THE PHYSICAL, CHEMICAL, AND MINERAL0G1CAL PROPERTIES OF LATERITE SAMPLES FORMED IN VARIOUS ENVIRONMENTS

by

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A thesis submitted to the Graduate Faculty of
North Carolina State University at Raleigh
in partial fulfillment of the
requirements for the Degree of
Doctor of Philosophy

DEPARTMENT OF SOIL SCIENCE

RALEIGH

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ABSTRACT

IBANGA, INIOBONG JIMMY. The Physical, Chemical, and Mineralogical Properties of Laterite Samples Formed in Various Environments. (Under the direction of STANLEY W. BUOL).

Samples of laterite were obtained from Australia, Bolivia, Brazil, Nigeria, Thailand, and the U. S. A. The laterite materials were found to have a *yery* wide range of chemical and morphological characteristics. A prominent feature of all samples is a high content of iron and/or aluminum, relative to other constituents. The amount of free iron varies from 4.7 to 44.6% on an oxide basis. Iron is present in the form of goethite, hematite, lepidocrocite, as poorly crystalline oxide compounds, and as unidentified coatings on other minerals. The other minerals identified in the laterite samples were kaolin minerals, which are common in all samples, quartz, feldspars, and micas. Quartz is an inert component and is believed to be derived from the underlying acidic rocks.

The structure of laterite as observed in thin sections and with the scanning electron microscope is complex and displays an even greater variety than the chemical composition. One structural extreme is the type composed largely of pisolitic bodies more or less closely packed in a matrix. The other extreme of structure is the vesicular type in which the cavities are either empty, filled or partly filled with clay minerals.

In addition, data obtained indicate a strong relationship between color and iron mineralogy. The reddish colored samples have a high content of hematite while the yellowish samples have a high goethite content. Also, samples with a low active iron ratio tend to have a reddish color

while those with a high active iron ratio *are* yellowish in color. Another relationship detected shows that samples that have a high content of kaolinite (- 60%) are dominated by hematite while those with < 30% kaolinite are dominated by goethite.

On an inter-regional scale, there is an apparent lack of relationship between laterite formation and lithology. But on a smaller scale the lithological control of the composition and form is more evident.

BIOGRAPHY

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ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation for the immense and valuable assistance provided by the following:

Dr. S. W. Buol, major professor, under whose guidance this study was undertaken.

Dr. S. B. Weed, Dr. H. J. Kleiss and Dr. V. V. Cavaroc, Jr., for serving on the author's advisory committee, and for their advice and assistance.

Mrs. Betty W. Ayers and Mrs. Jan D. Green for their assistance in various stages of laboratory analyses.

Dr. R. F. Isbell (Australia), Dr. Apisit Eiumnoh (Thailand), Mr. W. A. Hope (Nigeria) and Mr. K. E. Jaiyeola (Nigeria) for collecting and mailing the samples from their respective countries.

The Director, Institute for Agricultural Research, and the Registrar, Ahmadu Bello University, Zaria, Nigeria, for granting me leave of absence to undertake this academic program.

A special "thanks" goes to Mrs. Joan Buol for her hospitality to me. This has contributed greatly towards my successful stay in Raleigh.

And finally, my wife, Mkpangutong, and daughter, Unwana Maggie, who have always borne the brunt of my nocturnal and weekend absences from home. I dedicate this work to them.

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1. INTRODUCTION

What is laterite? This question has plagued geologists, geomorphologists and pedologists for a very long time. Various attempts have been made to define it on the basis of color, hardness, ability to harden, iron content, iron and aluminum content, aluminum content and many other ratios. In the present study, laterite will be recognized as iron-rich soil horizons composed of (1) soft mottled clays that change irreversibly to hardpans and crusts when dried; (2) cellular and mottled hardpans and crusts; (3) consolidated concretions; and (4) concretions and concretion-rich horizons which may still be unconsolidated.

Laterites are known to form in various environments or climatic regions, and so their morphology differs from place to place. Because laterite is a soil horizon, parent material and/or the other soil forming factors must play a significant role in their genesis. Uncertainty exists as to the role of each of the factors of soil formation, especially on an inter-regional scale.

Several processes and theories have been advanced to explain the exact nature of laterization. It is accepted, however, that laterization is a weathering process which takes place in the humid tropics and subtropics and which is characterized by the removal of bases and silica from, and the accumulation of the hydroxides and sesquioxides of aluminum and iron in, the soil solum. It has also been pointed out that the process of primary laterization may be followed by one of resilication; that the upward capillary movement of iron in the soil profile,

and subsoil exposure due to erosion, may be factors influencing laterization.

In order to gain further information relative to the laterization process, physical, chemical, and mineralogical studies were made of sixteen laterite samples collected from the five continents of Africa, Asia, Australia, North America and South America. The chemical analysis will provide information on the amount of leaching the reconcentration of materials that had occurred before the samples were formed. Mineralogical studies will indicate the nature and type of clay minerals and clay-sized materials present in the sample, which is another indication of "soil" maturity in the laterization process.

The objectives of the present study were:

(1) To characterize the samples

(2) To evaluate the relationship between the physical, chemical and mineralogical properties of the samples

(3) To determine the degree of similarity and/or differences between the samples based on their physical, chemical and mineralogical components

(4) To determine if a relationship exists between these lateritic properties and the dominant lithology of the locations where the samples were collected.

2. LITERATURE REVIEW

Literature concerning laterite is heavily encumbered by problems of terminology. Various names have been used for iron-containing materials occurring in tropical and subtropical soils. Concretions (Ho, 1960), iron concretions (Fiskell and Perkins, 1970; Frei, 1964; Hamilton, 1954), ferruginous concretions (Sherman and Kanehiro, 1954), lateritic concretions (Ho, 1957), iron-oxide mineral nodules (Sherman, Ikawa and Matsusaka, 1969), glaebules (Brewer and Sleeman, 1964; Gallaher et al., 1974), plinthite bodies, ironstone nodules, hardened sesquioxide nodules (Daniels et al., 1978) are some names used to refer to these formations.

2.1 What is Laterite

The word laterite was originally suggested by Buchanan in 1807 as a name for a highly ferruginous deposit first observed in Malabar, India. Because of the indefinite and often inexact uses of the term, it is worthwhile to turn back to Buchanan's original description.

> "Laterite. What I have called indurated clay is one of the most valuable materials for building. It is diffused in immense masses, without any appearance of stratification . . . It is full of cavities and pores, and contains a very large quantity of iron in the form of red and yellow ochres. In the mass, while extruded from the air, it is so soft that any iron instrument readily cuts it, . . . It very soon after becomes as hard as brick, and resists the air and water much better than any bricks that I have seen in India . . . As it is usually cut into the form of bricks for building, in several of the native dialets it is called brickstone, . . . The most proper English name would be laterite." (McFarlane, 1976).

The word is derived from the Latin - later, a brick, which applies to the use of laterite as a building material and not to its red color (Prescott and Pendleton, 1952).

Following Buchanan, the term was used largely by geologists. They regarded laterite as a rock type, and Newbold described it as a "purplish or brick-red porous rock" (McFarlane, 1976). Even after pedologists became interested in laterite, descriptions of it as a rock still persisted. Du Preez (1949) wrote that perhaps the fact that it is usually shattered when struck a sharp blow with a hammer is partially responsible for the persistence of this concept. Apart from the obvious property of hardness, the concept of it as a rock stemmed largely from the division of the weathering profile into two distinct horizons. In the upper parts processes due directly or indirectly to life, referred to as "soil-forming," predominated. This was regarded as the domain of the pedologists. The lower parts of the profile, characterized by inorganic processes of weathering, were the domain of the geologists. The occurrence of laterite at the surface was believed to be due to the removal of the soil. It was believed to form at depth and so properly belonged to the zone of inorganic alteration or weathering.

Attempts to define laterite by its hardness or ability to harden later became somewhat confusing. After the initial description of laterite, Buchanan subsequently found material in Malabar which was hard while still in the ground and not exposed to the air. He was apparently puzzles by this but recognized its relationship to his original laterite,

so he called it brickstone. Later the two words were used interchangeably since it was not possible for him to decide whether or not the indurated material found on the surface was formerly soft. The property of absolute hardness rather than the ability to harden rapidly gained popularity as a descriptive term. Pendleton and Sharasuvana (1946) defined laterite as "an illuvial horizon . . . with slag-like cellular or pisolithic structure, and of such a degree of hardness that it may be quarried out and used for building construction." Many authors compromised by including both the ability to harden and the property of hardness as definitive characteristics of laterite (Kellogg, 1949). And so, this leads to the use of the term laterite to describe a variety of hard and potentially hard materials.

The range of material described by the name laterite was further extended by efforts to use color as a definitive characteristic. Buchanan noted that laterite contains a very large quantity of iron in the form of red or yellow ochres. Newbold later described it as a "purplish or brick-red porous rock." Here the seeds were sown for the belief that laterite was so named because it was red, as are bricks. Walter is cited as the instigator of the assumption that Buchanan named it laterite because of its red color (Prescott and Pendleton, 1952). Walter then suggested that the word should be used for all red-colored alluvia. The subsequent adoption of the term by pedologists and introduction to cover several sorts of zonal and azonal soils furthered this indiscriminate use of the term. The result was that it became customary for travellers in the tropics to refer to anything red as laterite, and the term was rendered almost completely meaningless.

In an attempt to clear the confusion surrounding the terms laterite, ironstone and brickstone, the United States Soil Conservation Service has coined plinthite from a Greek word, plinthos, meaning brick as against the latin counterpart (Soil Survey Staff, 1975). Plinthite is used to refer to the soft iron-rich, humus-poor mixture of clay with quartz and other diluents. It changes irreversibly to ironstone hardpan on exposure to repeated wetting and drying. If a large amount of plinthite is present, it may form a continuous phase. However, if this continuous layer ever becomes indurated, it is not called plinthite but rather, a massive ironstone layer.

Sys (1968) introduced the term petroplinthite. Unlike plinthite, petroplinthite is hard--it does not break under pressure between the fingers and is not scratched readily with the fingernail. The petroplinthite only forms when an outer crust of about 0.2 to 2 mm develops. The crust may enclose one or more hardened cores with or without the enveloping soft material. The resulting petroplinthite is irregular in shape.

The term laterite as used here will refer to a highly weathered material: (1) Rich in secondary forms of iron, aluminum or both; (2) poor in humus; (3) depleted of bases and combined silica; (4) with or without non-diagnostic substances such as quartz, limited amounts of weatherable primary minerals or silicate clays; and (5) irreversibly hard. It excludes the soft material rich in iron, and subject to hardening upon exposure to alternate wetting and drying defined as plinthite (Soil Conservation Service, 1975).

2.2 Theories of Laterite Genesis

There is considerable lack of agreement concerning the genesis of laterite. Two very early models of laterite formation proposed marine and volcanic origins. These enjoyed little popularity and were readily dismissed by Oldham in 1893 (McFarlane, 1976). A third model involving termite activity received only limited support. Erhardt (McFarlane, 1976) suggested that one group of laterites might be "cuirasses termitiques," and that termites might be responsible for the general vacuolar structure of laterites. Earlier, Nazaroff (1931) had reported the occurrence of ferruginized termitaria in Angola. Goudie (1973) considered that termite channels may aerate the profile, encourage the development of vesicular laterites and promote the oxidizing of the ferrous compounds to form indurated ferricrete. It is possible that termites may contribute to laterite genesis by facilitating the reworking of a soil in which precipitates develop, thereby aiding their concentration at the base of the soil, but the belief that termites may actually be the cause of the laterite development is now largely discredited.

The early concept of laterite as a residuum attributed the accumulations to the relative immobility of the constituents. In 1932, the Imperial Bureau of Soil Science defined laterite as "a weathered rock product formed by the leaching of igneous and metamorphic rocks whereby the bases and much of the silica are removed leaving a residue containing alumina uncombined." Although laterites were believed to accumulate as a residuum, nevertheless, two phases of limited mobility of the constituents were implied. First, the materials to be concentrated were

released from their parent material by weathering processes and regrouped into relatively immobile precipitates; subsequently, a second mobile phase during the resolution or alteration of the residuum. This concept of laterite fitted well with the normal Davisian cycle of landscape development. During the reduction of a landsurface, slopes are reduced until they reach a critical value so that ingress is substantially greater than runoff, and laterite genesis begins (McFarlane, 1976). Laterite development was thus believed to be associated with a stage of landsurface development in which the relief is still being reduced.

From about 1906, the concept of laterite as a residuum was slowly losing ground to the precipitationary concept. This concept stressed the role of groundwaters in the formation of laterite. Maclaren (1906) stated that the laterite is not the result of deposition in situ of the rocks, but of the replacement of such decomposition products; the mechanism of the replacement being groundwaters. Iron and alumina in solution were believed to be moving into the enriched zones and there being precipitated.

Two mechanisms have been suggested for this enrichment of the laterite horizon--capillarity and the seasonal fluctuations of the water table. Laterite formation by capillary action was favored by Maclaren (1906), Wollnough (1927) and Holmes (1914). The evidence against the effectiveness of capillary action in laterite formation is overwhelming (Goudie, 1973; Sivarajasingham et al., 1962). Capillary movement as a major factor, has generally been discredited, but not

entirely abandoned as a mechanism by which some duricrusts are believed to accumulate (Loughnan et al., 1962).

The belief that upward movement of iron and aluminum was brought about by water table fluctuation was (and still is) more popular (Pendleton, 1941; Pendleton and Sharasuvana, 1946; Prescott and Pendleton, 1952; Alexander and Cady, 1962; Daniels et al., 1971). Essentially the theory is that enriched solutions are carried upwards in the profile with the seasonal rise of the water table and precipitated near the upper limits of the range of fluctuation. There is, however, a growing awareness that this method must be treated with reserve (Sivarajasingham et al., 1962; McFarlane, 1971; Goudie, 1973).

Detrital models of laterite formation have recently received some attention. Low-level laterites are regarded as absolute accumulations in that they have received a considerable contribution from topographically higher positions (where an older laterite may or may not occur). The contribution may be mechanical or in solution, or both (Maignien, 1966). Dispute arises, however, when this model is stretched to explain all laterite occurrences, especially the fossil "high-level" laterites. It has been explained that the low-level laterites can upon further erosion or lowering of the surrounding unlaterized areas be left standing above the adjacent country. In effect, the relief becomes inverted (McFarlane, 1976; Maignien, 1966; Goudie, 1973).

There is a compromise model between the original concept of laterite as a residuum and concepts of it as a precipitate. De Swardt (1964) favored this compromise for the development of the groundwater laterites

in Uganda. He suggested both an overhead source and underlying source. Trendall (1962), du Bois and Jeffrey (1955), and McFarlane (1971) have also compromised and regarded laterite as a residual precipitate. For example, the groundwater laterite accumulated as a mechanical residuum during the late stages of reduction of a down-wasting landsurface, while the original precipitates were formed as a result of the fluctuating groundwater table.

2.3 Laterite Structures

Laterite occurs in various morphological forms. The most commonly described is the "discrete concretion" variety, in which the bodies are often loosely described as nodules, pellets, concretions or shot. More specifically these bodies have been classified into pisoliths or ooliths, the former being over 2 mm diameter and the latter less than 2 mm as suggested by Twenhofel (du Preez, 1954). There is some confusion in the use of the terms pisolith and oolith (Johnson, 1959; Ollier, 1959; Pullan, 1967; Maignien, 1966). A "pisolithic laterite" is one composed of pisoliths, not necessarily cemented into a mass or pisolite, while a laterite composed of a cemented rock-like mass of pisoliths is a pisolite or "pisolithic laterite" (McFarlane, 1976).

The distinction of the terms oolith and pisolith based arbitrarily on size is sometimes ignored. For example, Hanlon (1945) says that the pisoliths vary from "microscopic dimensions to more than an inch in diameter." Further difficulties arise since many pisolithic laterites

contain both ooliths and pisoliths (Pullan, 1967). A further problem with these terms is the lack of agreement about whether or not a concentric laminar structure is diagnostic (Schieferdecker, 1959; Campbell, 1917; Pullan, 1967). Pullan (1967) suggested that the unbanded varieties be nodules and the banded variety be ooliths and pisoliths.

Pisoliths which form in the soil, the pedogenetic pisoliths, are often associated with manganese precipitates and are irregular in shape and size (Cornwall, 1958; Beater, 1940; Doyne and Watson, 1933). They enclose soil-like material and often have a dark outer layer of manganese. The truly pea-shaped pisoliths, groundwater precipitates which form in saprolite, are often very regular and well-rounded and enclose saprolite-like material.

The other main type of laterite structure is the continuous phase variety, in which the indurated elements form a continuous coherent skeleton. The terms used to describe the structures include vermicular (Hanlon, 1945; Stephens, 1961; Russell, 1962; etc.), vesicular (Brosh, 1970; Russell, 1962; Moss, 1965; Maud, 1965; Sivarajasingham et al., 1962, etc.), cellular (Brosh, 1970; de Preez, 1949; Falconer, 1911), vermiform (Johnson, 1960; Johnson and Williams, 1961; Hanlon, 1945; Goudie, 1973) and tubular (Fisher, 1958). The differences have never been clearly defined (Pullan, 1967). It is the shape of the cavities as opposed to the shape of the precipitates which is the main descriptive criterion. It seems that all of the terms describe the same structure, even though it is quite clear that the shape of such structures differs.

In general, truly vermiform or tube-like cavities seem to occur only in groundwater laterites. In Uganda (McFarlane, 1976) it was found that within the vermiform laterite profile the arrangement of the tubes varied with depth, being predominantly vertical in the upper parts and predominantly horizontal towards the base. Cellular laterites are usually pedogenetic and have a platy structure, often with horizontal tubes.

Somehow, it seems rather artificial to separate laterites into discrete concretions and continuous phase varieties, for these are merely the structural extremes which occur. Between them lies a whole range of structures in which both vermiform and pisolithic structures variously developed (Prescott and Pendleton, 1952).

2.4 Variations in the Nature of Laterite with Lithology

Laterite formation has often been related to what are described as "suitable rocks" (Woolnough, 1918; Hanlon, 1945) but different authors have conflicting opinions as to what constitutes suitability. Woolnough, for example, maintained that "there is very little tendency to laterite formation on anything but the basic rock types," (Woolnough, 1918). Simpson (1912) considered suitable rocks to be largely composed of metallic silicates, especially granite and common types of greenstones, as well as amphibolites, epidiorites, chlorite-schists and other similar rocks. Holmes (1941) noted that gneisses and basalts are particularly suitable, and Maud (1965) noted a preferential development on sandstones. Pallister (1954) observed a preference for metasediments.

Certain rocks were considered unsuitable for its formation. Holmes (1914) noted its absence on granite and metasediments. Maud (1965) also noted its absence and Pallister (1954) its poor development over granites. Only the suitability of basic volcanics appears to be uncontested, while the absolute unsuitability of quartzites has been denied (de Swardt, 1964; McFarlane, 1969).

It appears, therefore, that laterite formation is not restricted to certain rocks, but occurs over a great variety if not all rock types (McGee, 1880; de Preez, 1949; Mennel, 1909; Mulcahy, 1961; Scrivenor, 1933; Gozan and Vera, 1962; Campbell, 1917; Alley, 1970; Grubb, 1963; Mabbut, 1961). These anomalies are somehow, informative. It is likely that in one area laterite formation is favored by a particular lithology while in another its formation is apparently inhibited by the same lithology. This would suggest that other environmental factors are operative if not dominant in its development.

While on an inter-regional scale the variations of laterite with lithology suggest that environmental factors other than geology have had a more significant influence, on an intra-regional scale the lithological control is more evident. This is likely for within a limited area the other encironmental influences such as climate and vegetation might be expected to be less variable. Thus, Evans (1910) noted that the iron content of laterites could often be related to the parent material. Holmes (1914) noted that the ferruginous laterites common on the gneisses in Mozambique do not develop over granites.

Similar relationships have been noted by Fisher (1958), Warth and Warth (1903) and Alexander and Cady (1962).

Often the intra-regional variation of laterite with lithology is more apparent as differences in the appearance of the material. For example, Gozan and Vera (1962) noted form and color diffences in the laterites over different basalts and commented the content was remarkably similar despite this. Du Preez (1954) noted that concretionary laterite occurs on basement complex and metasediments, but that oolithic and pisolithic laterites are confined to the sediments. Goudie (1973) reported that in Nigeria, Uganda and Zambia laterites on crystalline basement rocks are nearly always concretionary and vesicular whereas those on limestone and dolomite are oolithic or pisolithic. Faniran (1971) noted that over shales the laterites are softer and more massive than over sandstone where they are more pisolithic.

The variations in the structures of the different rocks, and the way these respond to weathering, introduce micro-environmental controls in the form of differences in porosity and freedom of drainage. Thus, Pendleton and Sharasuvana (1946) noted that certain laterite structures (the concretionary structures) appear to form more readily in coarse grained and freely drained rocks than in finer grained rocks. Grubb (1963) further emphasized the role of permeability in determining the nature of the lateritic crust in Jahore. Therefore, such observations as those of Gozan and Vera (1962) that the laterite varies over different basalts, and Faniran's (1971) variations over shales and

sandstones, may be readily explainable in terms of the different micro-environments these produce rather than by other more direct geological controls such as the chemical content.

Similarly on a slightly larger scale, variations in lithology cause variations in topography, and so an apparent direct lithological influence on laterite formation might equally reflect the different topographies and their environmental variations. For example, Blondel (1954) recorded more iron-rich laterites on the higher parts of a certain terrain while less iron was in laterites on the lower parts. Since it is usual for the higher parts of a terrain to be occupied by more resistant rocks (McFarlane, 1976), such a pattern of variation might appear to relate directly to lithology. However, it is equally possible that the lithologically-induced topography is itself the major factor.

In summary, it appears that the reported relationship of laterite to lithology is neither so direct nor so consistent as has sometimes been suggested. Where an obvious relationship exists, for example, between the iron or alumina content of a laterite and that of the parent rocks, it appears to be largely a case of the lithology being such as to support the influence exerted by the environment. The obvious examples are the enormous deposits of bauxite where the environment was conducive to alumina concentration, in an area of alumina-rich parent material. More often the relationship between laterite and lithology is less clear and in many cases obscure. In general, a

stronger influence is exerted by the environment than the lithology, particularly on the iron and alumina content. This is clear on an inter-regional scale where variations may in fact reflect differences in the local environment rather than strictly geological influences.

2.5 Laterite and Topography

Laterite has long been associated with low relief, and occurs frequently on level or near level surfaces (Maclaren, 1906; Campbell, 1917; Pendleton and Sharasuvana, 1946; Mabbutt, 1961; Sombroek, 1971; Daniels et al., 1978). However, very few of the early workers believed that its formation was restricted to level surfaces. It was believed to be residual and the necessary conditions were visualized as merely a land-surface of sufficiently low relief to allow appreciable ingress of surface waters. Thus, the concept of laterite as a residuum fitted well with the normal Davisian cycle of landsurface development (Davis, 1920). During the reduction of the landsurface, slopes are reduced until they reach a critical level so that ingress is substantially greater than runoff, and laterite genesis begins. The laterite develops with the landsurface and the end-product is a planation surface blanketed by a thick sheet of residual material.

Contrary to the early concept of laterite developing with the landsurface, the later concept of laterite as a precipitate distinctly implies that laterite formation postdates the formation of the planation surface. In this theory it was only after the peculiar conditions

of a stable and fluctuating water table had been created by the formation of the planation surface that laterite genesis could begin. Thus, Woolnough (1918) noted that "laterization can occur only in areas where drainage is almost at a standstill. This usually involves the existence of a peneplain almost at sea level." Maclaren (1906) had also concluded that "only on a level surface can laterite form."

In the Coastal Plains of North Carolina, Daniels et al., (1978) found plinthite only the local swells or high parts of the landscape on the Coharie and Brandywine surfaces. It fades and disappears as the soils become somewhat poorly drained. The gentle swell and swale landscape in the middle coastal plain is in reality a miniature drainage system with the swells forming the drainage divide and the swales forming the valleys and internally drained basins. This is a good example of a low level laterite-geomorphic surface relationship.

Although laterite is commonly associated with low relief, it is by no means confined to it (Goudie, 1973). It occurs on mature (Fisher, 1958) and submature (Nye, 1954) landsurfaces and has recently been shown to occur on landsurfaces with considerable relief (Stephens, 1961; Johnson, 1954; 1959; Pallister, 1951; Bettenay, 1962; Bettenay et al., 1964). Up to 500 feet (152 m) of relief has been recorded on continuous sheets of laterite (Johnson and Williams, 1961; Trendall, 1962; de Swardt, 1964). The high relief of the high level laterite mesas must certainly be regarded with circumspection since they are extremely ancient features and much modified.

