X-RAY DIFFRACTION STUDIES OF CLAY MINERALS IN SELECTED SOILS OF CAPRICORN DISTRICT IN LIMPOPO PROVINCE

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A MINI DISSERTATION SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF: MASTER OF SCIENCE IN AGRICULTURE IN THE SCHOOL OF AGRICULTURAL AND ENVIRONMENTAL SCIENCES IN THE FACULTY OF HEALTH, SCIENCE AND AGRICULTURE AT THE UNIVERSITY OF LIMPOPO, TURFLOOP CAMPUS, SOUTH AFRICA

MAJOR COURSE: **SOIL SCIENCE**

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DECLARATION

I declare that the dissertation hereby submitted to the University of Limpopo for the degree of Master of Science in Soil Science has not previously been submitted by me for a degree at this or any other University, that it is my work in design and in execution, and that all material contained therein has been duly acknowledged.

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DEDICATION

To my loving mother

Nanikie Aksa Seabi

I would like to dedicate these lines

as a token of my love for you.

My journey as a scholar to this level was not a simple presumption of the future foretold, but was through your hard work and "dedication" to my success. Your sacrifices never went unnoticed and I would like to extend my sincere gratitude to your personal commitment in my upbringing and to all the wisdom you imparted in me. Along the road there have been many who took part in seeing that my end was successful and I appreciate their efforts, but you outstand them all. You have been a mother, a friend and a mentor through every step of the way, encouraging me all the time. Truly I am thankful.

Above all I would love to dedicate this to my loving and caring "Father" in Heaven, God Jehovah Elohim. I believe that my mother's ability and strength to love and support me was not a mere natural phenomenon of maternal instinct, but was indeed a mastering of your creative power in working through her to grant me all there is for me according to Your will and purpose in my life. I appreciate all the grace and favour You poured upon my life in strength and ability to accomplish the assignment that was before me. I appreciate also the favour you gave me with all people who took part in making sure that I reach the end of the journey in finishing the work at hand, most especially Prof. Georges-Ivo Ekosse. Truly he has been both an inspiration and a good friend, mentoring me with absolute excellence.

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ABSTRACT

Soil clay minerals are secondary minerals formed by low temperature reactions in the soil through weathering. These minerals are highly reactive and greatly influence the chemical and physical properties of many soils. Limpopo Province has a great diversity of soils that differ over a wide range of landscapes and climatic regions. Their diversity offer interesting research opportunities in terms of their physical and mineralogical properties. Weathering of the parent materials and soils over the past decades has lead to the production of a wide variety of soil clay minerals. The main chemical reactions, such as hydrolysis, hydration, dehydration, oxidation, reduction, and carbonation, take place in the solum as well as in the parent material and are responsible for the formation of new mineral products in the soil. Although clay minerals have been researched in South Africa, representation in terms of site specific research and their implication to agricultural practices is still lagging behind. This study investigated the distribution patterns of soil clay minerals and their agricultural implications on selected soils within Limpopo Province. Samples were obtained from 3 soil types namely, Inceptic, Oxidic and Plinthic soil types in the study area. X-ray diffraction (XRD) analyses, X-ray fluorescence spectrometry (XRF) and scanning electron microscopy (SEM) techniques were used in determining the soil mineralogy, soil chemistry and soil genesis of the samples. The selected soils were found to be dominated by kaolinite, smectite and quartz in their clay fraction with respect to XRD. Quartz were dominant within a percentage range of 50% – 75%, followed by kaolinite within the percentage range of 23% - 49%; and lastly smectite within the percentage range of 0% - 22%. Feldspar and mica were also present in trace to minor quantities. XRF analyses revealed a general decrease in the amount of SiO_2 in the clay fraction as compared to the whole soil and rock fractions. Al_2O_3 and Fe_2O_3 showed an increase in the clay fraction with other elements in negligible amounts. The SEM analyses revealed hexagonally shaped thin platelets which are typical of kaolinite. The weathering of feldspar and mica played a role in the quantities of kaolinite and smectite detected in the samples. The samples indicate that an alteration from primary to secondary minerals has taken place, but still lack satisfactory conditions for complete weathering. The booklet form of the kaolinite minerals in the area suggests their residual origin whereas the smooth booklet form suggests a sedimentary origin.

KEYWORDS: x-ray diffraction, kaolinite, smectite, feldspar, mica.

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CEC – Cation exchange capacity

CIA – Chemical index of alteration

DTA – Differential thermal analysis

FTIR – Fourier transform infra red spectroscopy

HIV – Hydroxyl-interlayered vermiculite

OM – Organic matter

PSA – Particle size analysis

S - Sample

SA – South Africa

SA – Surface area

SEM – Scanning electron microscopy

TEM – Transmission electron microscopy

XRD – X-ray diffraction

XRF – X-ray fluorescence spectrometry

CHAPTER 1

1. INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Studies on soil mineralogy in South Africa over the past 25 years in relation to soil properties such as erodibility, susceptibility of minerals to dispersion, and the importance of the clay mineral fraction to K-fixation were undertaken in an effort to achieve a better understanding of the soils and their behavior (Bühmann et al., 2004). Most studies were concerned with the clay size fraction and X-ray diffraction was the dominant technique used for mineral identification (Bühmann et al., 2004). The use of the X-ray diffraction (XRD) analysis method for the identification of clay minerals, amongst others, is perhaps the most widely used technique for soil mineralogical studies. In this method, x-rays are diffracted by atoms in a crystal plane, and producing characteristic patterns when recorded. The pattern is then used in the identification of mineral species.

In South Africa, XRD studies of clay minerals have been carried out over a wide extent on certain parts of the country and different types of clay minerals were identified. In all the investigations carried out, certain minerals were found to be dominant over a wide range of soil and land types, making them the most important clay minerals in South Africa. For example, studies on erosion and soil crusting in South Africa have highlighted the importance of smectite as one of the important clay minerals (Levy, 1988; Levy & Van der Watt, 1988).

Clay mineralogy was at times only an incidental part with data on clay composition in these studies, with generally wide distribution tendencies (Bühmann et al., 2004). Regional studies on clay mineralogy conducted in certain parts of the country revealed unexpected clay mineral compositions (Bühmann and Nell, 1999; Bühmann et al., 2002; Botha, 1992). The occurrence of the different types of clay minerals in nature varies over a wide variety of conditions and climatic factors. In South Africa, different types of clays have been identified from different types of parent materials (MacVicar et al., 1985; Bühmann et al., 2002), pedological horizons (Hawker, 1986; Hawker et al., 1992) and climatic conditions (Bühmann

& Nell, 1999). Limpopo Province alone has a wide diversity of soils with differing pedological properties. Soil types that generally occur in Limpopo Province include Oxisols, Melanic, Vertic, Calcic, Duplex and Iceptic soils. The Limpopo Province in South Africa covers an area of about 12,46 million hectares and these account for 10.2% of the total area of the Republic of South Africa. The province is one of the countries prime agricultural regions noted for the production of livestock, fruits and vegetables, cereals and tea. However there are two distinct types of agricultural production systems namely, the large commercial farming system and the small holder farming system. The dominating large scale commercial farmers who use the most advanced production technology occupy approximately 70% of the total land area of which much of it is prime land. The lesser smallholder farmers are located mostly in the former homeland areas and they cover approximately 30% of the provincial land surface area. Farming under the smallholder systems is characterized by low level production technology and small size of farm holding of approximately 1,5 hectares per farmer; with production primarily for subsistence and little marketable surplus.

Most of the smallholder rural farming communities in Limpopo province do not incorporate soil clay mineral data in their small scale farming production plans mainly because site specific data is not readily available for their application or simply a lack of knowledge about clays and their importance in agriculture. Only general knowledge about the texture of the soil is applied. A certain percentage of large scale commercial farmers incorporate soil clay mineral data in their annual farming plans, but site specific data still proves to be a challenge in many areas. Regardless of the numerous studies already undertaken on soil clay mineralogy in South Africa, awareness and knowledge of the farming community in Limpopo Province on the effect of soil clay minerals in their agricultural systems is generally on a minimal scale.

Agricultural development across the globe depends on a number of factors for its success. One of those factors is information or data and the application thereof of existing information. This necessitates a need for continuous derivation of information for the development of new strategies and practices in the agricultural sector in order to achieve a more sustainable and economically viable agriculture. In support of the above statements, the objective of this study was to identify the different types of clay minerals in selected areas of the Limpopo province and their related impact on the agricultural productivity of the soils in which they occur.

1.2 PROBLEM STATEMENT

South Africa has diverse soils with different physical and mineralogical properties over a wide range of land types. Most of the soil clay mineralogical information currently in use was derived from reports wherein clay mineralogy was not the core research objective, but only as incidental part of data acquired for the completion of reports. Applications of soil mineralogical data in agricultural systems in Limpopo Province, especially for small scale farmers, is but to a minimal scale if applied at all; perhaps due to a lack of site specific information of the areas concerned. Therefore this research concentrated on the derivation of site specific mineralogical data in selected soils of the Limpopo Province and their relevant implications on the agricultural systems of the province.

1.3 MOTIVATION OF THE STUDY

South Africa is a large country with a great variety of soils, the mineralogical composition of which undoubtedly influences agricultural, environmental and engineering properties. There have been a large number of references that report some mineralogical data, but far too commonly the data are not interpreted in sufficient detail to be useful (Bühmann et al., 2004). Limpopo Province alone holds a diverse range of soils that has undergone different soil formation processes within regions that differ greatly in terms of climate and topography. Without doubt, their clay mineralogical data will vary greatly either in terms of the dominant clay minerals or the transformation products thereof.

A complete land survey of selected areas within the province in terms of clay mineralogy has assisted in revealing variances that occur within the province and the implications thereof in terms of agricultural development and practice. The site specific clay mineralogical data collected for discrete areas within the country is of utmost significance for the development of a useful resource databank. The resource databank will assist greatly in the development of successful and sustainable agricultural soil management practices in Limpopo province.
Above all, the availability of site specific information on soil clays will encourage the farming community (both small and big scale framers) in Limpopo province to learn more about clay minerals and their influence on their farming systems. It is believed that this will further encourage farmers to apply their knowledge on clay minerals within their framing programs with an aim of a better output in terms of yield. Most of the rural community

farmers will benefit from this research project since most of them do not have sufficient funds available to commission a surveyor for the task of analyzing their soils. Rural development in terms of agriculture will be enhanced, with a promise of a better agricultural system in Limpopo province and increased levels of yields.

1.4 HYPOTHESIS

1.4.1 Soil clay minerals vary with respect to soil type and parent material.

1.4.2 Their mineralogy affect soil reactions and therefore land use.

1.5 MAIN OBJECTIVES

The main objectives of this study were:

- To identify different types of clay minerals prevalent in selected agricultural soils of Capricorn District in Limpopo Province.

- To investigate the distribution patterns of identified clay minerals within the district.

- To determine the implications of clay minerals on agriculture in Capricorn district based on their distribution patterns.

1.6 CONCLUDING REMARKS

The diversity of soils in Limpopo province and the variances that occur in terms of climate and topography points out a need for more research work to be done in order to nourish the already existing data on soil clay mineralogy and its impact on the farming systems of the province. Site specific survey of the areas selected in Limpopo province will not only improve the databank already existing, but will also enrich the knowledge of farming communities within the area surveyed who are directly affected by the results of the study. The acquisition of knowledge by farmers will encourage the application of soil clay mineral data in their farming systems, leading to a more prosperous and economically viable agricultural sector in Limpopo province.

CHAPTER 2

2. LITERATURE REVIEW

2.1 SOIL CLAY MINERAL REACTIONS

The structural and chemical properties of clay minerals exert an influence in the manner of behavior on soils they occur in. This behavior further determines the type of agricultural land use and the subsequent productiveness of the land. Crops depend on soil clay minerals due to their capability to store and release cations and other nutrients (CEC) and also for the storage of water. Knowledge of their distribution as well as their chemical and physical influence on soils due to their physicochemical characteristics has become an essential research route.

Soil clay minerals exhibit characteristic negative charges that attract cations which are held electrostatically on the surface of the clay. The adsorption and exchange of these cations are of great practical significance in nutrient uptake by plants, soil fertility, nutrient retension, and fertilizer application. Adsorbed cations are generally available to plants as nutrients by exchange with H^+ ions generated by the respiration of plant roots. Therefore, the cation exchange capacity (CEC) of soil clay minerals, which is the capacity of soils to adsorb and exchange cations, determines in part soil productivity through clay minerals. Soil cation exchange capacity depends largely on the surface area of its particles which leads to their chemical interaction with ions and water within the soil solution (Iwata et al. 1995). Banin and Amiel (1970) found high correlation between surface area (SA) and both clay content and cation exchange capacity. Curtin and Smillie (1976) found higher correlation between SA and CEC than between clay content or soil organic matter content and CEC for 10 Irish soils of varying mineralogy.

The cation exchange capacity of soils also depends on both the type and the amount of its clay and organic matter (OM) content. This is because most of the negative charges responsible for the CEC arise from the dissociation of carboxyl groups in organic matter molecules (Parfitt et al. 1995) and both permanent and variable charges on clay minerals (Russell, 1977). The contributory involvement of silt and sand in cation exchange reactions

has been already recognized (McAleese and Mitchell, 1958; Drake and Motto, 1982; Rusell, 1977). Surfaces of clay particles are also responsible for the chemical reactions that ultimately give rise to a net negative or positive charge of mineral surfaces. The siloxane and oxyhydroxy surfaces of minerals; forming the plane of oxygen atoms in the tetrahedral sheet and those of exposed hydroxyl, OH groups in the octahedral sheet respectively; interact directly with the electrolytes in the soil solution producing either a permanent or a variable charge/pH dependent charge. The third type of surface formed by hydroxides of Si, Al and Fe called silanol, aluminol and ferrol surfaces respectively is found in amorphous minerals and the broken edges of certain minerals (Mehlich, 1981; Greenland & Hayes, 1978; Tan, 1998; Sposito, 1989).

Of these surfaces, the oxyhydroxy, silanol, ferrol and aluminol are the ones that exhibit pH influence on their chemical reactions. The surfaces of various hydrous oxides commonly found in soils are similar in so far as the charge is dependent on pH and electrolyte concentration in the surrounding medium. The charge on these surfaces arises from the association or dissociation of protons and this is determined by the concentration of protons near the surface, and hence by pH and electrolyte concentration of the soil solution (Greenland & Hayes, 1978). In a study of the CEC of kaolinites, Ma & Eggleton (1999) found that the amount of negative charge on the edges and the exposed basal hydroxyls depends on pH and other ion concentrations. The study indicated that the charge from broken edges and exposed OH planes rather than from Al/Si substitution determines CEC, even at zero point of charge. The determination of the kinds and relative amounts of clay minerals is essential to understand more fully such soil physicochemical properties as shrink-swell potential, extreme crusting and cation exchange capacity amongst others (Mohamed et al., 1982). Knowledge of soil clay minerals is also needed for placing soils with more than 35% clay content into correct family classes according to Soil Taxonomy (Soil Survey Staff, 1975).

2.2 CLAY MINERALOGY OF SOUTH AFRICAN SOILS AND THEIR IMPLICATIONS TO AGRICULTURE

Munnik, Verster & Rooyen (1990, 1992, 1996) studied the textural and chemical properties of granite-derived soil profiles around Preytoriuskop, Pretoria/Johannesburg, and Phalaborwa, but provided only averaged clay mineralogical information from a few samples.

They were all dominated by kaolinite, with mica and quartz present in small amounts. Investigations of Bühmann & Nell (1999) on clay mineral associations in South African soils formed under the Mediterranean-type climate from the winter-rainfall area of the Western Cape Province revealed that most clay fractions were dominated by kaolinite. The clay mineral associations in 15 soil profiles from the Lusikisiki district in South Africa, which encompass all major soil profiles, have been identified and their related agricultural implications outlined (Bühmann et al., 2002). Their A-horizons were dominated by kaolinite, quartz or gibbsite with some soil profiles containing significant amounts of hydroxyl-interlayered vermiculite (HIV). Because of the tightness of the structural bonds in kaolinite, its particles are not easily broken down. Levy (1988) indicated that the susceptibility to crusting is highest in smectitic soils and lowest in soils dominated by kaolinite. Studies on erosion and soil crusting in South Africa have highlighted the importance of smectite as one of the important clay minerals (Levy, 1988; Levy & Van der Watt, 1988). Most soil smectites are dioctahedral with a negative charge arising from the isomorphous substitution. Buhman and Schoeman, (1995) determined the mineralogical characterization of vertisols from the northern regions of the Republic of South Africa. Their investigations on 76 samples from 38 benchmark vertisol profiles by means of XRD revealed that smectite constituted the dominant clay mineral component in most samples, whereas kaolinite was a common accessory mineral.

Stern et al. (1991) studied the effect of clay mineralogy on rain infiltration (IR), seal formation and soil loss on 19 cultivated soils from South Africa (SA). They compared the IR and soil losses with the same parameters of smectitic soils from Israel. The mineralogical composition of soils from South Africa comprised mainly kaolinite and illite as the predominant clay minerals with small amounts of smectite evident. Kaolinitic or illitic soils, which contain small amounts of smectite, are dispersive and as susceptible to seal formation as smectitic soils. The high swell-shrink potential of the soil make these soils plastic when wet and hard when dry, whereas wide cracks will form as soils dry out. The dry soil makes it difficult to till the land. According to the reports of work done on soil clay mineralogy in South Africa, vermiculite, mica and other clay minerals, such as the amorphous clays, imogolite, talc mixed layer silicates, and chlorites, were found to be widely distributed in the country but generally lacking the dominance such as in the case of kaolinite, illite, and or smectite (Du Plessis & Shainberg, 1985). Generally, their presence in the soil is comparatively smaller in percentage to the other dominant minerals. However, in certain

instances they were found to be dominant under certain conditions and their influence on soil properties was apparent. Cass & Johnston (1985) sampled areas where soils were prone to either swelling, dispersion or hard setting. Of the swelling soils 90% had smectite or vermiculite as essential components, dispersive clays contained at least some mica and were devoid of smectite.

Singer et al., (1995) investigated the characteristics and formation of fibrous clay minerals in the soils of Namaqualand, South Africa. Palygorskite or sepiolite dominated the clay fractions accompanied by illite and non – expanding minerals or mixed layer minerals. They found that the highest concentrations of the fibrous clay minerals commonly occurred in the bottom horizons. Van der Merwe et al. (2002), determined the clay mineral associations in melanic soils of South Africa and found that there was a large variation with regard to their mineralogical associations. More than half the soils were dominated by smectite, 30% by kaolinite, and the rest by an association of about equal proportions of mica, kaolinite, and smectite.

2.3 CLAY MINERAL GENESIS AND CHARACTERISTICS

Clay minerals are grouped as: kaolinite-serpentine, pyrophyllite-talc, smectite or montmorillonite, mica, illite, brittle mica, vermiculite, chlorite and palygorskite-sepiolite (Mackenzie, 1975; Brindley et al., 1968). The chemical structures of these minerals are very different depending on their atomic arrangements. They can either be categorized as diamorphic-1:1 (kaolinite), trimorphic-2:1 (montmorillonite) and tetramorphic-2:1:1 (chlorite) on the basis of the number of tetrahedral to octahedral sheets in one layer. They can further be subdivided into either dioctahedral or trioctahedral subgroups based on the occupation of the octahedral positions by either Al^{3+} or Mg^{2+} (Tan, 1998).

2.3.1 Kaolinite

Kaolinite is one of the dominant minerals found in kaolin deposits. Other minerals found in kaolin deposits include nacrite, dickite and or halloysite. The deposits can be classified as either primary or secondary depending on their genesis (Tan, 1998). Primary kaolin deposits are formed *in-situ*, by the alteration of feldspar-rich, Al-rich rocks such as granites and rhyolites; the parent minerals being feldspars and muscovite. Secondary kaolin deposits are

of sedimentary origin resulting from erosion and transportation of clay size particles, which are mineralogically altered, and deposited, in lacustrine, paludal, deltaic and lagoonal environments (Ekosse, 2005). Kaolinite is a 1:1 dioctahedral mineral with platy pseudo-hexagonal particles forming laths or vermicular books with irregular edges (Dixon, 1989). Kaolinite has a (001) basal spacing 7.14 Å and a second order spacing at 3.57 Å. The basic unit of kaolinite is made of a tetrahedral sheet of silica (SiO_2) and an octahedral sheet of gibbsite ($Al(OH)_3$) and both bonded by shared O atoms. Kaolinite units are held by hydrogen bonds. The layer stacking of kaolinite is controlled by repulsion between highly charged Si and Al cations which tend to avoid superposition (Dixon, 1989).

