side slope.

VEGETATION: Virginia pine and grasses.

SLOPE: 10 - 15%.

PARENT MATERIAL: Mica schist and colluvium.

CLASSIFICATION: Typic Hapludult, fine loamy, oxidic, mesic.

DESCRIPTION:

A — 0 to 4 cm, Very dark grayish brown (10YR 3/2) loam; strong fine granular structure; dry, very friable; very few coarse, few medium, many very fine and common fine roots; non-sticky and non-plastic; extremely acid; abrupt wavy boundary.

Ap — 4 to 12 cm, Dark yellowish brown (10YR 4/4) sandy clay loam; massive; dry, soft; many very fine and fine roots; non-sticky and non-plastic; extremely acid; abrupt wavy boundary.

Bt1 — 12 to 23 cm, Strong brown (7.5YR 5/6) sandy clay loam; weak medium subangular blocky structure; dry, slightly hard; few very fine and fine roots; slightly sticky and non-plastic; extremely acid; clear wavy boundary.

Bt2 — 23 to 49 cm, Yellowish red (5YR 5/6) clay loam; weak coarse subangular blocky structure; very few fine and very fine roots; dry, slightly hard; slightly sticky and slightly plastic; very strongly acid; gradual wavy boundary.

Bt3 — 49 to 66 cm, Strong brown (7.5YR 5/6) gravelly sandy clay; moderate coarse subangular blocky structure; dry, slightly hard; very few roots; slightly sticky and slightly plastic; very strongly acid; clear wavy boundary.

2Btb1	66 to 92 cm, Red (2.5YR 5/8) clay; weak medium subangular blocky structure; dry, slightly hard; sticky and plastic; very strongly acid; clear wavy boundary.
2Btb2	92 to 125 cm, Red (2.5YR 4/8) clay; moderate medium subangular blocky structure; dry, slightly hard; sticky and plastic; very strongly acid; gradual irregular boundary.
2BCb	125 to 150 cm, Red (2.5YR 4/8) sandy clay loam; weak coarse subangular blocky structure; dry, slightly hard; slightly sticky and slightly plastic; very strongly acid; gradual wavy boundary.
2Cb1	150 to 170 cm, Red (2.5YR 4/8) sandy loam; massive; dry, soft; non-sticky and non-plastic; strongly acid; clear wavy boundary.
2Cb2	170 to 196 cm, Strong (7.5YR 4/8) sandy loam; massive; dry, soft; non-sticky and non-plastic; many manganese nodules; strongly acid; clear wavy boundary.
2Cr	196 to 230 cm, Strong brown (7.5YR 4/8) with red (2.5YR 5/8) and reddish yellow (7.5YR 6/8) saprolite crushing to loamy sand; abundant manganese nodules.

Notes:

There is a gravel and cobble concentration at 66 cm which indicates the upper lag gravel of a past erosion surface and the underlying buried soil. The same coarse fragment concentration is also expressed on eroded ridges and side slopes over much of the Copper Basin.

PEDON CBOS 2C

DESCRIBED: August 4, 1980 by B.E. Nwadialo and R.D. Hammer.

LOCATION: Toe slope near CBOS 2B on the east side of road (See Figure 1).

PHYSIOGRAPHY: Toe slope.

VEGETATION: Grass.

SLOPE: 0 - 5%.

PARENT MATERIAL: Mica schist.

CLASSIFICATION: Typic Hapludult, fine loamy, mixed, mesic.

DESCRIPTION:

A11	0 to 5 cm, Very dark grayish brown (10YR 3/2) loam; weak fine granular structure; moist, friable; many very fine and fine roots; non-sticky and non-plastic; extremely acid; abrupt wavy boundary.
A12	5 to 16 cm, Brown (7.5YR 4/4) sandy loam; massive; abundant very fine and fine roots; moist, firm; non-sticky and non-plastic; extremely acid; clear wavy boundary.
Bw	16 to 35 cm, Yellowish brown (10YR 5/6) loam; massive; few fine and very fine roots; moist, firm; non-sticky and non-plastic; extremely acid; abrupt irregular boundary.
2Btb1	35 to 51 cm, Strong brown (7.5YR 5/6) clay loam; moderate fine to medium subangular blocky structure; moist, firm; slightly sticky and slightly plastic; extremely acid; clear wavy boundary.
2Btb2	51 to 73 cm, Strong brown (7.5YR 5/8) loam; moderate medium subangular blocky structure; few distinct yellowish brown (10YR 4/4) clay skins on ped faces; moist, firm; very strongly acid; gradual wavy boundary.
2Btb3	73 to 94 cm, Strong brown (7.5YR 5/8) clay; moderate coarse subangular blocky parting to medium subangular blocky structure; moist, firm; common distinct yellowish brown (10YR 4/4) clay skins on ped faces; sticky and plastic; very strongly acid; clear wavy boundary.