2.6 Laterite and Climate

The early accounts of laterite genesis implied that it could not form in extra-tropical environments, and certainly the belief that hot or warm environments favor its formation is widely popular (Fisher, 1958; Sanford, 1935; Sivarajasingham et al., 1962; du Bois and Jeffrey, 1955; Humbert, 1948; Nye, 1954; McNeil, 1964; etc.). There is less unanimity of opinion about the incidence of this heat. Pendleton (1941), for example, emphasized that continuity of high temperatures is favorable, while McNeil (1964) believed that high temperatures are only necessary "at least during part of the year." Van der Merwe and Heystek (1952) described current laterite formation where there are "high" summer temperatures and "mild" winter conditions. A minority believed that it may also form in temperate environments (Harrison and Reid, 1910; Scrivenor, 1910; Wolnough, 1927; Simpson, 1912; Prescott and Pendleton, 1952).

Studies of the conditions favorable for the development of laterite constituents, for example, the formation of alumina and kaolin and the development of low silica sesquioxide ratios, promised a contribution to the understanding of the temperature requirements for laterite formation. However, studies of the effects of temperature on the development of these components have yielded rather confusing results. Krauskopf (1956) showed that silica solubility is linearly related to temperature. This suggested that desilicification, widely believed to be synonymous with laterization, is aided by high temperatures. Jenny

(1929) had indicated this by showing that the SiO_2/Al_2O_3 ratio falls with increasing temperature. Robinson and Holmes (1924), using other methods, found no agreement between temperature increase and degree of laterization as expressed by this ratio. Crowther (1930) disputed the validity of Jenny's calculation and attempted to show that the relation was not negative but positive, that is, the ratio increases with temperature, the clays becoming more siliceous. Russell (1962), in turn, suggested that Crother's results were based on inadequate methods, and concluded that the effect of temperature on the formation of particular clays is uncertain.

It is, however, generally believed that the higher the temperature of percolating water the more effective it is in decomposing the rocks and lowering the silica content.

Rainfall conditions are generally accepted as being more critical to laterite formation than temperature conditions. Maclaren (1906) stated that a well-marked alternation of wetting and dessication is essential. Mennell (1909) agreed with this. Scrivenor (1909) repudiated this and stated that seasonal rainfall is not necessary and gave rainfall figures for Malacca where laterite was believed to be currently forming.

Water in some quantity is essential. As soon as this medium of transport is absent, there is no accumulation. It is also generally agreed that alternating wetting and drying conditions are needed for sesquioxide precipitation. Wet and dry seasons thus came to be considered favorable if not essential to laterite genesis (Martin and

Doyne, 1927; du Preez, 1954; Fisher, 1958; Humbert, 1948; Sabot, 1954). Many writers, although accepting that alternating seasons facilitate laterite formation, considered this to be nonessential (Fisher, 1958).

There are several ways of reconciling such a marked divergence of opinions. Climatic change may have occurred and current conditions are not necessarily those prevailing at the time of formation of the laterite. Goudie (1973) has emphasized the importance of plaeoclimates in the study of duricrust-forming conditions, and cited some Australian studies (Gentilli, 1961; Gill, 1961) indicating the considerable changes which have occurred since the Tertiary, the reputedly major crust formation period.

A more promising means of reconciling opposing views lies in recognizing the undue stress placed on atmospheric climate as opposed to what Maignien (1958) has described as "climat du sol." This distinction, discussed by Mohr and Van Baren (1954) is very important. Nye (1954) and Doyne and Watson (1933) describe laterite formation where there are "marked seasons," and added that the natural vegetation is forest. Clearly, to stress the atmospheric climate is deceptive, for the climate of the soil supporting a true forest cannot be markedly seasonal; and it is surely the soil climate which is more significant to laterite genesis.

Recently, a method devised by Kerner-Marilaum in 1927 to assess the climatic limits of laterite formation has aroused renewed interest (Goudie, 1973). This method considers (a) quantity of precipitation,

(b) seasonality, and (c) temperature, to be critical variables. Based on empirical evidence, it is proposed that laterite will form where L exceeds 50 in the formula:

$$L = R^{-1/4} \cdot (S_{-s}) \cdot t_m \cdot 100^{-1}$$

where L is the "laterite number"; R is the annual precipitation in mm; S is the wet season semiannual precipitation (mm); s is the dry season semiannual precipitation (mm); t_m is the minimum monthly mean temperature (degrees C). High L values, that is, favorable laterite formation conditions, would appear to be associated with a very high markedly seasonal rainfall and high temperatures. This method is reported (Goudie, 1973) to have met with some success in South Africa. Since it considers only atmospheric conditions and not those occurring at the locus of laterite formation, it is unlikely to be of very wide application (McFarlane, 1976). It may possibly be relevant to certain types of laterite formation, for example, the pedogenetic laterites.

2.7 Chemical and Mineralogical Constituents of Laterite

There has been various attempts to put laterite on a proper scientific basis and even to define it by its chemical content. Bauer in his work on the soils of the Seychelle Islands (Martin and Doyne, 1927) showed that, after the removal of the quartz grains, the laterite from granite contained 60 percent alumina, 9 percent Fe_2O_3, and 29 percent of combined water. The laterite from diorite contained 52 percent alumina, 21 percent iron oxide, and 27 percent water. He considered

quartz and iron to be non-essential constituents. The essential constituent was aluminum hydroxide. Papers by Warth and Warth (1903) and Holland (1903) showed that many of the laterite soils of India were of similar composition. Other papers by Scrivenor (1909), Harrison (1910), Crook (1909) and Maclaren (1906) showed that material previously described as laterite did not contain significant quantities of the oxides of aluminum.

Fermor (1911) proposed that the term "laterite" should be restricted to soils containing from 90 to 100 percent of lateritic constituents (these he defined as the oxides of Fe, Al, Ti and Mn more or less hydrated). Soils containing from 50 to 90 percent of lateritic constituents should be called siliceous laterites or lithomargic laterites; those containing from 25 to 50 percent be called lateritic soils or lateritic lithomarge, while those with less than 25 percent should receive no designation based on the presence of lateritic constituents.

Shantz and Marbut (loc. cit.) accepted the general classification of Fermor, and defined laterite as those soils containing 90 to 100 percent of lateritic constituents, while all soils containing 25 to 90 percent of lateritic constituents were described as "lateritic red loams." Thus, the definition of Fermor and Shantz and Marbut placed the terms "laterite" and "lateritic" on a definite chemical basis.

Other attempts were made to define laterite on the basis of iron content (Pendleton and Sharasuvana, 1946); alumina content (Martin and Doyne, 1927; Crook, 1909; Evans, 1910, etc.); both iron and alumina

content (Humbert, 1948; Farmor, 1911; Simmons, 1929; King, 1967, etc.); silica sesquioxide ratios - SiO_2/Al_2O_3, SiO_2/Fe_2O_3, $SiO_2/Al_2O_3 + Fe_2O_3$, etc. Martin and Doyne (1927) working in Sierra Leone reported soils with a silica/alumina ratio of less than 1.33 as laterites, while those with a ratio of more than 1.33 but less than 2.0 should be described as lateritic soils.

With a view to inter-regional comparison, these ratios have been found to be misleading. Crowther (1930) discussed the merits of ratios and concluded that they vary with circumstances, there being little to choose between them. Pendleton and Sharasuvana (1946) are of the opinion that all chemical definitions of laterite should be discarded as they are inadequate to explain the true nature of such soils. Their analytical results showed that, except in three cases, the iron content is much higher than the aluminum, Fe_2O_3 averaging from two to three times Al_2O_3.

Other than these attempts to define laterite chemically, laterites have been found to contain various forms of Fe oxides and other minerals. Sherman et al., (1969) found lateritic materials to contain hematite, maghematite, goethite and gibbsite. Gallaher et al., (1974) found iron glaebules to be highly amorphous; some were composed primarily of hematite, gibbsite, quartz and small amounts of kaolinite. Those glaebules with low Fe contents consisted of goethite, quartz, traces of gibbsite, and large amounts of kaolinite. Hallsworth and Ahmad (1958) also found hematite and goethite in ironstone.

Evans et al., (1978), studying the massive iron formations in some soils of Ontario, found that the contents of Fe_2O_3 and MnO_2 varied from 19.6 to 49.9 percent and 0.8 to 11.1 percent, respectively. They were unable to detect any crystalline oxides or hydroxides of Fe or Mn by X-ray diffraction. X-ray diffraction confirmed the presence of gibbsite, kaolinite and hematite in South African laterites (van der Merwe and Heystek, 1952).

Plinthite in the Southern Coastal Plains Province of Georgia (Wood and Perkins, 1976) showed greater iron segregation than non-plinthitic soil materials. Iron is present as hematite, goethite and amorphous hydrated oxides. Kaolinite in the clay fraction of plinthite is in a more disordered crystalline state than in the matrix soil. The silt fraction contains quartz, hematite, and goethite. Chemical and mineralogical properties of nodular materials (plinthite) in a Plinthaquult, North Trinidad (Ahmad and Jones, 1969) showed that the intensity of red coloration within the nodules was directly related to the amount of Fe present. All nodules were low in Mn; Ti was inversely related to Fe but Ca was evenly distributed throughout all nodules. No crystalline Fe minerals were found but lepidocrocite and goethite were present in the ochreous mottles. X-ray diffraction identified kaolinite, mica and quartz in the nodules.

Samples of laterite (petroplinthite) from India (Eswaran and Mohan, 1973) showed that the total SiO_2, Al_2O_3 and Fe_2O_3 content varied from 29 to 47 percent, 23 to 39 percent, and 2 to 33 percent, respectively.

Based on these figures, the kaolinite content was allocated as 58 to 97 percent, goethite as 2 to 35 percent, and quartz as 1 to 2 percent.

Manganese occurs in laterite in various forms, lithiophorite and birnessite being most common, and hollandite and tadorakite less so (Taylor and McKenzie, 1964). It frequently occurs as black nodules and concretions, usually smaller and less regular than the iron concretions (Cornwall, 1958; Taylor and McKenzie, 1964), and also as veins, coatings, linings and stains (Taylor and McKenzie, 1964; Nagell, 1962; McFarlane, 1971). Some laterites are sufficiently enriched by manganese to be ores (Fermor, 1911; Fisher, 1958; Nagell, 1962) while others have only slight concentrations (Holmes, 1914; McFarlane, 1971).

Titanium oxide (TiO_2) commonly occurs in laterites in small quantities (Goudie, 1973). Although absolute content is low and may appear insignificant (Pendleton and Sharauvana, 1946), it is nevertheless appreciable (Simpson, 1912; Harrison and Reid, 1910) and often represents a large accumulation relative to the parent material (Tiller, 1963; Harrison, 1911). For example, Mulcahy (1960) recorded 0.49 percent TiO_2 in laterite and described this quantity as large. Since the content of the parent material was only 0.01 percent, it does in fact represent a very large relative accumulation. Titanium often occurs as ilmenite (Maclaren, 1906; Fao, 1928; Hartman, 1955; du Bois and Jeffrey, 1955; Hanlon, 1945; Harrison and Reid, 1910). It can sometimes be shown to increase upwards in a laterite profile, indicating its residual nature (du Bois and Jeffrey, 1955; Hanlon, 1945). However, some laterites

contain little or no ilmenite (Simpson, 1912). Other forms include metatitanic acid, $TiO_2 \times H_2O$ (Simpson, 1912; Hanlon, 1945), rutile (Rao, 1928; Hartman, 1955), anatase (Rao, 1928), sphene (Rao, 1928), titaniferous magnetite (Rao, 1928), titaniferous hematite (Hartman, 1955), and leucoxene (Hartman, 1955).

Zircon, allied to titanium in its properties, also accumulates in some laterites and may be regarded as a resistant index mineral (Read, 1947; Tiller, 1963). Mulcahy (1960), for example, recorded up to 770 ppm in a laterite. The ratio of iron to zirconium showed that there was an absolute loss of iron from all weathering horizons, even from the laterite.

Chromium is an extremely resistant metal and the small quantities recorded in laterite by various authors (McFarlane, 1976) often represent appreciable relative concentrations. Iron and chromium have been observed to behave alike in the profile (Frasche, 1941) both rapidly increasing upwards as silica and magnesia are lost from the profile. Little is known of the form in which this element occurs, but Simpson (1912) suggested that it occurs predominantly as chromic hydrate and also a small percentage as chromite.

Laterite contains a great variety of other materials including nickel, cobalt, molybdenum, vanadium, copper and other trace elements, and phosphates. The mobilities of these are greatly varied. Some may be regarded as resistant index minerals, while others are mobile under a great variety of conditions.

There are evidently numerous studies on individual laterite occurrences. The problem remains in relating these data or information collected by various researchers under varying conditions. There is very limited composite information or data on various types of laterites derived from different parent materials in differing environments of formation, or on an inter-regional basis.

One of the few attempts was undertaken in 1951 by Overseas European Economic Community (OEEC) Technical Mission 47. This mission undertook a laterite study expedition in West Africa, and collected samples of laterite and associated soils, sediments and rock weathering products from Nigeria, Ivory Coast, French Guinea, and Dahomey (Alexander et al., 1956). The samples were examined by common mineralogical, chemical and physical procedures, and were found to have a very wide range of chemical and morphological characteristics. A prominent feature of all materials was a high content of either iron or aluminum, or both, relative to other constituents. Iron had been found in the form of goethite, hematite, as amorphous oxide compounds and as unidentified coatings on other minerals. Aluminum was found as gibbsite; boehmite was abundant in a few samples but generally absent. Kaolinite, quartz, anatase, zircon and amorphous materials were also identified in some laterites.

In their study of the engineering uses of laterite and lateritic soils and other problem soils of the tropics, Morin and Todor (1975) have reported that plinthic materials contain high percentages of sesquioxides. In most occurrences iron predominates. The most common

crystalline minerals in ironstones are hematite, goethite, gibbsite, and boehmite. Kaolinite is usually the predominant clay mineral and is followed by halloysite. Montmorillonite and vermiculite are not frequently identified. Quartz is mostly derived from underlying acidic rock. Their data were mostly compiled from various sources.

Laterites contain a great variety of materials and the mobilities of these are remarkably varied. Some may be regarded as resistant index minerals, while others are mobile under a great variety of conditions. Often it is the minerals present in small quantity which represent the largest relative accumlations. The study of their behavior may show that these lesser constituents in the weathering profile are more informative about laterite genesis than the more obvious accumulations which have been more thoroughly investigated.

3. MATERIALS AND METHODS

3.1 Selection of Sampling Sites

The aim of the present investigation was to study in detail a small number of samples which, cumulatively, represent a wide range of samples formed under differing parent materials, climatic conditions, vegetation and landscape relationships but yet similar enough to be called laterite. The first task in fulfilling this was to use information provided by various published reports on occurrence of laterite. Contacts were then made in various countries for collection of laterite samples that closely resembled those in the cited references.

A practical consequence of this is that the samples we received in Raleigh were based on the judgement of the people in the respective countries as to what we wanted. Finally, sixteen samples were chosen for this investigation, and are briefly described below:

Sample A was collected from Potiskum, in the northeastern part of Nigeria. The samples were exposed on the soil surface, and parent material is sandstone.

Sample B was collected at Samaru, near Zaria, in the north central part of Nigeria. It was part of an outcrop formed on crystalline acid rocks.

Sample C was from Thailand as an outcrop derived from basaltic rock.

Sample D was collected from an exposed laterite cap near San Ignacio, Bolivia. The parent material is basic igneous rock of Paleozoic age.

Sample E was collected from Jones County, North Carolina. The sample was found on Meggett loam soil and the parent material is probably Tertiary marls and clays.

Sample F was collected near Charters Towers (southwest of Townsville) North Queensland, Australia. Laterite formed on late Mesozoic or early Tertiary sandstone (Isbell, personal communication).

Sample G was colected from Neshoba County, Mississippi, on state highway 19, near its boundary with Winston County. It is formed on Winona sand underlain by Neshoba sands--both Eocene sands of the Claiborne Group.

Sample H was collected from Kemper County, Mississippi, near its boundary with Noxubee County, on U. S. Highway 45. The uppermost section of the Pasters Creek Formation (Tertiary) is thin-bedded silty, glauconitic, micaceous sandy clays with thick beds of iron oxide concretions derived from siderite (Soil Mineral Work Group, 1978).

Sample J was collected from the Temidire series, west of Ibadan, Nigeria. It occurred as boulders 25-50 cm below the soil surface.

Sample K was collected from the same profile as sample J, but occurred as a continuous sheet deeper than 50 cm.

Sample L was collected from Victoria Point, Brisbane, Southeast Queensland, Australia. It was formed in a deep weathered profile on

Table 3.1. Location of samples studied.

Sample Number	Location	Parent Material
A	Potiskum, Nigeria	Sandstone
B	Samaru, Nigeria	Igneous rocks
C	Thailand	Basaltic rocks
D	San Ignacio, Bolivia	Basic igneous rocks
E	Jones Co., N. C.	Calcium carbonate or marl
F	Charters Towers, Australia	Sandstone
G	Neshoba Co., Ms.	Sandy sediments
H	Kemper Co., Ms.	Sandy sediments
J	Ibadan, Nigeria	Granitic gneisses and schists
K	Ibadan, Nigeria	Granitic gneisses and schists
L	Victoria Point, Australia	Basalt
M	Brazil	Gneiss
N	Harnett Co., N. C.	Coastal sediments
P	Northampton Co., N. C.	Coastal sediments
Q	Pistol Range, Australia	Basalt
R	Wake Co., N. C.	Coastal sediments

basalt, and is probably of mid to late Tertiary age (Isbell, personal communication).

Sample M was collected near Brasilia, Brazil. The bedrock is primarily highly metamorphosed gneisses of early pre-Cambrian age.

Sample N was collected from Harnett County, North Carolina. Parent material is upper coastal plain sediments.

Sample P was collected from the Southgate Britt Farm, Northampton County, North Carolina. The parent material is coastal plain sediments.

Sample Q was collected from Pistol Range, Toowoomba, Southeast Queensland, Australia. It was collected from an exposure about 6 meters thick beneath 2-3 m of Oxisol; very deep profile on basalt, probably of mid-Tertiary age.

Sample R was collected in Wake County, North Carolina. It is formed in a Plinthic Paleudult typical of the upper coastal plain sediments.

3.2 Sample Preparation

Consolidated bulk samples were placed on 2 mm sieve and soaked in water for twelve hours. It was agitated occasionally to remove all adhering foreign particles. The samples were air dried and stored in plastic bags for use as desired. Samples used for scanning electron microscopy, bulk density, and thin section studies were left uncrushed.

The samples used for most of the physical, chemical and mineralogical studies were ground with a Spex Mixer/Mill for about 12 to 14 minutes to pass a 35-mesh sieve. Fifty to 60 g of these ground laterite

materials were weighed into 400 ml plastic beakers and 300 ml of distilled water were added to each. The suspensions were mixed with a teflon stirring rod and the pH of the suspensions were adjusted to 8.5 with N NaOH. The samples were dispersed with a Branson Sonifier Cell Disruptor (Model W-350, 1/2-inch tip, moderate power) for three minutes. The suspension was poured through a 300-mesh sieve into a 200 ml plastic beaker, and the sand fraction remaining on the sieve was washed free of silt and clay with distilled water and a rubber policeman. These sands were transferred to aluminum drying pans, dried at 110°C overnight, and stored.

The silt and clay suspensions were brought to volume, stirred, and allowed to settle until all the particles greater than 2 μ had settled out of suspension. Clay, < 2 μm effective diameter, was separated by repeated siphoning at a convenient depth and time interval calculated according to Stoke's Law (Jackson, 1974). The clay in suspension was flocculated by adding saturated NaCl solution, and the supernatant solution siphoned off. The flocculated clay was transferred to cellulose dialysis bags (average pore diameter = 4.8 nm) and dialyzed against distilled water until all excess salts were removed. The dialyzing medium had final conductivity readings below the equivalent of 0.5 ppm as NaCl. These salt-free clays were transferred to 400 ml disposable plastic cups, frozen in a dry ice-trichloroethylene slurry, and dried in a Virtis lyophilizer. These were stored in tightly capped bottles.

The silt-size fractions were later separated into coarse (20-50 m), medium (5-20 μm), and fine (2-5 μm) components. The coarse silt fraction was separated by gravity sedimentation while the medium and fine silt fractions were separated by centrifugation (Jackson, 1974). These fractions were all dried overnight at 110°C, and stored. The oven-dried sand fractions were separated into very fine, fine, and medium sands by sieving at the appropriate size limits.

Analyses were conducted on air-dry materials (unless otherwise stated). The air-dry values were adjusted to corresponding oven-dry weights after prior determination of the moisture content by gravimetric weight loss at 110°C.

3.1 Physical Analyses

3.3.1 Resistance to Disintegration Tests

Before the laterite samples were ground (Section 3.2), they were subjected to a slaking test. Laterite fragments were placed on a 10-mesh sieve and soaked in 10 percent calgon. The samples were shaken on a reciprocating shaker for 24 hours. All samples that after the slaking test could not be crushed by the thumb and forefinger were truly irreversibly hardened.

Samples were further subjected to the CBD treatment (Section 3.4.3) to see if they could be disintegrated chemically. About 10-15 g samples were used, and the treatment was repeated twice.

3.3.2 Bulk Density Determinations

Bulk densities of all samples were obtained by the saran-coated clod procedure. Air-dry laterite fragments were weighed, coated with saran and allowed to dry, reweighed, and finally weighed while immersed in a beaker of water. The saran was prepared using one part by weight of Dow Saran Resin F-220 to 5 parts methyl ethyl ketone, and was assumed to have a density of 1.3 g/cm^3. Clod samples were run in triplicate.

3.3.3 Color of Ground Whole Samples

Air-dry and moist colors of laterite samples to ground to pass a 35-mesh sieve were determined using the standard Munsell soil color charts and natural sunlight. Dry colors of unground crusts were also determined.

3.3.4 Weight Loss Determinations

Weight losses were determined gravimetrically after extraction of free iron, silicon, aluminum and manganese from the clay fraction using the CBD method (Jackson, 1974). This was also determined for materials lost during the 0.5 N KOH boiling (Section 3.4.4).

Two-hundred to 250 mg of clay (110°C, oven-dry basis) were weighed into pre-weighed 50 ml stainless steel centrifuge tubes. Free oxides of iron, aluminum, silicon, and manganese were extracted as described in Section 3.4.3. The supernatant solution was discarded and the residue was washed twice in the 1N NaCl, twice in absolute methanol and once in 60 percent methanol. The clay residue was oven-dried in the steel

centrifuge tube at 110°C for 12 hours. The tube and clay were cooled over $CaCl_2$ in a dessicator and weighed. Each sample was run in triplicate.

The weight of material lost during the 0.5N KOH boiling was determined using deferrated clay (Section 3.4.3). About 100 mg (110°C, oven-dry basis) were boiled in a nickel beaker as described in Section 3.4.4. The clay was quantitatively transferred from the nickel beakers to a 100 ml polyethylene centrifuge tube, and centrifuged until the supernatant liquid was clear. The residue was washed twice with absolute methanol, transferred to a pre-weighed aluminum drying pan, and dried at 110°C. The weight loss resulting from the 0.5 N KOH boiling was calculated by difference from the original weight of the deferrated clay sample. All determinations were done in triplicate.

3.3.5 Surface Area by Adsorption of Ethylene Glycol Monoethyl Ether

Total (internal plus external) surface areas of the undeferrated and CBD-extracted (Section 3.4.3) clay fractions were estimated by adsorption of ethylene glycol monoethyl ether (EGME). The method used was adapted from those of Carter, Heilman and Gonzalez (1965) and Heilman, Carter and Gonzalez (1965).

Duplicate samples of oven-dried clays were weighed into clean, pre-weighed aluminum weighing pans. From 200 to 250 mg samples were used, 2 ml of EGME were added to each pan, and the resulting slurries were allowed to equilibrate for one hour in an evacuable desiccator ($CaCl_2$). The deferrated clays required 4 ml of EGME to completely wet them. After

12 hours under vacuum, the samples were weighed, returned to the desiccators, and re-evacuated. This procedure was repeated until a constant weight was obtained. Specific surface areas were calculated by dividing the weight of EGME retained per g of clay by the factor 2.86×10^{-4} g EGME/m^2 (Carter et al., 1965).

3.3.6 Surface Area by Nitrogen Gas Adsorption

External surface areas of undeferrated and deferrated clays obtained as indicated in Sections 3.2 and 3.4.3, respectively were obtained by a single point nitrogen adsorption technique using a Quantasorb surface area analyzer (Quantachrome Corporation).

An oven-dry (110°C) clay sample was placed in a pre-weighed adsorption cell and "outgassed" at 110°C until all water vapor had been removed. Nitrogen was adsorbed on the sample by allowing a gaseous mixture of 30% nitrogen gas in helium to flow through the adsorption cell while immersed in liquid nitrogen. Thus, the clay was allowed to adsorb the nitrogen gas to an extent dependent upon its partial pressure. The weight of gass adsorbed can be determined using the B. E. T. equation (Brunauer, Emmett, and Teller, 1938). After adsorption was complete, the liquid nitrogen was removed and the adsorption cell immersed in a beaker of water at room temperature. The volume of desorbed gas was measured with a thermal conductivity detector and calibrated against a comparable signal from a known volume of pure nitrogen gas manually injected into the sample stream with a gas syringe.