The chemical formula for kaolinite is $Al_2Si_2O_5(OH)_4$. The lattice chemistry of kaolinite consists of tetrahedral and octahedral sheets in the *a* and *b* directions positions which are stacked one above another in the *c* direction (Fig.1). Charges within the structural formula units are balanced, and there is very little substitution within the lattice structure. The regular stacking and close spacing of layers creates strong H bonds between successive layers (Tan, 1998). Kaolinite has a low CEC of 3-15 meq/100g with a pH of 6.8-7.3 (Murray and Keller, 1993)

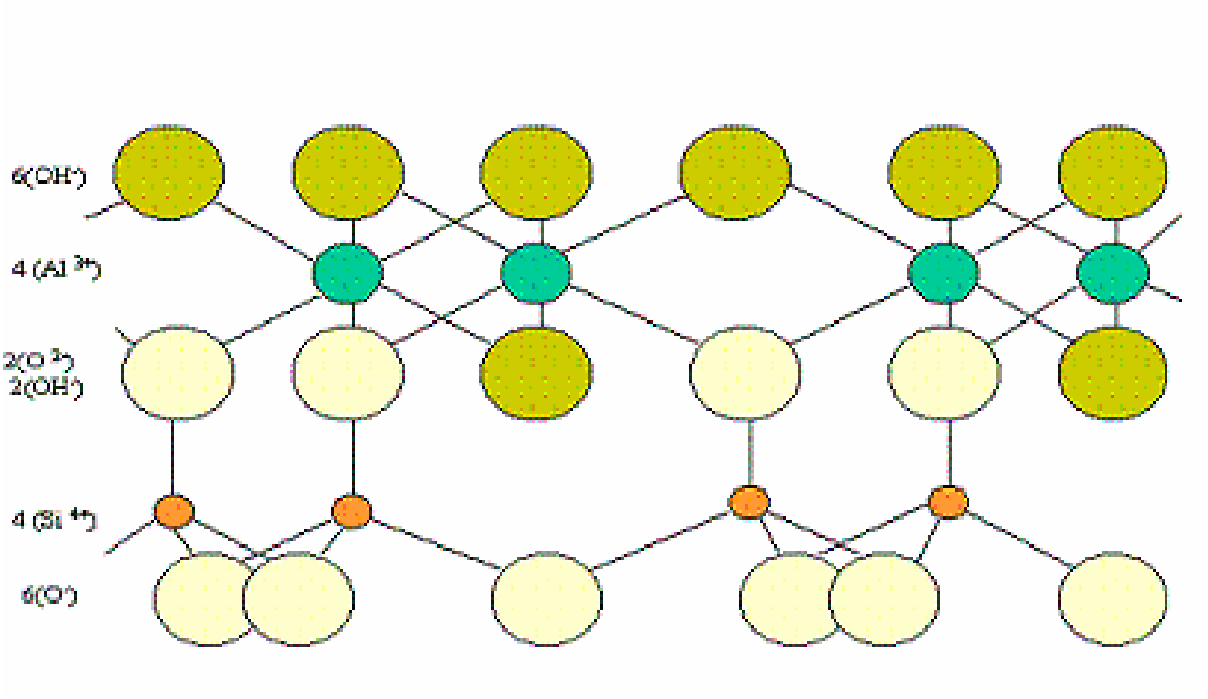

Fig.1: Chemical Structure Representation of Kaolinite
(University of Wisconsin-Madison, 1999)

2.3.2 Smectites

Smectites are formed from the alteration of volcanic ash or transformed from feldspars, micas, various FeMg silicates and silication of detrital phylosilicates (Weaver, 1989). Mineral species of di-octahedral smectites are montmorillonite, beidellite and nontronite, whereas tri-octahedral smectites include saponite, hectorite and sauconite. Low energy environment under temperate climatic conditions (low relief, low permeability, low temperature and low rainfall) are necessary for deposition and formation. Colloidal silica from altered volcanic ash combines with colloidal $Al(OH)_3$ gels to form smectites. Smectites are capable of shrinking and swelling depending on the moisture content. Van Olphen showed in his studies that smectites can double their dry volume by adsorbing water molecules in the interlayers of the clay units. Smectites have a high CEC at 50-150 meq/100g with a pH of 9.0-10.5 (Murray and Keller, 1993).

Smectites are made up of mainly 2:1 structural type clay minerals of the smectite dioctahedral layered subgroup (Bailey, 1980; Thorez, 1976). Their basal spacing is influenced by exchangeable cations, relative humidity, association with organic molecules and heat treatment (Wilson, 1987). The basal spacing of beidellite is 17.6 Å and that of nontronite is between 14.6 Å and 15.2 Å. The basal spacing of Na-montmorillonite of Wyoming bentonite if treated with ethylene glycol is 16.9-17 Å, and treated with glycerol is 17.8 Å (Wilson, 1987). Smectites are composed of units made of two silica tetrahedral sheets with a central alumina octahedral sheet (Fig.2). All tetrahedron apexes point to the same direction and towards the center of the unit. Their composition and lattice structure usually differ because of substitution of Al with Fe and/or Mg in the octahedral sheet of the crystal lattice. Only 2/3 of the possible positions in the octahedral sheet are filled for di-octahedral smectites. The layers are continuous in the *a* and *b* direction and are stacked one above another in the *c* direction in which lattice expansion occurs. Smectites derive about half of their negative charge from the octahedral sheet and half from the tetrahedral sheet (Bohn et al, 2001).

The chemical formula of Na-montmorillonite is $Na_{0.3}(Al,Mg)Si_4O_{10}(OH)_2.xH_2O$. The chemical composition of the parent rock, the cooling rate of the glass, the pH of the solution and the conditions of fluid flow prevailing during mineral formation may determine the original interlayer cation chemistry of the mineral. The chemical composition, mineral type and structural characteristics of smectites affect its surface reactions and influence the

resulting high temperature mineral phases (Brindley and Lemaitre, 1987). Interlayer water is given off at 180 ºC, and dehydroxylation occurs at 720 ºC.

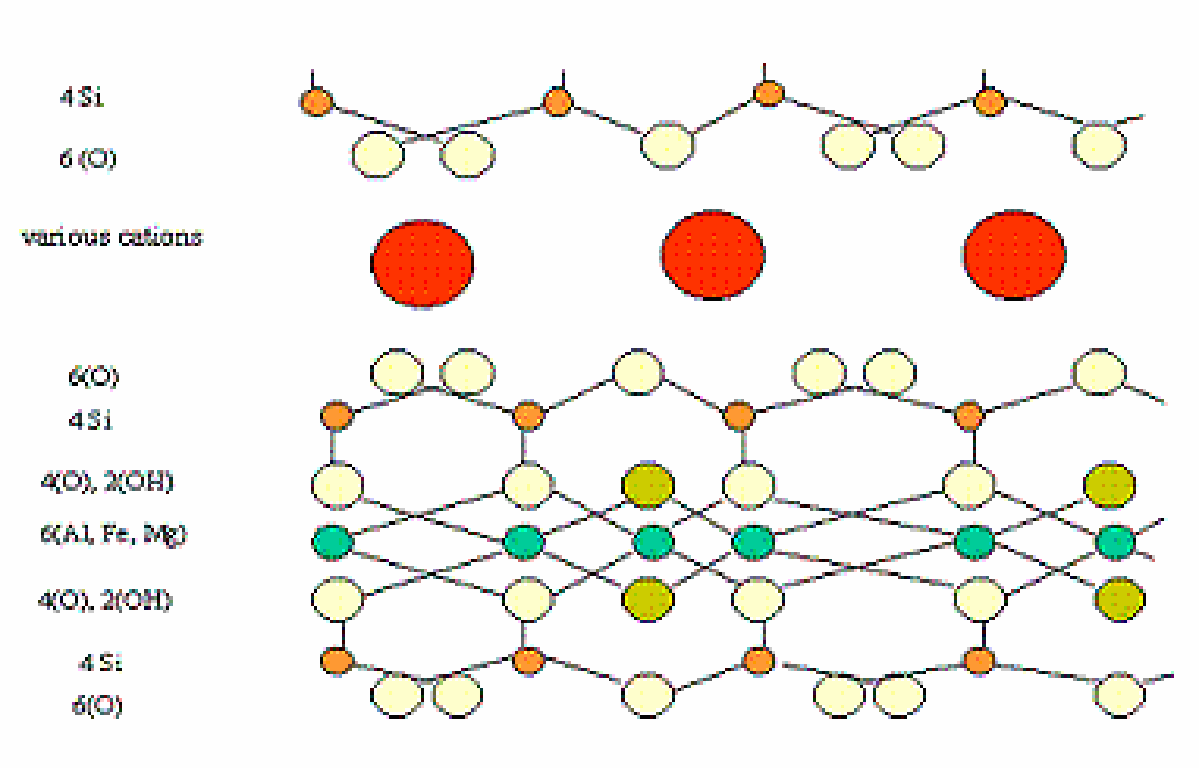

Fig.2: Chemical Structure Representation of Montmorillonite
(University of Wisconsin-Madison, 1999)

2.3.3 Hydromica

Biotite, illite and muscovite form members of the hydromicas group. Illite is a micaceous clay mineral (Fig.3) with similar chemical and mineralogical composition as muscovite, but slightly smaller in particle size. Differences of hydromicas and especially muscovite and illite occur in their physical properties such as their particle size. The hydromicas occur in low to medium grade metamorphic and igneous rocks. Their layer charges result from isomorphous substitution taking place in the octahedral sheet of the unit cell (Dixon, 1989). Illites are very fine, and the only reliable forms of identification are XRD and differential thermal analysis (DTA). Muscovite is di-octahedral whereas biotite is tri-octahedral with its octahedral positions filled with Mg and Fe. The unit layers of illite extend in the *a* and *b* direction and are stacked in the *c* direction. Potassium ions occur between the unit layers where they fit into hexagonal distribution along the surface of the O layer. This arrangement gives illite the

thickness of 10 Å with a very strong reflection and this makes its identification easy through XRD. The diffraction patterns of the hydromicas are almost similar. Illite can be distinguished from muscovite by the difference in the first order basal peak.

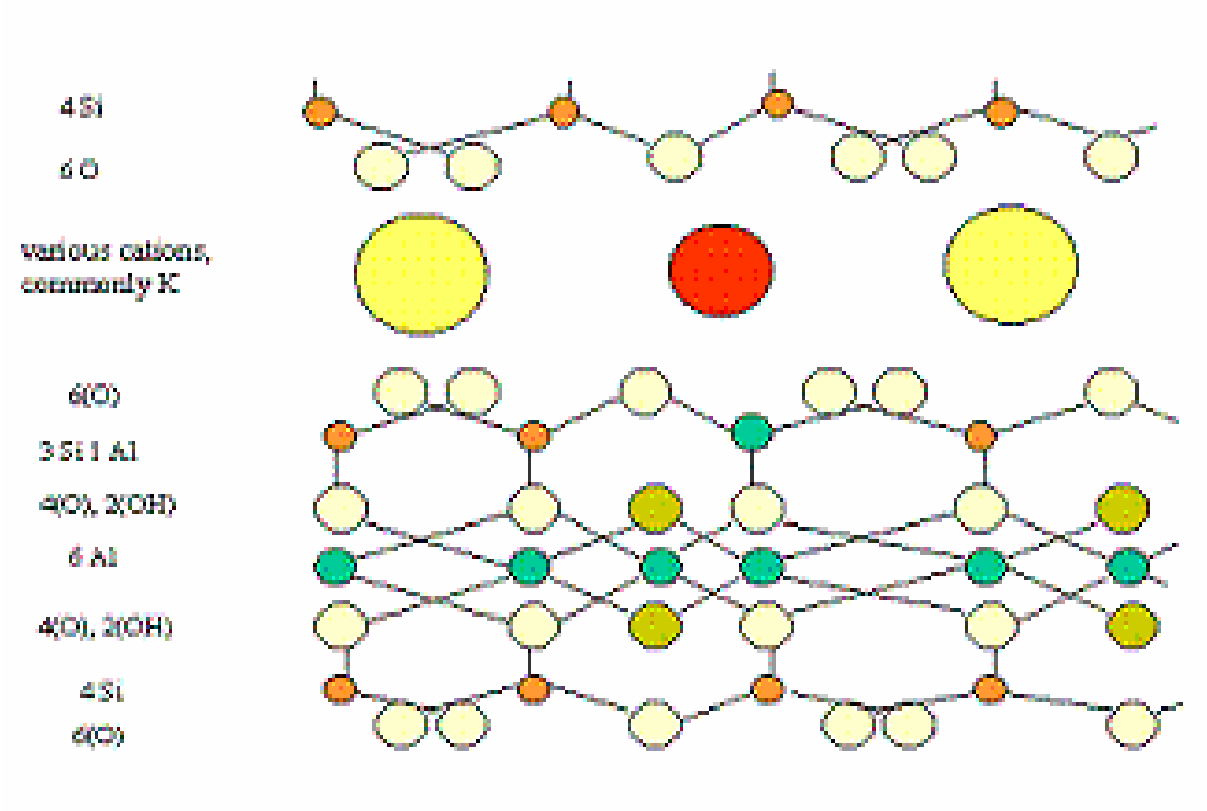

Fig.3: Chemical Structure Representation of Illite
(University of Wisconsin-Madison, 1999)

The chemical formula of illite and muscovite are $K_{1-1.5}Al_4[Si_{7-6.5}Al_{1-1.5}O_{20}](OH)_4$ and $K_2Al_4[Si_6Al_2O_{20}](OH,F)_4$ (Gallon, 1986). An illite unit cell consists of two Si tetrahedral sheets with a central octahedral sheet. The tips of all the tetrahedrons in each of the silica sheet point towards the center of the unit, and combined with the octahedral sheet in a single layer.In some cases part of the Si is replaced by Al and the resultant charge deficiency is balanced by the K ions. The CEC of micas are slightly higher than that of kaolinite but lower than the values of smectites. Al^{3+} and Si^{4+} substitution reactions with micas are less as compared to smectites (Murray an Keller, 1993). Soils rich in micas experience permanent and pH dependent charges, resulting from isomorphous substitution at the time of argillisation and transformation from 2:1 to 1:1 clay minerals (Bailey, 1980).

2.3.4 Vermiculites

Vermiculite can be categorized into true vermiculite and clay vermiculite. True vermiculite is considered as a rock forming mineral and not a clay mineral. The clay sized vermiculite is found in soils formed by weathering or hydrothermal alteration of micas. The layer structure of vermiculite resembles that of mica from which the mineral is derived (Fig.4). They are 2:1 layer minerals with a d spacing (001) of 14 Å (Tan, 1998).

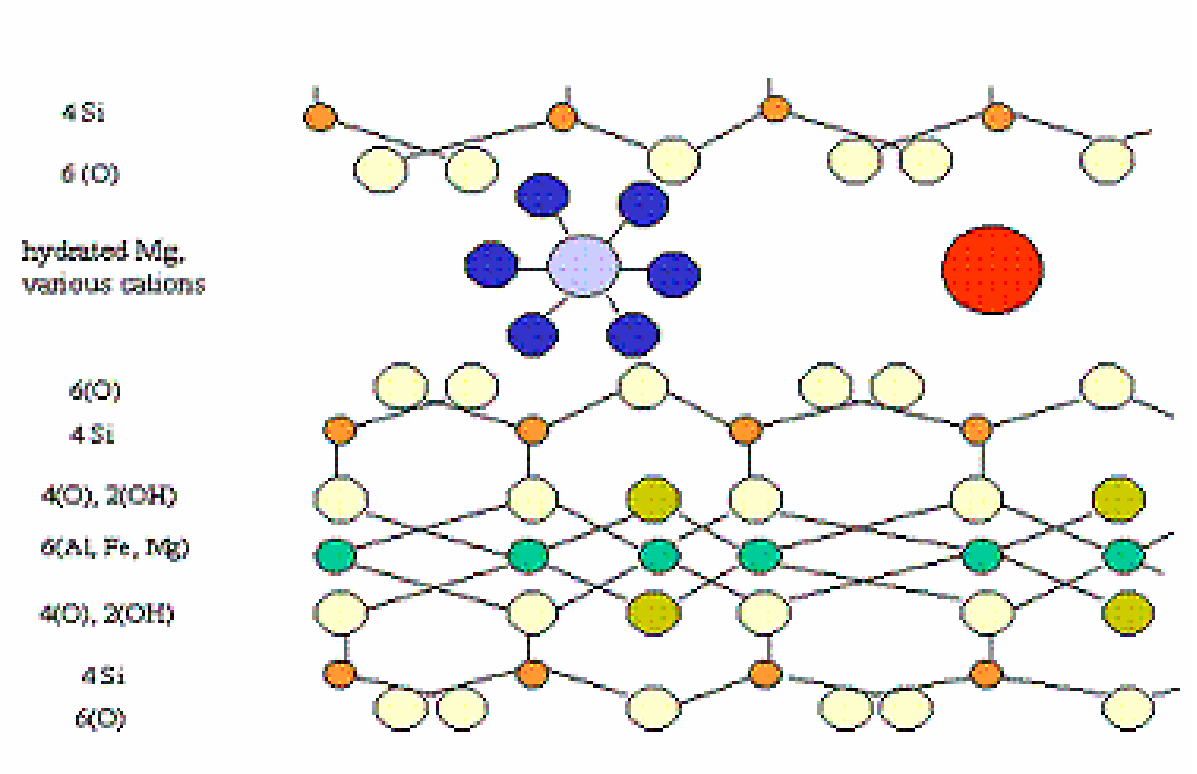

Fig.4: Chemical Structure Representation of Vermiculite
(University of Wisconsin-Madison, 1999)

Vermiculite is a magnesium aluminum silicate, with Mg occupying the octahedral positions between two silica tetrahedral sheets. Generally the chemical formula is $22MgO.5Al_2O_3.Fe_2O_3.22SiO_2.4OH_2O$. Substitution of Al for Si takes place in the tetrahedral sheet and this gives rise to a high negative charge of this mineral with a CEC of approximately 150meq/100g, which is the highest CEC of all minerals. The presence of hydroxyl-Al interlayers usually reduces the CEC of the mineral.

2.3.5 Chlorite

Chlorites are hydrated magnesium and aluminum silicates, which are related to mica minerals in appearance. They are 2:2 (or 2:1:1) layer silicates, and are common in sedimentary rocks and productive soils derived there from. Octahedral sheets composed of $Mg(OH)_2$, are sandwiched between the two silica tetrahedral sheets (Fig.5). The $Mg(OH)_2$ sheet, formerly called the brucite sheet (Tan, 1998), occupy the intermicellar spaces, hence the term 2:2 layer silicates. The characteristic d spacing (001) of chlorite is 14.0 Å.

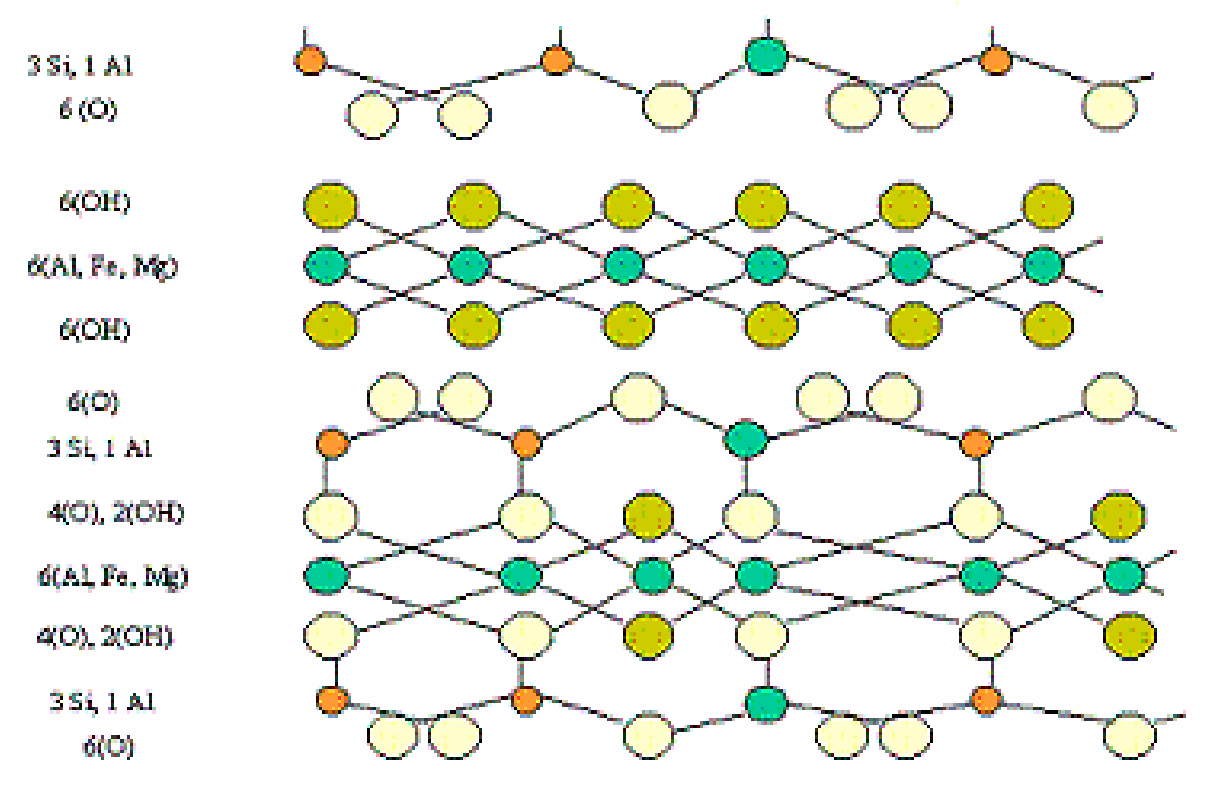

Fig.5: Chemical Structure Representation of Chlorite
(University of Wisconsin-Madison, 1999)

The chemical formula of chlorites is $(Mg, Fe, Al)_6(Si, Al)_4O_{10}(OH)_8$. The brucite sheet between the two tetrahedral layers restricts swelling, decreases the effective surface area, and reduces the effective CEC of the mineral. The replacement of Mg by Al occurring in the brucite sheets accounts for the development of a positive charge in this mineral. The positive charge neutralizes the negative charge in the 2:1 layer. Therefore chlorites have a small negative and consequently a small CEC (Bohn et al., 2001; Tan, 1998).