2Btb4	94 to 105 cm, Red (2.5YR 4/6) clay loam; weak medium subangular blocky structure; moist, firm; slightly sticky and slightly plastic; common distinct yellowish brown (10YR 4/4) clay skins on ped faces; very strongly acid; clear wavy boundary.
2Cb	105 to 129 cm, Brownish yellow (10YR 6/8) sandy clay; massive; moist, firm; very strongly acid; clear wavy boundary.
3BAb	129 to 141 cm, Light yellowish brown (10YR 6/4) sandy clay loam; massive parting to weak coarse subangular blocky structure; moist, firm; very strongly acid; clear wavy boundary.
3Bwb	141 to 157 cm, Light yellowish brown (10YR 6/4) sandy clay loam; moderate coarse subangular blocky structure; moist, firm; common faint brownish yellow (10YR 6/8) mottles; very strongly acid; clear wavy boundary.
3BCb	157 to 170 cm, light yellowish brown (10YR 6/4) sandy clay loam; moderate coarse subangular blocky structure; moist, firm; common distinct brownish yellow (10YR 6/8) mottles, very strongly acid; clear wavy boundary.
3Bwb1	170 to 195 cm, Light yellowish brown (10YR 6/4) sandy loam; weak medium subangular blocky structure; few medium faint brownish yellow (10YR 6/8) mottles; strongly acid; gradual wavy boundary.
3Bwb2	195 to 213 cm, Reddish yellow (10YR 6/8) sandy loam; weak medium subangular blocky structure; common coarse prominent dark reddish brown (2.5YR 3/4) mottles; strongly acid; clear wavy boundary.
3Bwb3	213 to 230 cm, Reddish yellow (10YR 6/8) sandy loam; weak medium subangular blocky structure; common coarse prominent dark reddish brown (2.5YR 3/4) mottles; strongly acid; abrupt smooth boundary.
3BC'b	230 to 248 cm, Yellowish red (5YR 5/8) with red (2.5YR 4/6) sandy loam; massive; very strongly acid; clear wavy boundary.
3C	248 to 260 cm, Brownish yellow (10YR 6/8) with red (2.5YR 4/6) sandy loam; massive; very strongly acid.

PEDON CBNS 3A

DESCRIBED: August 5, 1980 by B.E. Nwadialo and R.D. Hammer.

LOCATION: Closest to new smelter (See Figure 1).

PHYSIOGRAPHY: Foot slopes.

VEGETATION: Grass.

SLOPE: 10 - 15%.

PARENT MATERIAL: Alluvium over colluvium and mica schist.

CLASSIFICATION: Typic Hapludult, fine-loamy, oxidic, mesic.

DESCRIPTION:

A	0 to 6 cm, Dark brown (7.5YR 3/2) sandy clay loam; fine granular structure; dry, soft; many fine and very fine roots; non-sticky and non-plastic; extremely acid; clear wavy boundary.
Bw1	6 to 15 cm, Reddish brown (5YR 4/3) sandy clay loam; weak medium subangular blocky structure; many fine and very fine roots; dry, soft; non-sticky and non-plastic; very strongly acid; clear wavy boundary.
Bw2	15 to 34 cm, Reddish brown (5YR 4/3) loam; weak medium subangular blocky structure; many fine and few very fine roots; dry, slightly hard; non-sticky and non-plastic; strongly acid; abrupt smooth boundary.
2Ab	34 to 50 cm, Dark reddish brown (5YR 3/4) loam; weak fine granular structure; very many fine and very fine roots; dry, soft; non-sticky and non-plastic; very strongly acid; clear wavy boundary.
2Btb1	50 to 62 cm, Reddish brown (5YR 4/4) clay loam; weak medium subangular blocky structure; dry, slightly hard; non-sticky and non-plastic; very many fine and very fine roots; very strongly acid; clear wavy boundary.
2Btb2	62 to 69 cm, Yellowish red (5YR 4/6) clay loam; weak medium subangular blocky structure; dry, slightly hard; slightly sticky and slightly plastic; many fine and very fine roots; very strongly acid; abrupt wavy boundary.