The total surface area of the sample was calculated from the equation:

$$S_T = (1-P/P_o) \cdot (A/A_c) \cdot V_c \cdot (NA_{cs} \cdot P_a/RT)\ m^2$$

where: S_T = total surface area of sample,

P = partial pressure of adsorbate (N_2),

P_o = saturated pressure of adsorbate,

V_c = volume of calibration,

A = signal area,

A_c = area of calibration,

P_a = ambient pressure, atmosphere,

N = Avogadro's number,

R = gas constant = 82.1 cc atm/^oK mole,

A_m = cross sectional area of an N_2 molecule in monolayer ($16.2 \times 10^{-20}\ m^2$), and

T = temperature of calibration volume (^oK).

The specific surface area was obtained by dividing the total surface area by the weight of the sample in the adsorption cell.

The single adsorption point technique assumes that the intercept of the linear B. E. T. equation is essentially zero. A few determinations were performed with three adsorption points (P/P_o = 0.299, 0.201, and 0.100), and these agreed well with the single-point (P/P_o = 0.299) determinations.

3.4 Chemical Analyses

3.4.1 Reaction of Ground Whole Samples

The pH was determined in water (1:1 ratio) and in 1 N KCl solution (1:1 ratio) using laterite samples that were ground to pass a 35-mesh sieve. The suspension was stirred and allowed to equilibrate for one hour. All measurements were made on a Fisher Accumet pH meter (Model 320) calibrated at pH 4 and at pH 7.

3.4.2 Acidified Ammonium Oxalate Extractions

Ammonium oxalate-oxalic acid buffer was prepared by the method of Gorbunov et al., (1961). The final pH was adjusted to 3.0 with concentrated HCl. Clay samples weighing 150 to 200 mg (110°C, oven-dry basis) were placed in 15 ml glass centrifuge tubes, and 10 ml of the acidified ammonium oxalate buffer were added. The tubes were tightly closed, placed horizontally in a covered box on a reciprocating shaker, and shaken for four hours. The sample suspensions were not exposed to sunlight since the reaction is photosensitive. After the shaking period, the suspension was centrifuged at 1500 rpm for 10 minutes. The supernatant solution was decanted into a 100 ml volumetric flask, made up to volume with distilled water, and analyzed for Fe, Al, and Si using a Perkin Elmer atomic absorption spectrophotometer, Model 403.

The 100 ml extracts were further diluted by a factor of 25 for Fe determinations while no further dilutions were required for Al and Si determinations. Concentrations of Fe, Al, and Si determined from the extracts were compared to standard solution ranging from 0 to 5 ppm

in Fe, 0 to 50 ppm in Al, and 0 to 10 ppm in Si. All standards were prepared using Fisher certified atomic absorption stock solutions. Samples were analyzed in duplicate, and residual clay was discarded.

3.4.3 Sodium-Citrate-Bicarbonate-Dithionite Extractions

Sodium-citrate-bicarbonate-dithionite extractions (CBD) were performed on the sand; coarse, medium, and fine silt; and the clay fractions of all the 16 samples. The process was repeated twice on the sand fractions reserved for petrographic microscope study (Section 3.5.4).

Sample weights ($110^{o}C$, oven-dry basis) used ranged from 1 to 1.2 g for the coarse silt, 0.5 g for the medium silt, 0.2 g for the fine silt, and 0.2 to 0.3 g for the clay fractions. The extraction procedure was adapted from that described by Mehra and Jackson (1960). Forty-five millimeters of a sodium-citrate-bicarbonate buffer (pH 7.3) were added to the pre-weighed samples in 100 ml polyethylene centrifuge tubes. These suspensions were swirled by hand and heated at about $80^{o}C$ in a water bath, and 1 g of sodium dithionite (low in Fe) was added to each. The sample suspensions were stirred and heated for about 30 minutes, or until the samples turned whitish or greyish in color. Some samples required an additional 1 g of sodium dithionite to effect the color change. The samples were then centrifuged until the supernatant solution was clear. All samples were washed once with 45 ml of the citrate-bicarbonate buffer solution. The supernatant and citrate-bicarbonate washing were combined and brought to 500 ml volume with deionized water.

The solutions were analyzed directly for Al, Si, and Mn, while the silt extracts were diluted 100 times and the clay extract diluted 50

times for Fe determination. The analyses were performed in duplicate using a Perkin Elmer atomic absorption spectrophotometer, Model 403. Standards for each element were prepared using Fisher certified atomic absorption reference solutions and blank CBD, and ranges were 0-5, 0-50, 0-10, 0-3 ppm for Fe, Al, Si, and Mn, respectively.

The residues remaining in the centrifuge tubes were washed twice with absolute methanol, once with distilled water, and saved for X-ray diffraction analysis (Section 3.5.1).

3.4.4 Dissolution of Poorly Crystalline and Amorphous Aluminosilicates

Poorly crystalline and amorphous aluminosilicates were removed according to the procedure of Hashimoto and Jackson (1960). Approximately 100 mg of deferrated (Section 3.4.3), and freeze-dried (Section 3.2) clays were accurately weighed and transferred to nickel beakers. One hundred millimeters of 0.5 N KOH were added, the suspension swirled, rapidly brought to boiling and then boiled for exactly 2-1/2 minutes. A round-bottomed flask, through which cold water was flowing, was placed on top of each beaker to reduce evaporation loss of water from the boiling 0.5 N KOH. The beakers were rapidly cooled in an ice bath. The contents were quantitatively transferred into 100 ml polyethylene centrifuge tubes, and centrifuged at 1500 rpm for five minutes. The supernatant solution was transferred to a 200 ml volumetric flask and brought to volume with distilled water. Duplicate samples were analyzed for Si and Al on a Perkin Elmer atomic absorption spectrophotometer, Model 403. Standards were made using Fisher certified atomic absorption reference solutions and 0.5 N KOH, and ranged from 0-50 ppm in both Si and Al.

3.4.5 Total Chemical Analysis

Approximately 50 mg of ground whole laterite samples (Section 3.2) were decomposed with 0.5 ml aqua-regia and 3 ml HF at 110°C in a Parr digestion bomb (Bernas, 1968). The bomb was heated for one hour and then cooled in a conventional freezer for about 30 minutes. Boric acid (2.8 g) was added, the final solutions made to 100 ml, and stored in 125 ml polyethylene bottles.

The dissolved Fe, Al, Si, Mn, K, Na, Ca, Mg and Ti were determined using a Perkin Elmer 403 atomic absorption spectrophotometer. Calcium and Mg were analyzed from 1:1 dilutions; Al, Si, Mn, Na, K, and Ti from 1:5 dilutions; and Fe from 1:25 dilutions. Standard solutions were prepared from Fisher certified atomic absorption reference solutions, and ranged from 0-5 ppm Fe, 0-50 ppm Al, 0-50 ppm Si, 0-5 ppm Ca, 0-2 ppm Mg, 0-2 ppm Na, 0-2 ppm K, 0-5 ppm Mn, and 0-10 ppm Ti.

The percent water in the whole samples was determined by heating at various temperature intervals. Approximately 0.5 to 1 g of these samples was accurately weighed into pre-weighed ceramic crucibles, and heated in a furnace at 110°C (for 12 hours), and at 300°C, 540°C and 1000°C for two hours. All samples were cooled in a desiccator over $CaCl_2$, and weighed. The amount of water lost at each temperature was determined. Each sample was run in duplicate.

3.5 Mineralogical Analyses

3.5.1 X-Ray Diffraction Analysis

X-ray diffraction analyses were conducted using a Diano XRD 700 diffractometer employing Ni-filtered CuKα radiation. The diffraction

tube was operated at 45 kv and 16 ma for all samples. All diffractograms were recorded from 3^{o} 2θ at a scanning speed of 2^{o} 2θ per minute and recorder speed of one inch per minute.

Diffractograms were obtained for undeferrated clay samples, and deferrated clays, medium silts and fine sands. Approximately 300 mg (110^{o}C, oven-dry basis) of Na-saturated undeferrated clay was weighed into a 50 ml polyethylene centrifuge tube. The sample was washed in 20 ml N KCl, dispersed on a vortex mixer, and centrifuged at 1500 rpm for 10 minutes. The supernatant solution was discarded. The procedure was repeated twice. The K-saturated clay was then washed several times with distilled water until it was salt-free, the actual number of washings being determined by testing with 0.1 N Ag NO_3 as a Cl indicator. After the final washing, the K-saturated clay was "smeared" on a glass slide (25 x 75 mm) using a stainless steel spatula, and allowed to dry. The same procedure was repeated in preparing Mg-saturated clays except that N $MgCl_2$ was used instead of N KCl.

Deferrated clay samples preserved from Section 3.4.3, after being both K- and Mg-saturated, were dispersed in 10 ml of distilled water, and 2 ml of the resulting suspension were pipetted on a 25 x 75 mm microscope slide. After air-drying, the oriented mount was X-rayed.

Clay samples (deferrated and undeferrated) were X-rayed in the following conditions: (1) Mg saturation, (2) Mg saturation plus solvation with ethylene-glycol in an oven at 70^{o}C, (3) K saturation at room temperature, and (4) K saturation and heating at 350 and 550^{o}C for two hours.

The medium-silt fraction (deferrated) was similarly Mg-saturated, "smeared" on a microscope glass slide, and X-rayed at room temperature.

The fine sand fraction (CBD treated) was mounted on glass slides using a double-stick Scotch tape. It was neither K- nor Mg-treated. The mounted samples were X-rayed at room temperature.

3.5.2 Differential Thermal Analysis

A DuPont Model 900 Differential Thermal Analyzer with a calorimeter cell operating at a heating rate of 25^{o}C per minute in an air atmosphere was used.

Approximately 10 mg of freeze-dried clay samples were gently packed into a platinum sample pan and positioned in the high temperature cell of the analyzer. All samples were previously dried at 150^{o}C for 12 hours, and stored over $CaCl_2$ until required for analysis.

Each sample was heated from room temperature to approximately 640^{o}C or until after the kaolinite endotherm. Absolute temperatures were measured against an ice water slurry, and relative temperature differences were measured against an inert sample of calcined alumina. Endotherms resulting from the dehydroxylation of goethite, gibbsite and kaolinite were recorded on chart paper. Areas under the appropriate endotherms were determined using a Keuffel and Esser planimeter. Areas of appropriate endotherms were then compared with those produced by known amounts of gibbsite and kaolinite mixed with calcined alumina.

3.5.3 Scanning Electron Microscopy

Small laterite fragments were cemented to aluminum stubs using Dag graphite cement. These were allowed to dry and coated with gold using a Polaron E5000 Sputter coater for three minutes at 1.2 kv and 40 ma.

All specimens were then observed in an Autoscan Scanning Electron Microscope (ETEC Corporation) at 20 kv accelerating voltage and various levels of magnification.

3.5.4 Mineralogy of the Fine-Sand Fraction

The deferrated fine-sand fractions (Section 3.4.3) of all 16 samples were examined with a petrographic microscope using the oil immersion technique. Oil with a refractive index of 1.544 was used, and a total of about 500 grains was identified and counted for each sample.

3.5.5 Thin Section Analysis

Unground laterite samples were oven-dried at 110^{o}C for 24 hours and impregnated under vacuum in an apparatus described by Buol and Fadness (1961). A mixture of Castoline resin (300 ml), methyl methacrylate (200 ml), and benzol peroxide (3 g) was used.

The impregnated samples were mounted on glass slides (27 x 46 mm) using epoxy cement. Each mounted sample was ground to approximately 30 µm thickness using Ingram Laboratories Model 103 thin section saw, Model 303 thin section grinder, and 320 grit.

3.6 Statistical Analysis

The sixteen samples were subjected to a cluster analysis using the Statistical Analysis Systems (SAS) and computer facilities at North Carolina State University, Raleigh, North Carolina.

Cluster analysis is used primarily where no a priori or theoretical classification information about the data is available. The cluster procedure is designed to help identify clusters of observations that have similar attributes. Using the cluster map and distance between two clusters, it is possible to show the degree of similarities and/or differences between the various samples.

The following 21 variables (components) were used to perform the analysis: Percent CBD extractable Fe, Al and Si; 1 N KCl pH values; bulk density; % quartz and iron stained undifferentiated grains; surface areas of undeferrated samples - EGME and N_2 adsorption; total Fe, Al, Si, Ti, Mg, K, Na, and H_2O; % kaolinite by DTA; and percent amorphous Fe, Al, and Si. This program differentiates the samples based on their physical, chemical and mineralogical properties.

4. RESULTS AND DISCUSSION

4.1 Physical Properties

Only the three physical properties considered relevant to the characterization and differentiation of the laterite samples are discussed under this heading. The bulk density is especially important as a measure of the degree of cementation or massiveness of the samples. Structure is an inherent property of laterites and so reflects the local environment of formation. It could serve as a useful tool in the genetic classification of laterites.

Color is used as a measure of the type and form of iron in soils. A measure of the color is also useful in characterizing laterite samples.

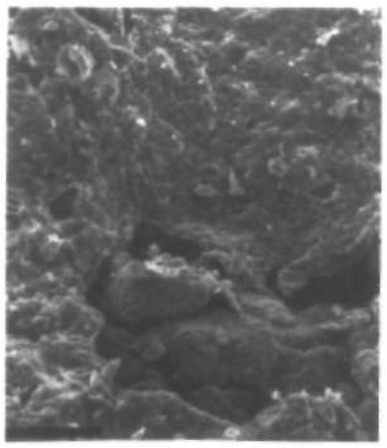
4.1.1 Studies of Laterite Structures

Laterites in various forms were studied both in thin sections and also using the scanning electron microscope (SEM). The structure as observed in thin sections and SEM is very complex and displays an even greater variety than the chemical composition.

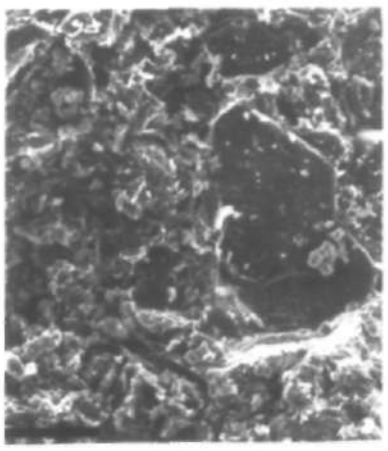
One structural extreme is the type composed largely of pisolitic bodies more or less closely packed in a matrix (Figure 4.1A). The matrix of the sample is composed of a very homogeneous mass with micro to meso, irregular vughs. This type commonly contained many iron minerals and formed from a variety of parent materials. Pisoliths have the ability to envelop and preserve relatively coarser or unweathered material as shown in Figure 4.1M. This ability of pisoliths to protect relatively fresh

Figure 4.1. Scanning electron micrographs of some unground laterite samples (black bar represents 50 μm).

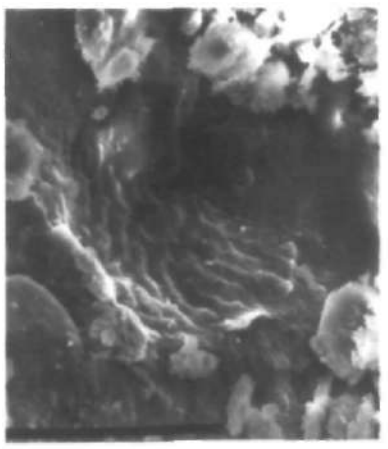
A



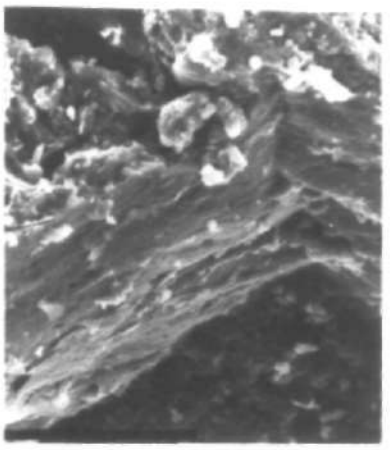
M



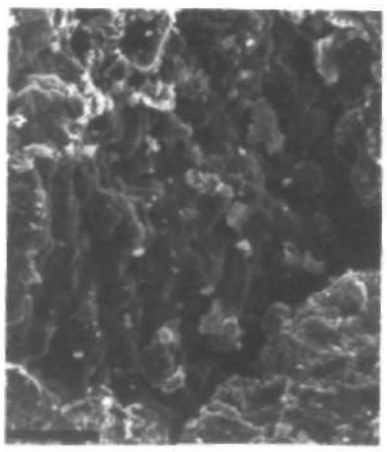
L



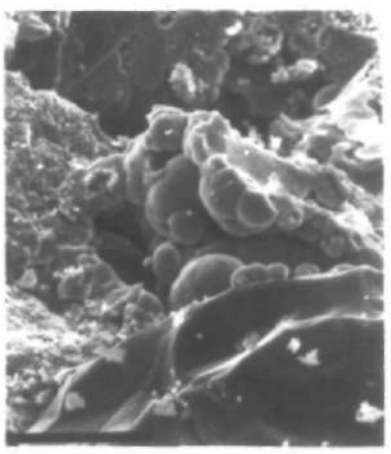
K



H



R



material within them has led to the conclusion that they form early in the process of laterization (Alexander and Cady, 1962).

The other extreme of structure is displayed by samples from Ibadan, Nigeria, and Wake County, North Carolina (K and R). The structure resembles the saprolite derived by weathering of coarse grained rocks. These samples show lattice-type network of oriented films of kaolinite upon which is overlaid the impregnating iron mineral, goethite. The iron-stained kaolinite mass can be observed as linings of pores and channels in Figure 4.1R. The goethite crystals forming the boundary of the pores are segregated on a minute scale to give the effect of small round aggregates a few microns in size, closely packed. This is the type of laterite described as vesicular. The vesicles or cavities are either empty, filled or partly filled with kaolinite clay. Quartz is present as an inheritance of the parent material.

Between these two extremes lies a wide range of structures. Figures 4.1H and 4.1L show some structures typical of low level laterites. The cement is frequently laminated, indicating several fluxes of iron. The laminated layer is made up of goethite and hematite. In thin sections, the lamina are homogeneous. The iron colloids are supplied either from the parent material or outside sources.

4.1.2 Bulk Density Determinations

Bulk densities of the samples obtained by the clod method are given in Table 4.1. The bulk densities ranged from 1.87 to 3.10 g/cm^3 with a mean of 2.34 g/cm^3. Bulk densities of 1.6 g/cm^3 and over have been reported to restrict root penetration (Blanchar *et al.*, 1978).

Table 4.1. Bulk densities of sample clods.

Sample	Bulk Densities
	--- g/cm^3 ----
A - (Potiskum, Nigeria)	2.30
B - (Samaru, Nigeria)	2.32
C - (Thailand)	2.38
D - (Bolivia)	2.12
E - (Jones Co., N. C.)	2.26
F - (Charters Towers, Austr.)	1.87
F - (Neshoba Co., Ms.)	2.54
H - (Kemper Co., Ms.)	3.10
J - (Ibadan, Nigeria)	2.32
K - (Ibadan, Nigeria)	2.18
L - (Victoria Pt., Austr.)	2.14
M - (Brazil)	2.51
N - (Harnett Co., N. C.)	2.75
P - (Northampton Co., N. C.)	2.18
Q - (Pistol Range, Austr.)	2.03
R - (Wake Co., N. C.)	2.47

* The high density of the laterites results in "soil" strengths that limit root penetration. Figure 4.2 is a good example of such a restriction, and because of the shallow rooting system the tree was tipped over by the wind.

4.1.3 Colors of Ground Whole Samples

In all samples studied colors of the ground unfractionated samples varied from strong brown (10 YR 5/8) to red (10 YR 4/8). Dry and moist Munsell color notations for the various samples are given in Table 4.2. Studying the colors in conjunction with the X-ray diffractogram and DTA patterns, reveals a close relation between the colors and the dominant iron mineralogy. Those samples having moist colors of strong brown and sometimes yellowish red show dominance of goethite while the light red, red, and dark red colors correlate with high hematite and low goethite contents. This agrees well with the findings of Bigham (1977) that the red and yellow colors of clays are related to the iron mineralogy. There is no relationship between the amount of iron (Table 4.3) and the "redness" of the colors. For example, the clay fraction of the sample from Charters Towers, Australia (sample F) contains 4.7% Fe_2O_3 and the moist color is red (2.5 YR 5/6), the sample from Thailand (sample C) contains 27.3% Fe_2O_3 and the moist color is yellowish red, while the samples from Jones County, North Carolina and Neshoba County, Mississippi contain 43.8% and 44.6% Fe_2O_3, respectively but the moist color is strong brown (7.5 YR 5/6).

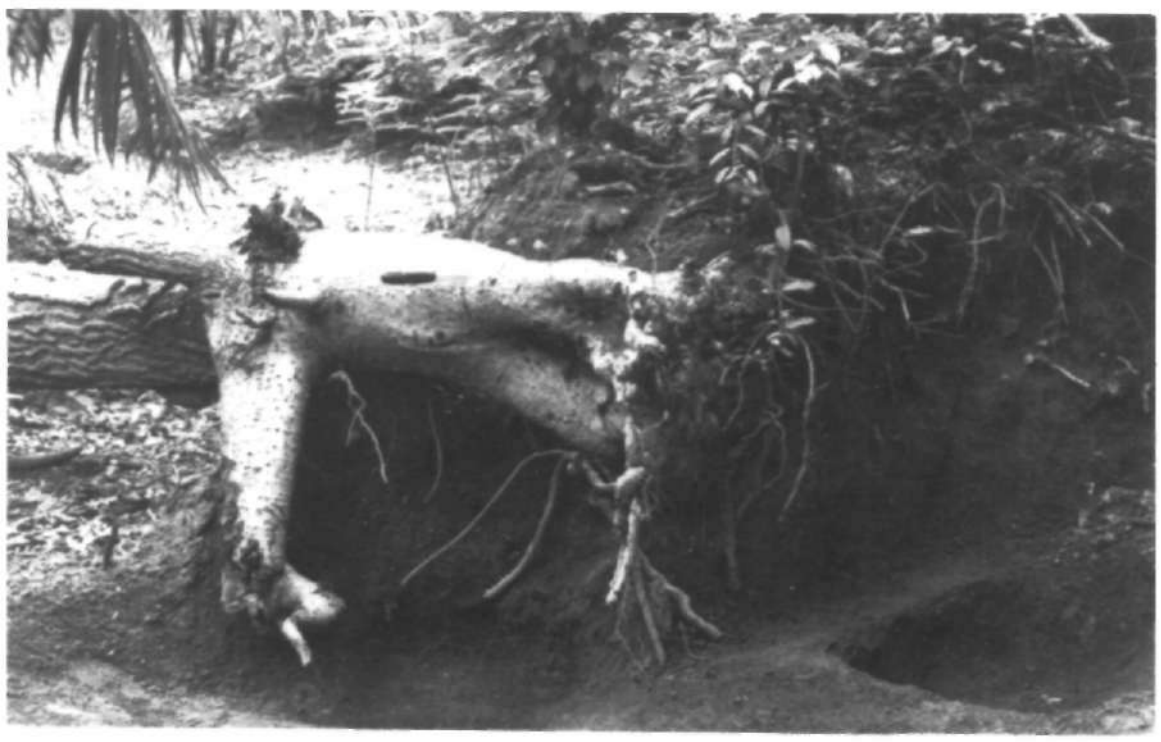


Figure 4.2. A tree that was growing above the laterite layer in the Gambari soil near Ife, Nigeria.

Table 4.2. Color of ground whole sample and the dominant iron mineral.

Sample	Munsell Color		Dominant Iron Mineralogy
	Dry	Moist	
A - (Nigeria)	5 YR 5/8	5 YR 5/6	Hematite
B - (Nigeria)	5 YR 5/8	5 YR 5/6	Hematite
C - (Thailand)	5 YR 5/6	5 YR 4/5	Goethite
D - (Bolivia)	2.5 YR 5/6	2.5 YR 4/6	Goethite
E - (N. C.)	7.5 YR 5/8	7.5 YR 5/6	Goethite
F - (Austr.)	2.5 YR 6/6	2.5 YR 5/6	Hematite
G - (Miss.)	7.5 YR 5/8	7.5 YR 5/6	Goethite
H - (Miss.)	10 YR 6/6	10 YR 5/6	Goethite
J - (Nigeria)	5 YR 5/8	5 YR 4/6	Goethite/Hematite
K - (Nigeria)	7.5 YR 5/8	5 YR 4/6	Goethite/Hematite
L - (Austr.)	10 YR 4/8	10 YR 4/6	Hematite
M - (Brazil)	2.5 YR 4/6	2.5 YR 3/6	Hematite
N - (N. C.)	10 YR 5/8	7.5 YR 5/8	Goethite
P - (N. C.)	7.5 YR 5/8	5 YR 5/6	Goethite
Q - (Austr.)	2.5 YR 4/8	2.5 YR 3/6	Hematite
R - (N. C.)	5 YR 5/8	5 YR 4/6	Goethite

Table 4.3. Citrate-bicarbonate-dithionite extractable oxides of iron from different fractions.

