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For the degree of Doctor of Philosophy

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EFFECT OF SOIL PROPERTIES ON BIOAVAILABILITY OF ALUMINUM AND PHOSPHORUS IN SELECTED KENYAN AND BRAZILIAN ACID SOILS

A Dissertation

Submitted to the Faculty

of

Purdue University

by

Pamela Achieng Obura

In Partial Fulfillment of the

Requirements for the Degree

of

Doctor of Philosophy

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To my dear husband Tom and my daughter Lyne.

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This study was supported by a scholarship from The McKnight Foundation, through the Collaborative Crop Research Project (CCPR), I believe it will go a long way to help uplift food security of smallholder farmers in Kenya.

Glory to God.

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ABSTRACT

Obura, Pamela Achieng. Ph.D., Purdue University, West Lafayette, August, 2008. Effect of soil properties on bioavailability of aluminum and phosphorus in selected Kenyan and Brazilian acid soils. Major Professor: Darrell G. Schulze.

Declining agricultural productivity in many parts of Africa is negatively affecting the livelihood of many people. Information on the fertility status of many of these fragile soils is scarce. To determine the soil factors responsible for the decline in soil productivity in the Kenyan highlands, 11 representative sites were selected, described in the field, and sampled for laboratory analyses. They were compared with selected soils from the Cerrado region of central Brazil where crop production has increased significantly since the 1960s due to improved crop varieties and soil nutrient management strategies. Soils east of the Rift Valley (Mt. Kenya region) were significantly different from those west of the Rift Valley. The topsoils of the pedons east of the Rift Valley had andic properties, were 0.75 pH_{H2O} units more acidic, had 37% higher aluminum (Al) saturation, and about two to three times greater phosphorus sorption capacity (PSC) than the topsoils west of the Rift Valley. The soils from western Kenya were generally comparable to the Brazilian Cerrado soils with the exception that the exchange properties of the Brazilian soils were lower. Overall, Al saturation of both the Kenyan and

Brazilian soils varied from 0-69%, and PSC ranged from 426-3333 mg kg^{-1}. The PSCs of the Brazilian topsoils were, however, not significantly different from the western Kenya soils. Both the Kenyan and Brazilian soils were generally high in dithionate-citrate-bicarbonate and ammonium oxalate extractable iron (Fe) and Al. X-ray diffraction, electron microscopy and thermal gravimetric analyses indicated that the clay fractions of both the Kenyan and Brazilian soils were dominated by kaolinite. In addition, spheroidal and rolled-up sheets of halloysite were also identified in the Kenyan soil clays. Among the Kenyan soils, gibbsite was relatively abundant in the volcanic ash derived soils east the Rift Valley, while soils west of the Rift Valley contained appreciable amounts of 2:1 phyllosilicates inherited from the parent rocks. Most of the Brazilian soils contained significant amounts of gibbsite, and in some cases, minor amounts of 2:1 phyllosilicates. In light of these findings, the western Kenya soils are likely to respond to nutrient management practices that are similar to those used in central Brazil, while the soils from the Mt. Kenya region will require crop varieties and management strategies tailored to higher Al toxicity and phosphorus sorptive capacity.

CHAPTER 1. BACKGROUND

1.1. Introduction

The extent to which physical resources (soil, climate, terrain and water) can be utilized to produce food and agricultural products is limited. The ecological limits to production are set by soil and climatic conditions as well as by specific production inputs and management. Soils are irreplaceable natural resources, and increasing population pressure is constantly making these resources more and more valuable. From a nutrient management standpoint, land use systems are characterized by nutrient inputs (mineral fertilizer, manure, atmospheric deposition, biological nitrogen fixation, sedimentation) and nutrient outputs (removal of harvested crop parts and residues, leaching, denitrification, erosion), and the balance between the two.

Large proportions of the world's population and agricultural activities occur on tropical and subtropical soils. About 20 % of maize production and 13% of rice production worldwide is on acid soils (Uexküll and Mutert, 1995). Many of these soils are in an advanced stage of soil weathering as they proceed through the development stages of soils (Jackson and Sherman, 1953). This advanced stage of soil weathering is characterized by Oxisols and Ultisols. Based on the global soil regions (World Soil Resources, 1998) soil orders found in the tropics consist mainly of Oxisols, Ultisols, Entisols, Inceptisols, Aridisols, and Alfisols (Soil Survery Staff, 1999). The vast extent of Oxisols and Ultisols occurs in tropical America and Africa. In Africa, they extend from the Congo Basin toward the Southeast and Northeast of the continent. The problem of plinthite grading into iron stones is common throughout drier areas of Africa. Plinthite is humus-poor, Fe-rich soil material thar hardens irreversibly if exposed to repeated wetting and drying in place. Plinthite forms by alternating oxidation and reduction reactions, mostly due to fluctuation of the water table through a layer containing some iron oxides (Buol, et al., 2003). In South America, vast areas of Oxisols cover most of Brazil, especially in the Amazon Basin. In Asia, Ultisols are the major soil group, with a few patches of Oxisols. Ultisols are also found in the northern part of Australia (USDA-NRCS, 2005).

Approximately 30% of the world's total land area consists of strongly acid (pH < 5.5) soils (Uexküll and Mutert, 1995), of which 60% are in the tropics. Eswaran et al., (1997), estimate that 28.8% of the African continent has acid topsoils and 19.6% has subsoil acidity problems. Acid soils cover more than a third of sub-Saharan Africa (Depauw, 1994) and are widely distributed in the highland areas of East Africa. Approximately 20% of the total arable land in Kenya is acidic (FURP, 1987; Kanyanjua et al., 2002) and covers significant parts of Central, Rift Valley, Western, and Nyanza provinces (Jaetzold and Schmidt, 1983), which are the major maize growing regions of the country.