2.4 TECHNIQUES IN THE IDENTIFICATION OF CLAY MINERALS

Different instrumentation and techniques are used for the characterization of clay minerals such as transmission electron microscopy (TEM), Fourier transform infra red spectroscopy (FTIR), differential thermal analyses (DTA) and particle size analyses (PSA). In this study, focus will be on X-ray powder diffraction (XRPD), X-ray fluorescence spectrometry (XRF) and scanning electron microscopy (SEM) techniques and their related instruments.

2.4.1 X-Ray Powder Diffractometry

Diffraction in x-ray diffraction (XRD) occurs as waves interact with a regular structure whose repeat distance is about the same as the wavelength. X-rays have wavelengths of a few angstroms, which are also the typical inter atomic distances in crystalline solids. When certain geometric requirements are fulfilled, x-rays scattered from a crystalline material can constructively interfere, producing a diffracted beam. The distance between similar planes in a crystalline material, the angle of diffraction in degrees and the wavelength of the incident X-radiation are important components of the geometric requirements.

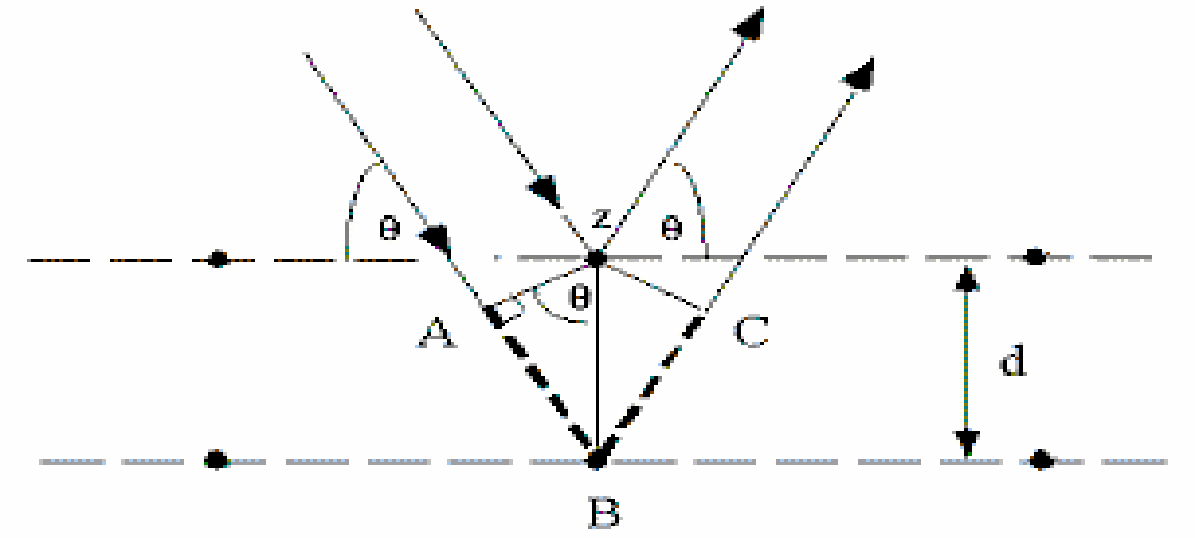

Fig.6: Diffraction from crystal planes according to Bragg's law, AB and BC = distance traveled by the lower beam, θ = angle of diffraction, d = interlayer spacing (Mineral Physics Institude, 2007)

Bragg W.L. (1912) quantitatively related the reinforcement of scattered rays to the distance of separation of atomic planes and defined the relation as,

$$n\lambda = 2d \sin \theta \,, \qquad (1)$$

where n = an integer determined by the order given, λ= wavelength, d = the interplanar spacing, and θ = the critical angle at which rays scattered from successive planes will be in phase along a front as they leave the crystal (Fig.6). The phenomenon of diffraction involves the scattering of x-rays by atoms of a crystal and the reinforcement of scattered rays in definite directions away from the crystal.

Figure 7 below shows an example of an X-ray diffractogram of a sample containing smectite, kaolinite and quartz.

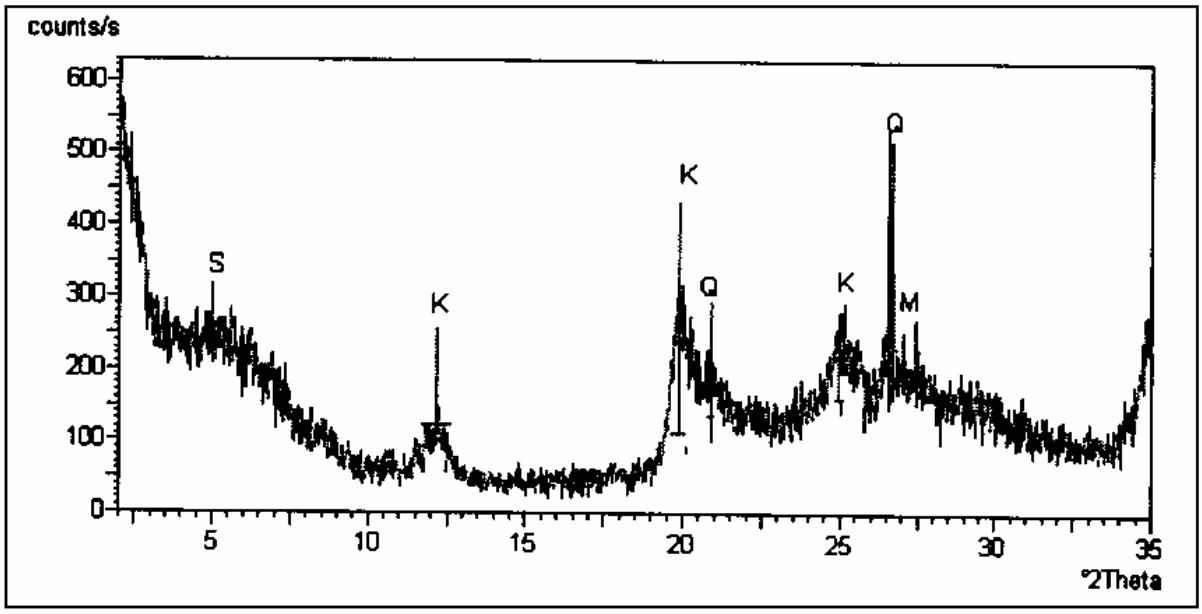

Fig.7: X-ray diffractogram of < 2.0 μm fraction of a representative soil sample from Gaborone, Botswana (S = smectite, K = kaolinite, Q = quartz) (Ekosse, 2005)

In XRD, the application of Bragg's law is by having a fixed wavelength while measuring the diffraction angle. In this case, the results give values for a set of d spacings, which are dependent on the structure of phases in the material being analyzed. With the advancements in XRD technology, today x-ray diffraction studies include thin films and amorphous to highly crystalline materials. X-ray diffractometry has got an accuracy of tens of percent, and a sensitivity of 0.1% to 100% (Jenkins and Snyder, 1996). Even though an appreciable number of investigations has been carried out, a direct research on site specific clay

mineralogical data commands attention for the improvement of the database and site-specific management principles within the agricultural systems of the Limpopo Province.

2.4.2 X-Ray Fluorescence Spectrometry

X-ray fluorescence spectroscopy (XRF) is widely used to measure the elemental composition of materials. This method is fast and non-destructive to the sample, and therefore it is a method of choice for field applications. Depending on the application, XRF can be produced by using not only x-rays but also other primary excitation sources like alpha particles, protons or higher energy electron beams. The XRF technique is based on the absorption of energy by atoms and their subsequent emissions for the measurement of the elemental compositions of materials. When a primary x-ray excitation source from an x-ray tube or a radioactive source strikes a sample, the x-ray can either be absorbed by the atom or scattered through the material. The process in which an x-ray is absorbed by the atom by transferring all of its energy to an innermost electron is called the photoelectric effect. During this process, if the primary x-ray had sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells and in the process give off a characteristic x-ray whose energy is the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces x-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of the sample. The process of emissions of characteristic x-rays is called X-ray Fluorescence (XRF).

2.4.3 Scanning Electron Microscopy

Scanning electron microscopy is an analysis tool that permits the observation and characterization of heterogeneous organic and inorganic materials on a nanometer (nm) to micrometer (μm) scale. It is one of the most versatile instruments available for the examination and analysis of the microstructural characteristics of solid objects. This technique is capable of obtaining three-dimensional-like images of a wide range of materials. In the SEM, the area to be examined or the microvolume to be analysed is irradiated with a finely focused electron beam, which may be swept in a raster across the surface of the specimen to form images or may be static to obtain an analysis at one position. A variety of

signals such as secondary electrons, backscattered electrons, characteristic x-rays, and other photons of various energies are produced from the interaction of the electron bean with the sample. These signals are obtained from specific emission volumes within the sample and can be used to examine many characteristics of the sample. The imaging signals of greatest interest are the secondary and backscattered electrons because these vary primarily as a result of differences in surface topography (Goldstein et al., 2003).

The basic components of the SEM are the lens system, the electron gun, the electron collector, the visual and photorecording cathode ray tubes, and the associated electronics. The development and addition of instruments such as the electron probe microanalyzer (EPMA) and energy dispersive spectrometer (EDS) greatly enhanced the capabilities of the SEM. The EPMA makes it possible for SEM to obtain compositional information using characteristic x-rays by localized chemical analysis of solid samples. The EDS system offers a means of rapidly evaluating the elemental constituents of a sample. In addition to rapid qualitative analysis, accurate quantitative analysis can also be achieved with EDS x-ray spectrometry (Goldstein et al., 2003).

A major reason for the SEM's usefulness is the high resolution which can be obtained when bulk objects are examined with an instrumental resolution in the order of 1-5 nm (10-50Å). Another important feature of the SEM is the large depth of field, which is responsible, in part, for the three dimensional appearance of the specimen image. The greater depth of field of the SEM provides much more information about the specimen as compared with other microscopes such as the light microscope. The SEM is also able to examine objects at very low magnification. The following are examples of scanning electron photomicrographs of some clay minerals.

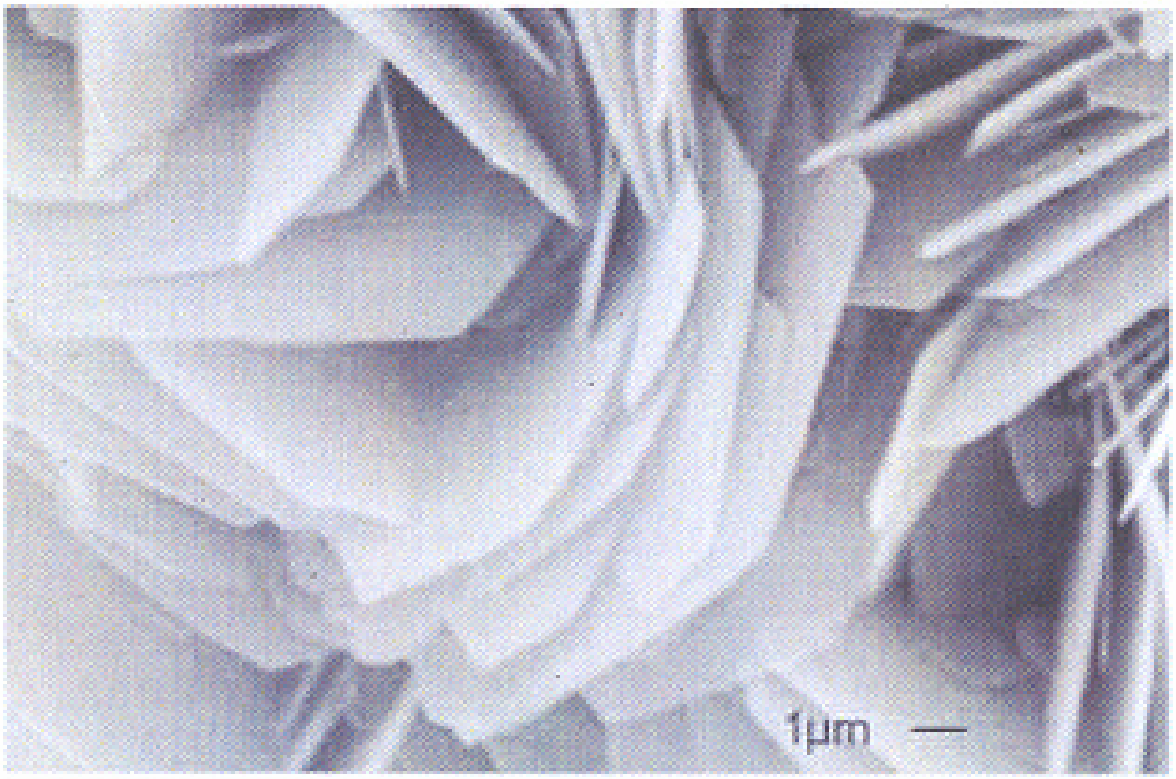

Fig.8: Scanning electron micrograph of chlorite flakes (Barthelmy, 2005).

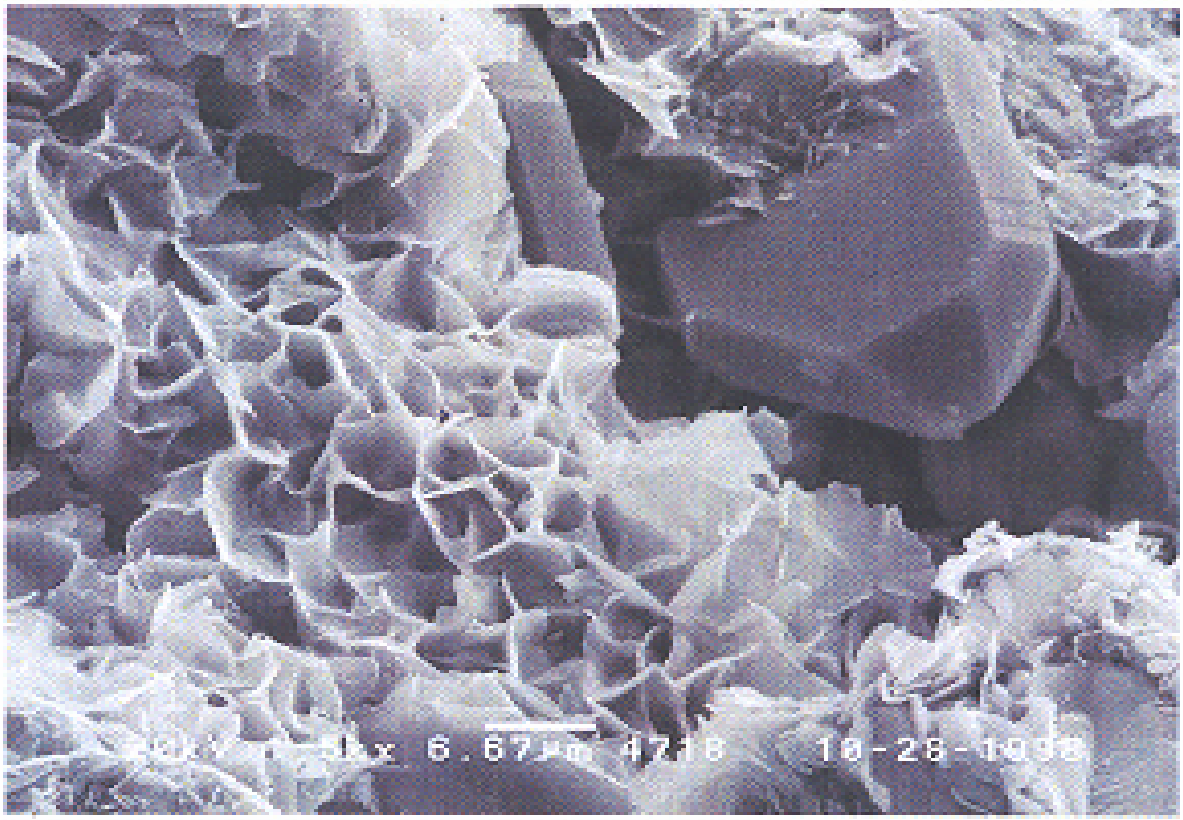

Fig.9: Scanning electron micrograph of montmorillonite honeycombs (Barthelmy, 2005).

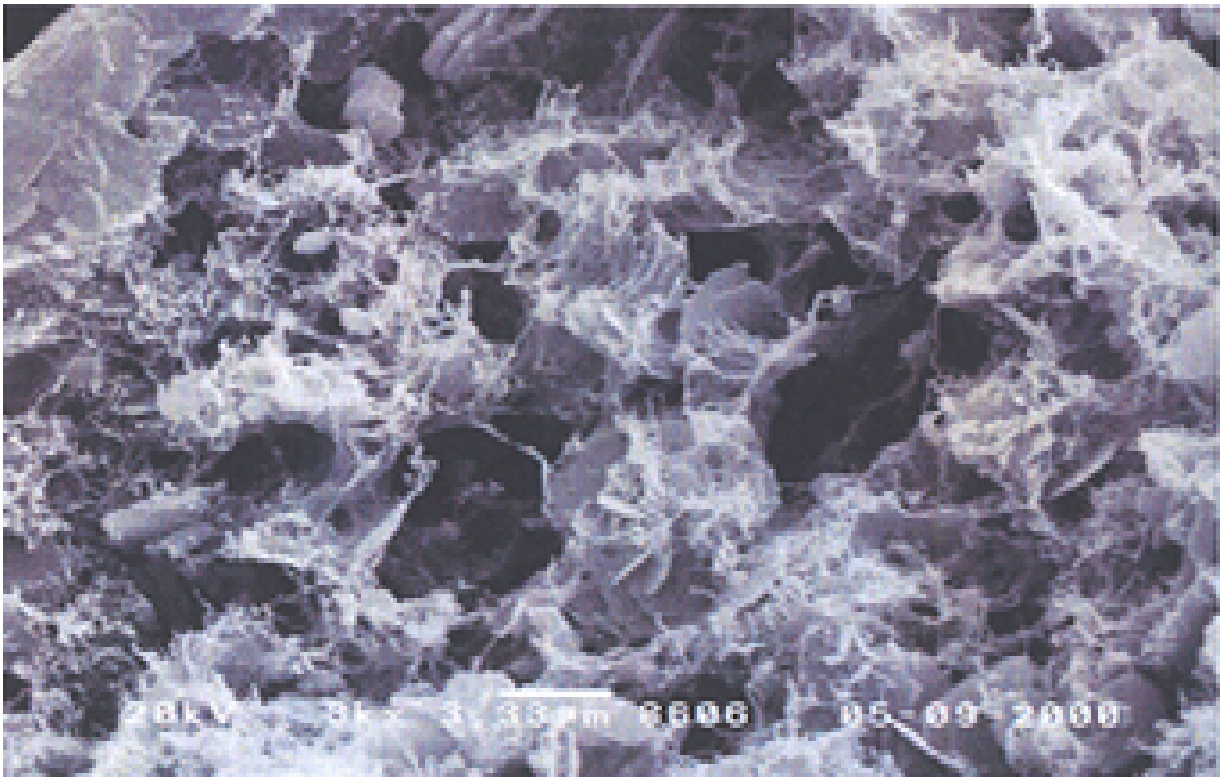

Fig.10: Scanning electron micrograph of spongy illite (Barthelmy, 2005).