Sample	Coarse Silt (50-20 μm)	Medium Silt (20-5 μm)	Fine Silt (5-2 μm)	Clay (2 μm)
	---------- Fe_2O_3 weight % ----------			
A-(Nigeria)	20.1	30.6	35.2	31.5
B-(Nigeria)	10.8	19.6	23.4	15.6
C-(Thailand)	19.6	28.9	38.4	40.5
D-(Bolivia)	14.8	19.6	28.1	21.3
E-(N. C.)	21.4	29.6	36.3	43.8
F-(Austr.)	6.8	2.6	6.5	4.7
G-(Miss.)	42.3	34.0	54.7	44.6
H-(Miss.)	17.4	12.6	34.1	32.2
J-(Nigeria)	13.3	25.8	30.2	23.2
K-(Nigeria)	12.9	17.6	33.5	22.9
L-(Austr.)	46.5	35.6	37.4	32.2
M-(Brazil)	28.2	31.8	37.7	32.1
N-(N. C.)	23.4	24.9	30.9	30.0
P-(N. C.)	22.3	27.9	33.7	27.3
Q-(Austr.)	25.9	21.5	23.4	19.2
R-(N. C.)	35.2	27.8	33.6	36.4

4.2 Secondary Iron Content

The distribution of secondary (CBD extractable) iron in the samples is given in Table 4.3. The CBD treatment was not sufficient to remove all the free iron oxides from the sand fractions and so the content of iron in these fractions was not measured.

In general, the iron oxide content of the coarse, medium and fine silt fractions seemed to increase with a decrease in particle size. This is as would be expected. If the extractable Fe_2O_3 contents of the clay and silt fractions are compared, the < 2 μm clay fractions generally contained less than the fine silt (5- 2 μm) fractions. The Fe_2O_3 content of the fine silt ranges from 6.5% to 54.7% while that of the clay fractions ranges from 4.7% to 44.6%. Apart from quartz, the iron cement and iron nodules would be the next hardest materials in the laterite samples. Hence, the grinding process seemed to concentrate the iron minerals in the silt fractions while the kaolin minerals (very easy to grind) concentrated in the clay fractions. This is evident from the X-ray diffractograms of the medium silt and clay fractions.

There is, however, no detectable relationship between bulk density and the free iron content of the samples excepting that the sample with the lowest bulk density (sample F from Charters Towers, Australia) contained the least amount of free iron oxides.

4.3 Chemical Composition of the Clay and Ground Whole Samples

The elements dissolved along with iron by the CBD treatment of the clay fractions are given in Table 4.4 on an oxide bases. Substantial

Table 4.4. Citrate-bicarbonate-dithionite extractable oxides of aluminum, silicon, titanium, and manganese in the clay fraction (< 2 μm).

Sample	Al_2O_3	SiO_2	MnO_2	TiO_2
	weight %			
A - (Nigeria)	4.8	1.9	1.7	0.07
B - (Nigeria)	5.6	1.4	—[a]	0.06
C - (Thailand)	6.2	2.0	0.2	0.05
D - (Bolivia)	5.7	2.2	—	0.06
E - (N. C.)	2.3	1.9	0.2	—
F - (Austr.)	1.1	1.3	—	—
G - (Miss.)	3.9	3.4	—	0.04
H - (Miss.)	1.8	1.5	0.1	—
J - (Nigeria)	6.1	2.4	1.5	0.06
K - (Nigeria)	5.8	2.4	1.5	0.07
L - (Austr.)	2.0	1.1	—	0.04
M - (Brazil)	2.4	1.6	—	0.05
N - (N. C.)	3.3	3.2	—	—
P - (N. C.)	4.9	2.2	—	—
Q - (Austr.)	2.7	1.1	—	0.30
R - (N. C.)	3.8	2.2	—	—

[a]No measurable amount.

amounts of aluminum were detected in the CBD extracts--1.1 to 6.2% Al_2O_3 by weight. Since the samples contain very little or no gibbsite, much of this Al is probably derived from the iron oxides. According to Jackson (1974) an appreciable amount of Al may substitute for Fe in the structure of soil goethite as well as in amorphous iron oxides. The CBD procedure is known to extract considerable Al in the above minerals but crystalline gibbsite is little attacked. Except for the Charters Towers sample (F), all the amounts of Si detected (Table 4.4) were less than the amounts of Al. Only minor amounts of manganese and titanium were solubilized by the CBD treatment.

The total chemical components of the samples are given in Table 4.5. The iron and silicon contents are consistently the highest and account for 61 to 85% of the chemical compositions of the various samples. Much of the remaining fraction is contributed by aluminum and adsorbed and structural water. All of the samples are quite low in their total contents of manganese, calcium, magnesium, potassium and sodium. If one considers the length of time required for the formation of laterites, it is almost certain that their "parent materials" have passed through very intense processes of weathering and mineral transformation. All processes involve the removal of almost all bases and much of the combined silica. The titanium content ranges from 0.11 to 4.36%, the highest amounts being detected in the three samples (F, L and Q) from Australia. Generally, titanium occurs in laterites only in small quantities, and the absolute content may appear insignificant, but it is nevertheless appreciable relative to its content in the parent material (Tiller,

Table 4.5. Total elemental analysis of the ground whole samples expressed as weight percent of the oxides.

Samples	Fe_2O_3	Al_2O_3	SiO_2	MnO_2	TiO_2	CaO	MgO	K_2O	Na_2O	H_2O^a	Total
						%					
A	46.58	8.73	30.78	2.12	0.76	0.01	0.10	0.37	0.26	8.85	98.56
B	38.68	6.78	47.14	-	0.22	-	0.03	0.11	0.11	5.07	98.14
C	56.40	7.87	20.58	0.61	0.42	-	0.10	0.62	0.15	9.74	96.49
D	49.31	7.54	28.64	-	0.78	-	0.10	0.34	0.10	9.41	96.22
E	48.11	6.33	30.50	0.40	0.15	0.03	0.02	0.07	0.09	8.88	94.48
F	27.87	16.01	38.41	0.05	1.58	-	0.06	0.92	0.15	12.24	96.29
G	50.72	6.94	32.80	-	0.05	0.01	0.06	0.14	0.08	9.14	99.94
H	48.89	5.64	18.51	0.27	0.28	0.70	0.71	0.76	0.17	23.61	99.54
J	29.90	13.34	42.28	2.30	0.28	0.03	0.07	0.58	0.13	7.78	96.69
K	30.77	13.86	41.34	2.30	0.30	0.02	0.07	0.50	0.10	7.59	96.85
L	53.63	12.31	19.64	0.03	3.09	-	0.13	0.06	0.08	9.73	98.70
M	48.92	8.07	25.03	1.53	0.72	0.01	0.04	0.23	0.09	12.45	97.14
N	38.56	8.31	40.19	-	0.20	0.01	0.03	0.32	0.14	7.57	95.33
P	38.30	7.80	45.46	-	0.11	0.03	0.07	0.55	0.11	7.54	99.97
Q	27.32	12.50	36.54	0.05	4.36	-	0.11	0.08	0.11	12.95	94.02
R	43.42	4.44	41.69	-	0.04	0.02	0.02	0.06	0.09	7.17	96.95

[a]Water content between 110 and 1000°C.

1963). An accumulation of titanium in laterites, if shown to be a primary stable form, can be used as evidence of a residual origin.

The summation of the oxides is consistently less than 100%. Two reasons could be advanced for this. It is possible that other constituents of laterite, for example, zircon, chromium, nickel, cobalt, molybdenum, vanadium, copper and phosphates would make up this difference. Secondly, Calvert (1978) noted that loss of Si by volatilization during dissolution in the acid bomb could be a factor.

4.4 Mineralogical Analyses

4.4.1 Mineralogy of the Sand and Silt Fractions

X-ray diffractograms (Section 3.5.1) were obtained for the fine sand and medium silt fractions as representative of the sand and silt fractions, respectively. Both size fractions were CBD-treated. All minerals observed in the sand, silt and clay fractions, along with their observed d-spacings, relative intensities and Miller indices, are summarized in Table 4.6.

The fine sand fractions (Figures 4.3) contain mostly quartz, with minor traces of kaolinite, dehydrated halloysite and goethite. The treatment of the fine sand fraction with the CBD procedure was not sufficient to remove all the free iron oxides from the samples. The X-ray diffraction procedure was still able to detect some goethite in many samples. Quartz shows its relative resistance to grinding by dominating the fine sand mineralogy of most samples. Surprisingly, no mineral was detected in this size fraction in the sample from Victoria Point, Australia (Sample L).

Table 4.6. X-ray diffraction data for observed minerals.

Mineral	Observed d value	A.S.T.M.[a] d value	I/I_1	hkl
Hydroxy Interlayered Vermiculite	14.72-15.22	-	-	001
Kaolinite	7.19	7.15	100	001
	3.52-3.58	3.57	100	002
	2.36-2.39	2.37	70	003
Halloysite	7.2-7.4	7.15	90	001
	4.41-4.47	4.42	100	110
Muscovite	10.04-10.15	9.97	100	003
	4.95-5.01	4.99	100	006
	3.32-3.35	3.33	53	009
Quartz	4.25-4.27	4.26	35	100
Lepidocrocite	6.24-6.27	6.26	100	020
Goethite	4.15-4.18	4.21	100	110
	2.67-2.69	2.69	80	130
	2.43-2.46	2.44	70	111
Hematite	2.67-2.69	2.69	100	104
	2.51	2.51	80	110
K-Feldspar (Microcline)	3.24-3.27	3.24	100	220,002, 040
Apatite	2.78-2.79	2.77-2.83[b]		

[a]X-ray Power Data File, American Society for Testing Materials.

[b]M. L. Jackson (1974), p. 221.

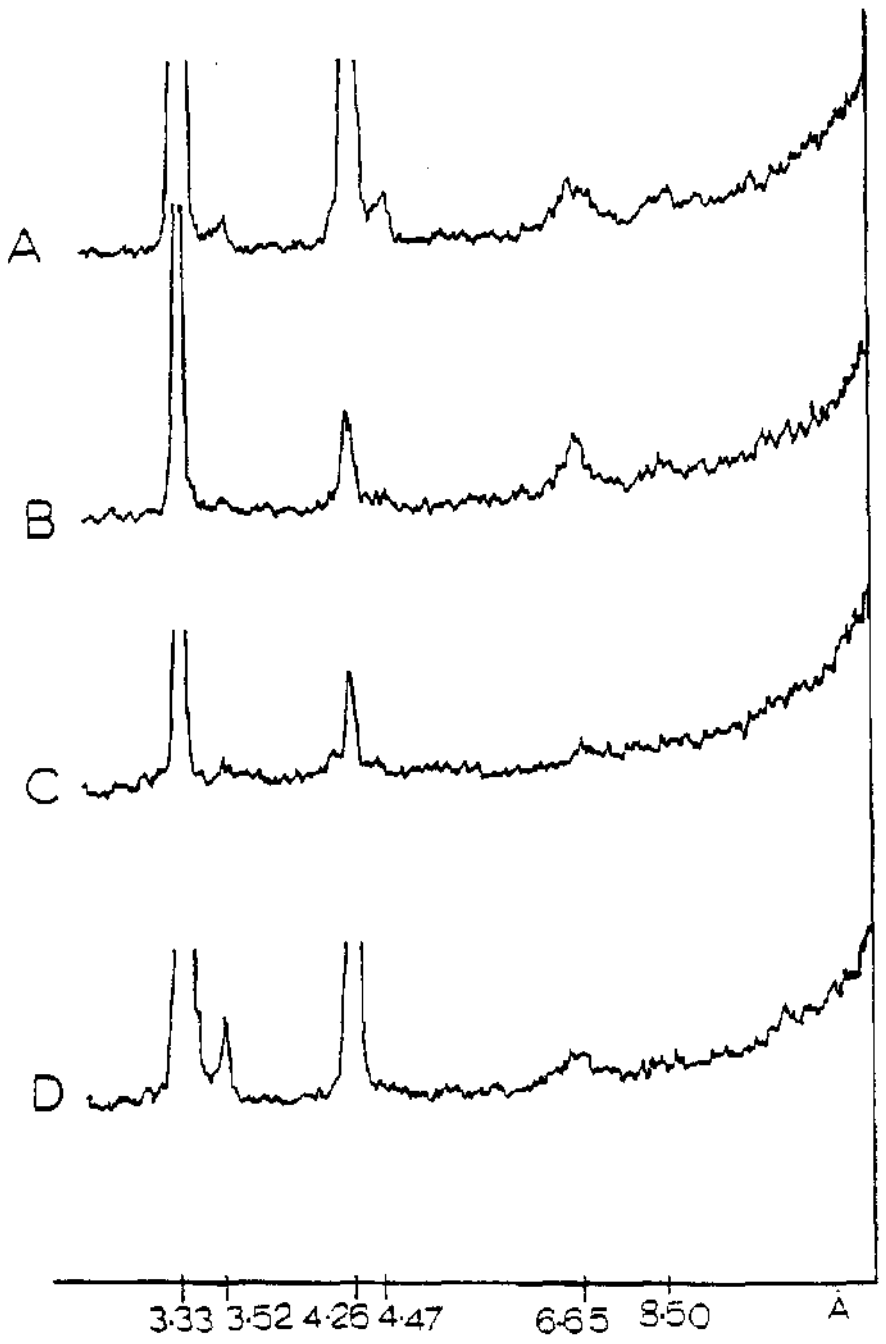


Figure 4.3. X-ray diffractograms of deferrated fine sand (100-250 µm) fractions, 25°C; run at a 1000 counts-per-second range factor and a one-second time constant.

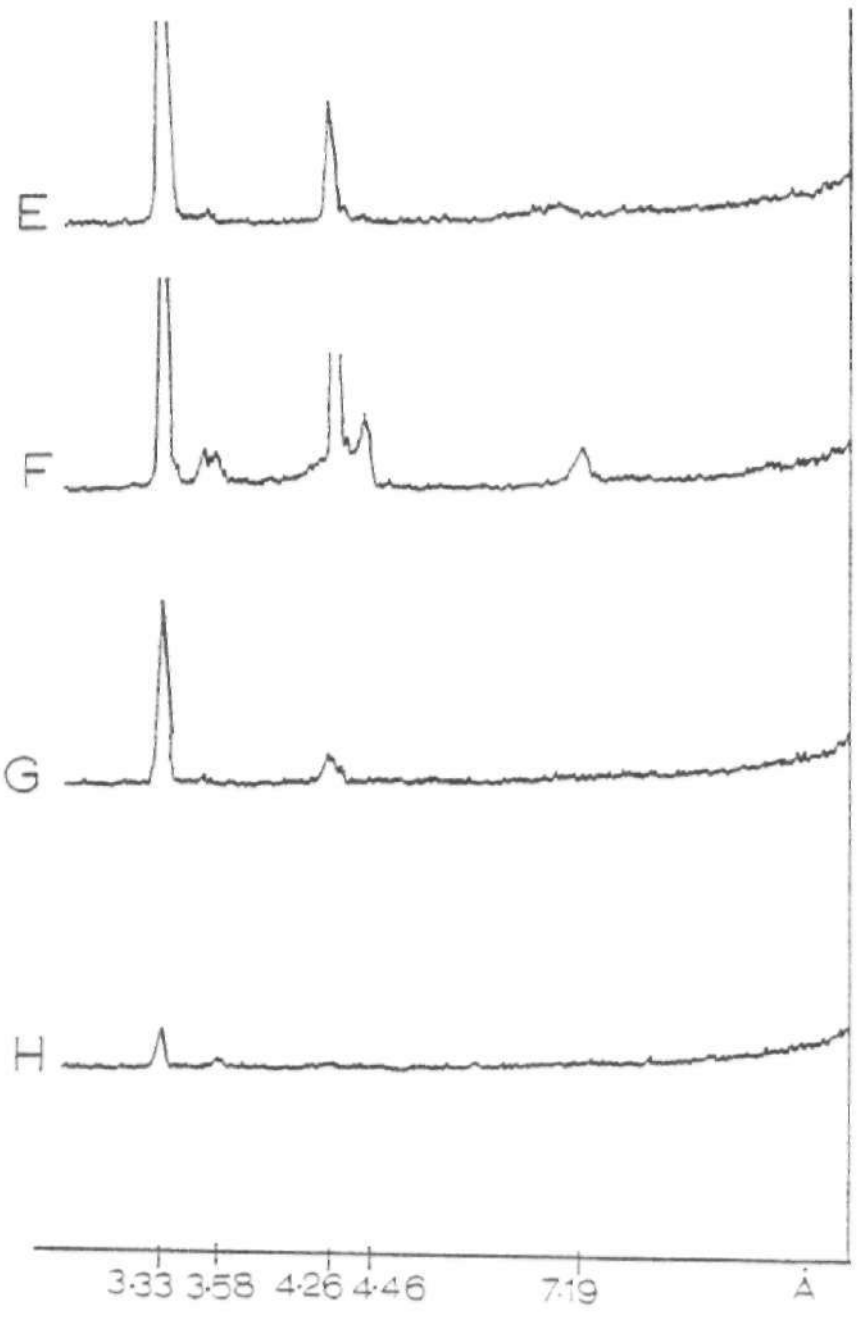


Figure 4.3 (continued)

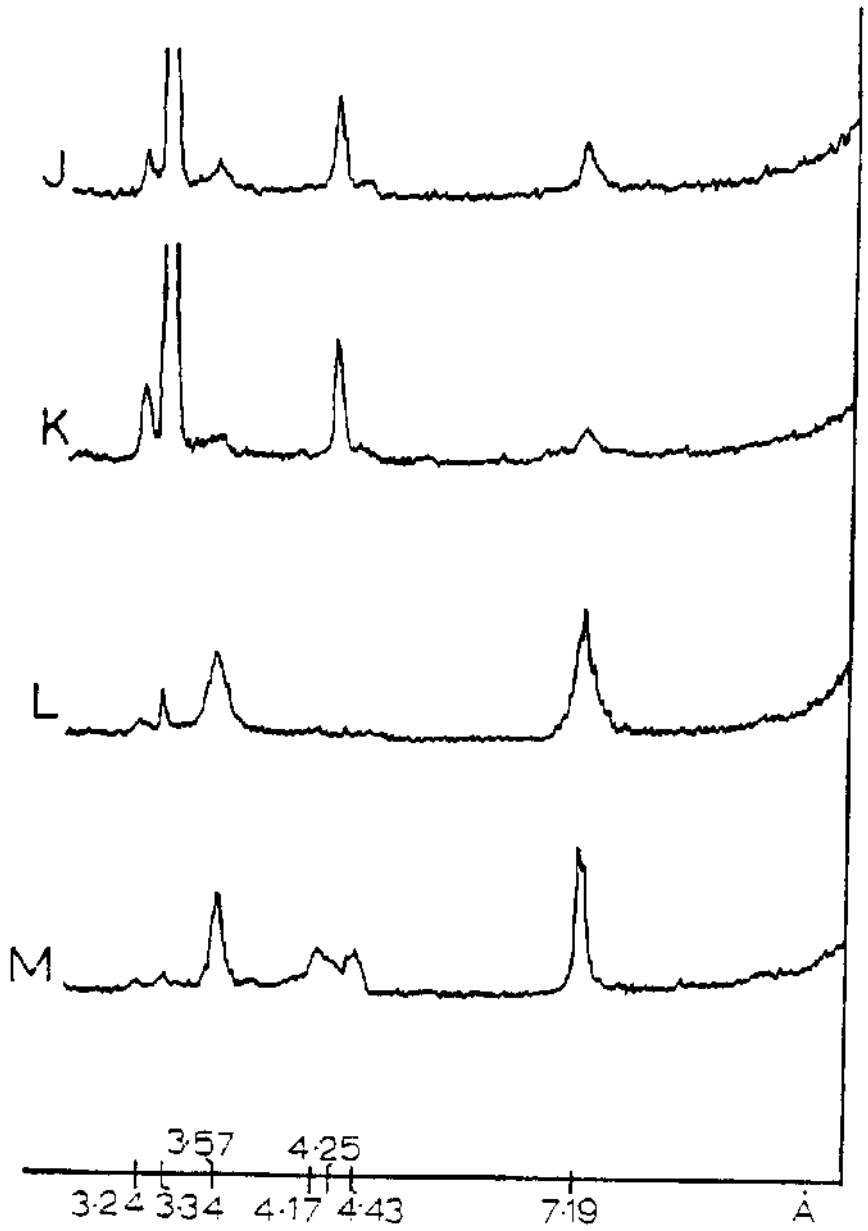


Figure 4.3 (continued)

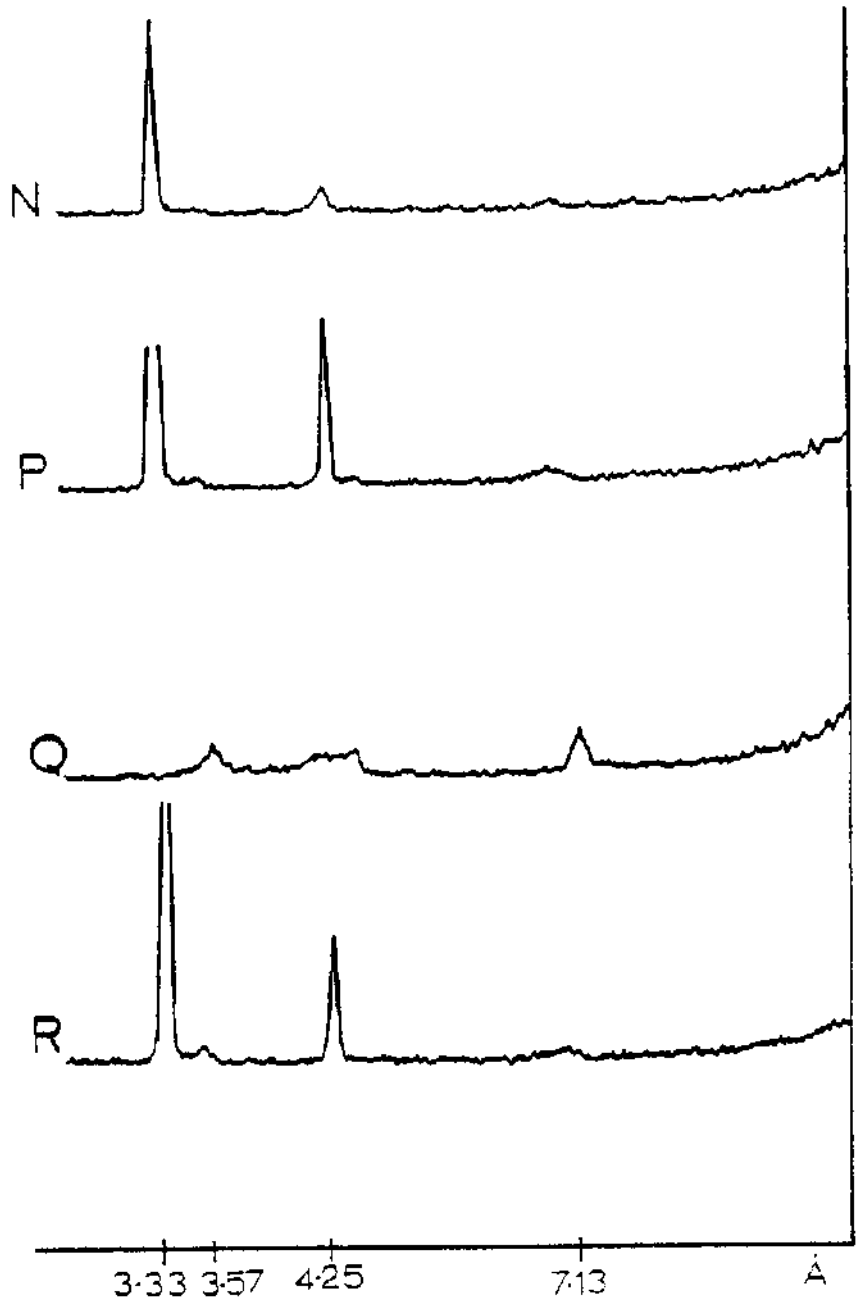


Figure 4.3 (continued)

Table 4.7. Modal analysis of the fine-sand fraction.

Sample	Quartz	Feldspar	Mica	Opaque	Iron-stained aggregates (undifferentiated)
	---------- % ----------				
A	64.2	0.2	-	-	35.6
B	92.1	-	0.6	-	7.3
C	23.2	-	-	-	76.6
D	77.4	-	-	0.2	22.4
E	93.3	-	-	0.4	6.3
F	81	0.8	-	-	18.2
G	60.2	0.2	0.2	0.2	39.2
H	27.1	0.2	0.4	0.2	72.1
J	81.6	-	0.4	-	18.0
K	90.4	0.2	-	-	9.4
L	5.9	-	0.4	0.2	93.5
M	4.6	-	-	-	95.4
N	60.0	-	0.4	-	39.6
P	79.4	0.4	-	0.6	19.6
Q	2.0	-	-	4.0	94.0
R	8.6	-	-	-	14.0

Both the X-ray diffractograms (Figure 4.3) and the grain counts of the fine sand fraction (Table 4.7) indicate that the three samples from Victoria Point, Australia, Brazil and Pistol Range, Australia (L, M and Q, respectively) contain the least amounts of identifiable quartz. These same samples also contained the highest amounts (93.5%, 95.4% and 94.0%, respectively) of unidentified iron-stained aggregates. The grain count data support the very minor amounts of feldspars and micas identified from the X-ray diffractograms.