2Btb3	69 to 96 cm, Yellowish red (5YR 4/6) clay loam; weak medium subangular blocky structure; dry, slightly hard; slightly sticky and slightly plastic; many fine and very fine roots; very strongly acid; irregular boundary.
2BCb	96 to 132 cm, Yellowish red (5YR 4/6) gravelly sandy clay loam; weak medium to coarse subangular blocky structure; dry, slightly hard; non-sticky and non-plastic; very few roots; strongly acid; clear wavy boundary.
3Bwb1	132 to 158 cm, Red (2.5YR 4/6) sandy clay loam; weak medium subangular blocky structure; dry, slightly hard; non-sticky and non-plastic; strongly acid; clear wavy boundary.
3Bwb2	158 to 170 cm, Red (2.5YR 4/6) sandy clay loam; weak medium subangular blocky structure; dry, slightly hard; non-sticky and non-plastic; strongly acid; clear wavy boundary.
3CBb	170 to 181 cm, Strong brown (7.5YR 5/8) sandy loam; massive; dry, slightly hard; non-sticky and non-plastic; strongly acid; abrupt smooth boundary.
3Cb1	181 to 199 cm, Red (2.5YR 4/6) sandy loam; massive; dry, hard; non-sticky and non-plastic; strongly acid; clear wavy boundary.
3Cb2	199 to 225 cm, Red (2.5YR 4/6) sandy loam; massive; dry, hard; non-sticky and non-plastic; strongly acid; clear wavy boundary.
3Cb3	225 to 240 cm, Yellowish red (5YR 4/6) sandy loam; massive; dry, hard; non-sticky and non-plastic; strongly acid; clear wavy boundary.
3Cr	>240 cm, Brown (7.5YR 4/4) saprolite that crushes to sandy loam; massive; strongly acid.

PEDON CBNS 3C

DESCRIBED: December 16, 1980 by B.E. Nwadialo and R.D. Hammer.

LOCATION: Closest to new smelter in the drainageway about 3 meters from stream bank (See Figure 1).

PHYSIOGRAPHY: Drainageway.

VEGETATION: Grasses and loblolly pine.

SLOPE: 0 - 2%.

PARENT MATERIAL: Colluvium over alluvium and bedrock.

CLASSIFICATION: Typic Udifluvent, coarse loamy, mixed, mesic.

DESCRIPTION:

Bt1 — 0 to 18 cm, Red (2.5YR 4/6) silty clay; weak to moderate medium subangular blocky structure; moist, firm; slightly sticky and slightly plastic; very many fine and very fine roots; extremely acid; clear wavy boundary.

Bt2 — 18 to 23 cm, Yellowish red (5YR 3/8) sandy clay loam; weak medium subangular blocky parting to weak fine granular structure; moist, firm; slightly stick and non-plastic; few fine faint light yellowish brown (10YR 6/4) mottles; many fine and very fine roots; extremely acid; clear wavy boundary.

Bt3 — 23 to 31 cm, Light yellowish brown (10YR 6/4) silty clay; weak medium subangular blocky parting to weak fine granular structure; moist, firm; slightly sticky and slightly plastic; many coarse distinct strong brown (7.5YR 5/8) mottles; extremely acid; abrupt smooth boundary.

2Ab — 31 to 38 cm, Dark gray (5YR 4/1) sandy loam; weak fine subangular blocky structure; moist, friable; non-sticky and non-plastic; few fine distinct red (2.5YR 4/8) mottles; very strongly acid; clear wavy boundary.

2Cb1 — 38 to 43 cm, Yellowish brown (10YR 5/6) sandy loam; massive; moist, friable; non-sticky and non-plastic; many medium prominent yellowish red (5YR 4/6) mottles; very strongly acid; abrupt smooth boundary.

2Cgb1	43 to 61 cm, Olive gray (5Y 5/2) sandy loam; massive; few medium prominent yellowish red (5YR 5/8) mottles along root channels; very strongly acid; clear irregular boundary.
2Cgb2	61 to 69 cm, Dark grayish brown (10YR 4/2) sandy loam; massive; few coarse prominent yellowish red (5YR 5/8) mottles; very strongly acid.

Notes:

Horizon 2Cgb2 is intermittent between rock fragments. The Bt3 horizon was originally A and Bt horizons of upland soil washed downslope. The Bt2 horizon was a mid argillic horizon washed downslope while the Bt1 horizon was mid to lower argillic horizon of upland soil washed downslope.

VITA

Bernard-Shaw E. Nwadialo was born in Lagos, Nigeria on August 16, 1946 but his parents originally came from Oguta. He completed his elementary school education at Sacred Heart School, Oguta and went on to complete his secondary school education at Holy Ghost College, Owerri where he received the West African School Certificate in 1964 and Higher School Certificate in 1966.

His education was interrupted by the Nigerian civil war between 1967 and 1970. He entered the University of Nigeria, Nsukka in October 1970 and received the Bachelor of Science degree in Plant and Soil Science in June 1973. After graduation he compulsorily registered for the National Youth Service Corps for one year, worked briefly with the Ministry of Education and accepted a fellowship from the University of Nigeria, Nsukka.

He entered the graduate school of the University of Wisconsin, Madison, in August 1976 and received the Master of Science degree in Soil Science in May 1978. He went on to the University of Tennessee where he received the Doctor of Philosophy degree in Plant and Soil Science in June 1982.

The author is a member of the Soil Science Society of America, American Society of Agronomy, Klobb 41, and Phi Kappa Phi.

He is married to the former Prisca Oputa of Oguta.