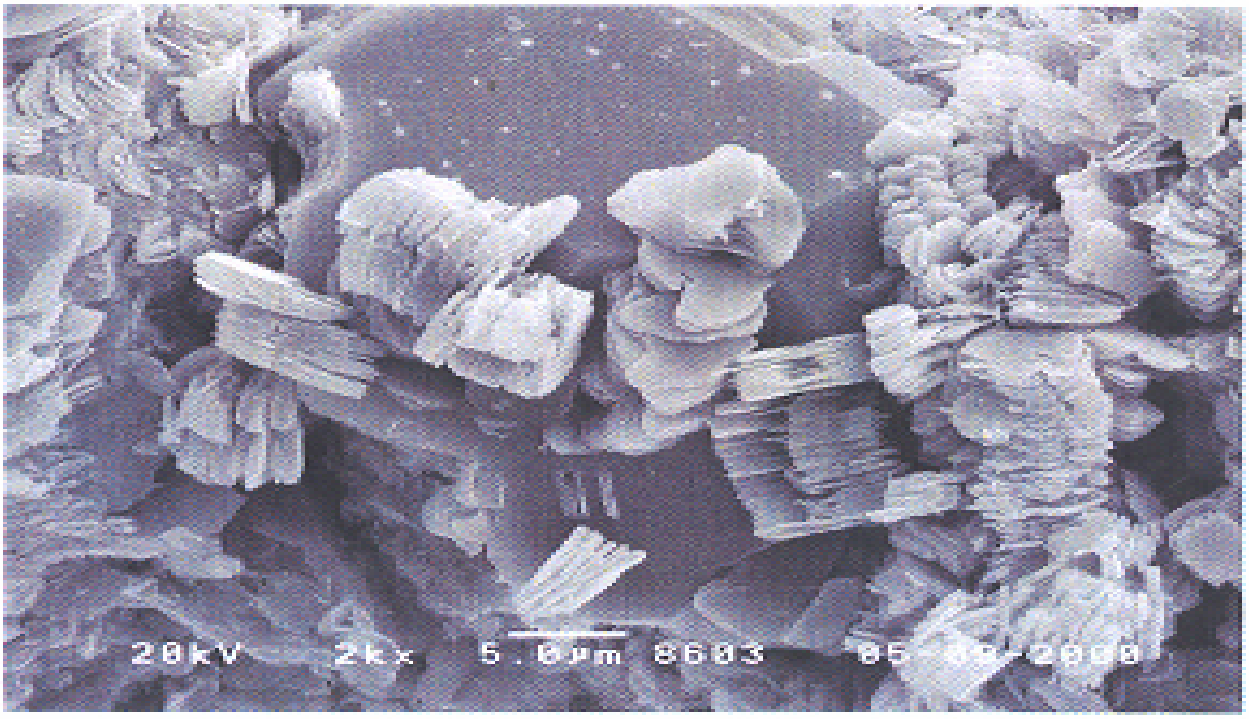

Fig.11: Scanning electron micrograph of kaolinite booklets (Barthelmy, 2005).

Figure 8 depicts paper like flakes of chlorite minerals. Figure 9 portray the honeycombed shaped platelets of montmorillonite overgrown on pore spaces and quartz grains in a sandstone. Figure 10 reveals the spongy nature of illite particles lining a pore space in a sandstone. Figure 11 shows kaolinite booklets covering a quartz grain.

2.5 CONCLUDING REMARKS

The clay minerals occur in nature in different forms according to their formation reactions and the conditions in which they were formed. Their distribution is wide spread and produces a diversity of soils with varying characteristics according to the type of clay mineral dominating the soil. The diversity that occurs in Limpopo province indicates for a fact that the most recently acquired data on soil clay minerals does not satisfactorily give a good description of the distribution in the province. More research is required to understand better the implications of clay minerals in the agricultural systems of the province. The use of different techniques and also the availability of relevant equipment in the province for the identification of clay minerals is important for the derivation of more information about the status of our soils.

CHAPTER 3

3. MATERIALS AND METHODS

3.1 STUDY AREA DESCRIPTION

South Africa falls within the longitudes 26°14' E and 32°10' E, and latitudes 25°25' S and 21°49' S, and it is divided into nine provinces. Limpopo Province is located north of South Africa, sharing boarders with Botswana, Mozambique and Zimbabwe in the north. Limpopo Province covers an area of 12,46 million ha and this accounts for 10.2% of the total land area of the Republic of South Africa.

In Limpopo Province, arid to semi-arid and sub-humid climatological regions can be identified with daily temperatures varying between an average of 17ºC and 27ºC in the summer and 4ºC to 20ºC in winter. The rainfall varies between 350 to 650 mm, occurring in summer. Limpopo Province is comprised of 5 districts, namely Sekhukhune, Mopani, Vhembe, Capricorn and Waterberg (Fig.12). The study area is located in the Capricorn district (Fig.13) comprising a total area of 316053 ha. The area falls within the longitudes 28º35'52,34"E and 30º7'1,19"E and within the latitudes 23º10'0,72"S and 24º3'11,57"S. As can be shown on the map, the area is comprised of different types of soils over a wide area of the district. Only three different soil type areas, as indicated on the map, were used for this study. The selected soils (mostly oxidic and inceptic soils) are believed to have formed on migmatite and gneiss parent materials. Their clay content ranges from 10 to 25% with soil depths of up to 1200 mm. Apparent soil forms/land classes include clovelly, bainsvlei, hutton, mispah and glenrosa.

The geology of the study area (Fig.14) is comprised predominantly of the Hout River Gneiss, with radiometric ages clustering around 2 750 Ma. Intrusions, largely as granites, occur and form scattered bodies of various size from large batholiths to small circular or oval stocks. Hout River Gneiss is itself intrusive into the Pietersburg group. Leucocratic migmatite and gneiss, grey and pink hornblende-biotite gneiss, grey biotite gneiss and pegmatic rocks form part of the granitoid rocks found under Hout River Gneiss. Leucocratic migmatite and gneiss consist typically of quartzo-feldspathic layers and thin parallel streaks, mainly of biotite. Muscovite-bearing granite and pegmatite occur throughout the Hout River Gneiss. Intrusive Moletsi and Matlala granites occur and forming large bodies towards the south.

Goudplaats Gneiss and intrusive Matok Porphyroblastic Granite succeed the Hout River Gneiss to the east of the map (Brandl, 1986). Most of the area forms undulating country with the altitude varying between 900m and 1300m. The monotony of the plains is occasionally broken by ridges and iselbergs. Along the northern edge, resistant sediments give rise to a mountainous landscape with the highest point being 2051 m above sea level. A large part of the western half of the area comprises a plateau, with an altitude between 1100 and 1400 m, which is bounded on the left by a conspicuous escarpment (Brandl, 1986). The vegetation type of the study area is predominantly mixed bushveld. This bushveld represents a great variety of plant communities, with many variations and transitions. The vegetation varies from a dense, short bushveld to a rather open tree savanna. On shallow soils Red Bushwillow *Combretum apiculatum* dominates the vegetation. Other trees and shrubs include Common Hook-thorn *Acacia caffra, Sickelbush Dichrostachys cinerea* and *Live-long.* Fingergrass *Digitaria erianth* and Kalahari Sand Quick *Schmidtia pappophoroides* are some of the grasses that dominate these soils. On deeper and more sandy soils, Silver Clusterleaf *Terminalia sericea* becomes dominant.

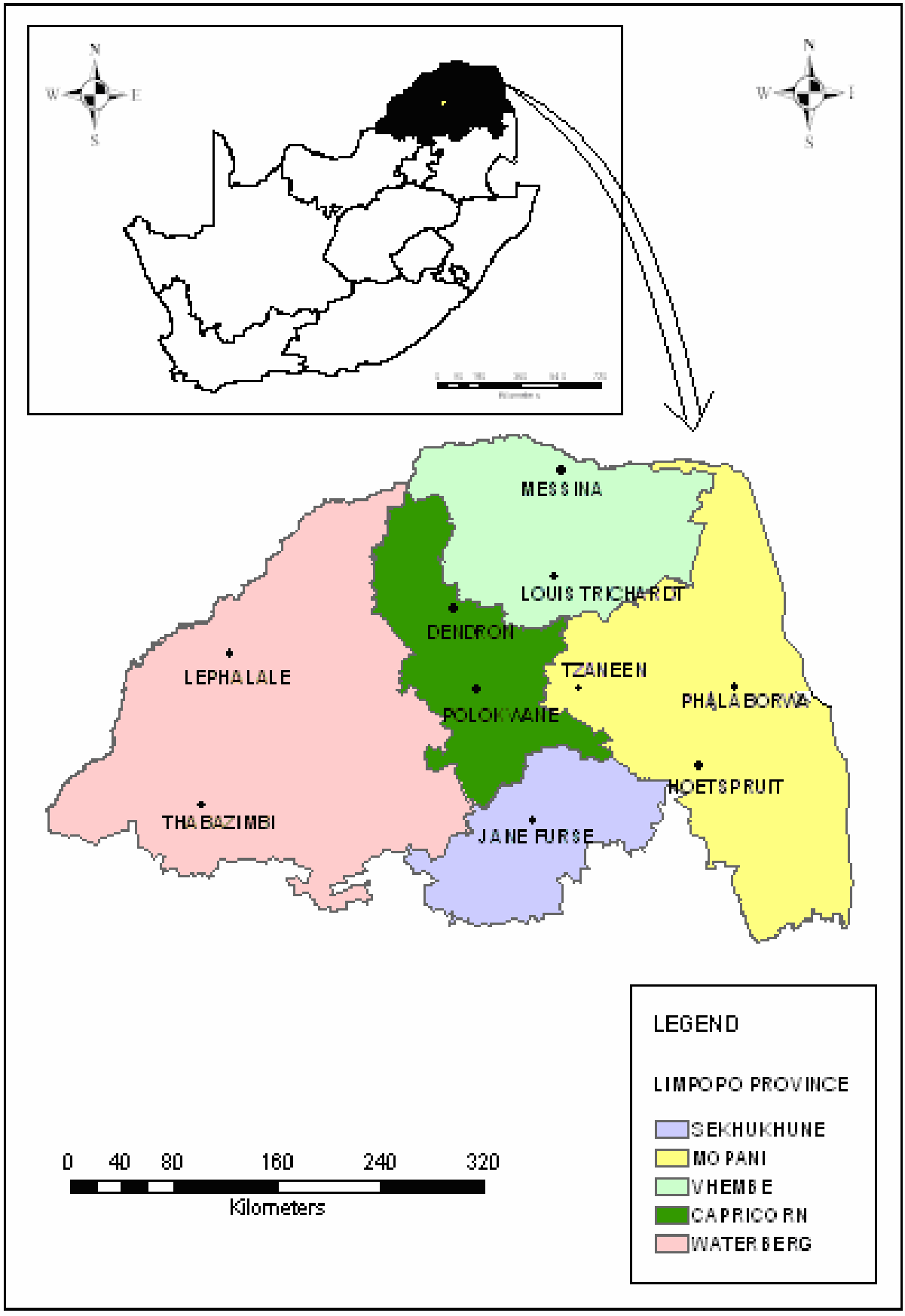

Fig.12: Map of Limpopo Province showing the five districts.

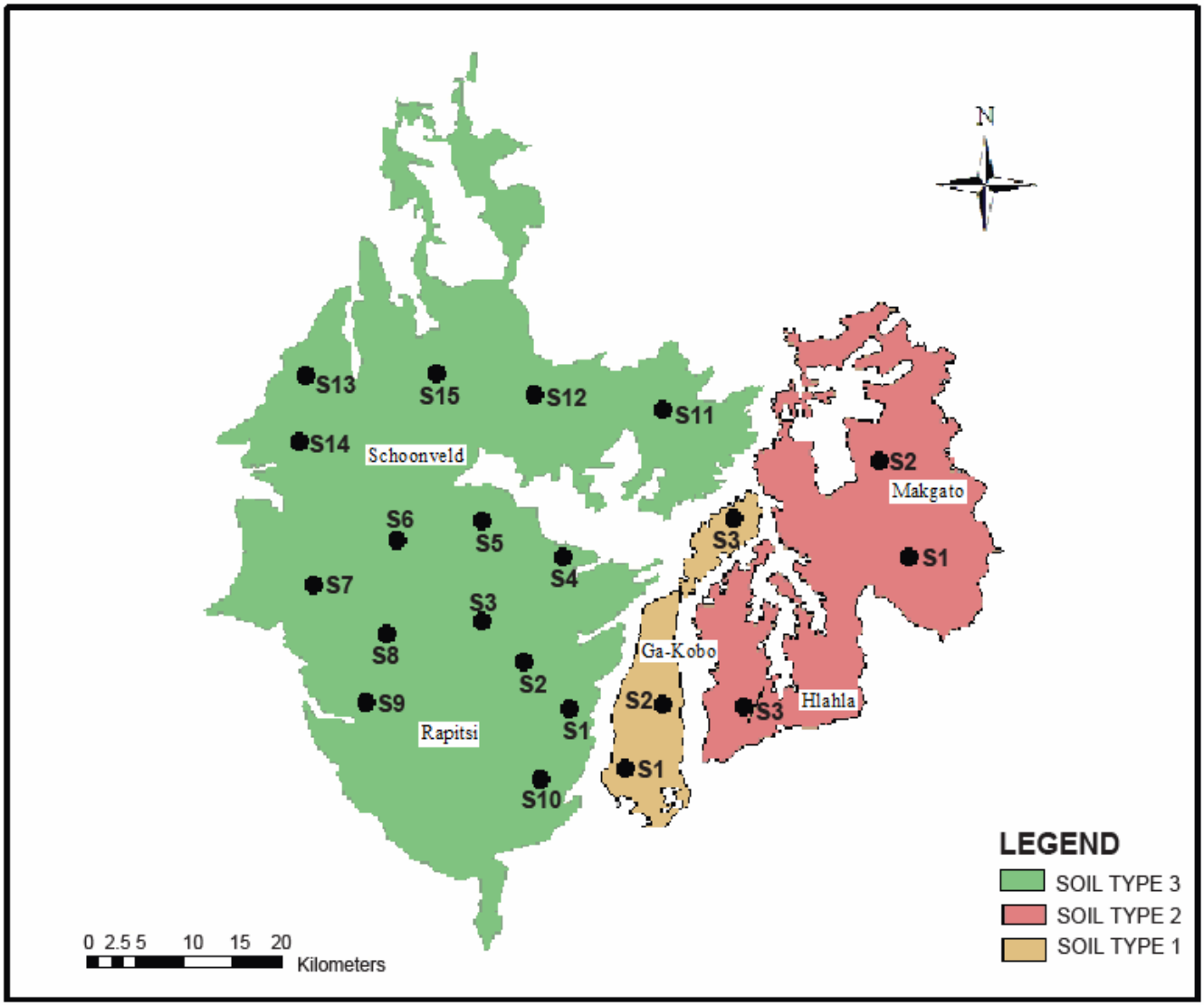

Fig.13: Map of the study area showing the soil types and their sample locations.

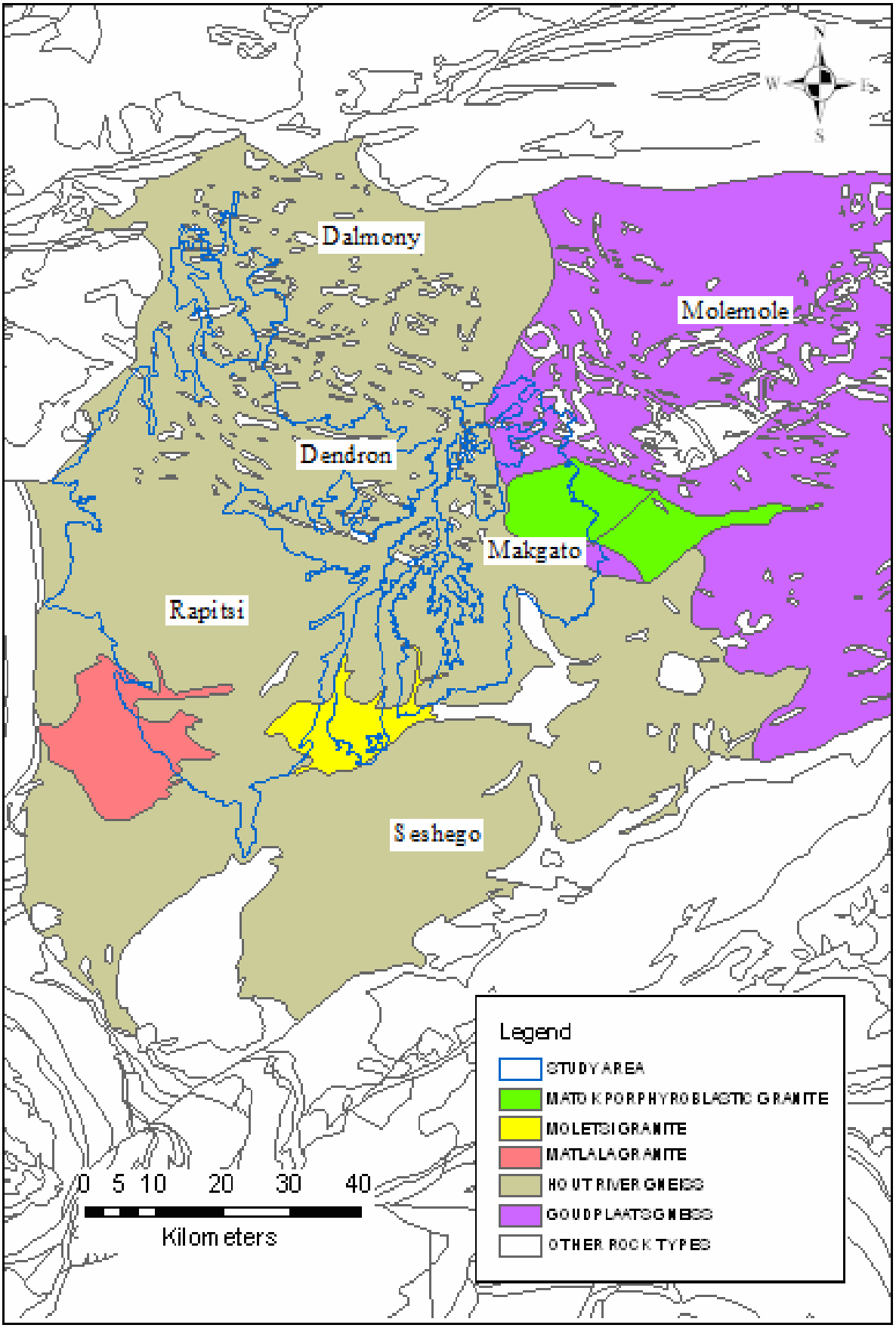

Fig. 14: Geology map of the study area

3.2 SAMPLE COLLECTION

A random sampling method was used to sample soils to a depth of 20cm, on an area of 316053 ha. To minimize sampling error, all the units of the survey area were included to cover the inherent variations among soil units. A soil auger and a geological hammer were used for the collection of samples. Table 1 gives sample numbers and sample coordinates in each soil type of the study area.

Table 1: A table of sample coordinates and sample numbers in each soil type.

Sample identity	**Coordinates**	**Sample identity**	**Coordinates (ctd)**
Soil type 1 (Inceptic)		**Soil type 3 (Oxidic)**	
S1	S23°31,957E029°35,690	S5	S23°27,112E029°12,801
S2	S23°26,680E029°34,794	S6	S23°29,337E029°06,946
S3	S23°23,343E029°07,252	S7	S23°31,334E029°02,040
Soil type 2 (Plinthic)		S8	S23°34,149E029°05,717
S1	S23°38,432E029°03,454	S9	S23°37,805E029°04,037
S2	S23°24,365E029°33,094	S10	S23°38,434E029°03,458
S3	S23°39,368E029°24,481	S11	S23°21,858E029°21,434
Soil type 3 (Oxidic)		S12	S23°20,414E029°14,336
S1	S23°54,734E029°27,197	S13	S23°17,163E029°07,695
S2	S23°54,737E029°27,197	S14	S23°17,163E02°907,695
S3	S23°33,671E029°11,200	S15	S23°23,344E029°07,252
S4	S23°30,380E029°15,286		

3.3 SAMPLE PREPARATION FOR CLAY MINERALS ANALYSIS

3.3.1 Dissolution of carbonates and soluble salts with sodium acetate buffer

The collected samples were ground and passed through a 2-mm sieve into a dialysis membrane, one end of which is tied with a rubber band. 0.5 *M* of Na-acetate buffer solution was added to the sieved samples in a glass container of appropriate size and allowed to hang. After all carbonates were dissolved, the samples were desalted against tape water to wash away all salts. Electrical conductivity measurements on small volumes of the supernatant liquid of the sample were done to check ionic concentration. The procedure was continued until the concentration was lowered to10 meq/L.