The X-ray diffractograms of the medium silt fraction are presented in Figure 4.4. These patterns show more intense peaks for kaolinite, muscovite and feldspars than the fine sands. Quartz in the medium silt is not as dominant mineralogically as in the fine sand. This again shows the discriminatory effect of the grinding process which allows the quartz to concentrate in the larger size fractions. The K-feldspar peaks were most intense in the samples from Ibadan, Nigeria (J and K), and Northampton County, North Carolina (P).

4.4.2 Mineralogy of the Clay Fraction

X-ray diffraction analysis of the clay (< 2 μm) fraction was conducted under the various conditions given in Section 3.5.1. Only the diffraction patterns from Mg-saturated nondeferrated and deferrated; deferrated Mg-glycolated; K-saturated nondeferrated (at 25°C and 350°C); and K-saturated deferrated (at 25°C and 550°C) clays are reproduced, and shown in Figures 4.5 through 4.11.

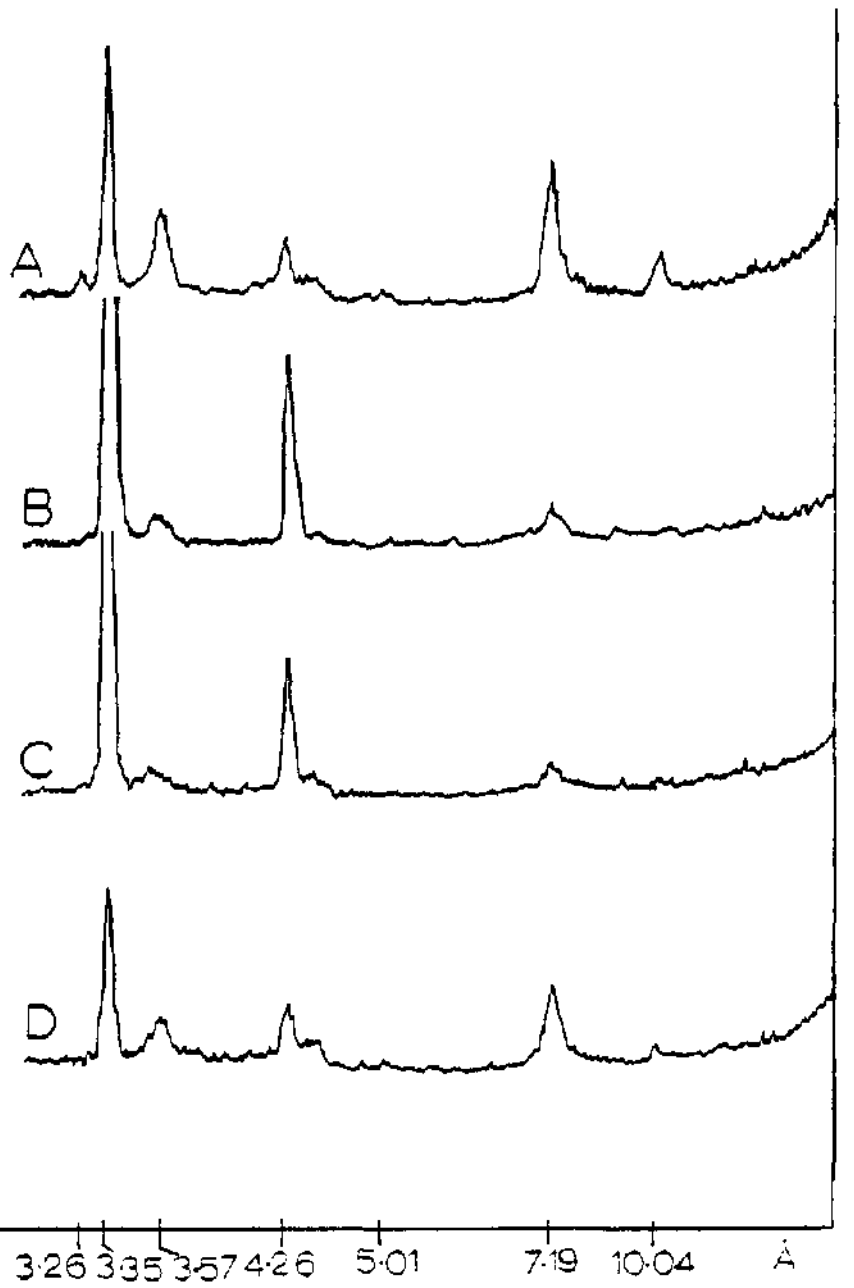


Figure 4.4. X-ray diffractograms of deferrated medium silt (5 μm-20 μm) fraction at 25°C; run at a 1000 counts-per-second range factor and a one-second time constant.

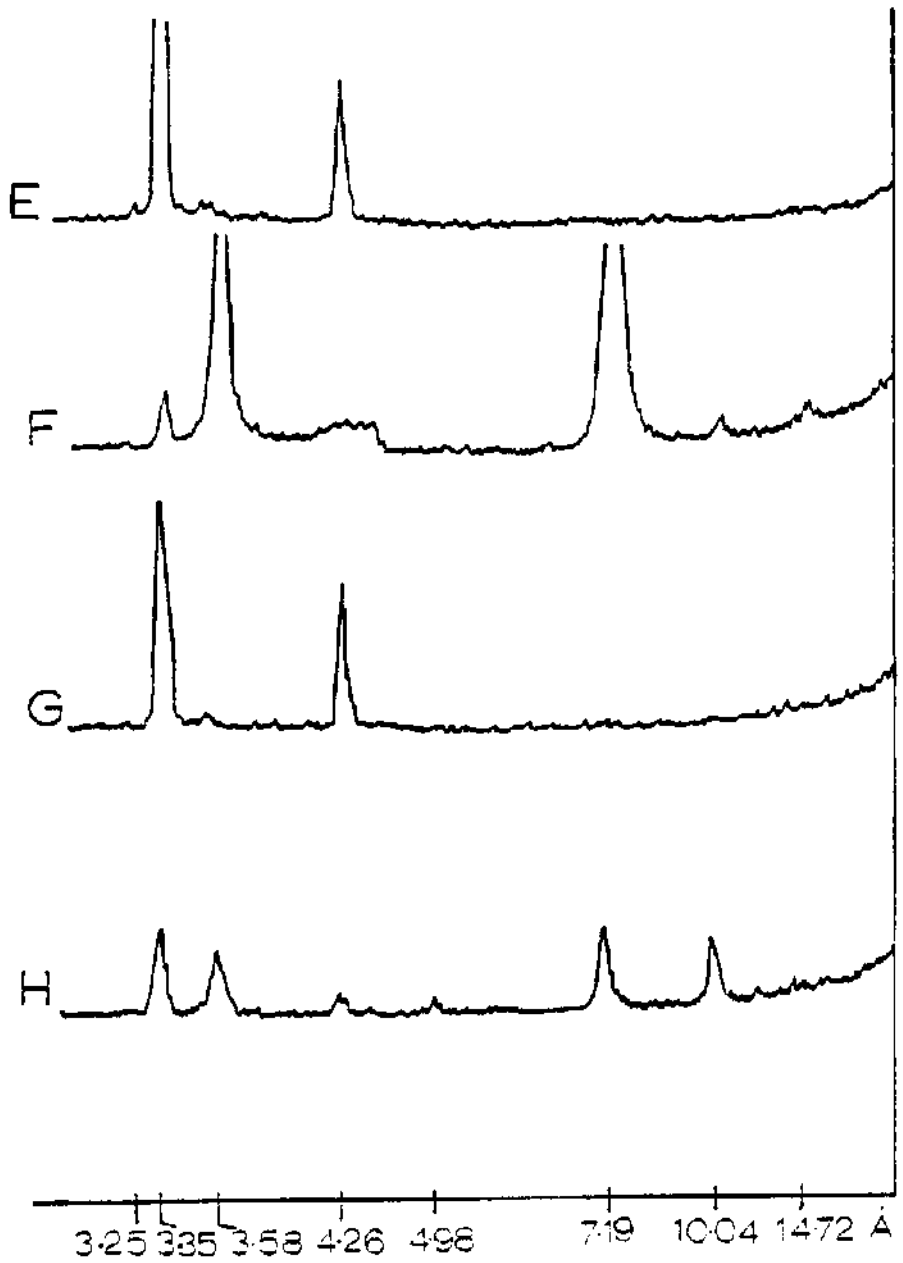


Figure 4.4 (continued)

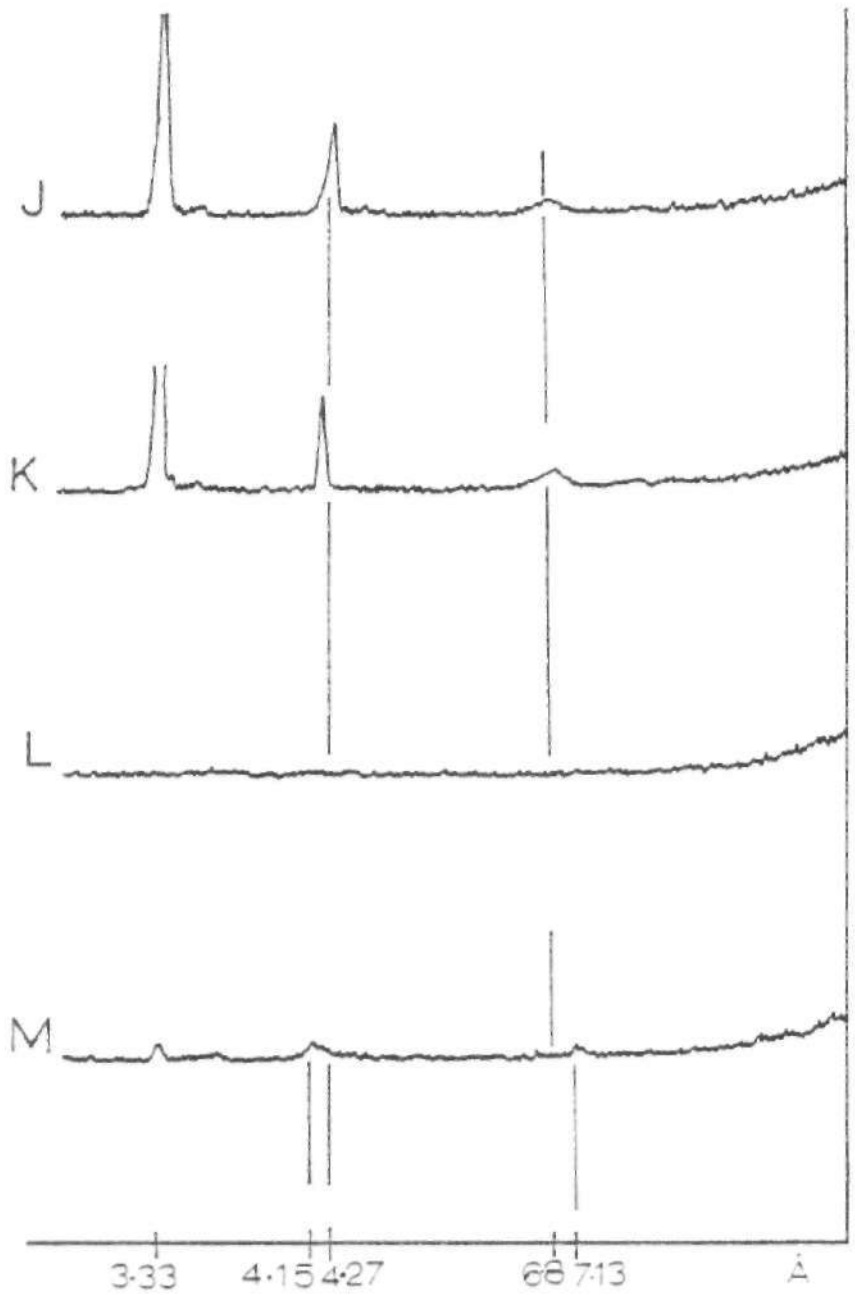


Figure 4.4 (continued)

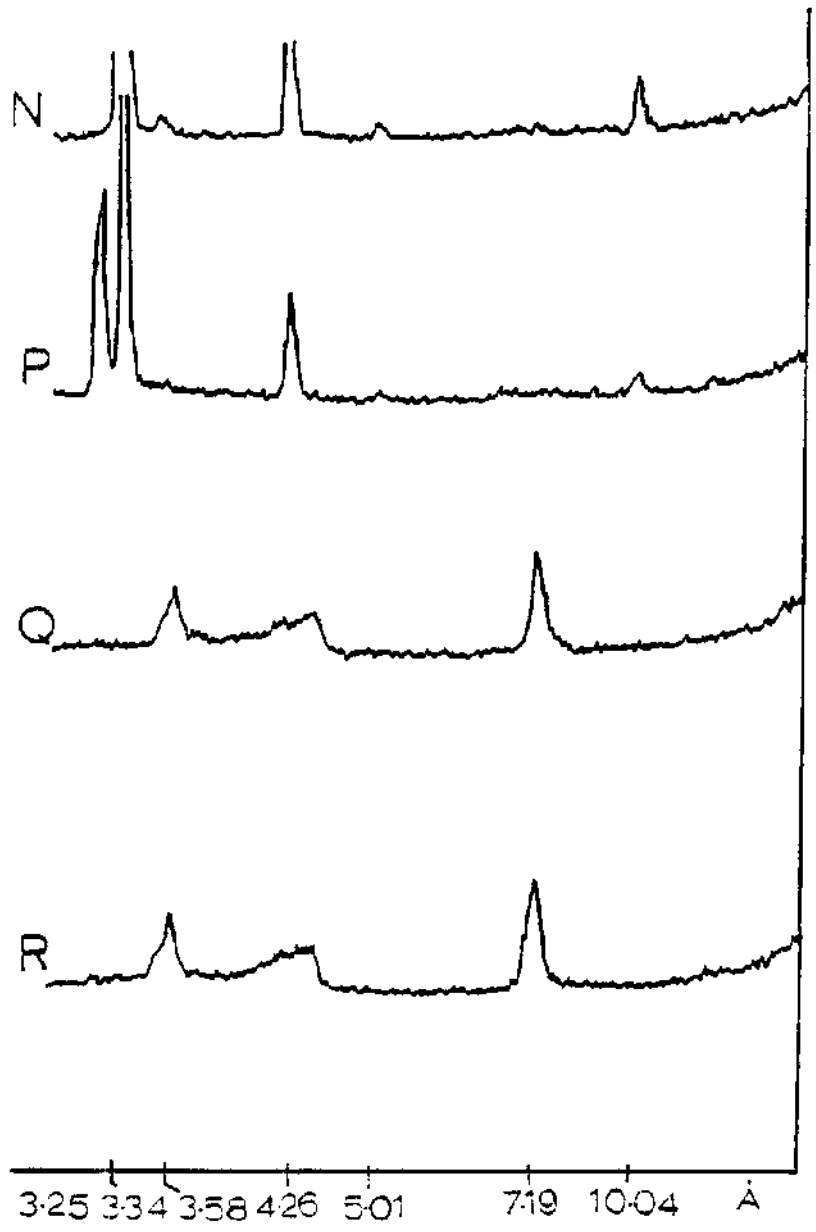


Figure 4.4 (continued)

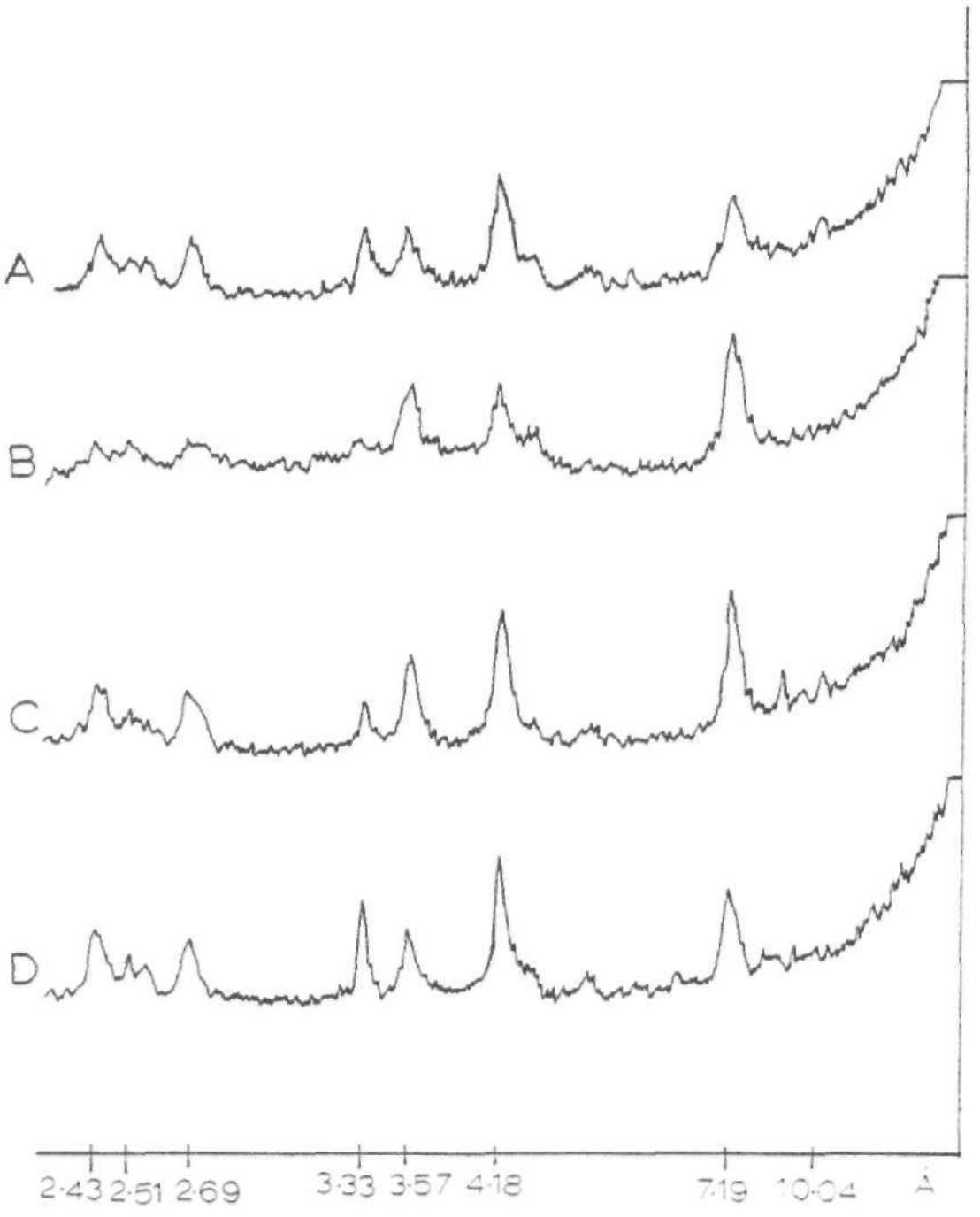


Figure 4.5. X-ray diffractograms of nondeferrated, Mg-saturated clays (<2 μm); run at a 250 counts-per-second range factor and a 2.5 seconds time constant.

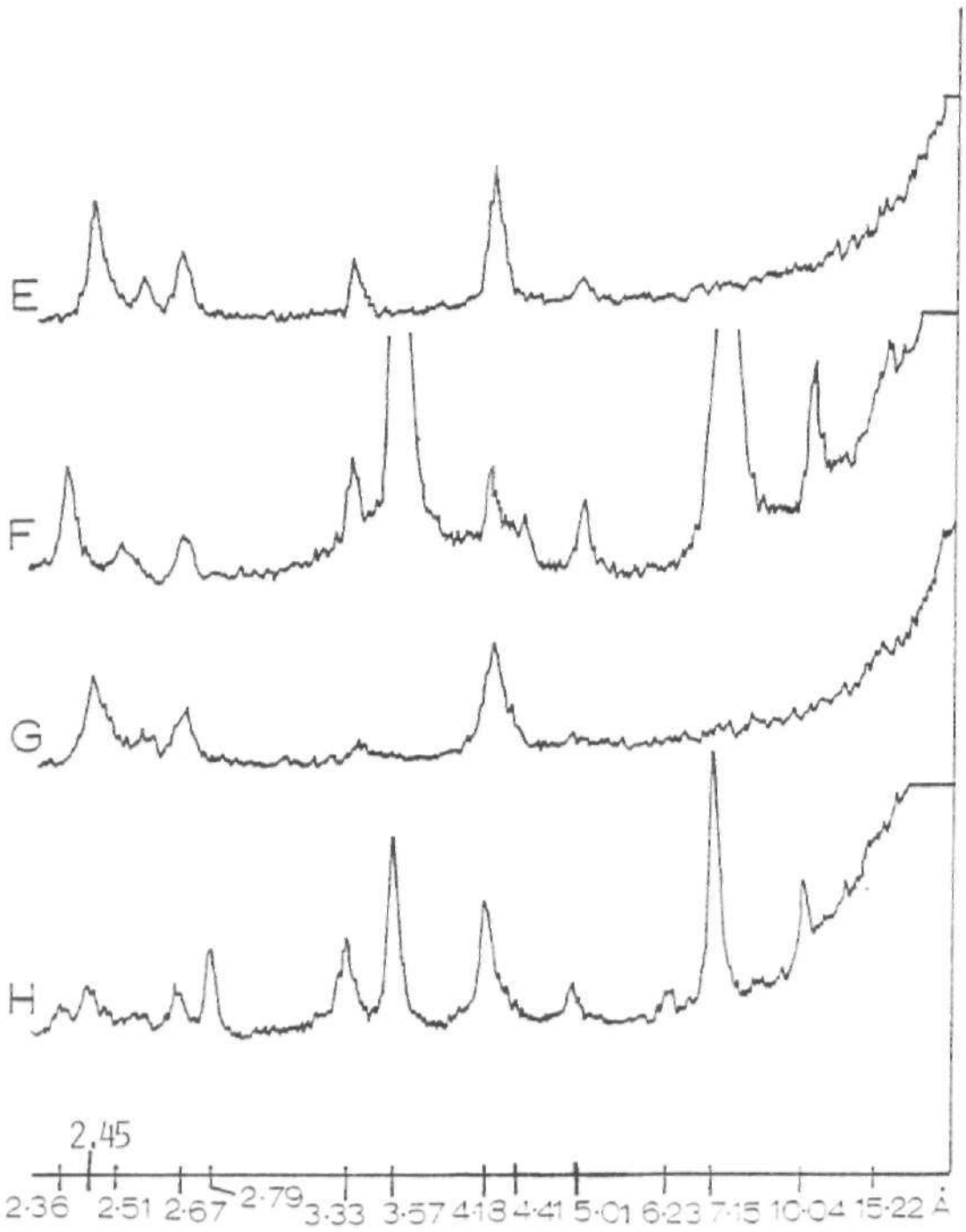


Figure 4.5 (continued)

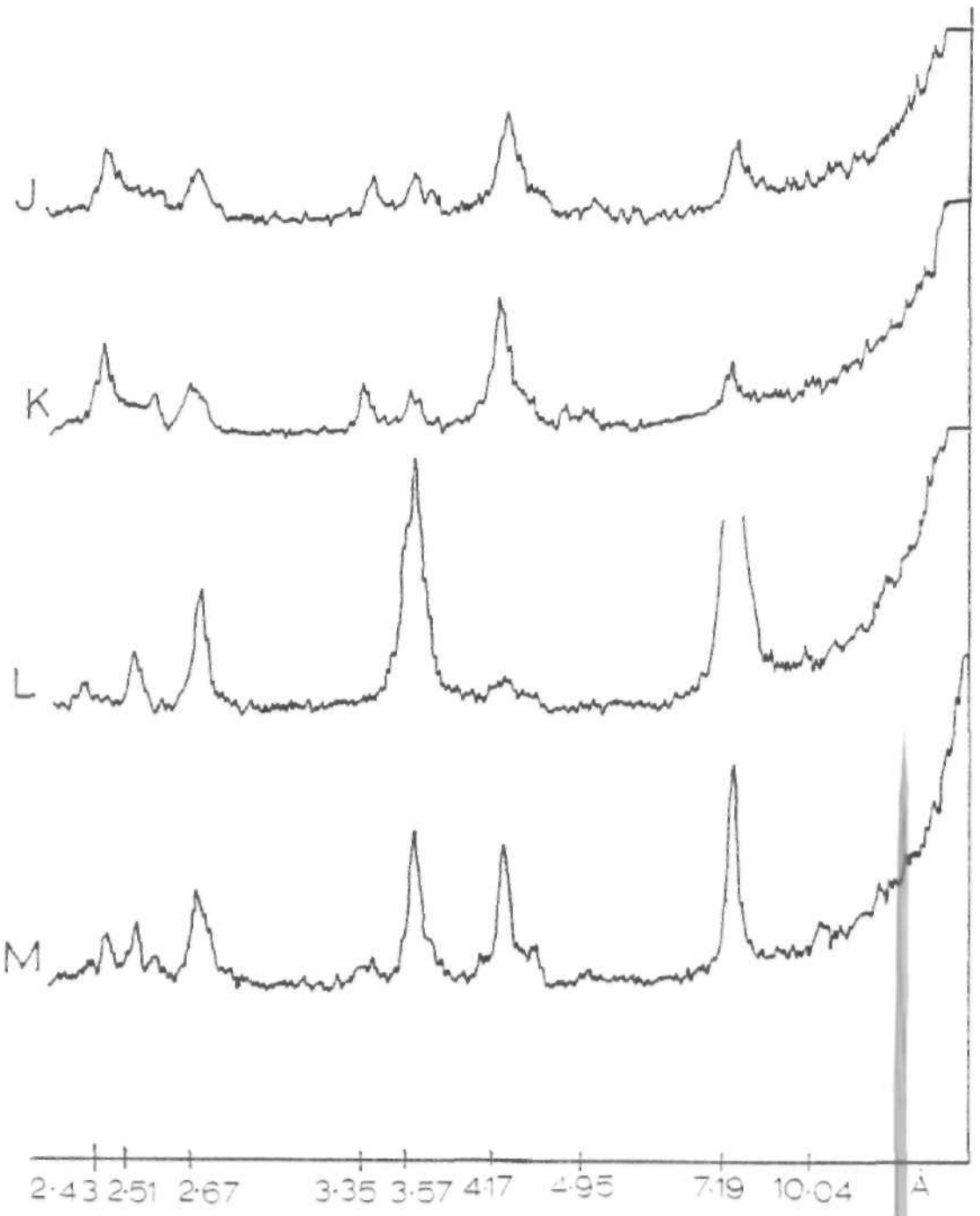


Figure 4.5 (continued)

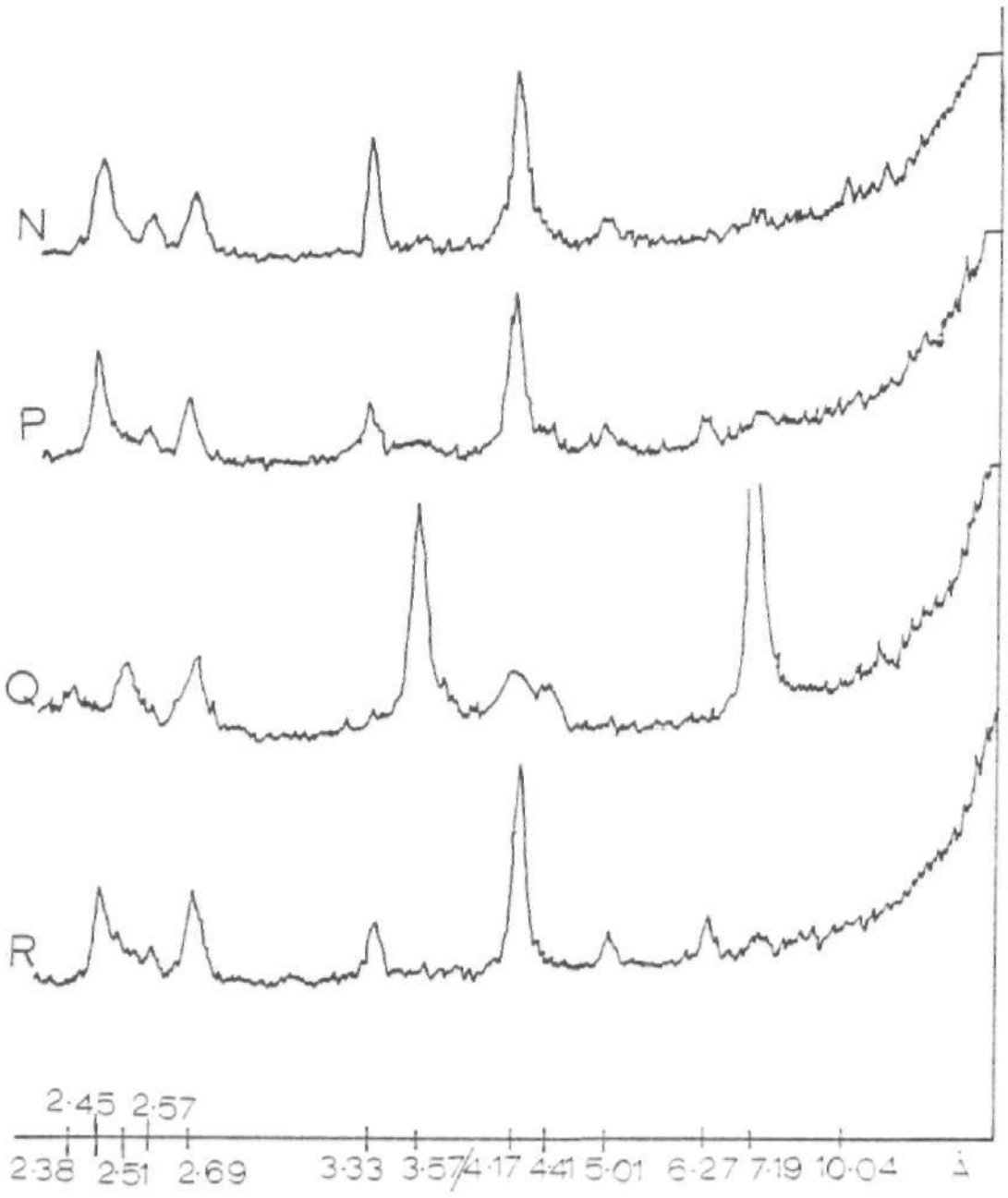


Figure 4.5 (continued)

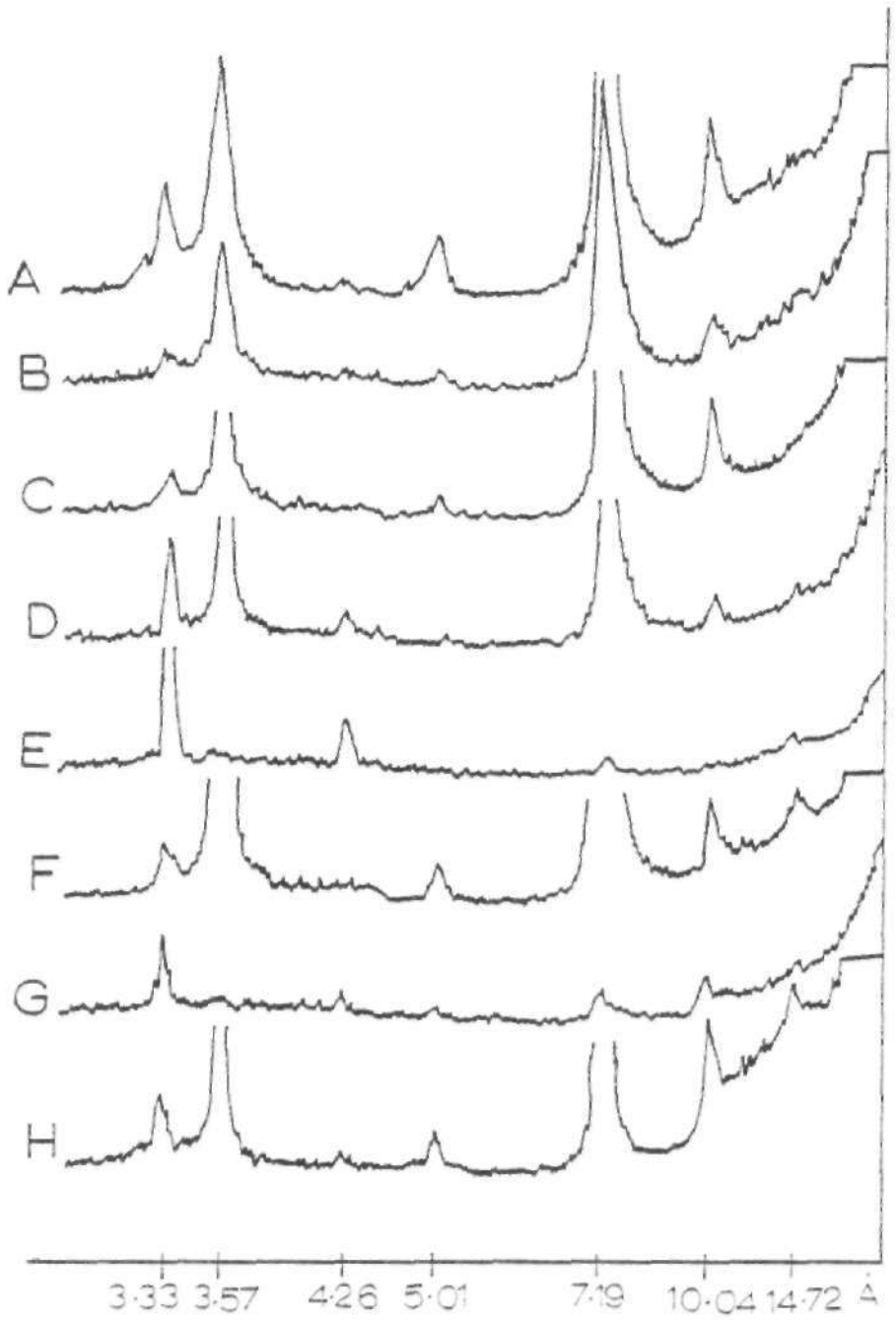


Figure 4.6. X-ray diffractograms of deferrated, Mg-saturated clays (< 2 μm); run at a 1000 counts-per-second range factor and a one-second time constant.

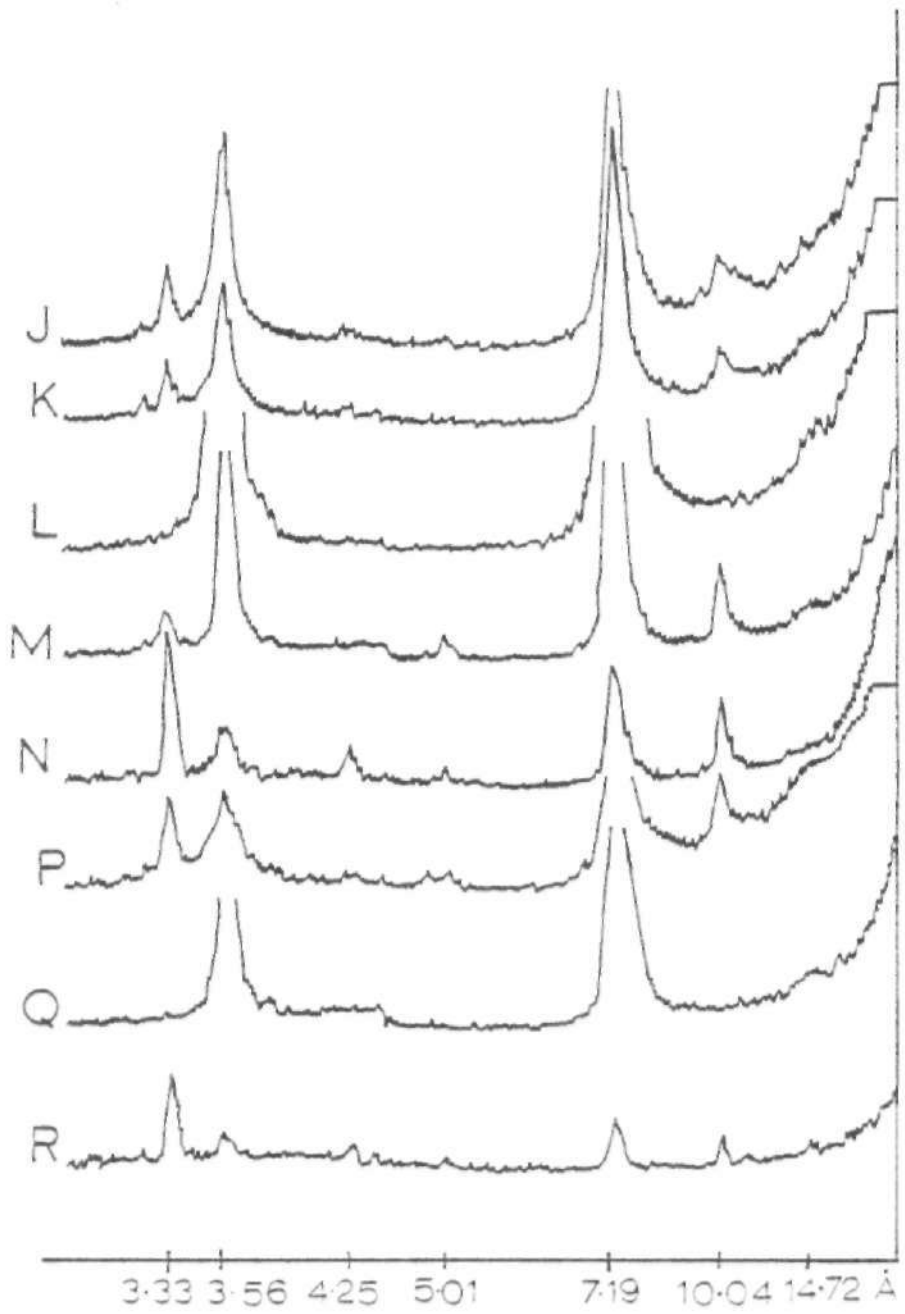


Figure 4.6 (continued)

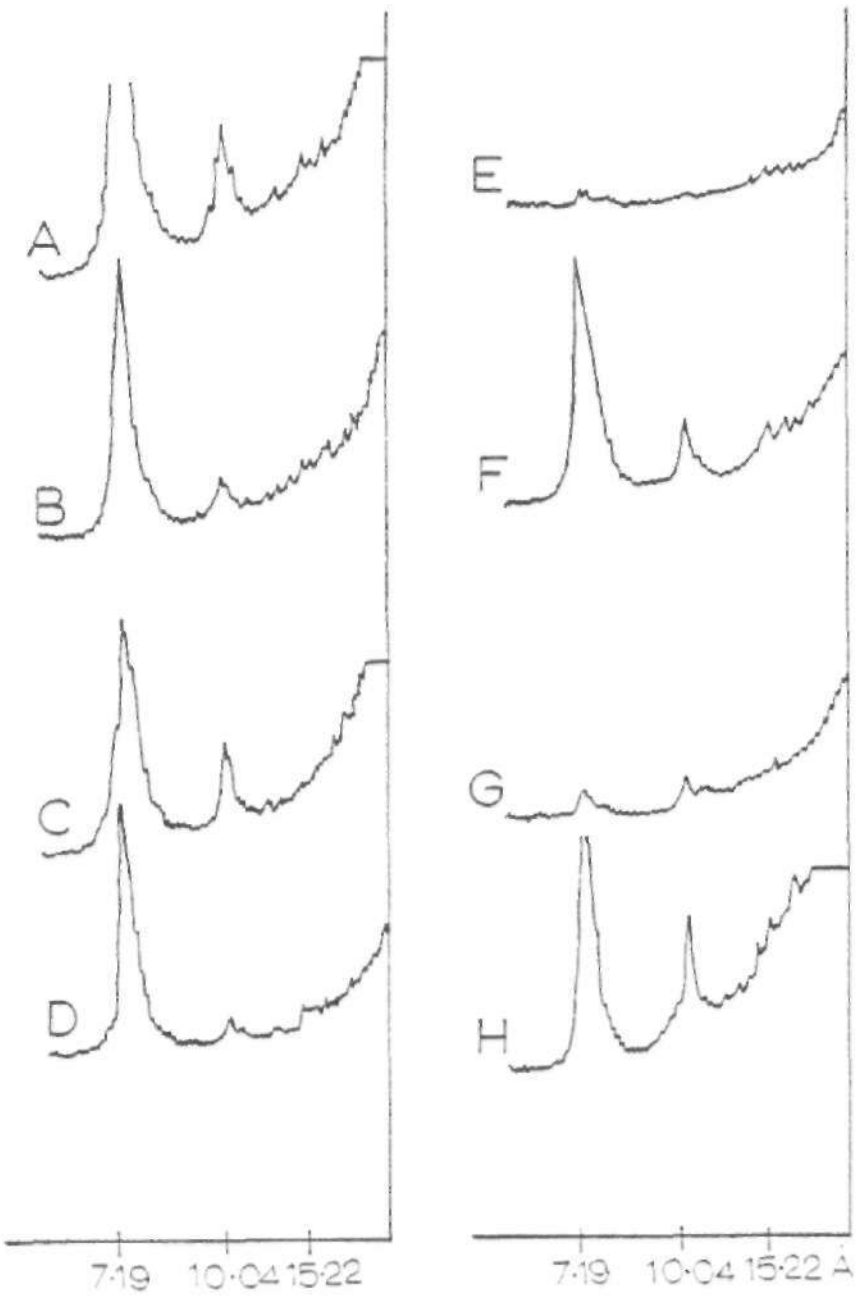


Figure 4.7. X-ray diffractograms of deferrated, Mg-glycolated clays (<2 μm); run at a 1000 counter-per-second range factor and a one-second time constant.

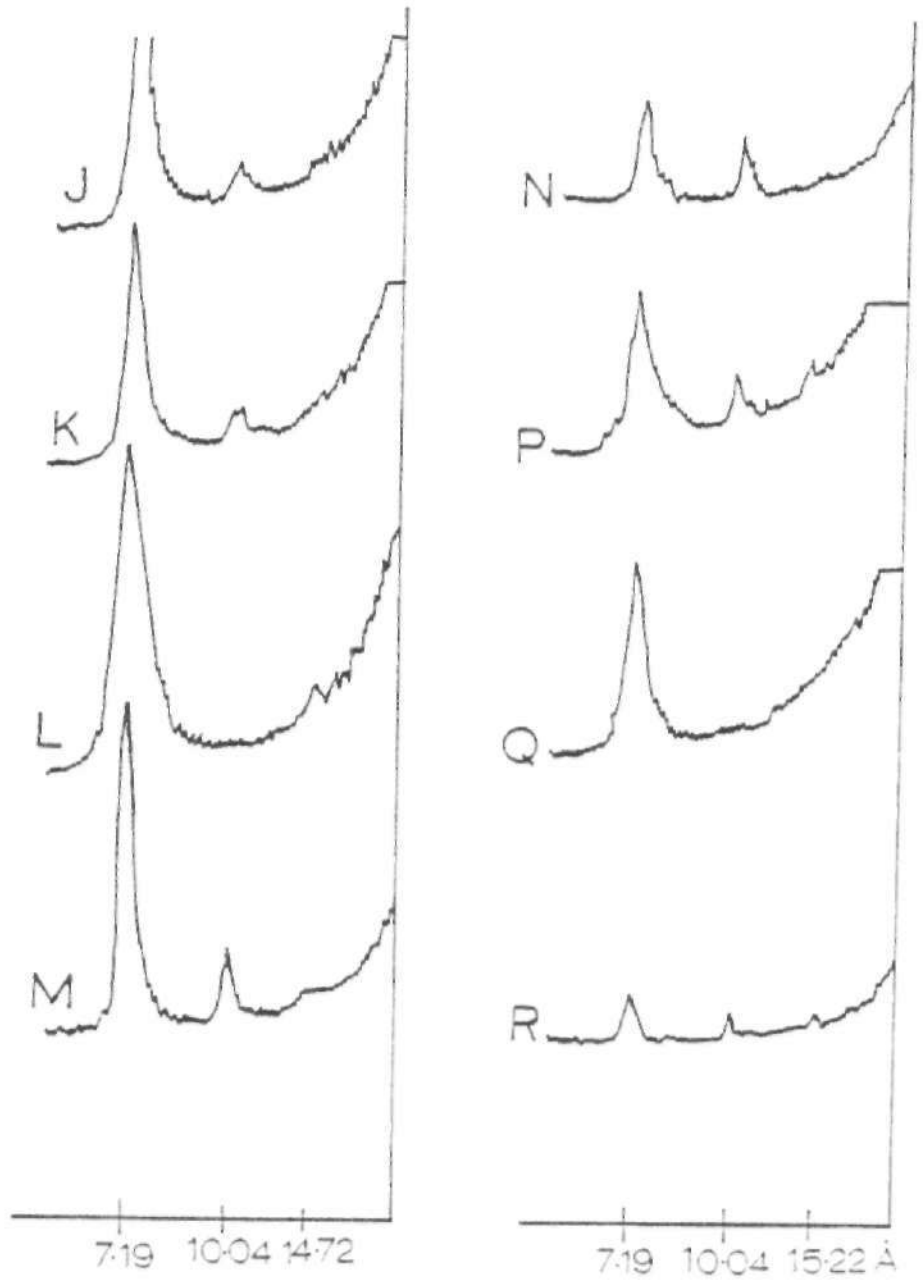


Figure 4.7 (continued)

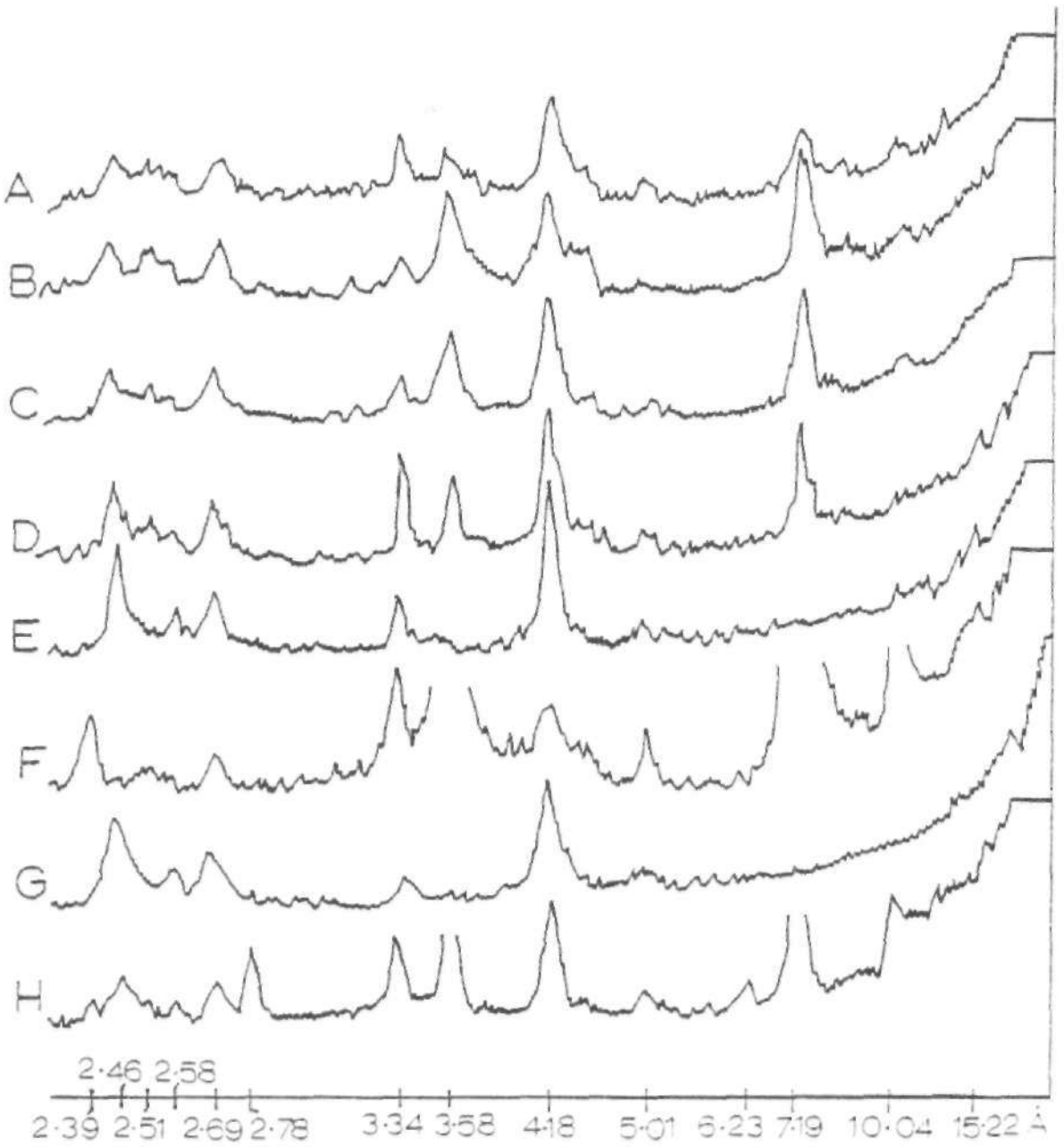


Figure 4.8. X-ray diffractograms of nondeferrated, K-saturated clays (<2 μm) at 25°C; run at a 250 counts-per-second range factor and a 2.5 second time constant.