3.3.2 Removal of organic matter

The samples were then transferred to a beaker with a minimum quantity of distilled water. Excess water was evaporated using a steam bath or hot plate to a soil-water ratio of 1:1 to 1:2. Thirty percent of hydrogen peroxide (H_2O_2) was added in increments of 5 to 10 mL and stirred. Additions of H_2O_2 and subsequent heating was done until frothing ceased. When the reaction of the soil with H_2O_2 was completed, the sample was transferred to centrifuge tubes for centrifugation at 1600 to 2200 rpm for 10 to 15 min. The supernatant liquid was then decanted and discarded.

3.3.3 Removal of free iron oxides

One gram of clay sample was transferred to a 100mL centrifuge tube. 40 mL of 0.3*M* Na-citrate solution and 5mL of 0.5*M* $NaHCO_3$ solution was added to the sample. The suspension was warmed up to 80ºC in a water bath and 1g of solid $Na_2S_2O_4$ added. The suspension was stirred constantly for 1 min and then occasionally for a total of 15 min. Ten milliliter of a saturated NaCl solution was added to flocculate the suspension. The sample was finally washed with Na-citrate solution.

3.3.4 Separation of particle size fractions (< 2 μm)

The pretreated soil sample was transfered quantitatively into a blender cup. After the the soil sample was transferred, the blender cup was filled with distilled water to about 10cm of the top (rim) and metaphosphate solution was added. The solution was blended mechanically on a blending machine for 15 min and the soil suspension was transferred into a soil testing cylinder. The remaining soil residue in the cylinder was washed with water from a water bottle. The volume in the cylinder was made up to a 1L level with water. The suspension was mixed thoroughly using a stirring rod so that all sediment disappeared from the bottom of the cylinder. Then the solution was allowed to stand for 2 hours. After the appropriate sedimentation time, the supernatant suspension was decanted into the vessel reserved for the < 2 μm particles. The procedure was repeated 5 to 8 times to effect complete separation.

3.3.5 Separation of particle size fractions (< 0.2 μm)

The < 2 μm suspension clay was transferred to a group of 100mL centrifuge tubes, keeping the depth of suspension in the tubes to exactly 10cm. The suspension was centrifuged to

allow > 0.2 μm particles to sediment to the bottom. The procedure was continued until all the clay suspension was collected in the tubes. The sediment was then resuspended in the tubes in Na_2CO_3 solution and the centrifugation and decantation repeated until separation was essentially complete. 5 to 8 repetitions were done. After the last decantation, the sediment in the bottom of the tubes was transferred to a flask and saved for x-ray analysis.

3.4 ANALYTICAL TECHNIQUES

3.4.1 X-ray Diffraction Analyses

The clay fraction of the samples for minerals identification was obtained based on the principle of sedimentation according to Stoke's law (Gaspe et al., 1994). The clay fraction of samples were mixed with a few drops of epoxy glue to control particle orientation. The dried samples were gently crushed to fine samples in an agate mortar, and then mounted on the sample holder with very little pressure for analyses (Ekosse, 2005). Samples were scanned from 2º 2θ to 70º 2θ for bulk and < 2-μm fraction, and their diffractograms recorded.

The presence of kaolinite in the samples was identified by its (001) d spacing of 7.14 Å diffraction in oriented samples. Samples were subjected to a 500˚C treatment to distinguish kaolinite from serpentine in the kaolinite-serpentine group. Kaolinite was further reacted with formamide for 10 minutes to allow the recognition of halloysite (a member of the kaolinite group) which expanded from 7 to 10 Å in a shot time.

The swelling clays, smectite and vermiculite, were identified by their (001) d spacing of 14 Å. Hydrous mica was identified by a (001) basal spacing of 10 Å. The 10 Å peak does not shift or collapse after heating the mineral at 500˚C or after salvation with glycerol or ethylene glycol. Chlorites were identified by their non-changing basal spacing at 14 Å irrespective of solvation and heat treatment. The 500˚C heat treatment causes a change in the peak intensity ratios, the (001) reflection while the other reflections are weekend and commonly disappear (PDSA, 1994; Tan, 1998).

3.4.2 X-ray Flouorescence Spectroscopy Analyses

The samples were ground to < 75 μm in a Tungsten Carbide milling vessel, and were roasted at 1000˚C to determine loss on ignition value. 1g of sample was added to 9g of $Li_2B_4O_7$ and the mixture fused into a glass bead. Analyses of the major elements were executed on the

fused bead using the ARL9400XP+ spectrometer. Another aliquot of the sample was pressed in a powder briquette for trace element analyses.

3.4.3 Scanning Electron Microscopy Analyses

The SEM produced images by detecting secondary electrons which are emitted from the specimen surface due to excitation by the primary electron beam. The electron beam was rastered across the sample, with detectors building up an image by mapping the detected signals with beam position. Particle images were obtained using a secondary electron detector. Samples were mounted on Al stumps using a conductive glue. A thin coating of Au and Pd, about 10nm thick, was applied to the surface of the stumps. This prevented the accumulation of static electric fields at the specimen due to the electron irradiation required during imaging. This ensured a good yield of secondary electrons and thereby a good quality image.

CHAPTER 4

4. RESULTS

4.1 FIELD OBSERVATION

4.1.1 Soil profile

The studied soils present, to a greater extent in soil type 3, a soil profile that is similar in properties to oxidic soils. The oxidic group comprises soils having a B horizon that is uniformly pigmented with red and/ or yellow oxides of iron, with an orthic A horizon. The concept underlying the group is one of relative maturity (although not all members would conform to this description) coupled with free drainage and aeration. The apedal soils in this group are characterized by a relatively low CEC reflecting oxidic mineralogy in association with a predominantly kaolinitic mineral assemblage (sometimes referred to as kandic or low activity clays). The stable micro-aggregates of oxides and silicate clay are responsible for the strong and fine granular condition of these soils. Some areas (mostly in soil type 3) were found to have soil properties similar to the $CaCO_3$-containing soils of arid regions that exhibit at least some subsurface development. These soils contain subsurface horizons in which clays, calcium carbonate, silica, salts, and/ or gypsum have accumulated. They are characterized by being dry most of the year and expirience limited leaching. Soil type 2 has most of its area dominated by soils representing characteristics of a plinthic soil type. These soils consist of an orthic A horizon which grades into a soft or hard plinthic Bhorizon either directly, or indirectly via a red apedal B, yellow-brown apedal B or E horizon. The properties of plinthic soils are very similar to those of oxidic soils. The plinthite in plinthic soils indicates periodic saturation with water (Soil Classification Working Group, 1991). Soil type 1 on the other hand has most of its area composed of youthful soils perhaps because of limited weathering or on account of rejuvenation through natural erosion on steeper, convex slopes. Even were rock is weathered the subsoil has a predominantly geogenic character. These soils portray characteristics of inceptic soils with a lithocutanic B subsoil horizon, categorizing the soils to be of a lithic subgroup.

Generally, the soils have their B horizon as either red apedal B or yellow-brown apedal B, with small scale appearances of related horizons such as the red structured B horizon, E horizon and lithocutanic B horizon. The red and yellow-brown apedal B horizons have more or less uniform colors. The concept of these macroscopically weakly structured or

structureless materials embraces that kind of weathering that takes place in a well drained oxidizing environment to produce coatings of iron oxides on individual soil particles (hence the diagnostic red colors in the case of red apedal B horizon) and clay mineral suites dominated by 1:1 types (hence the lack of structural development). A 2:1 layer smectite clay was found in some samples, indicating the presence of some coarse textured red apedal horizons, but in fine textured horizons, 1:1 layer clays dominate the clay fraction. These horizons appear to have developed easily under a wider range of climatic conditions from siliceous parent materials such as granite, gneiss and quartzite which are prevalent in the area. These parent materials have a lower content of weatherable minerals and thus a lower clay forming potential.

4.1.2 Sampling techniques

Random soil sampling technique was carried out in all the three soil types surveyed. Samples were taken to a depth of 20cm as this depth correlates well with planting depth of most crops. Three samples were taken from study area 1 to represent the whole area. The sampling pattern in this area was more or less a straight line sampling from the northern part of the area to the southern part of the area. It was found that samples from the northern part contained concretions whereas those from the southern region had negligible to non presence of concretions. The sampling pattern of study area 2 was erratic with no particular pattern. Three soil samples were taken and were found to be uniform in texture. Study area 2 had much of its soils utilized as farm lands and this made sampling difficult in some areas. Study area 3 was the most sampled portion of the three study areas mainly because of its size compared to the other study areas. A total of 17 samples were taken in a random pattern to represent the different soil types that are prevalent in the area. Soil samples were found to be uniform in texture. Only a small number of the samples were found to be slightly clayey.

4.1.3 Study area soil profile variations

Soil type 1 (Inceptic) consists of soils with a general yellow-brown apedal B horizon. In some areas a variation in color from yellow-brown to reddish soils exists. In general the soils are deep to accommodate hutton and clovelly as some of the soil forms prevalent in the area. On the other hand, some areas are shallow with concretions near the surface or on the surface of the soil to form Lithocutanic B horizon as the apparent soil form (Fig. 15 & 16).

Soil type 2 (Plinthic) consists of largely deep red soils portraying mainly red apedal B horizon. Appearance of yellow-brown apedal B horizon is minimal in this area. The topsoil is mainly orthic A horizon rich in organic matter. The soils are sandier and well drained. Again, with respect to slope, some soils portray a lithocutanic character in their B horizon and therefore restricting the soil to a minimal depth (Fig. 17 & 18).

Soil type 3 (Oxidic) is made up of largely flat plains with soils exhibiting a high degree of weathering. Soil texture ranges from sandy to slightly clayey in some areas although the clay content is minimal. Yellow-brown apedal B horizon is dominant in the B horizon of these soils (Fig. 19, 20, 21 and 22). Table 2 below lists soil sample colors in each soil type of the study area.

Table 2: A table of soil sample colors in soil type 1, 2 & 3.

SAMPLES	**HUE**	**VALUE/CHROMA**	**COLOR**
Soil Type 1			
S1	7.5YR	7/4	Dull orange
S2	7.5YR	7/6	Reddish yellow
S3	7.5 YR	5/6	Brown
Soil Type 2			
S1	7.5 YR	7/4	Dull orange
S2	10 YR	6/6	Brownish yellow
S3	10 YR	7/4	Dull yellow orange
Soil Type 3			
S1	7.5 YR	5/6	Brown
S2	7.5 YR	6/2	Greyish brown
S3	7.5 YR	5/6	Brown
S4	7.5 YR	8/4	Light yellow orange
S5	7.5 YR	4/4	Dark brown
S6	7.5 YR	7/4	Dull orange
S7	7.5 YR	6/6	Reddish yellow
S8	7.5 YR	7/4	Dull orange
S9	7.5 YR	5/6	Brown
S10	7.5 YR	6/2	Greyish brown
S11	7.5 YR	6/6	Reddish yellow
S12	10 YR	6/4	Greyish yellow brown
S13	7.5 YR	4/3	Dark brown
S14	10 YR	4/3	Dark brown
S15	7.5 YR	5/4	Brown

Figure15: A photograph of soil type 1 (*Inceptic soil*) depicting imaturity of the soils

Figure 16: A photograph of soil type1 (*Inceptic soil*) showing concretions as a result of the lithic nature of the soils.

Figure 17: A photograph of soil type 2 (*Plinthic soil*) showing grass from a bushveld vegetation.

Figure18: A photograph of soil type 2 showing a plinthic soil with less vegetation.

Figure19: A photograph of soil type 3 (*Oxidic soil*) showing a calcareous soil.

Figure 20: A photograph of soil type 3 (*Oxidic soil*) showing calcium carbonate nudules.

Figure 21: A photograph of soil type 3 showing a lithic horizon..

Figure 22: A photograph of soil type 3 showing a reddish yellow soil color along the horizon.

4.2 X-RAY DIFFRACTION ANALYSES

The results of the chemical analyses carried out on all three soil types in the study area are reported in Table 3 & 4.

4.2.1 X-ray diffraction analyses on soil type 1 samples

The sample with the highest % of quartz in the clay fraction was sample S3 with the value of 75%, and the sample with the lowest value was sample S1 with the value of 54%. Sample S2 had the highest value of kaolinite at 33% as compared to a low of 4% in S3. Feldspar minerals were prevalent with a high of 18% in S1 and a low of 10% in S3. Smectites were not present at all in study area 1 with mica present in negligible amounts of 11% in S3 only. The rock samples in Table 4 showed the dominance of quartz minerals at a high of 82% in S1 and a negligible amount of mica with a low of 4% in S3. The rock samples proved to have higher amounts of both feldspar and mica as compared to the clay fraction samples.

4.2.2 X-ray diffraction analyses on soil type 2 samples

Soil type 2 portrayed smaller amounts of quartz as compared to soil type 1 with a high of 60% in S1 and a low of 47% in S3. Kaolinite percentages were also small as compared to those in soil type 1 with the highest value at 18% and the lowest value at 7%. Feldspar figures are almost the same as those in soil type 1 with the highest value at 18% in S1 and the lowest value at 9% in S2. Soil type 2 results show the presence of smectite in negligible amounts with a high of 9% in sample S3 and a low of 6 in sample S1. Mica appears more strongly in soil type 2 with a high value of 17% in S2. The quartz content of the rock samples was still high at a value of 88%, but the feldspar minerals were more or less similar in content with the clay fraction samples with a high value of 15% in S2. Mica had a higher % value of 27% in S2 as compared to the values in the clay fraction. An unusual smectite content of 3% was identified in sample S2.

4.2.3 X-ray diffraction analyses on soil type 3 samples

Soil type 3 had its highest quartz percentage at a value of 75% in S6 (similar to that of soil type 1 sample S3) and its lowest value at 27% in sample S8. Kaolinite content was high in sample S1 with a value of 41% and a lowest value of 8% in sample S2. Feldspar content, as in soil type 1 and 2, was in negligible amount with a high value of 12% in both sample S8

and sample S14 and low value of 4% in sample S7. Soil type 3 had higher values of smectite compared to soil type 1 and 2 with a high value of 30% in sample S1 and a lower value of 3% in sample S10. Mica has a high value of 26% in sample S2 and a lower value of 7% in sample S12. Based on the contents of the different minerals, soil type 3 clay fraction samples can be divided into two categories in each mineral. In quartz, the first category was samples which had a % ≥ 51%, and these are samples S2, S3, S4, S6, S7, S10, S11, S12 and S14. The second category was made up of quartz % ≤ 51%, and the samples were S1, S5, S8, S9, S13 and S15. In kaolinite, the first category was samples which had a % ≥ 18%, and these are samples S1, S3, S5, S7, S8, S13, S14 and S15. The second category was made up of % ≤ 17%, and the samples were S2, S4, S6, S9, S10, S11 and S12. In feldspar, the first category was samples which had a % ≥ 10%, and these are samples S4, S8, S9, S11, S13 and S14. The second category was made up of % ≤ 9%, and the samples were S1, S2, S3, S5, S6, S7, S10, S12 and S15. In smectite, the first category was samples which had a % ≥ 19%, and these are samples S1, S5, S9 and S20. The second category was made up of % ≤ 18%, and the samples were S2, S3, S4, S6, S7, S8, S10, S12, S13, S14 and S15. In mica, the first category was samples which had a % ≥ 15%, and these are samples S2, S5, S8 and S10. The second category was made up of % ≤ 14%, and the samples were S1, S3, S4, S6, S7, S9, S11, S12, S13, S14 and S15.

The rock samples of soil type 3 had negligible contents of mica with the highest value at 6% in sample S14 and a low value of 4% in sample S12 and S13. There was no evidence of smectite in these samples.

4.3 X-RAY FLUORESCENCE SPECTROMETRY ANALYSES

The XRF results for the survey area are shown in Tables 5, 6 and 7 for the clay fraction, whole soil and rock samples respectively. Generally the results show a decrease in the amount of SiO_2 in the clay fraction of samples as compared to those in the whole soil and rock samples. But the whole soil sample results differ only slightly with the rock sample results. The Al_2O_3 results also show the same pattern, with the amount increasing in the clay fraction. Fe_2O_3 also shows an increase in the clay fraction as compared to the whole soil and rock samples. The behavior of other elements such as MgO, MnO, CaO, Na_2O, K_2O and P_2O_5 are in negligible amounts and show a very small change in the XRF clay fraction results.

4.3.1 X-ray fluorescence spectrometry analysis on soil type 1

Sample S1 contains a highest amount of SiO_2 at a percentage of 69.89% in the clay fraction. Its lowest value is 69.05% in sample S2. The highest value in the whole soil samples is 86.80% in sample S1, with its lowest as 83.78% in sample S2. The highest value of Al_2O_3 in the clay fraction is 14.43% in sample S1 and the lowest value as 12.89% in sample S3. The whole soil samples had their highest value as 6.98% in sample S3 and their lowest value as 5.87%. The Fe_2O_3 content was smaller as compared to the Al_2O_3 and SiO_2 contents in these samples. The clay fraction samples had their highest value in sample S2 with 4.95% and their lowest in sample S1 with 4.16%. The whole soil samples had smaller contents with highest value as 3.16% in sample S2 and the lowest as 1.47% in sample S1. The amounts of MnO, MgO, CaO, Na_2O, P_2O_5 and K_2O remained more or less the same with slight increments in the clay fraction results although Na_2O and K_2O had slightly higher contents than the rest.

4.3.2 X-ray fluorescence spectrometry analyses on soil type 2

Soil type 2 shows slight variances with respect to chemical contents to those of soil type 1. Its highest SiO_2 value is 65.71% in sample S1 and its lowest is 57.99% in sample S2. The whole soil samples have their highest value in sample S3 as 87.32% and their lowest in sample S2 as 78.76%. The highest value for Al_2O_3 in the clay fraction was 15.57% in sample S1 and the lowest as 14.85% in sample S3. For the whole soil samples, the highest value was 8.30% in sample S2 and the lowest value as 5.62% in sample S3. Fe_2O_3 content in the clay fraction had its highest value as 9.28% in sample S2 and its lowest value as 5.23% in sample S3. On the other hand, the highest value in the whole soil fraction is 4.21% in sample S2 and the lowest is 1.58% in sample S1. The increment in the amount of MnO, MgO, CaO, Na_2O, P_2O_5 and K_2O in soil type 2 is slightly higher compared with those for soil type 1 in both the whole soil and clay fraction samples.

4.3.3 X-ray fluorescence spectrometry analyses on soil type 3

The SiO_2 content in soil type 3 has its highest value in sample S4 as 77.35% and its lowest value as 60.81% in sample S8. The highest value in the whole soil fraction is 90.79% in sample S4, which is higher than the samples of both soil type 1 and 2, and its lowest value as 76.89% in sample S11. Al_2O_3 in the clay fraction was found to be highest in sample S1 as 17.33% and lowest in sample S4 as 10.59%. The whole soil fraction has its highest value as 8.46% in sample S5 and its lowest value in sample S4 as 3.19%. Fe_2O_3 in the clay fraction

had its highest value as 10.68% in sample S8 and its lowest value as 2.69% in sample S10. The whole soil fraction had their highest Fe_2O_3 value as 9.78% in sample S3 and their lowest value as 1.23% in sample S9. The MnO, MgO, CaO, Na_2O, P_2O_5 and K_2O values in the clay fraction had many variations that represented, in similarity, samples from both soil type 1 and 2. The whole soil samples had almost uniform values as compared with the clay fraction values.

4.4 SCANNING ELECTRON MICROSCOPY ANALYSES

The scanning electron micrographs (Fig. 23, 24 and 25) of the clay fraction reveal hexagonally shaped thin platelets which are typical of kaolinite. However, these platelets are sometimes interbedded with semi rounded particles of smectites.

SEM micrographs of the study area show euhedral to subhedral pseudo-hexagonal flakes with relatively very rough surfaces and ragged edges (Fig. 26). The general appearance of the images portray larger, thin particles together with smaller micro islands attached or intergrown to the larger particle surfaces. Some of the larger particles portray a high frequency of steps (Fig 23 & 24). The overall particle shapes are therefore relatively complex, ragged with comparatively thin edges giving higher aspect ratios. The vermicular book structure of kaolinites is clearly distinct in figure 24, clearly revealing the right angled edges and the steps characteristic of kaolinite minerals. Figure 25 & 29 depicts quartz minerals with rough surfaces, attesting to the presence of the minerals in the clay fraction. Soil type 2 SEM photomicrographs show nearly well developed euhedral, hexagonal to pseudohedral shaped platelets with slightly smooth surfaces (Fig. 27 & 28). Figure 30 & 31 show semi rounded particles of smectite mixed with platelets of kaolinite and quartz minerals.

Table 3: Semi-quantitative analyses of the clay fraction for XRD.

Wt%	Soil type 1			Soil type 2			Soil type 3													
	S1	S2	S3	S1	S2	S3	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15
Qz	54	66	75	60	53	47	29	58	54	69	28	75	62	27	32	55	55	57	41	62	50
Kt	28	33	4	7	9	18	41	8	23	10	30	9	20	28	17	9	15	17	24	26	25
Fs	18	0	10	18	9	13	0	8	7	10	0	8	4	12	11	9	10	9	11	12	0
St	0	0	0	6	7	9	30	0	0	0	22	8	11	0	19	3	20	10	11	0	0
Mi	0	0	11	0	17	13	0	26	0	11	20	0	0	21	0	24	0	7	13	0	13

Qz = quartz, Kt = kaolinite, Fs = feldspar, St = smectite and Mi = mica

Table 4: XRD clay fraction descriptive statistics.

MINERALS	MEAN	MEDIAN	MODE	RANGE	STANDARD DEVIATION	COVARIANCE	VARIANCE
Qz	52.81	55	54	48	14.42	-79.46	208.06
Kt	19.09	18	9	37	9.96	-22.53	99.29
Fs	8.52	9	0	18	5.27	-13.65	27.86
St	7.42	6	0	30	8.85	-16.49	78.35
Mi	8.38	7	0	26	9.23	DIV/0	85.25

Qz = quartz, Kt = kaolinite, Fs = feldspar, St = smectite and Mi = mica

Table 5: Selected rock samples from the three soil types of the study area.

Wt%	Soil type 1		Soil type 2		Soil type 3			
	S1	S3	S1	S2	S12	S13	S14	S15
Qz	82	66	88	41	65	71	51	96
Fs	10	30	12	15	31	20	43	0
Mi	7	4	0	27	4	4	6	0
St	0	0	0	3	0	0	0	0

Qz = quartz, Kt = kaolinite, Fs = feldspar, St = smectite and Mi = mica

Table 6: XRD rock samples descriptive statistics.

MINERALS	MEAN	MEDIAN	MODE	RANGE	STANDARD DEVIATION	COVARIANCE	VARIANCE
Qz	70	68.5	N/A	55	18.47	-146.37	341.14
Fs	20.125	17.5	N/A	43	13.83	1.31	191.26
Mi	6.5	4	4	27	8.65	7.68	74.86
St	0.37	0	0	3	1.06	DIV/0!	1.12

Qz = quartz, Kt = kaolinite, Fs = feldspar, St = smectite and Mi = mica

Table 7: XRF results for the clay fraction.

	Soil type 1			Soil type 2			Soil type 3														
Wt %	**S1**	**S2**	**S3**	**S1**	**S2**	**S3**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**	**S11**	**S12**	**S13**	**S14**	**S15**
SiO_2	69.89	69.05	69.70	65.71	57.99	65.44	63.99	71.01	66.52	77.35	62.89	69.12	68.81	60.81	66.96	71.46	65.30	61.79	67.35	64.49	65.11
TiO_2	1.27	1.37	1.07	1.41	2.30	1.31	1.10	1.01	1.44	1.35	1.33	0.99	1.19	0.98	0.93	0.80	1.52	1.20	1.15	0.95	0.99
Al_2O_3	14.43	13.06	12.89	15.57	15.22	14.85	17.33	13.09	14.29	10.59	15.24	12.99	14.79	15.90	14.81	14.04	15.53	16.61	16.22	17.50	16.50
Fe_2O_3	4.16	4.95	4.19	5.74	9.28	5.23	5.46	3.80	5.66	3.28	7.63	4.66	4.63	10.68	3.67	2.69	5.83	6.60	4.22	4.19	4.57
MnO	0.05	0.12	0.09	0.09	0.17	0.09	0.06	0.09	0.10	0.07	0.13	0.12	0.08	0.16	0.09	0.04	0.09	0.12	0.07	0.08	0.08
MgO	0.29	0.75	0.66	1.10	1.41	0.46	0.43	0.46	0.33	0.37	1.30	0.56	0.40	0.42	0.49	0.27	1.11	0.61	0.44	0.64	0.94
CaO	0.00	0.48	0.45	1.10	2.16	0.07	0.02	0.28	0.00	0.00	1.02	0.31	0.00	0.12	0.88	0.21	1.09	0.36	0.24	0.26	0.43
Na_2O	1.06	1.74	1.92	2.70	2.01	1.10	0.57	1.53	0.67	1.24	1.34	1.51	0.78	1.20	2.25	2.85	2.68	0.86	1.15	1.23	1.69
K_2O	3.07	2.37	2.30	1.58	2.06	2.01	1.95	2.28	1.73	1.83	1.51	2.29	1.84	2.11	2.64	3.32	1.61	1.65	2.25	1.87	1.65
P_2O_5	0.05	0.09	0.09	0.07	0.46	0.10	0.07	0.09	0.13	0.08	0.13	0.13	0.07	0.11	0.09	0.06	0.09	0.08	0.06	0.05	0.08
Cr_2O_3	0.02	0.04	0.03	0.04	0.03	0.03	0.03	0.02	0.03	0.04	0.05	0.04	0.04	0.05	0.01	0.01	0.05	0.06	0.03	0.04	0.06
NiO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.02
V_2O_5	0.01	0.02	0.01	0.02	0.03	0.02	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.03	0.01	0.01	0.02	0.02	0.01	0.01	0.01
ZrO_2	0.18	0.18	0.10	0.13	0.19	0.11	0.08	0.11	0.12	0.19	0.09	0.11	0.10	0.09	0.12	0.11	0.14	0.09	0.09	0.05	0.09
LOI	5.71	4.96	5.60	5.55	6.24	7.33	9.19	6.55	8.19	4.13	7.50	6.85	7.28	7.49	7.59	4.37	5.83	8.82	7.59	8.88	7.34
TOTAL	100.18	99.19	99.11	100.82	99.56	98.15	100.31	100.34	99.24	100.54	100.19	99.70	100.04	100.15	100.54	100.24	100.89	98.90	100.88	100.24	99.57

Table 8: Clay fraction descriptive statistics

ELEMENTS	MEAN	MEDIAN	MODE	RANGE	STANDARD DEVIATION	COVARIANCE	VARIANCE
SiO_2	66.70	66.52	N/A	19.36	4.23	-0.47	17.93
TiO_2	1.22	1.19	0.99	1.5	0.31	-0.02	0.10
Al_2O_3	14.83	14.85	N/A	6.91	1.67	1.12	2.81
Fe_2O_3	5.29	4.66	4.19	7.99	1.93	0.05	3.74
MnO	0.09	0.09	0.09	0.13	0.03	0.00	0.00
MgO	0.64	0.49	0.46	1.14	0.34	0.15	0.11
CaO	0.45	0.28	0	2.16	0.53	0.20	0.28
Na_2O	1.53	1.34	N/A	2.28	0.67	0.08	0.45
K_2O	2.09	2.01	1.65	1.81	0.48	-0.00	0.23
P_2O_5	0.10	0.09	0.09	0.41	0.08	-2.7E-05	0.01
Cr_2O_3	0.03	0.04	0.04	0.05	0.01	3.4E-05	0.00
NiO	0.01	0.01	0.01	0.01	0.00	-2.9E-06	1.9E-05
V_2O_5	0.01	0.01	0.01	0.02	0.01	6.01E-05	4.62E-05
ZrO_2	0.12	0.11	0.09	0.14	0.04	-0.04	0.00
LOI	6.81	7.28	7.59	5.06	1.43	-0.15	2.05
TOTAL	99.94	100.18	100.54	2.74	0.72	DIV/0!	0.51

Table 9: XRF results for the whole soil fraction.

	Soil type 1			Soil type 2			Soil type 3													
Wt %	**S1**	**S2**	**S3**	**S1**	**S2**	**S3**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**	**S11**	**S12**	**S13**	**S14**	**S15**
SiO_2	86.80	83.78	85.56	87.05	78.76	87.32	80.14	88.09	79.52	90.79	79.84	86.83	88.78	84.32	83.07	83.53	76.89	81.04	84.69	83.43	85.67
TiO_2	0.36	0.46	0.32	0.32	1.25	0.43	0.47	0.17	0.47	0.21	0.46	0.19	0.28	0.26	0.25	0.17	1.21	0.43	0.27	0.31	0.23
Al_2O_3	5.87	6.39	6.98	6.15	8.30	5.62	8.45	5.50	4.94	3.19	8.46	5.69	4.27	6.76	8.32	7.79	8.11	7.82	8.36	8.24	7.21
Fe_2O_3	1.47	3.16	1.69	1.58	4.21	1.74	3.87	1.43	9.78	1.31	3.87	1.66	2.93	2.77	1.23	1.65	5.65	2.89	1.83	2.01	1.93
MnO	0.02	0.06	0.03	0.02	0.08	0.03	0.06	0.03	0.04	0.02	0.06	0.05	0.02	0.04	0.03	0.04	0.09	0.07	0.02	0.03	0.03
MgO	0.00	0.23	0.18	0.21	0.56	0.05	0.70	0.03	0.01	0.03	0.68	0.05	0.01	0.07	0.06	0.08	0.52	0.25	0.05	0.19	0.33
CaO	0.00	0.00	0.07	0.32	1.12	0.00	0.81	0.00	0.00	0.00	0.77	0.00	0.00	0.00	0.14	0.00	0.90	0.24	0.42	0.00	0.13
Na_2O	0.46	0.86	1.44	1.82	1.76	0.48	1.11	1.13	0.22	0.51	1.11	0.84	0.35	0.74	1.54	1.34	1.51	1.36	0.92	1.13	1.33
K_2O	2.75	1.68	1.81	0.60	1.85	1.78	1.22	1.46	0.65	0.59	1.21	2.12	0.80	1.40	2.82	3.03	1.42	1.27	3.21	1.50	0.78
P_2O_5	0.01	0.03	0.03	0.01	0.12	0.03	0.05	0.03	0.07	0.02	0.05	0.05	0.02	0.03	0.02	0.02	0.20	0.03	0.03	0.02	0.03
Cr_2O_3	0.01	0.03	0.02	0.02	0.02	0.01	0.03	0.01	0.05	0.02	0.03	0.01	0.04	0.02	0.00	0.01	0.02	0.03	0.02	0.03	0.04
NiO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
V_2O_5	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.00	0.03	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.02	0.01	<0.01	0.01	<0.01
ZrO_2	0.06	0.05	0.04	0.04	0.08	0.05	0.03	0.03	0.05	0.04	0.03	0.03	0.04	0.03	0.04	0.03	0.04	0.05	0.02	0.03	0.03
LOI	1.51	2.15	1.50	1.08	1.45	2.02	2.72	1.32	3.38	1.40	2.90	1.54	1.95	2.70	1.91	1.70	2.65	2.61	<0.01	2.90	2.15
TOTAL	99.33	98.92	99.67	99.24	99.56	99.57	99.68	99.23	99.21	98.15	99.49	99.07	99.51	99.16	99.44	99.40	99.23	98.12	99.85	99.85	99.89

Table 10: Whole soil fraction descriptive statistics

ELEMENTS	MEAN	MEDIAN	MODE	RANGE	STANDARD DEVIATION	COVARIANCE	VARIANCE
SiO_2	84.09	84.32	N/A	13.9	3.66	-0.72	13.39
TiO_2	0.40	0.32	0.46	1.08	0.29	0.13	0.08
Al_2O_3	6.78	6.98	N/A	5.27	1.53	0.05	2.36
Fe_2O_3	2.79	1.93	3.87	8.55	1.98	0.02	3.92
MnO	0.04	0.03	0.03	0.07	0.02	0.00	0.00
MgO	0.20	0.08	0.05	0.7	0.22	0.07	0.05
CaO	0.23	0	0	1.12	0.36	0.08	0.13
Na_2O	1.04	1.11	1.11	1.6	0.46	0.04	0.22
K_2O	1.62	1.46	N/A	2.62	0.79	-0.00	0.63
P_2O_5	0.04	0.03	0.03	0.19	0.04	4.56E-05	0.00
Cr_2O_3	0.02	0.02	0.02	0.05	0.01	-1.3E-05	0.00
NiO	0.01	0.01	0.01	0.01	0.00	-1.2E-05	4.76E-06
V_2O_5	0.01	0.01	0.01	0.03	0.01	1.99E-05	6.49E-05
ZrO_2	0.04	0.04	0.03	0.06	0.01	-0.00	0.00
LOI	1.98	1.98	2.15	2.3	0.65	0.03	0.42
TOTAL	99.31	99.4	99.23	1.77	0.47	DIV/0!	0.22

Table 11: XRF results for rock samples.

	Soil type 1		Soil type 2		Soil type 3			
Wt %	**S1**	**S3**	**S1**	**S2**	**S12**	**S13**	**S14**	**S15**
SiO_2	85.49	92.86	98.87	59.35	91.59	80.33	89.00	99.09
TiO_2	0.30	0.01	<0.01	1.64	0.02	0.03	0.01	<0.01
Al_2O_3	7.09	3.68	0.32	13.47	4.70	9.86	6.38	0.30
Fe_2O_3	2.51	0.38	0.53	9.53	0.70	1.42	0.47	0.44
MnO	0.02	0.01	0.02	0.14	0.01	0.04	0.01	<0.01
MgO	0.14	0.00	<0.01	3.05	0.00	<0.01	0.00	<0.01
CaO	0.00	0.00	0.06	4.39	0.00	<0.01	0.00	0.05
Na_2O	1.85	1.65	<0.01	3.09	2.11	1.63	2.31	<0.01
K_2O	1.91	0.32	<0.01	2.16	0.34	5.75	1.53	0.04
P_2O_5	0.01	0.01	<0.01	0.56	<0.01	<0.01	<0.01	<0.01
Cr_2O_3	0.01	0.00	0.02	0.02	0.01	0.01	0.01	<0.01
NiO	0.01	0.01	<0.01	0.01	0.01	0.01	0.01	<0.01
V_2O_5	<0.01	0.00	<0.01	0.03	<0.01	<0.01	<0.01	<0.01
ZrO_2	0.04	0.01	<0.01	0.06	0.01	0.01	0.01	<0.01
LOI	1.01	0.16	0.19	1.95	0.52	0.55	0.26	0.06
TOTAL	100.39	99.10	100.00	99.47	100.02	99.65	100.00	99.97

Table 12: Rock samples descriptive statistics

ELEMENTS	MEAN	MEDIAN	MODE	RANGE	STANDARD DEVIATION	COVARIANCE	VARIANCE
SiO_2	87.07	90.30	N/A	39.74	12.86	-6.33	165.39
TiO_2	0.25	0.03	0.01	1.63	0.65	1.59	0.42
Al_2O_3	5.72	5.54	N/A	13.17	4.52	9.58	20.46
Fe_2O_3	1.99	0.61	N/A	9.15	3.13	0.13	9.79
MnO	0.03	0.02	0.01	0.13	0.05	0.06	0.00
MgO	0.40	0	0	3.05	1.35	2.12	1.82
CaO	0.56	0	0	4.39	1.65	0.78	2.73
Na_2O	1.58	1.98	N/A	1.46	0.55	-0.16	0.30
K_2O	1.50	1.53	N/A	5.71	1.97	0.13	3.86
P_2O_5	0.07	0.01	0.01	0.55	0.32	0.00	0.10
Cr_2O_3	0.01	0.01	0.01	0.02	0.01	0	4.76E-05
NiO	0.01	0.01	0.01	0	0	0	0
V_2O_5	0.00	0.01	N/A	0.03	0.02	0.00	0.00
ZrO_2	0.02	0.01	0.01	0.05	0.02	0.01	0.00
LOI	0.59	0.39	N/A	1.89	0.63	-0.02	0.40
TOTAL	99.82	99.99	100	1.29	0.40	DIV/0!	0.16

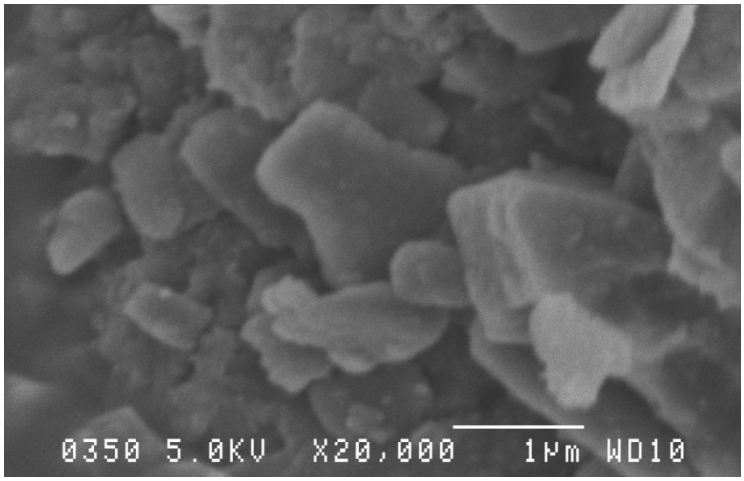

Fig 23: SEM photomicrograph of soil type 3 showing pseudohexagonal shapes of kaolinite.

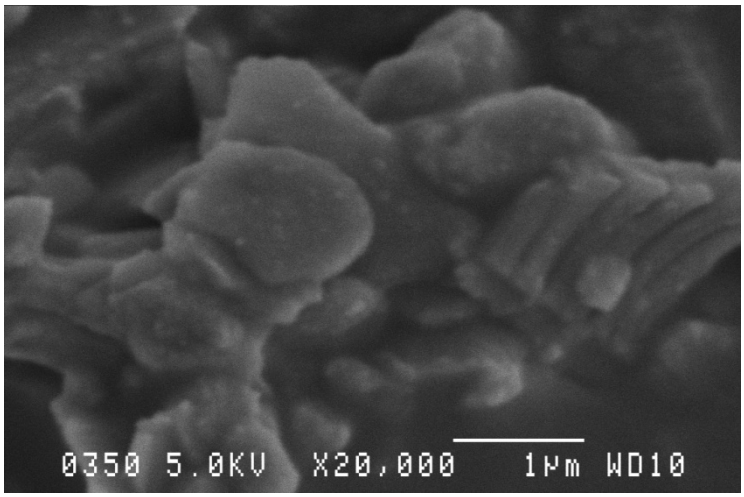

Fig 24: SEM photomicrograph of soil type 3 showing the vermicular books of kaolinite.

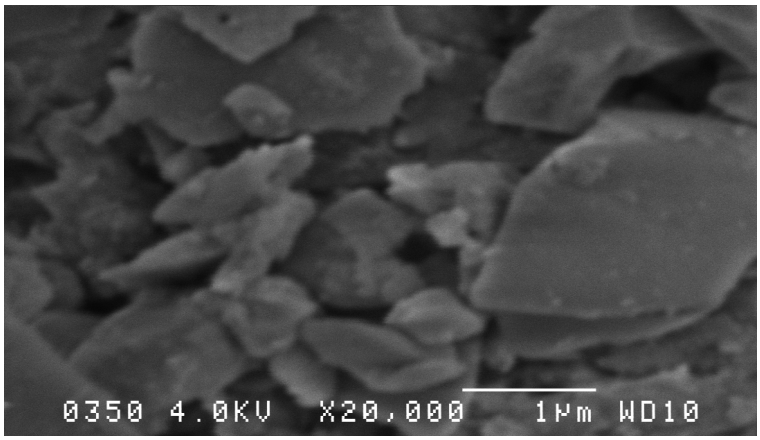

Fig 25: SEM photomicrograph of soil type 3 depicting quartz crystals with smaller crystals on their surfaces.

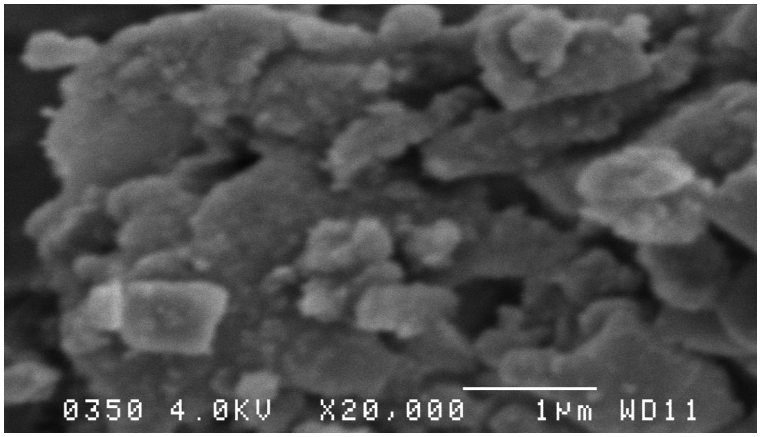

Fig 26: SEM photomicrograph of soil type 3 portraying pseudohexagonal kaolinite crystals with rough surfaces and ragged edges.