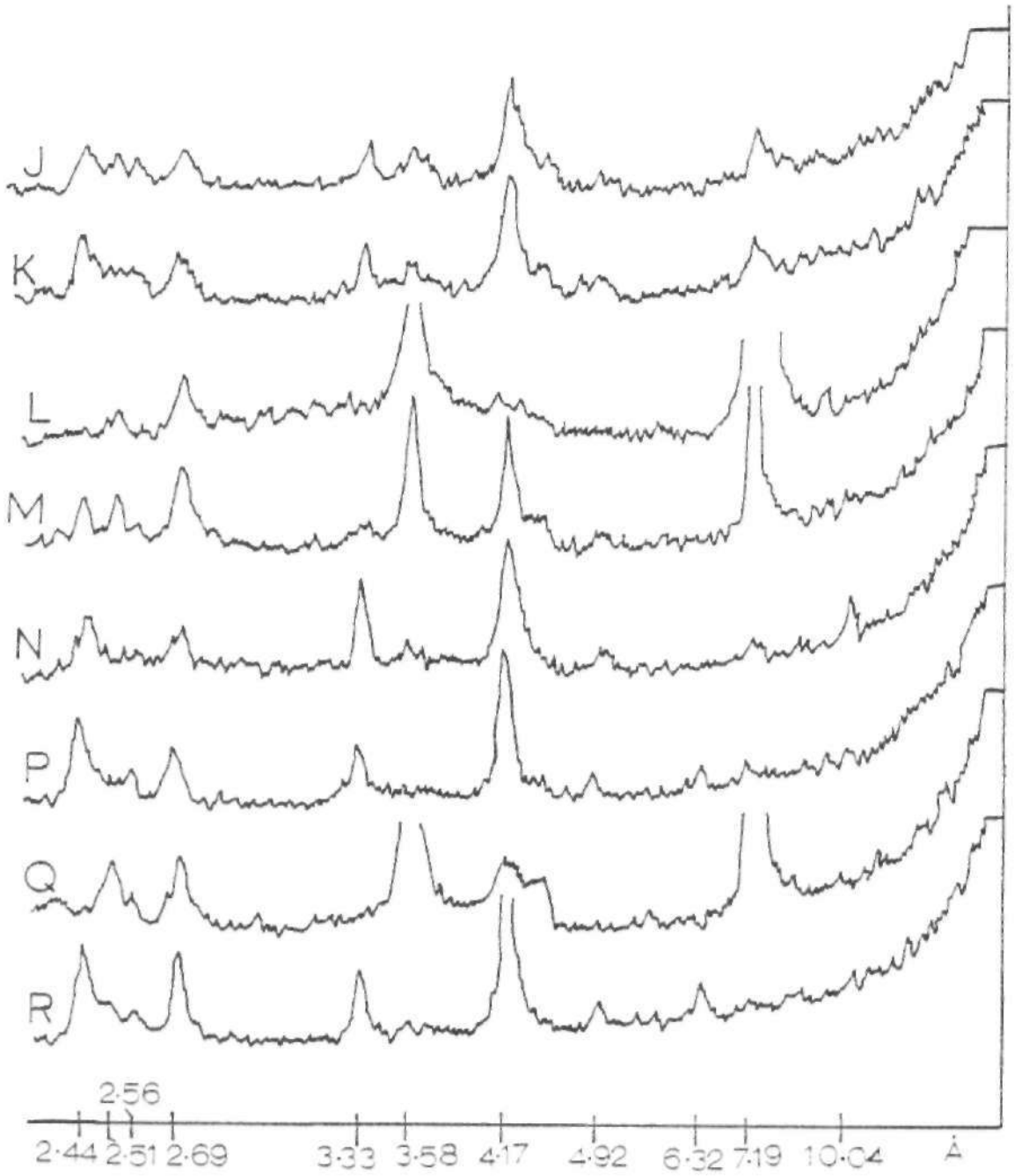


Figure 4.8 (continued)

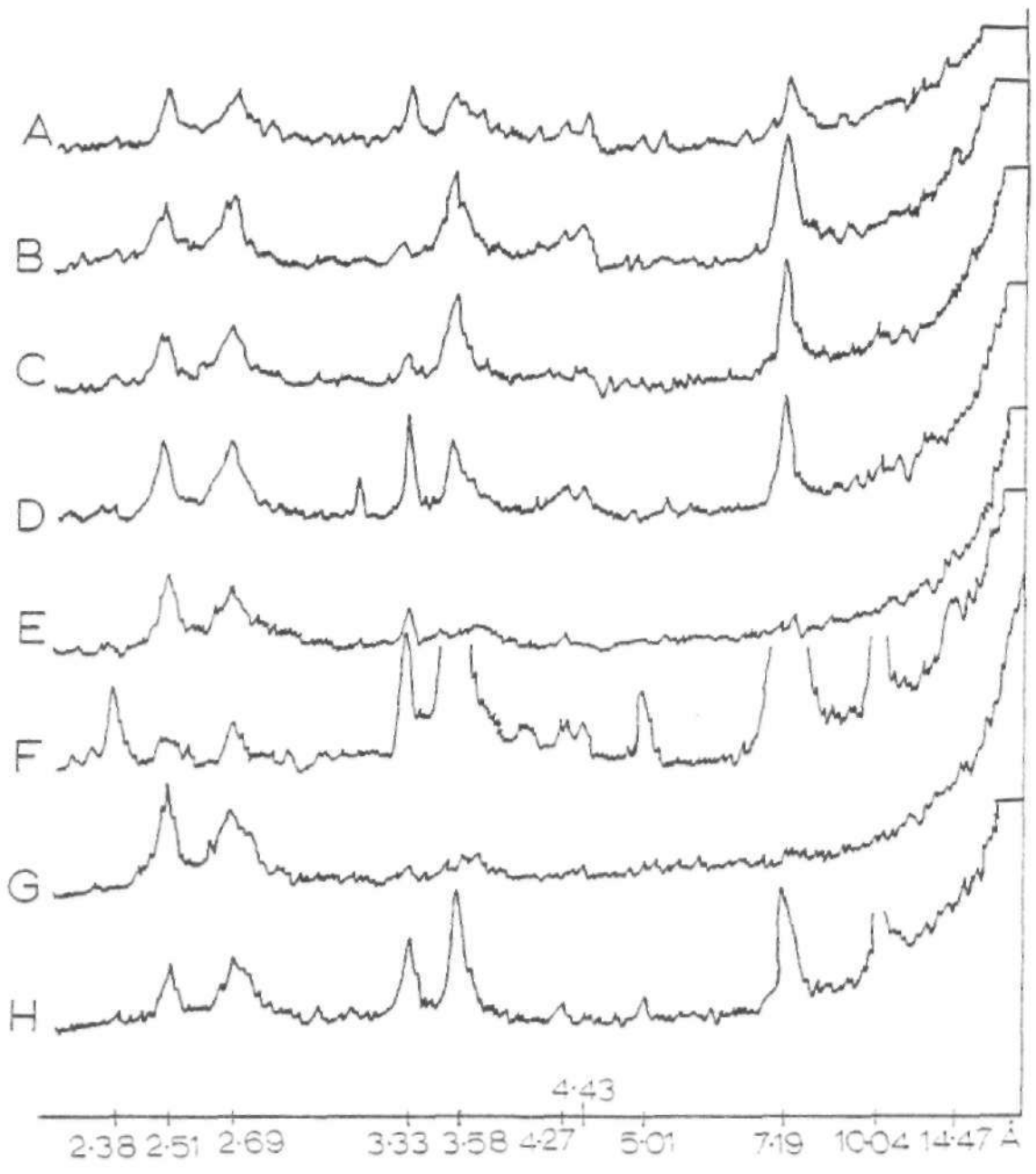


Figure 4.9. X-ray diffractograms of nondeferrated, K-saturated clays (<2 μm) at 350°C; run at a 250 counts-per-second range factor and a 2.5 second time constant.

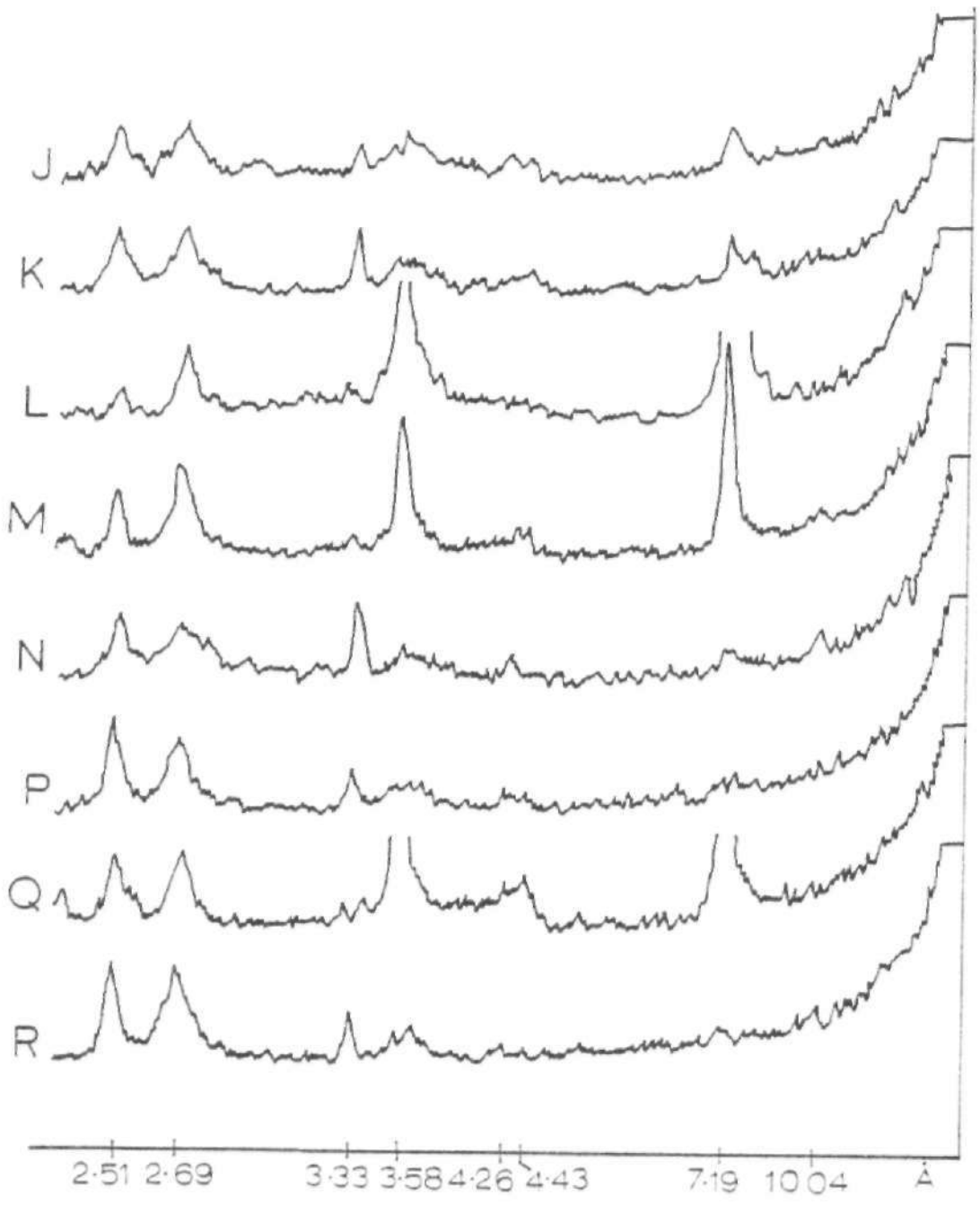


Figure 4.9 (continued)

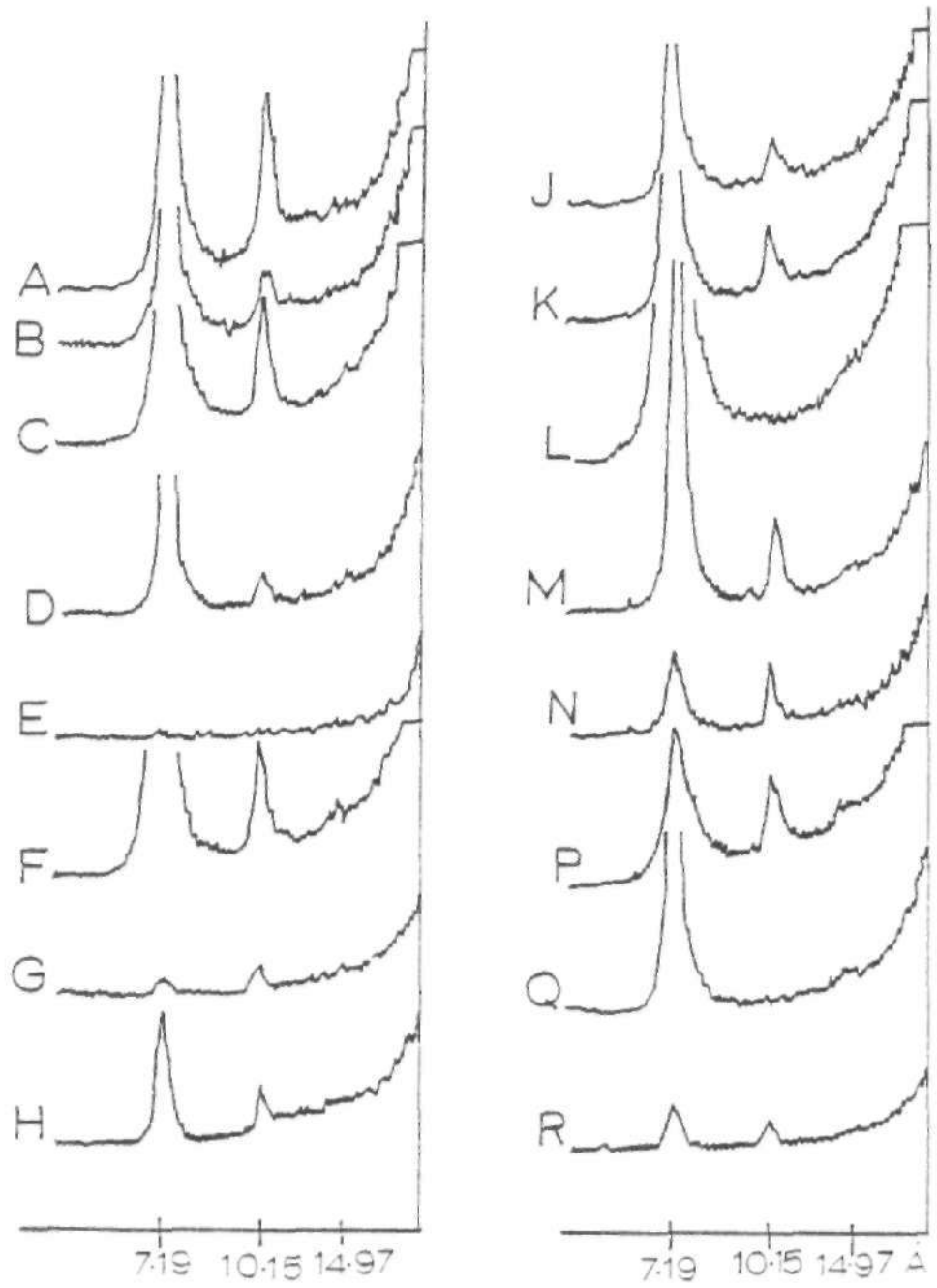


Figure 4.10. X-ray diffractograms of deferrated, K-saturated clays (<2 μm) at 25°C; run at a 1000 counts-per-second range factor and a one-second time constant.

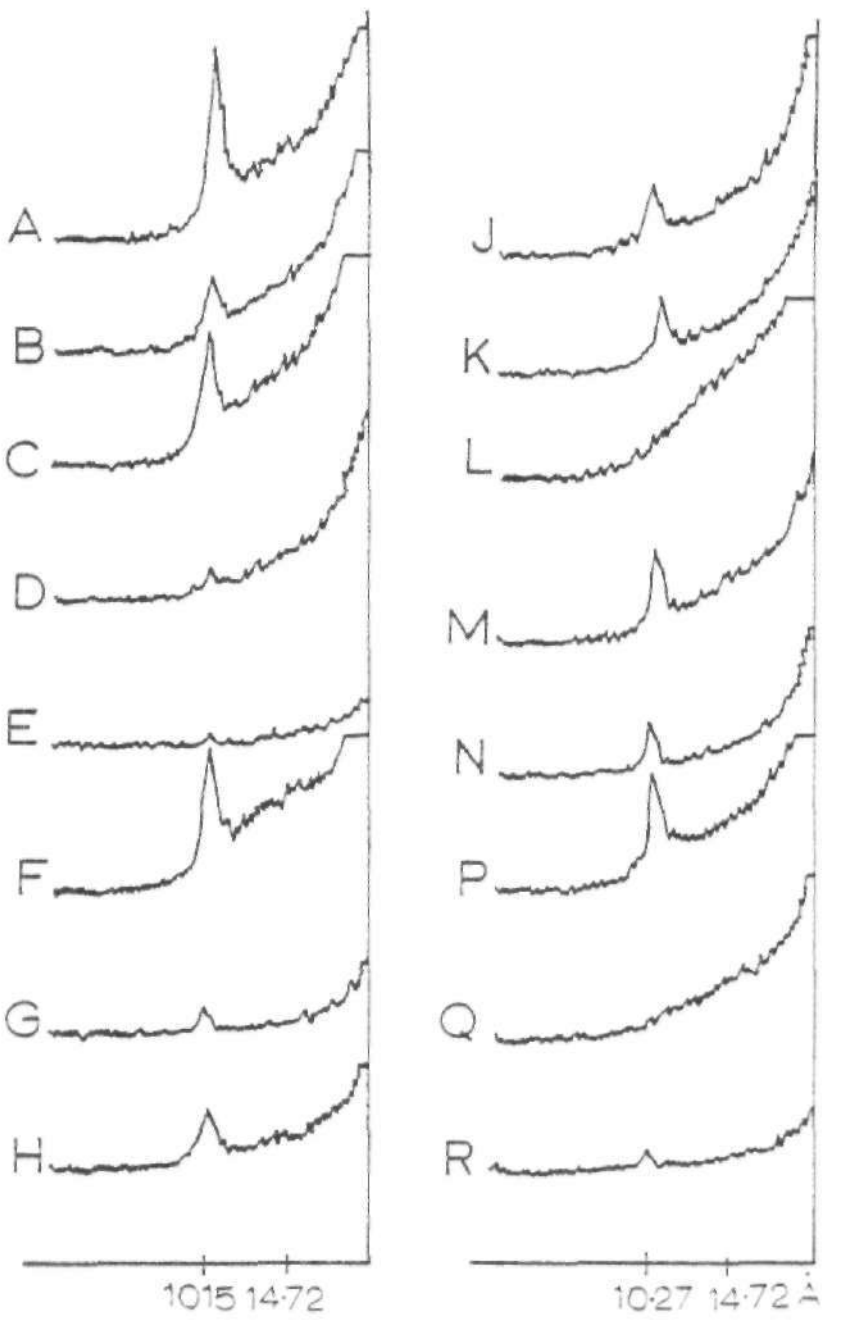


Figure 4.11. X-ray diffractograms of deferrated, K-saturated clays (<2 μm) at 550°C; run at a 1000 counts-per-second range factor and a one-second time constant.

This size fraction (< 2 μm) represents the active constituents (plasma) of the laterites. The clay fractions of the samples contain variable quantities of kaolinite, halloysite, goethite, hematite, hydroxy-interlayered vermiculite, lepidocrocite, quartz, muscovite and apatite. The dominant minerals common to all samples are few--kaolinite, goethite and hematite.

The 7.19, 3.57 and 2.37-A peaks are considered diagnostic of kaolinite. On heating (K-550^{o}C, Figure 4.11) the 7.19 A peak is absent. This provides additional evidence since the crystalline structure of kaolinite is destroyed with 550^{o}C heating. Mica was identified by the 10.04 and 5.0 A peaks. The intensities of these peaks were increased with iron removal and were not destroyed on heating. Biotite is unstable in weathering and occurs near its source in igneous or metamorphic rocks. Because of the length of time and intensity of weathering required for laterites to form, the mica peaks are identified as muscovite, although biotite could not be excluded from the analysis carried out. Reflections at 4.26 and 3.33 A are for quartz, those at about 4.17, 2.69 and 2.45 A in Figures 4.5, 4.8 and 4.9 indicate the occurrence of goethite (α-FeOOH) and the reflection doublet at 2.69 and 2.51 A represents hematite (α-Fe_2O_3).

Diffractograms of K-saturated and 350^{o}C-treated clay fraction (Figure 4.9) resulted in the conversion of goethite to hematite. The reaction 2 (α-FeOOH) + heat $\xrightarrow{\text{--------}}$ α-Fe_2O_3 + H_2O is used to demonstrate the reaction involved. The 4.18 and 2.45 A peaks present in Figure 4.8 are conspicuously absent in Figure 4.9 (after heating). Also in samples higher in goethite than hematite, (for example, samples C, D, E, G, H, N, P and R), the intensity of the 2.51 A peak of hematite increases after heating

at 350°C. However, in samples proportionately more in hematite than goethite, (for example, samples A, B, F, L, M and Q), there is no significant difference in the 2.51 A peak intensity before heating (Figure 4.8) and after heating at 350°C (Figure 4.9).

Lepidocrocite (α-FeOOH) was identified only in trace amounts in the three samples from Kemper County, Mississippi; Northampton County, North Carolina and Wake County, North Carolina (samples H, P, and R, respectively). An orange color in the field gives a good indication of the presence of lepidocrocite (Schwertmann and Taylor, 1977). The three samples above have a dry color of brownish yellow (10 YR 6/6), strong brown (7.5 YR 5/8) and yellowish red (5 YR 5/8), respectively. Soil lepidocrocite can be transformed into goethite although at a very slow rate (Schwertmann and Taylor, 1977).

Apatite $\{Ca_2\ Ca_3\ [PO_4]_3\ (OH, F)\}$ was identified only in one sample (from Kemper County, Mississippi) by its 2.79 A peak in Figures 4.5 and 4.8.

DTA thermograms of the untreated clay fraction are not reproduced. Data obtained by comparison of the endothermal peak areas of samples with those of kaolinite standards are given in Table 4.8. The range is from a low of about 4% to a high of 80%. The thermograms do not show any measurable quantities of gibbsite and quartz in the clay fraction. The dominant iron mineralogy was obtained by examining the DTA thermograms together with the X-ray diffractograms.

An estimate of the "amorphous" constituents present in the samples was obtained by alkali boiling of the samples (Section 3.4.4). The

Table 4.8. DTA determined content of kaolin minerals and iron minerals in the clay fraction (< 2 μm).

Sample	Kaolin Minerals	Dominant Iron Mineralogy
	----- % -------	
A - (Potiskum, Nigeria)	60	Hematite
B - (Samaru, Nigeria)	73	Hematite
C - (Thailand)	44	Goethite
D - (Bolivia)	44	Goethite
E - (Jones, Co., N. C.)	16	Goethite
F - (Charters Towers, Austr.)	76	Hematite
G - (Neshoba Co., Ms.)	9	Goethite
H - (Kemper Co., Ms.)	30	Goethite
J - (Ibadan, Nigeria)	43	Goethite/Hematite
K - (Ibadan, Nigeria)	31	Goethite/Hematite
L - (Victoria Pt., Austr.)	61	Hematite
M - (Brazil)	62	Hematite
N - (Harnett Co., N. C.)	7	Goethite
P - (Northampton Co., N. C.)	35	Goethite
Q - (Pistol Range, Austr.)	80	Hematite
R - (Wake Co., N. C.)	4	Goethite

results are presented in Table 4.9. The molar SiO_2/Al_2O_3 ratio ranges from 1.89 to 5.69. Tables 4.8 and 4.9 indicate that the samples with high contents of kaolinite (≥ 31%) have a SiO_2/Al_2O_3 ratio close to two. The SiO_2/Al_2O_3 molar ratio of kaolinite is 2:1. The odd sample is F (from Charters Towers, Australia) which has an estimated 76% kaolinite and a SiO_2/Al_2O_3 molar ratio of 5.69. It has the highest absolute amount of SiO_2 (13.7%) but a low value of Al_2O_3 (4.1%). This may suggest dissolution of highly siliceous aluminosilicates. The X-ray diffractograms (Figures 4.5 through 4.11) also indicate that the Charters Towers sample (F) is the only one with significant 14-15 Å peak intensity. Hence, the high SiO_2/Al_2O_3 ratio could indicate dissolution of poorly crystalline hydroxy-Al interlayered silicates.

Samples showing high absolute values of SiO_2 and Al_2O_3 but low SiO_2/Al_2O_3 molar ratios are assumed to contain high amounts of amorphous aluminosilicates due to very intense weathering conditions in their various environments of formation. Conversely, the low absolute amounts of SiO_2 and Al_2O_3 dissolved but high SiO_2/Al_2O_3 ratios suggest more highly crystalline minerals.

Hashimoto and Jackson (1960) stated that the selective dissolution method with 0.5 N KOH dissolved amorphous materials completely while only slightly attacking the highly crystalline layer silicates. However, Calvert et al., (1979) noted that this method also dissolved gibbsite and some poorly crystalline 1:1 minerals. The samples used in the present study did not contain measurable amounts of gibbsite and so no portion of

Table 4.9. Quantitative analysis of the deferrated clay minerals dissolved in boiling 0.5 N KOH.