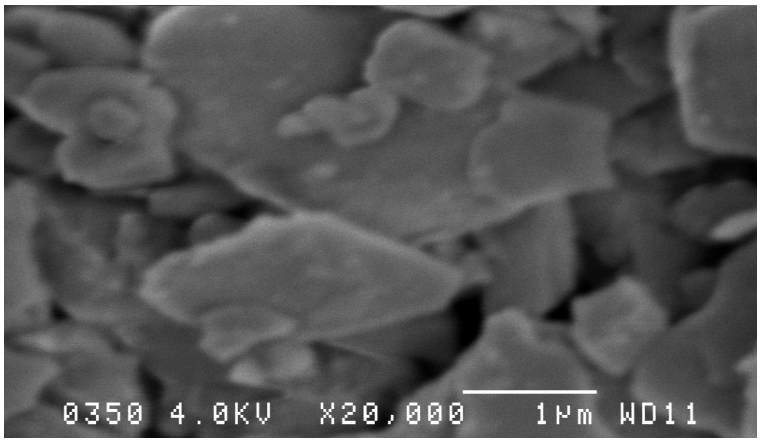

Fig 27: SEM photomicrograph of soil type 2 showing well developed euhedral, hexagonal to pseudohexagonal shaped plates.

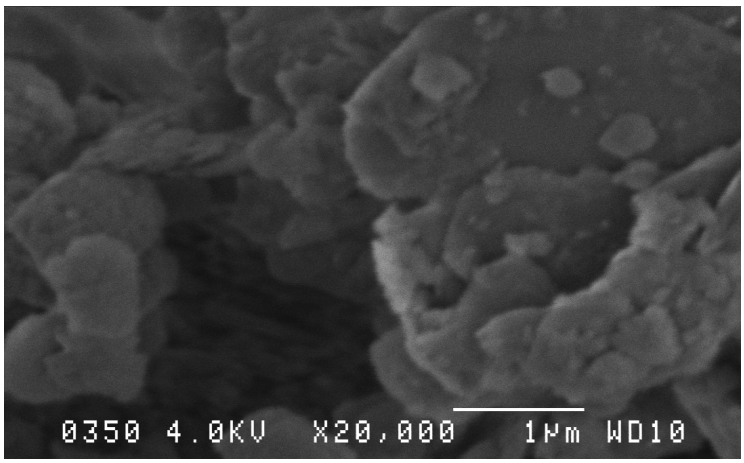

Fig 28: SEM photomicrograph of soil type 2 depicting the field of depth with smaller platelets on top of lager platelets.

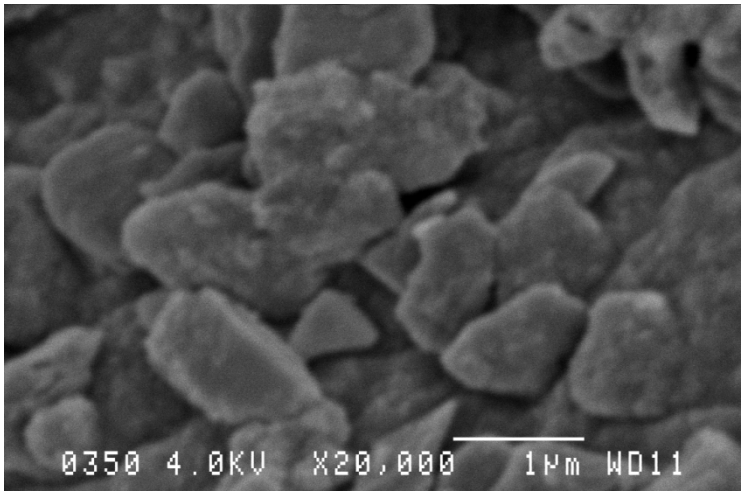

Fig 29: SEM photomicrograph of kaolinite flakes of soil type 2 with rough surfaces.

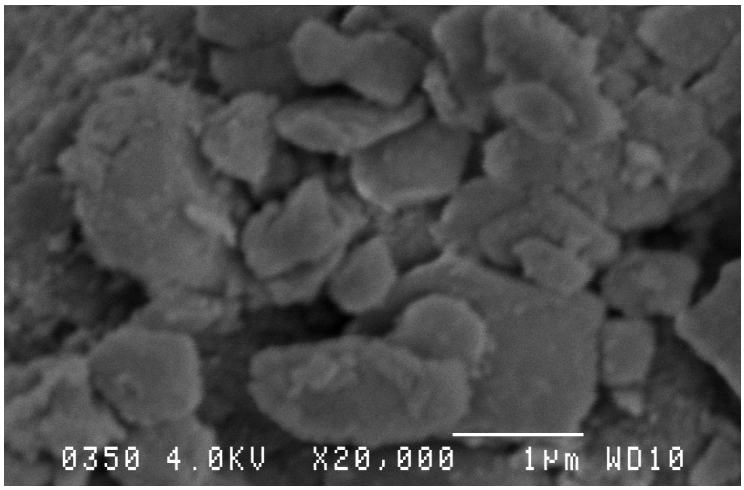

Fig 30: SEM photomicrograph of soil type 1 quartz minerals mixed with kaolinite flakes.

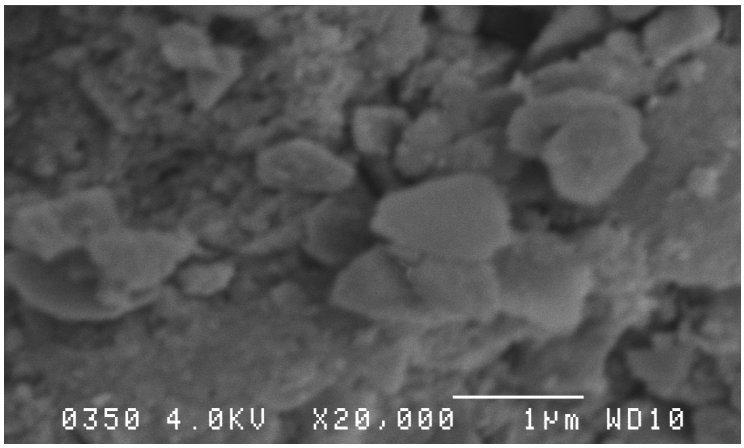

Fig 31: SEM photomicrograph of soil type 1 showing kaolinite flakes with smectite particles.

4.5 CONCLUDING REMARKS

The soils in the study area show a slight variation in their clay mineral constituents with kaolinite being the dominant clay mineral in the three study area sites surveyed. The XRD and XRF results provide a good picture with regards to the origin of the secondary clay minerals encountered in the area. The results show a weathering sequence relating to the weathering of the igneous rock with the subsequent release of its primary minerals, namely feldspars, quartz and mica. Further weathering of the primary minerals produced kaolinite and smectite as the secondary minerals. The results do not give any record of the other primary or secondary minerals known to occur in the weathering of igneous rocks. An assumption can only be made that the weathering process completely removed some of the secondary and primary minerals or the amounts are too small to be detected.

CHAPTER 5

5. DISCUSSIONS

5.1 CLAY MINERALS CHARACTERISATION BASED ON MINERALOGY

X-ray diffraction studies on soil samples in the research area revealed varying mineralogical results with respect to the type and amount of clay minerals present in the soil and more so in the clay fraction. On a general level, kaolinite was the dominant secondary clay mineral in all three soil types, showing to be comparatively higher in soil type 3 and lowest in study area 2. Quartz on the other hand dominated the primary clay minerals in all the soil types. The primary minerals dominating the soils constituted quartz, feldspar and mica whereas the secondary clay minerals constituted predominantly kaolinite and smectite. The presence of other possible primary and secondary minerals was not indicated in the results possibly because they are present in smaller insignificant quantities to be detected or not present at all. Table 3 & 4 shows the varying XRD quantities of the different minerals in varying locations of all three soil type areas surveyed.

Soil type 1 and 3 clay fraction contain higher quantities of quartz ranging between 29 – 75 % compared to soil type 2 with a high percentage of 60%. The rock samples slightly vary indicating a high percentage of quartz in soil type 3 with a range between 51 - 96% and a lower percentage range of 66 – 82% in soil type 1. The clay fraction results indicate a high kaolinite percentage range in soil type 3 at 0 – 41% and a lower percentage range in soil type 2 at 7 – 18 % with an intermediate range of 4 – 33% in soil type 1. Feldspar concentrations were comparatively high in the clay minerals of both soil type 1 and 2 with percentage ranges between 0 – 18% and 9 – 18% respectively. The rock sample results varied numerically with a high of 0 – 43% in soil type 3, 10 – 30% in soil type 1 and a low of 12 – 15% in soil type 2. Smectite quantities in the clay fraction of all study areas showed an interesting contrast with a comparative high percentage range of 0 – 30% in soil type 3 and an intermediate range of 6 – 9% in soil type 2. Soil type 1 indicated no presence of smectite in their clay fraction according to the XRD results obtained as indicated in table 3. The rock samples of soil type 2 indicated an interestingly small amount of smectite present in a range of 0 – 3%. On the other hand soil type 1 and 3 rock samples indicated no presence of smectite at all. Mica percentages ranged from 0 – 26% in the clay fraction of soil type 3 with most of the locations in this area presenting insignificantly lower percentages to a total absence in some areas.

Mica percentages in the clay fraction of both soil type 1 and 2 are 0 – 11% and 0 – 17% respectively. Mica rock mineral percentages were high in soil type 2 at 0 – 27%, intermediary in soil type 3 at 0 – 10% and lower in soil type 1 at 4 – 7%.

The high percentage range of kaolinite in the clay samples of soil type 3 and 1 may be because of both the weathering of feldspar minerals producing kaolinite and the direct weathering of biotite in mica to produce kaolinite. The non-presence of smectite in soil type 1 indicates that the weathering of mica directly produces kaolinite and perhaps smaller insignificant amounts of smectite that cannot be detected. The lower percentages of kaolinite minerals in the clay fraction of soil type 2 samples results from the lower quantities of feldspar and mica minerals both in the rock and soil portions of this area. However the other reason may be due to the fact that weathering has progressed slowly to produce both the primary and secondary minerals discussed in this paper.

5.2 CLAY MINERALS CHARACTERISATION BASED ON CHEMICAL COMPOSITION

The XRF results support the presence of kaolinite and smectite in these soils showing the evidence of desilicification leading to the formation of the dominant clay types. Desilicification is a process in which silica is released from soil silicates, where part of the released silica reacts with alumina to form clays, whereas the remainder is subject to leaching. The soil thus exhibits a loss of silica and at the same time has a residual accumulation of stable weathering products, including sesquioxides (Tan, 1998). The study area exhibit different soil types in the three portions surveyed and also within each area individually. Most areas are well drained and permeability is rapid, and therefore the activities of dissolved ions and H_4SiO_4 are kept low by leaching. This condition lead to the production of kaolinite clay types through weathering and later gibbsite will be realized as the end product. Some areas on the other hand are poorly drained and have low permeability. In these areas leaching is inhibited, and silica is not leached. This results in an increase in H_4SiO_4 activity and K^+/H^+ ratio, leading to formation of smectites (Van Schuylenborgh, 1971). This process is the reverse of desilicification and it is called silicification. These transformation processes (Singer, 1979), under changing physical and chemical conditions, can convert smectite to kaolinite and kaolinite into smectite. As a result, some of the kaolinite clay in the study area could be a conversion from smectite through these processes in time or vice versa. The high percentage of quartz minerals as fine silica particles found in the clay

fraction, and also the whole soil and rock samples give evidence of their origin from a granite parent material. The XRF results show an increase in the amount of aluminium and iron compounds in the clay fraction as opposed to the whole soil and rock samples. This provides evidence of the formation of octahedral layers of both the smectite and kaolinite. Even so, there is more increase in the Al^{3+} content as compared to the Fe^{3+} content possibly because more alluminium is required for both kaolinite and smectite as compared to Fe^{3+} which is mostly needed for the smectite structures.

The Chemical Index of Alteration (CIA) as proposed by Nesbitt and Young (1982) was used to study the degree of alteration of the primary minerals to the secondary minerals (Ericksson *et. al.*, 1990). CIA is based on the equation

$$CIA = 100 \text{ X } Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O) \quad (2)$$

When the value of CIA is 100%, it is an indication that a complete weathering of minerals has taken place due to the fact that ions of Ca, Na and K are very mobile. CIA value for kaolinite, gibbsite and other secondary minerals is 100. The upper continental crust has a CIA value of 50 (Taylor and McLennan, 1985). The CIA values for the study area in the clay and whole soil fraction samples are reported in Tables 8 and 9. The values for the clay fraction were between 68.74 and 87.2, and the values for the whole soil fraction were between 63.71 and 84.96 (Fig 26 and 27). The CIA values of the clay fraction samples indicate that a shift from primary to secondary minerals has occurred, even though conditions for complete weathering were not satisfied. Generally, the higher CIA values in soil type 3 samples indicate a greater degree of alteration on average compared to soil type 2 and 1 with the highest value of 87.2. Soil type 1 and 2 indicate more or less the same CIA values ranging from 70.98 to 77.74. An exception occurs in S 3 of soil type 2 with a value of 82.4, indicating a higher degree of weathering than the other samples. This may be indicative of the climatic and geological properties of the area being susceptible to weathering than those in the other samples of soil type 1 and 2. The lower CIA values in the whole soil fraction compared to those of the clay fraction indicate the resistance of certain primary minerals, mainly quartz, feldspar and mica, to weathering even though alteration has taken place. Similarly to the clay fraction samples, soil type 1 and 2 CIA values are more or less the same at lower levels compared to those of soil type 3 at slightly higher levels. The alteration of primary minerals to secondary minerals as weathering progresses results in an increase in the CIA values as a

result of a decrease in primary mineral content and accumulation of secondary minerals (Nesbitt & Wilson, 1992).

Table 13: Chemical Index of Alteration values of the clay fraction samples

Sample identity	**CIA**	**Sample identity**	**CIA**
Soil type 1		**Soil type 3**	
S1	77.74	S5	79.77
S2	74.01	S6	75.97
S3	73.44	S7	84.94
Soil type 2		S8	82.28
S1	74.33	S9	71.96
S2	70.98	S10	68.74
S3	82.4	S11	74.27
Soil type 3		S12	85.28
S1	87.2	S13	81.66
S2	76.19	S14	83.92
S3	85.62	S15	81.4
S4	77.52		

Table 14: Chemical Index of Alteration values of the whole soil fraction samples

Sample identity	**CIA**	**Sample identity**	**CIA**
Soil type 1		**Soil type 3**	
S1	64.63	S5	73.3
S2	71.5	S6	65.75
S3	67.79	S7	78.81
Soil type 2		S8	75.9
S1	69.14	S9	64.93
S2	63.71	S10	64.04
S3	71.3	S11	67.89
Soil type 3		S12	73.13
S1	72.91	S13	64.77
S2	67.99	S14	75.81
S3	84.96	S15	76.27
S4	74.29		

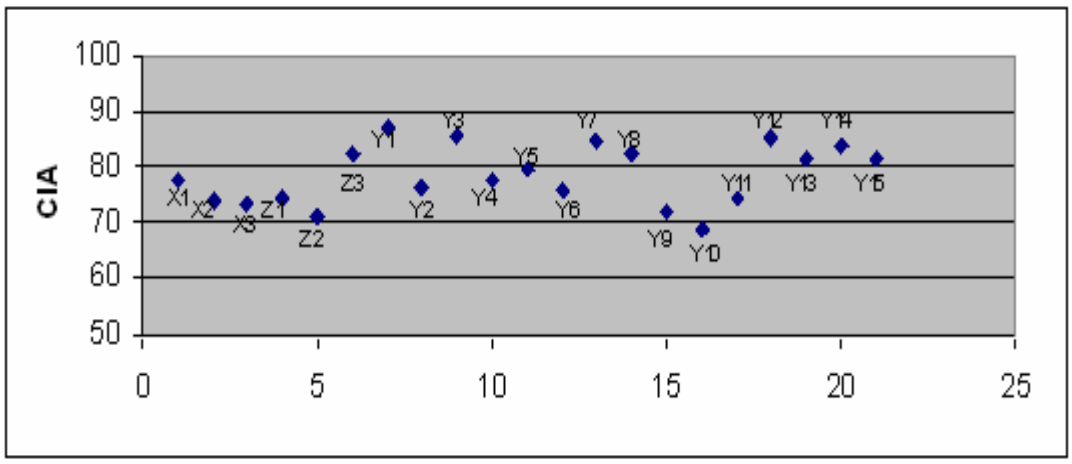

Fig 32: Chemical Index of Alteration graph for the clay fraction samples.
X = soil type 1, Z = soil type 2 and Y = soil type 3.

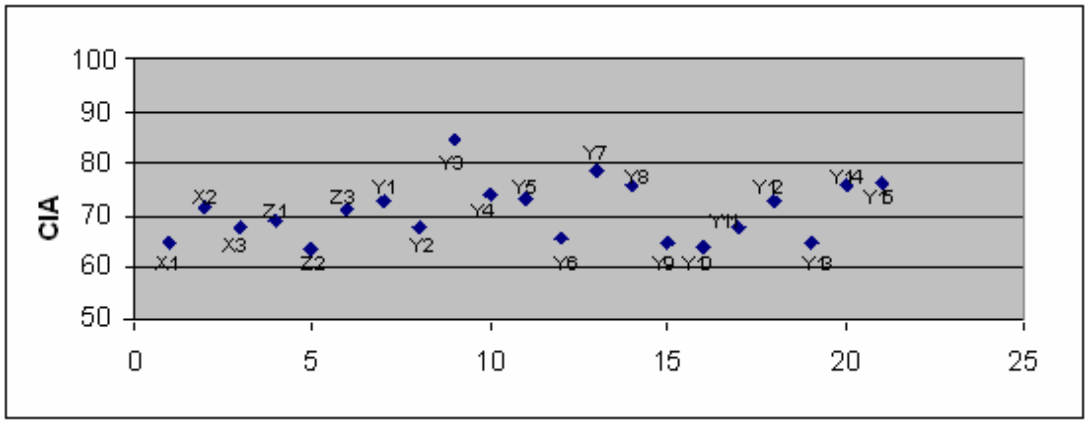

Fig 33: Chemical Index of Alteration graph for the whole soil samples.
X = soil typ1, Z = soil type 2 and Y = soil type 3.

Table 15: SiO_2/Al_2O_3 ratio of the clay fraction

Sample identity	**SiO_2/Al_2O_3**	**Sample identity**	**SiO_2/Al_2O_3**
Soil type 1		**Soil type 3**	
S1	4.84	S5	4.13
S2	5.29	S6	5.32
S3	5.41	S7	4.65
Soil type 2		S8	3.83
S1	4.22	S9	4.52
S2	3.81	S10	5.09
S3	4.41	S11	4.2
Soil type 3		S12	3.72
S1	3.69	S13	4.15
S2	5.42	S14	3.69
S3	4.65	S15	3.95
S4	7.3		
Theoretical kaolinite	1.16		

Table 10 indicates values of SiO_2/Al_2O_3 ratio of the clay fraction as well as some of bentonitic clays (Murray, 1993; Parras et. al., 1996, Fentaw and Mengistu, 1998; Galan et.al., 1996; and Dondi, 1999). The SiO_2/Al_2O_3 ratio of the clay samples had a range from 4.84 to 5.41 in soil type 1, 3.81 to 4.41 in soil type 2 and 3.69 to 5.42 in soil type 3.

5.3 CLAY MINERALS CHARATERIZATION BASED ON MICROMORPHOLOGY

The SEM photomicrographs of the study area samples portray, in most of the area, pseudohexagonal platelets of kaolinite. The booklet form of kaolinite was only depicted in few samples of the study area compared with the platelet form. The platelets depict smoothness and reworking, possibly as a result of transportation of kaolinite from their source of formation to deposition. On the other hand the booklets are micro massive collection of several kaolinite particles undisturbed from their source of formation. The samples from soil type 3 depicted mostly the booklet form (Fig. 24) whereas those from the other soil types (soil type 1 and 2), depicted the platelet form (Fig. 23 and 25). Therefore this qualifies soil type 3 kaolinite to be considered as residual and soil type 1 and 2 kaolinite to be of sedimentary origin.

The representative samples also reveal the vermicular book nature of kaolinite crystal with irregular edges (Dixon, 1989). In some samples stacks of kaolinite flakes are evident, which may range from a few tenths of micrometer to a couple of hundreds of micrometer in width.