Sample	SiO_2	Al_2O_3	Molar[a] SiO_2/Al_2O_3
A - (Potiskum, Nigeria)	8.82	7.35	2.04
B - (Samaru, Nigeria)	10.51	9.46	1.89
C - (Thailand)	9.05	7.26	2.12
D - (Bolivia)	8.24	6.54	2.14
E - (Jones Co., N. C.)	5.92	3.05	3.30
F - (Charters Towers, Austr.)	13.65	4.08	5.69
G - (Neshoba Co., Ms.)	10.07	3.48	4.92
H - (Kemper Co., Ms.)	3.03	1.62	3.18
J - (Ibadan, Nigeria)	11.14	7.84	2.42
K - (Ibadan, Nigeria)	11.41	7.92	2.45
L - (Victoria Pt., Austr.)	6.73	5.45	2.10
M - (Brazil)	7.09	6.08	1.98
N - (Harnett Co., N. C.)	7.83	3.69	3.61
P - (Northampton Co., N. C.)	9.19	7.07	2.21
Q - (Pistol Range, Austr.)	12.56	10.09	2.12
R - (Wake Co., N. C.)	4.78	2.60	3.13

[a]No adjustment made for gibbsite content since very few samples contained any trace of it.

Table 4.10. Partial mineralogy of the clay fraction: Kaolinite by DTA, iron by CBD extraction, and mica by K_2O content.

Sample	Kaolin Minerals	Fe_2O_3	Muscovite	Sum
	---------- % ----------			
A - (Potiskum, Nigeria)	60	32	4	96
B - (Samaru, Nigeria)	73	16	1	90
C - (Thailand)	44	41	6	91
D - (Bolivia)	44	21	3	68
E - (Jones Co., N. C.)	16	44	1	61
F - (Charters Towers, Austr.)	76	5	9	90
G - (Neshoba Co., Ms.)	9	45	1	55
H - (Kemper Co., Ms.)	30	32	8	70
J - (Ibadan, Nigeria)	43	23	6	72
K - (Ibadan, Nigeria)	31	23	5	59
L - (Victoria Pt., Austr.)	61	32	1	94
M - (Brazil)	62	32	2	96
N - (Harnett Co., N. C.)	7	30	3	40
P - (Northampton Co., N. C.)	35	27	6	68
Q - (Pistol Range, Austr.)	80	19	1	100
R - (Wake Co., N. C.)	4	36	1	41

the Al_2O_3 dissolved by this procedure is attributable to gibbsite dissolution.

The partial mineralogy of the clay fractions of all 16 samples is summarized in Table 4.10. The 1:1 type minerals were obtained by DTA (Table 4.8), the iron oxides were determined by CBD extraction (Table 4.3), and mica was calculated from the weight percent K_2O (Table 4.5), assuming mica contains 10 percent K_2O (Jackson, 1974).

Koalin minerals make up the major component in most of the samples. Iron oxides follow closely and exceed the kaolin content of five samples (E, N, R, G, and H)--from Jones, Harnett and Wake Counties in North Carolina, Neshoba and Kemper Counties in Mississippi, respectively. Mica content is negligible in some and rises to a high of 9 percent. Together these minerals account for 40 to 100 percent of the clay mineralogy.

4.5 Activity of the Iron Oxides

The high amount of total iron in many soils associated with laterite is of great concern in soil development and classification. However, the total amount is probably not as important as its effects on certain soil properties (Lutz, 1938). Several lateritic soils have been described that owe their properties to their high iron content. However, some soil properties, including color are not directly proportional to the amount of iron present in these soils.

4.5.1 Acid Ammonium Oxalate Data

The acid ammonium oxalate method extracts mainly the amorphous forms of inorganic Fe and Al (McKeague and Day, 1966; Juo et al., 1974). The

Table 4.11. Acid ammonium oxalate extractable Fe, Al, and Si.

Sample	Fe	Al	Si	$\frac{Fe_{ox}}{Fe_{CBD}}$
	---------- % ----------			
A - (Potiskum, Nigeria)	0.67	0.50	0.26	3.04
B - (Samaru, Nigeria)	0.22	0.49	0.22	2.02
C - (Thailand)	0.22	0.44	0.21	0.78
D - (Bolivia)	0.44	0.76	0.33	2.95
E - (Jones Co., N. C.)	2.29	0.12	0.11	7.48
F - (Charters Towers, Austr.)	0.05	0.39	0.13	1.52
G - (Neshoba, Ms.)	0.95	0.15	0.14	3.05
H - (Kemper, Ms.)	11.18	0.43	0.32	49.64
J - (Ibadan, Nigeria)	0.78	0.78	0.35	4.81
K - (Ibadan, Nigeria)	0.71	0.81	0.34	4.43
L - (Victoria Pt., Austr.)	0.15	0.27	0.09	0.67
M - (Brazil)	0.20	0.43	0.19	0.89
N - (Harnett Co., N. C.)	1.09	0.29	0.18	5.20
P - (Northampton Co., N. C.)	2.75	0.91	0.37	14.41
Q - (Pistol Range, Austr.)	0.28	0.36	0.15	2.08
R - (Wake Co., N. C.)	1.82	0.17	0.12	7.15

data obtained by extraction of the clay fractions of the laterite samples is given in Table 4.11.

The amounts of Fe, Al and Si extracted by this method are relatively smaller than that extracted by the CBD treatment. Generally, the amount of Si solubilized by this method was consistently lower than the amount of Fe and Al. The relative distribution of amorphous to total free Fe oxides (CBD extracted Fe) within each sample is expressed as "active Fe ratio" (Juo et al., 1974), which is obtained as follows:

$$\text{active Fe ratio} = \frac{\text{oxalate Fe}}{\text{dithionite Fe}} \times 100$$

Results are also given in Table 4.11. Except for two of the samples (H and P), the active iron ratio was not more than 7.5 percent. This clearly indicates that higher proportions of Fe oxides in the samples are present as crystallized forms rather than in a disordered state. The environmental conditions (high temperature and prolonged dry season) have been suggested by Juo et al., (1974) as being responsible for the low content or amorphous Fe and Al in their samples from Nigeria. As pointed out by Sherman et al., (1964), drying at elevated temperature causes the amorphous Fe and Al oxides to dehydrate and subsequently shift to a system of greater crystallinity.

Karamanova (1978) also showed that soils with a higher moisture content in all natural zones have a considerably higher absolute and relative content of amorphous iron than automorphic soils. The amount of this iron increases with the degree of hydromorphism, reaching 50-60 percent of the content of non-silicate iron (free iron) in strongly gleyed soils.

Table 4.12. Total and external surface areas of the clay fraction (< 2 μm).

Sample	With Fe		Without Fe		Iron[a] oxides
	EGME (total)	N_2 (external)	EGME	N_2	
	m^2/g				
A - (Potiskum, Nigeria)	83	68	26	14	144
B - (Samaru, Nigeria)	72	62	23	14	214
C - (Thailand)	69	60	24	23	96
D - (Bolivia)	65	48	11	7	136
E - (Jones Co., N. C.)	55	50	8	4	92
F - (Charters Towers, Austr.)	37	35	31	15	278
G - (Neshoba, Ms.)	85	79	4	4	139
H - (Kemper, Ms.)	93	89	9	7	227
J - (Ibadan, Nigeria)	78	75	51	25	165
K - (Ibadan, Nigeria)	72	60	22	12	150
L - (Victoria Pt., Austr.)	82	54	10	8	136
M - (Brazil)	54	43	10	5	103
N - (Harnett Co., N. C.)	48	45	21	11	103
P - (Northampton Co., N. C.)	62	48	17	11	112
Q - (Pistol Range, Austr.)	69	59	28	24	163
R - (Wake Co., N. C.)	39	38	8	5	77

[a]Calculated from the formula:

$$A = \frac{S_N - S_{CBD}\,(1-W)}{W}$$

where A = derived surface area of Fe_2O_3,

S_N = specific surface area of nondeferrated clay,

S_{CBD} = gravimetric weight loss due to CBD treatment per gram of clay.

W

Studying the water content of the 16 laterite samples (Table 4.5) in relation to the active iron ratio (Table 4.11) does not show a definite trend. However, the sample from Kemper County, Mississippi (sample H) that had the highest water content of 23.6% also contains the highest amount of amorphous iron as well as the highest active iron ratio. This may be tortuitous.

There is some relationship between color of the samples and the active iron ratios. Samples with more yellowish hues (7.5 YR and 10 YR) have high active iron ratios while those with reddish hues (2.5 YR and 10 R) have low active iron ratios (Figure 4.12).

4.5.2 Surface Area Determinations

Surface area data for the nondeferrated and deferrated (CBD-treated) clay fractions are given in Table 4.12. The EGME surface areas are consistently higher than those obtained by N_2 adsorption. In this study the EGME values are higher than the N adsorption values by a factor of 1.0 to 1.5 for the nondeferrated samples. This little difference (low ratio) can be indicative of the degree of association of the iron hydroxides with clay surfaces. The surface areas seem to indicate that most of the iron was present as coatings binding together or physically blocking clay surfaces.

Gallez et al., (1976) reported that the EGME surface areas of some Nigerian soils were higher than corresponding N_2-adsorption values by a factor of 2.5. They reported surface areas of iron oxides as high as 324 m^2/g and concluded that in such soils a large portion of the Fe oxides existed in fine, discrete particles. The calculated surface areas of the laterite samples under investigation are reported in Table 4.13. The

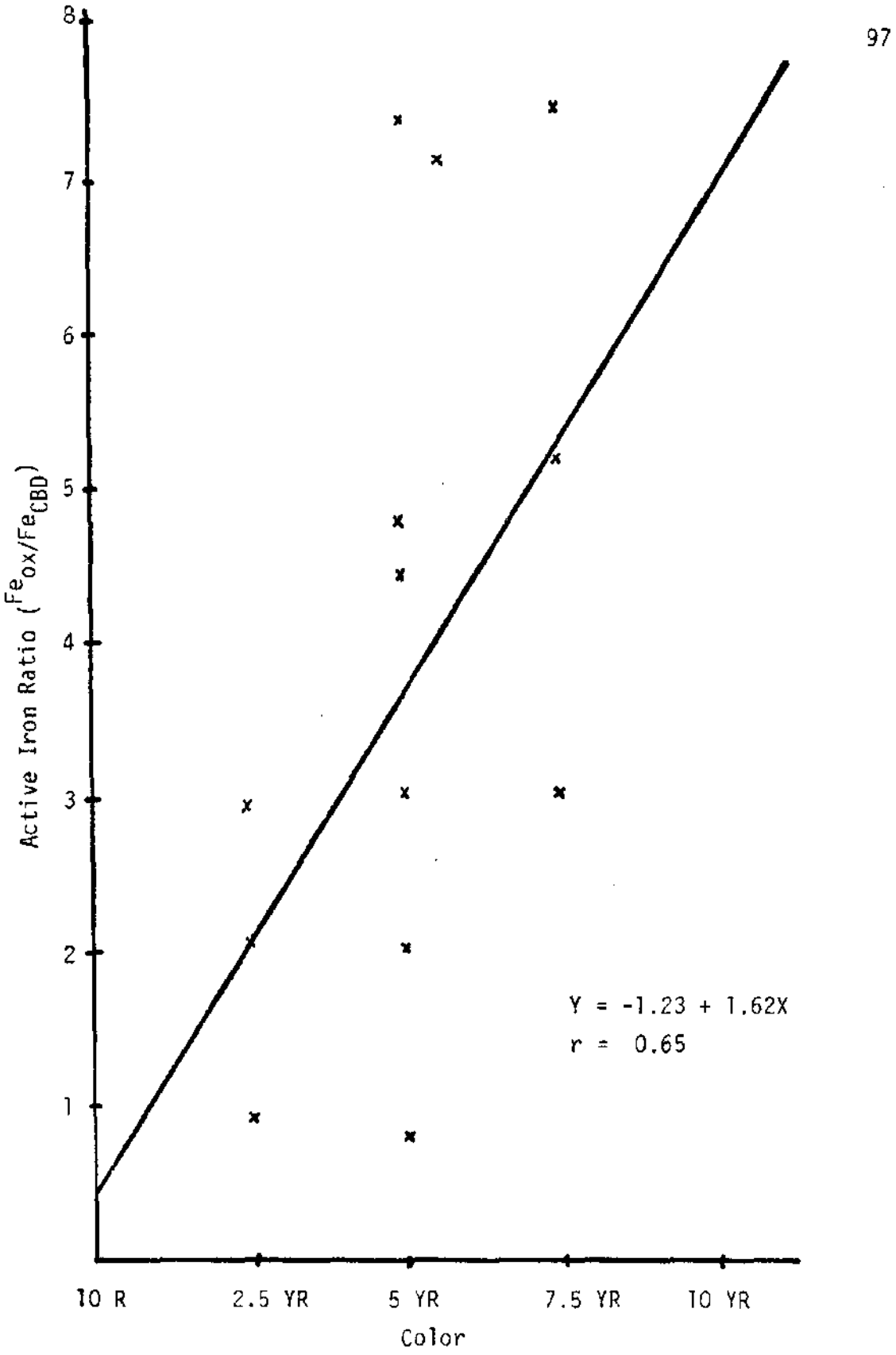


Figure 4.12. Plot of color of samples against the active iron ratio.

Table 4.13. Comparison of gravimetric and calculated weight losses resulting from CBD extraction of the clay fraction.

Sample	Gravimetric weight loss (1)	Calculated weight loss (Fe_2O_3 + Al_2O_3 + SiO_2) (2)	(1) - (2)
	---------- % ----------		
A - (Potiskum, Nigeria)	41.4	39.9[a]	1.5
B - (Samaru, Nigeria)	24.0	22.6	1.4
C - (Thailand)	50.8	48.9[a]	1.9
D - (Bolivia)	31.8	29.2	2.6
E - (Jones Co., N. C.)	52.0	48.2[a]	3.8
F - (Charters Towers, Austr.)	7.6	7.1	0.5
G - (Neshoba Co., Ms.)	55.7	51.9	3.8
H - (Kemper Co., Ms.)	37.2	35.6[a]	1.6
J - (Ibadan, Nigeria)	35.7	33.2[a]	2.5
K - (Ibadan, Nigeria)	34.7	32.6[a]	2.1
L - (Victoria Pt., Austr.)	36.0	35.3	0.7
M - (Brazil)	38.8	36.1	2.7
N - (Harnett Co., N. C.)	37.0	36.5	0.5
P - (Northampton Co., N. C.)	36.8	34.4	2.4
Q - (Pistol Range, Austr.)	25.1	23.0	2.1
R - (Wake Co., N. C.)	45.9	42.4	3.5

[a]Includes % MnO_2

values range from 77 to 278 m^2/g, with the majority of the samples ranging between 103 and 165 m^2/g. An interesting aspect of the present data is that the largest surface area of values of iron are observed in two categories of samples: Those with low amount of CBD extractable Fe (B and F), and those with high active iron ratio (H in Table 4.11). Thus, the larger the surface area of the iron oxides, the larger the proportion of iron oxides remaining as fine, discrete particles. This is in agreement with the findings of Greenland and Oades (1968) and Gallez et al., (1976) who reported interactions among amorphous materials and crystalline minerals in the clay fraction, for example, kaolinite-goethite interaction, may result in mere mechanical complexes whereby the kaolinite surfaces did not become coated by iron oxyhydroxide.

Probably only three samples (B from Samaru, Nigeria; F from Charters Towers; and H from Kemper County, Mississippi) have most of their iron oxides in fine, discrete particles, while the remaining 13 samples have a large proportion of their iron oxides either as aggregates or coatings over the silicate minerals.

4.6 Statistical Analysis

Using the 21 laterite components given in Section 3.6 with no a priori weighting of data a computer-generated cluster map was reproduced (Figure 4.13), together with the maximum distance within a cluster "d." One cluster is formed for each sample in the analysis. The two closest clusters are combined into one cluster, then the closest of the new set of clusters are combined into a single cluster, and so on.

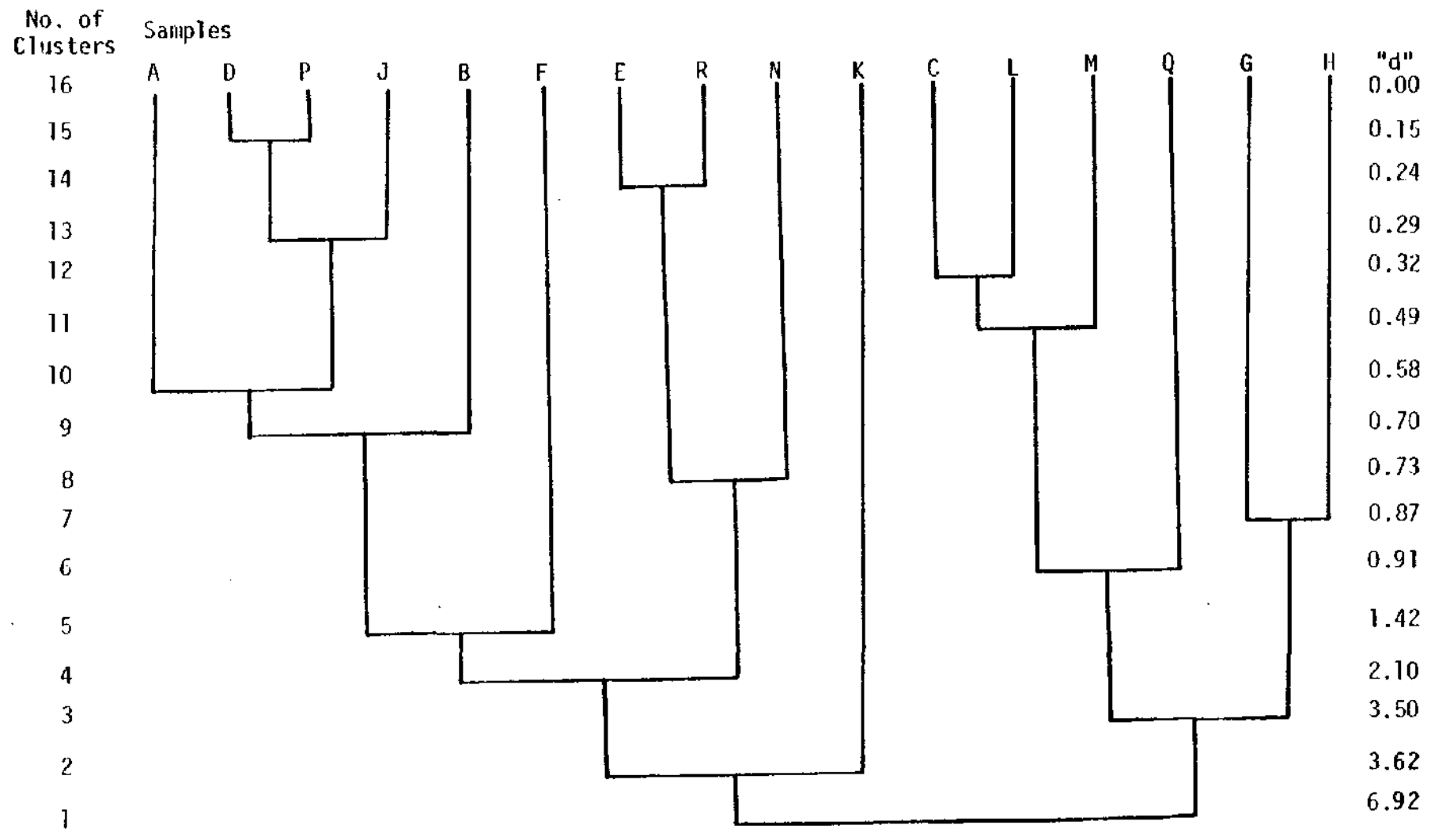


Figure 4.13. Cluster map.

The small "d" values indicate that the samples so connected together are very similar with respect to the parameters studied. For example, the samples from Bolivia (D) and Northampton County, North Carolina (P) are the most similar, with a "d" of 0.15. Conversely, a large "d" value indicates that the samples are highly dissimilar, for example, the sample from Ibadan, Nigeria (K), is very dissimilar to the sample from Thailand (C) having a "d" value of 6.92.

Based on the cluster map (Figure 4.13), which itself is derived from the physical, chemical and mineralogical components, the samples have been grouped into five similarity groups as follows:

Group 1 comprises samples A, D, P, H, and B;

Group 2 comprises samples E, R, and N;

Group 3 comprises samples C, L, M, and Q;

Group 4 comprises samples G and H; and

Group 5 comprises samples F and K that cannot fit into the other four groups.

Group 1 is made up of three samples from Nigeria, and one each from Bolivia, and Northampton County, North Carolina. Group 2 consists of three samples from North Carolina (Jones, Wake and Harnett Counties). Group 3 consists of two samples from Australia, and one each from Thailand and Brazil. Group 4 consists of the two samples from Mississippi together with one sample each from Australia and Nigeria. In terms of differences between the samples, samples in Groups 1 and 2 are most dissimilar to samples in Groups 3 and 4, as shown by the large d of 6.92.

5. SUMMARY AND CONCLUSIONS

The word laterite covers a rather large succession of weathering products. Yet all these products are colored red or dark brown. In many areas of the world scientists have routinely identified laterites either on the basis of color or on its ability to harden irreversibly.

The present study was, therefore, concerned in determining if materials called laterites in one region or continent is the same as those bearing the same name in other regions. The samples used for this study were from five continents: Africa - 4 samples, Australia - 3 samples, Asia - 1 sample, North America - 6 samples, and South America - 2 samples.

Laterite crusts occupy distinct topographical sites. These sites are the uplands or high grounds, and the lower slopes or low grounds. Accordingly, such laterites are called high and low level laterites. The samples used for this study were definitely from both topographic locations. If the samples were formed where they were collected, then they formed over various parent materials, for example, granites, basalts, schists, sandstones and coastal plain sediments. This shows an apparent lack of a direct relationship between laterites and lithology. Figure 4.13 shows that the sample from Bolivia formed over basalt is very similar to the sample from Northampton County, North Carolina, formed from coastal plain sediments. Conversely, the samples from Wake and Jones Counties of North Carolina (R and E) are formed from coastal plain sediments, the same as the two samples from Mississippi (G and H), yet they are shown to be very dissimilar. This is accounted for by the fact that the same rocks weather

to form different materials in different areas, and that quite different rocks weather to similar materials. This certainly implies that the other environmental factors are of greater significance to the nature of the end-product than is the lithology, and thus dictate the ultimate nature or occurrence of a laterite.

On a smaller scale the lithological control is more evident, for within a limited area the other environmental influences such as climate and vegetation might be expected to be less variable. Thus, the three samples from Wake, Jones and Harnett Counties are in the same similarity group. Likewise, the samples from Neshoba and Kemper Counties in Mississippi fall into the same similarity grouping. The directness of the lithological control may be debatable but geology to some extent controls the local environment.

Chemically, lateritic materials are composed of a high percentage of sesquioxides. In most occurrences iron oxides, aluminum oxides and silica predominate. The present study indicates that not only iron rich (44.6% Fe_2O_3), but also iron poor materials (4.7% Fe_2O_3) can be described as laterites. The ability of the clay to harden irreversibly or en masse with such a low iron content is interesting. This suggests that it is something more than the absolute iron content which is responsible for the characteristic ability to harden en masse. It is, therefore, not possible to define laterite on the basis of iron distribution.

The low contents of magnesium, calcium, sodium, potassium and manganese in these samples can be used as evidence of the long and intense

weathering processes that have to take place before laterites are formed. The bases are removed or lost during laterization.

The mineralogical data indicate that the most common crystalline minerals are hematite and goethite. The resultant color of the samples is directly related to the dominant iron mineralogy, but not the amount of free iron oxides. Lepidocrocite is a minor component of the iron oxides. Kaolinite is usually the predominant clay mineral and is followed by halloysite and muscovite. Vermiculite, apatite and microcline are only infrequently identified. Quartz is frequently identified but is assumed to be only an inert component of laterites. Quartz is believed to be derived from the underlying acidic rocks and so could be a good indication of the nature of the parent material. The accumulation of these resistant or inert materials points to a severe weathering process.

Correspondingly small amounts of "amorphous" iron were extracted by chemical techniques. The low values for calculated surface areas for the iron oxides suggest that a large proportion of their constituent iron oxides are closely associated with the surfaces of silicate minerals (possibly as coatings). The frequent occurrence of iron-oxide coatings on quartz grains would seem to support this conclusion. These oxides also act as cementing agents binding resistant soil minerals together, and upon dehydration become irreversibly hardened.

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7. APPENDIX

Appendix Table 7.1. Reaction of Ground Samples.

Sample	1:1 Sample/N KCl	1:1 Sample/water	Δ(1-2)
	pH		
A	5.42	6.47	-1.05
B	5.33	5.84	-0.51
C	5.17	5.73	-0.56
D	4.89	5.69	-0.80
E	5.65	6.07	-0.42
F	4.07	5.35	-1.28
G	5.95	6.27	-0.32
H	4.63	5.04	-0.41
J	5.77	6.82	-1.05
K	4.85	5.55	-0.70
L	4.77	5.25	-0.48
M	5.62	6.42	-0.80
N	5.91	6.07	-0.16
P	5.66	6.30	-0.64
Q	4.76	5.25	-0.49
R	6.28	6.38	-0.10