5.4 DISTRIBUTION PATTERNS OF CLAY MINERALS

The distribution patterns of the five minerals detected in the clay fraction of the study area samples were clearly evident when comparing different percentage ranges of each mineral in each sample. Percentage ranges of 0% – 22%, 23% - 49% and 50% - 75% were used to assess the distribution of each mineral in the study area. Quartz was present in all the samples with a percentage range of 50% to 75%. S1, S5, S8, S9 and S13 in soil type 3; and S3 in soil type 2 fell within the percentage range of 23-49%. Kaolinite was present in most of the samples in mixed percentage ranges. Samples S1 and S2 of soil type 1; and S1, S3, S5, S8, S13, S14 and S15 of soil type 3 were within the range of 23% - 49%. S3 of soil type 1; and S1, S2 and S3 of soil type 2; and S2, S4, S6, S7, S9, S10, S11 and S12 of soil type 3 were found within the range of 0% – 22%. Feldspar and smectite were well within the range of 0% - 22% except for S1 of soil type 3 in smectite. Mica also fell within the range of 0% - 22% except for S2 and

S10 in soil type 3. Table 11 below summarizes the distribution and dominance of the clay minerals according to XRD analyses results.

Table16: Clay minerals distribution and dominance.

Soil Type	Minerals				
	Quartz	Kaolinite	Feldspar	Smectite	Mica
Soil type 1	+++	+++	++	nd	+
soil type 2	+++	++	++	+	+
soil type 3	+++	+++	+	+	+

+++ = major, ++ = minor, + = trace and nd = not detected.

Quartz was dominant in all the samples except for S1 and S8 of soil type 3 possibly because they are the most common mineral on the face of the earth, being found in nearly every geological environment. It is at least a component of almost every rock type; igneous, metamorphic and sedimentary rocks; and is frequently the primary mineral, > 98%. Its presence in the clay fraction has been observed by many workers to this date (Bohn et al., 2001).

Kaolinite was found to be dominant only in samples S1 and S8 of soil type 3. However kaolinite was second dominant in samples S1 and S2 of soil type 1; S3 of soil type 2; and S3, S5, S6, S7, S12, S13, S14 and S15 of soil type 3. Soil type 2 had lower values of kaolinite on average compared to soil type 1 and 3. This may be an indication that feldspar weathering was not intense compared to the other soil types. Soil type 3 exhibits a variation in terms of the quantities of kaolinite in various samples showing the differences that occur in the area. The variation may be ascribed to the variation in the parent material composition in terms of the parent materials (Wilson, 2004).

Feldspar was only second dominant in S1 of soil type 2. The lower values compared to those of kaolinite are in correlation with the weathering sequence yielding kaolinite as secondary clay mineral from feldspars (Wilson, 2004). Variation among the soil types is minimal on average, with values ranging from 0% to 18%. Smectites were second dominant in samples S1, S9 and S11 of soil type 3. Their distribution over the three soil types was found to be variable. Soil type 1 virtually had no smectite detected, whereas soil type 2 contained only trace amounts. Soil type 3 varied greatly with the values ranging from 0% to 30%. However, most of the samples had no smectite detected possibly due to the kaolinization process of mica minerals leading to the formation of kaolinite minerals (De Kimpe & Tardy, 1968).

Mica was second dominant in samples S3 of soil type 1; S2 of soil type 2; and S2, S4 and S10 of soil type 3. The variations in mica in all the three soil types may be ascribed to the dissolution rates of mica group minerals namely biotite and muscovite. Biotite is known to be easily weathered compared to muscovite (Wilson, 2004). Therefore the lower values or virtually complete absence of mica in samples of all the three soil types may relate to the presence of mica minerals in the samples whereas the higher values may relate to the presence of muscovite mica in the relevant samples. Overall, mica distribution depicts a similar pattern to that of smectite showing almost non detection of mica in soil type 1 and trace amounts in soil type 2. This was expected considering the weathering sequence of mica to smectite. Soil type 3 also showed similar patterns to smectite with variations ranging from 0% to 26%.

5.5 GENESIS OF THE CLAY MINERALS

The XRD results of the clay minerals in the study area provide evidence of the genesis of the minerals with regards to their formation. The high percentage of quartz and the presence of feldspar and mica as primary minerals support the relation that these minerals were formed from igneous rock minerals.

Granite rocks, which are prevalent throughout the study area, are igneous rocks which were formed by slowly cooling pockets of magma that were trapped beneath the earth's surface. These rocks are subdivided into basic and acid rocks. Basic rocks contain a high percentage of Ca and Mg- rich primary minerals like pyroxene, amphibole, olivine and a Ca-rich plagioclase. Mica and K-feldspar are low to absent and the quartz content is, per definition, <5%. Acid rocks contain free quartz (>30%), Na-rich plagioclase, K-feldspar and mica, generally an association of biotite and muscovite (Bühmann et. al., 2004).

Kaolinite, as the dominant secondary mineral, can be formed from either acid or basic igneous rock. It is formed from acid igneous rocks if the weathering conditions are such that potash and magnesia are rapidly removed after the breakdown of the parent minerals. Under conditions of poor drainage and low rainfall, which allow the potash and magnesia to remain in the weathering environment, smectite and illite are formed. Similarly, kaolinite is formed from basic igneous rocks if the magnesia is removed as soon as it is released (Heckroodt, 1991). Kaolinite deposits can be classified as primary or secondary depending on their genesis. Primary kaolinite could be hydrothermal, residual or both hydrothermal and residual.

It could also be formed *in-situ*, by the alteration of feldspar-rich and Al-rich rocks such as granite; the parent minerals being feldspars (3) and micas (muscovite) (4).

$$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O \rightarrow 3Al_2Si_2O_5(OH)_4 + 2K^+ \quad (3)$$

K-feldspar kaolinite

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2K^+ \quad (4)$$

Muscovite kaolinite

The weathering of feldspars is known to produce commonly kaolinite and halloysite. Eswaran & Bin (1978) demonstrated that feldspar weathered primarily to halloysite in a weathered granite in Malaysia, but additionally showed that both halloysite and kaolinite could occur in the same feldspar pseudomorph. Robertson and Eggleton (1991) showed that plagioclase feldspar in deeply weathered granite in Queensland was converted to kaolinite, which then altered to spiral halloysite rods through a process involving hydration. An interesting finding was found by Rodgers & Holland (1979) in their investigation of the weathering products of micro-cracked feldspar in tonalite cobbles from a morainic deposit in Montana. They found only kaolinite in orthoclase, whereas in oligoclase there was both kaolinite and smectite. On the other hand the weathering of mica minerals depends highly on the susceptibility of its component minerals mainly biotite and muscovite. Biotite weathers very easily and may progress to advanced stages even at the base of the weathering profile. In contrast, muscovite is often extremely resistant to weathering and may persist unaltered to the top of the weathering profile.

Mica, through the weathering of biotite, may produce either kaolinite or smectite depending on the weathering method undertaken. Vermiculitization of mica, which is the exchange of the interlayer K of the mica for ions of the external solution (Barshad, 1948), can produce smectite through the weathering of biotite. Fordham (1990b) explained the conversion of biotite to dioctahedral clay minerals in a soil developed on granite gneiss. Both dioctahedral vermiculite and smectite-like minerals were identified primarily on the basis of electron probe microanalysis. Smectites may certainly form as a consequence of biotite weathering as concluded by Ismail (1969, 1970) under arid and alkaline conditions and Kapoor (1972) under humid acidic conditions. MacEwan (1954) described trioctahedral smectite derived by weathering of biotite in poorly drained soils. Under more intensive weathering conditions, vermiculitization may be bypassed and conversion of biotite directly to kaolinite may occur

(De Kimpe & Tardy, 1968). This process is termed kaolinization of mica. In fact, biotite may be completely pseudomorphed by kaolinite (Mitsuda, 1960) and this transformation may take place within a few centimeters of fresh rock (Eswaran & Heng, 1976).

5.6 IMPLICATIONS OF CLAY MINERALS IN AGRICULTURE

In managing soils for agricultural production, soil texture or particle size distribution, and the amount and type of clay present are very important. Soil structure depends on clay: soils with little clay have simple structures whereas soils with much clay have complex structures. Clays have a large specific surface, often predominantly negatively charged, that retains nutrients against leaching and reacts with hydrogen and aluminium ions, while buffering the soil against extreme pH changes (Newman, 1984). Agricultural productivity varies widely in many areas. One intrinsic factor in yield variation is soil type, which is related to soil's composition and its position in the landscape (Burnham, 1974). The amount and type of clay present is a prime consideration in the composition of the soil and has a highly important effect on its properties. A soil usually contains at least some clay, and its clay content strongly influences its management and productivity (Davies et al., 1972). Soils with little clay, for example loam soils containing 15-25% clay with particle sizes of under 2 μm and a larger proportion of silt particles sized 2-60 μm are the most productive and easy to work with. Soils with more than 30-35% by mass weight of clay tend to take on the properties of the clay itself and thus create difficulty in management.

The buffering action of mineral clays in the soil plays an important role in eliminating toxic substances that might be harmful to plants. Soil forming processes usually cause an accumulation of hydrogen ions in the soil. Organic acids and HCO_3^- released into the soil through biological activity and rain water contain acids and CO_2. When there is leaching through the soil, bases are carried down with the leachate and there is a net accumulation of hydrogen ions. Thus in soils not containing free calcium carbonate, colloids in the upper soil layers tend to retain aluminium compounds complexed with organic matter and sorbed on clay surfaces (Newman, 1984). This process of acidification and the consequent formation of hydroxyaluminium coatings on the surface of soil colloids is fundamentally important in pedogenesis and determining soil properties of agricultural importance (Jackson, 1963).

Clay minerals have net negative charge at soil pH-values and in natural conditions the cations countering this charge are Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+ and Al^{3+} with its hydrolysed

derivatives. Soils with kaolinite as the predominant clay mineral also contain iron oxides as important accessory minerals. The pH-dependent charge characteristics of the combination are effectively the sum of the component parts, so that they appear to behave as a mixture. However, because soil kaolinites have a relatively large specific surface, the negative charge is considerably larger than usual with mineral kaolinites (Greenland, 1975). Soils with 2:1 minerals as the dominant clays have larger exchange capacities and pH-dependent charge contributes a much smaller fraction of the total than with kaolinitic soils.

The reaction that occur between clays and phosphates depends both on the nature of the clay surface and concentration of the phosphate. Relative to alumina, kaolinite sorbs much less phosphate per unit of surface (Chen et al., 1973). Few studies have have been made of the sorption of phosphate by 2:1 clay minerals. Hall and Baker (1971) investigated the effect of laboratory-synthesized Al-OH interlayers in montmorillonite and vermiculite on phosphate sorption. They found that increasing amounts of phosphate were fixed by montmorillonite as the pH was raised, but that the opposite occurred with vermiculite. A wide range of interactions occurs between the organic pesticides and clay minerals, depending on the nature of the compounds. The extremes are exemplified by paraquat, which is cationic and strongly sorbed, and picloram, which is acidic and repelled from the clay surface. In deciding what may be the principal interaction mechanism between clay and a pesticide, the main points to consider are the acidity of the clay and the chemical nature of the pesticide.

In terms of plant available water, Greene-Kelly (1974) found that both total and available water contents were poorly related to mineralogy. Equally, soils with widely different mineralogies may show little difference in water held between specific suctions. The soil containing the mixed-layer smectite has relatively little plant available water presumably because microstructural arrangement of the clay particles affects the release of available water more than loss of interlamellar water from smectite layers. The mechanical effort needed to draw a plough through soil depends on several factors, one of which is the amount of clay in the soil (Haines & Keen, 1925). Soil consistency and the change in liquidity or solidity of soils with water content are related to the amount and type of clay in the soil (Spoor & Muckle, 1974). The preparation of a satisfactory seedbed depends on cultivating at a soil water content at which the soil is friable, but not sticky. The range of water content over which the soil remains in a friable state is related to its mechanical composition, and also to the mineralogical and structural composition of the colloid fraction (Newman, 1984).

The study area contains soils that are dominated mostly by kaolinite, with smectite in appreciable quantities. The chemical properties of both minerals as the secondary clay minerals characterize and also affect the nature and status of the soils they dominate.

Kaolinite has little isomorphous substitution, and the permanent charge per unit cell is very small. Its cation exchange capacity is very small and may change with pH. Because of the tightness of the structural bonds, kaolinite particles are not easily broken down. This is also the cause for low plasticity and shrinkage and swelling properties of this mineral. Its restricted surface area limits the adsorption capacity of cations. These properties make these soils inefficient holding and exchanging important crop nutrients in the soil. Generally these soils are susceptible to leaching. Therefore, soils dominated by kaolinite need a constant fertilizing program to replenish both the leached ions and also those absorbed by the previous crop if cultivation was implemented the previous season (Bohn, 2001; Tan, 1998; Bühmann et al., 2004, Newman, 1984).

On the other hand, the component layers of smectites are not bonded strongly. In contact with water, the mineral exhibits interlayer swelling, causing the volume of the clay to double. The high swell-shrink potential makes the mineral able to admit and fix metal ions and organic compounds. Smectite also has a large specific surface area, approximately 700-800 m^2/g, and therefore a higher cation exchange capacity than kaolinite. Because of this large surface area, smectites exhibits strong plasticity and stickiness when wet. Soils dominated by smectites require minimal constant fertilizer input compared to kaolinite dominated soils, because of the ability to hold nutrients in the soil. Their water holding capacity is very efficient compared to kaolinitic soils due to their ability to expand. However, their strong plasticity and stickiness when wet may create mechanical problems during cultivation, making the soils difficult to work with. The quartz silica minerals present in both the clay fraction and the whole soil fraction are generally considered inert, or chemically inactive, material. They have only a slight effect on physicochemical properties of soils. Soils dominated by silica minerals are usually nonplastic and have a small swell-shrink capacity. Therefore silica minerals enhance the drainage of the soils and may be useful in clayey areas where drainage is a problem (Bohn, 2001; Tan, 1998; Bühmann et al., 2004, Newman, 1984).

CHAPTER 6

6. CONCLUSIONS

The geographical characterization and attributes of the study area; in terms of topography, climate, soil type, vegetation and time; without any scientific study or survey undertaken, assumes the truth that variations in terms of clay mineralogy exists. This research project provided the opportunity to verify and report on this assumption of the existence of variations. According to the clay fraction XRD results, the study area consists of variable weight percentages of existing clay minerals in various locations of the area surveyed. It must however be noted that the variations were not too extreme, perhaps due to the fact that the soils in the study area originated from more or less the same parent material, as revealed by the geological map in figure 14. Even so, other factors influencing the soil formation such as geological time sequence, climate, vegetation and topography and the accumulation and losses of substances within the soil profile, often related to its position in the landscape; seem to have played a role in the existence and the chemical and also the physical reactions leading to the production of the existing clay minerals in the area.

6.1 CONCLUSIONS BASED ON X-RAY DIFFRACTION

The XRD results reveal the existence of kaolinite and smectite as the prevailing secondary minerals in the study area. These minerals are believed to have originated from their parent materials of which the igneous rock is the dominant rock type in the area. Other primary minerals such as quartz, mica and feldspar were also detected possibly because the weathering process has not progressed well enough for a greater alteration of the minerals into secondary minerals. It is also assumed that the existence of other intermediate minerals leading to the formation of the detected minerals (using XRD) might have taken place for the completion of soil reactions. On the other hand, the intermediate minerals might be in smaller quantities and too fine to be detected using the XRD analyzing equipment. Kaolinite is dominant in all soil types compared to smectite which correlates well with the amount of feldspar and mica detected. This dominance of kaolinite over smectite may reveal the strong dependence of soil formation on the parent material as one factor of soil formation. The presence of quartz minerals both in the primary and secondary minerals relates well with their resistance to weathering due to their inert nature. The existence of kaolinite as the dominant secondary mineral may have serious implications with regards to the agricultural potential of

the land mainly because of its low CEC. As a result, agricultural management must take this factor into consideration if good yields are envisaged.

The distribution pattern of the studied clay minerals correlates well with the known soil reactions believed to have affected their formation from the parent material and the interaction between the individual minerals themselves. Topography and climate, among other factors, seem to have played a big role in the distribution of the minerals since parent material was more or less the same in the area. Even so, the influence of the mineralogical composition of the parent rock (Table 4) on the clay mineral assemblages cannot be ignored. The mineralogical composition of the parent rock correlates well with the distribution pattern observed from the clay mineral XRD results. Taking all factors in consideration, it could be concluded that the distribution of the clay minerals in the study area was controlled by the physical and chemical environment present during the alteration process.

6.2 CONCLUSIONS BASED ON X-RAY FLUORESCENCE SPECTROSCOPY

The chemical composition of the samples supports the existence of both the primary and secondary minerals detected in the XRD analyses. The decrease in the amount of SiO_2 in the clay fraction as compared to the whole soil fraction and the rock samples may be due to two reasons, firstly due to leaching of the soils and secondly due to the restricted use of the minerals in the elemental composition of the secondary clay minerals. More over the huge amount of SiO_2 in all the samples verify the existence of the silicate clays and the minerals from which they were derived, and also in their importance in the structural formulation of silica tetrahedron sheets. The contribution of the quartz minerals to the quantity of SiO_2 must also be taken into consideration regarding the amount of SiO_2 detected. The results also show an increase in the amount of Al_2O_3 and Fe_2O_3 in the clay fraction with Al_2O_3 being in greater quantity compared to Fe_2O_3. The greater amount of Al_2O_3 over Fe_2O_3 may be due to the fact that both kaolinite and smectite contain Al_2O_3 in their octahedral layers whereas Fe_2O_3 occurs most often in the octahedral sheet of smectites due to their isomorphic substitution character. Kaolinite on the other hand has little isomorphic substitution in its octahedral sheets and therefore often lacks Fe_2O_3. The behavior of other elements such as MgO, MnO, CaO, Na_2O, K_2O and P_2O_5 are in negligible amounts and show a very small change in the XRF clay fraction results. This may be attributed to the low CEC nature of the kaolinite minerals as the dominant clay minerals.

6.3 CONCLUSIONS BASED ON SCANNING ELECTRON MICROSCOPY

The SEM photomicrographs clearly revealed the abundance of both the quartz and kaolinite minerals with respect to the shapes of the particles observed. The subhedral pseudo-hexagonal flake shapes associated with kaolinites was apparent in most samples analyzed. The rough surfaces and ragged edges of the flakes observed in the images may relate to the progress in alteration of the minerals to form secondary clay minerals. The detection of smectite minerals proved to be a difficult task since they existed in smaller quantities compared to the other minerals. This may be because they experienced a shadowing effect from other minerals with regards to the scanning electron microscope beam. The detection of quartz minerals in all the samples testify to the abundance of the mineral in the study area.

RECOMMENDATIONS

It is without doubt that the variation and existence of the different minerals in the study area has a marked influence in terms of the fertility and productivity of the land. The different types of clay minerals found in the study area individually affect the physical and chemical reactions in the soil and therefore soil type. With other parameters constant, the clay mineral quantities in different locations of the study area in terms of the analyzed weight percentages will have a direct influence on the dominance of a specific mineral and therefore the chemical and physical behavior of the soil. This will in turn affect the fertility and productivity of the soil in question. With the soil affected, vegetation and agricultural production is implicated, revealing the importance of clay minerals in the soil and the environment as a whole.

The degree of weathering in the three soil types surveyed implicates the agricultural potential and land use differently. The samples from soil type 3 indicate a greater degree of alteration from primary to secondary minerals compared to soil type 1 and 2, which have more or less the same CIA values in their samples. This in turn indicates that the degree of weathering in soil type 3 is greater than in soil type 1 and 2. The resulting implications of this condition to agriculture is varied with the fact that the weathering of some minerals may have progressed to an extend that some of the nutrients are leached from the soils and therefore becoming unavailable to plants. On the contrary, the weathering process may have progressed well enough to cause some of the resistant minerals to become soluble and therefore supply the nutrients most needed by plants. Soil type 1 and 2 soils may require greater quantities of fertilizer than soil type 3 soils to improve the overall potential of the soils.

Even so, little is still known about the implications of clay minerals to the overall production in agriculture. Much work has been concentrating on the structural and chemical study of clay minerals, and their existence in nature. This has been beneficial contribution to the mineralogical sciences since little was known about this important fraction of our soils. In the same sentiment, knowledge of the correlations in the implications of clay minerals in the world's agricultural systems is still lacking behind. More work needs to be done in order to fully comprehend the relationships that occur between clay minerals and soil fertility which eventually affects the productivity of the land. Relationships of clay minerals and the production of certain agricultural commodities also must be investigated if proper agricultural practices are to be put in place.

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