Despite favorable temperature and moisture conditions in the tropics, these soils are considered to be highly marginal for the production of most food crops unless special management strategies are employed. Low crop production in acid soils is rarely the result of a single factor, but is rather more probably due to several factors affecting different physiological and biochemical processes, both in the soil and plant (Foy, 1984). Many properties of Oxisols and Ultisols relate directly or indirectly to the dominant mineralogy, consisting primarily of kaolinite, gibbsite and iron oxides (Schwertmann and Herbillon, 1992). Typically, plant growth limiting properties of these soil orders may include: low pH and weak buffering capacity; low P bioavailability due to high P fixation capacity; toxicities of Al, Fe, Mn (occasionally H); deficiencies of Ca, Mg, K, Zn, S, and Mo; low cation exchange capacity (CEC); and low populations of beneficial soil microorganisms (rhizobia, mycorrhiza) (Sanchez, 1976; Sanchez and Uehara; 1980; Sanchez and Salinas, 1981; Clark et al., 1988; Ta et al., 1989). These deficiencies or toxicities often act together or independently, consequently limiting plant growth (Clark, 1982). However, plant growth in acid soils may vary among species and even among genotypes (Clark, 1982).

Nutrient mining of tropical soils is threatening food security, sustainability of agricultural production systems and agricultural development in developing countries (Smaling, et al., 1993; Sanchez et al., 1997). The problem is particularly acute in sub-Saharan Africa where farmers are faced with a dilemma of feeding an ever-increasing population, while the land resources are declining and food production is subsequently inadequate. Studies undertaken at a variety of scales: from plot and catchments to regional analyses and, even continent-wide assessments, point to widespread processes of nutrient mining and soil fertility decline in Africa. Stoorvogel et al. (1993) showed that outputs exceed inputs all over the continent. One such study from the Kisii district, Kenya, found consistently negative balances for all major nutrients at the aggregate district level, with estimated balances for the major nutrients at -112 N, -3 P and -70 K kg ha^{-1} yr^{-1} (Smaling et al., 1993). This indicates a rapid rate of soil nutrient mining in agricultural systems in a well-endowed and densely populated part of the Kenyan Highlands.

There is a critical need to reverse this trend to meet basic food requirements and to protect the environment for future generations. Research is therefore needed to develop appropriate nutrient management options that are specific for well-defined agro-ecological environments that are characterized by a specific set of soil and climatic properties. Information gathered and presented in this study is therefore intended to provide the necessary framework to facilitate transfer of efficient nutrient management technologies.

1.2. Research needs

An opportunity exists to increase food production in the acid soils of Africa by capitalizing on existing technologies. Use of lime, fertilizer and organic amendment are some of the conventional agronomic approaches that can increase productivity. Liming strongly acid soils can eliminate the aluminum toxicity problem and increase the range of crop types that can be grown. Liming, however, does not correct subsoil acidity below the plow layer where root growth of susceptible cultivars is restricted. Moreover, soil acidity is a significant constraint in many poorer areas of the world where agricultural lime and fertilizer inputs are not readily available or affordable.

In recent years, great research effort has been made to develop soil and crop management systems that maximize the absorption of nutrients either native or applied as fertilizers to cultivated soils. Although the mechanism of Al-toxicity is not yet clearly understood, researchers in the fields of agronomy, plant physiology and molecular biology have made substantial contributions to our understanding of the mechanism of Al toxicity and tolerance in plants. Plant species and genotypes within species differ significantly in their tolerance to Al (Foy, 1988; Taylor, 1987). Aluminum-tolerant genotypes have also been identified within otherwise Al-intolerant crop species, such as maize and sorghum (McKnight CCRP, 2004). Research on the fundamental processes that confer Al-resistance in crop plants via plant breeding and biotechnology is already underway (Kochian, 1995). The Al-tolerant genotypes can modify the rhizosphere environment by secreting organic acids from their roots in response to Al treatment (Ryan et al., 2001). Succinate, citrate, oxalate, malate, lactate and fumarate are some of the organic acids which have been identified in the rhizosphere of many Al-tolerant, plants (Ma et al., 2001). Organic acids play an important role in both the internal and external detoxification of Al (Ma, 2000) and allow the plant to access P more efficiently. Where subsoil liming is not economical, use of Al-tolerant plants may therefore be a viable option to achieve good crop productivity.

Farmers and plant breeders working in areas with acid soils have been able to select Al-tolerant crop genotypes. Plant breeders hope to accelerate the development of Al-tolerant and P-efficient food crop varieties by using marker-assisted breeding and genetic transformation. The Collaborative Crop Research Program (CCRP) of the McKnight Foundation is an example of such an effort. The project, "New approach for improving phosphorus acquisition and aluminum tolerance of plants in marginal soils" is an undertaking of a team of researchers at Embrapa in Brazil, Moi University in Kenya, and Purdue University and USDA-Cornell University in the USA. The main aim of this project is to improve the productivity of maize and sorghum in Brazilian and East African acid soils. The focus of the breeding efforts is on selection of maize and sorghum genotypes, which are both Al-resistant and P-efficient. A study at Purdue University (Rana, 2007) has been investigating the potential of physiologically relevant concentrations of low-molecular weight organic acids such as malate, citrate and oxalate to simulate and evaluate the ability of these organic acids to complex Al and release P into the soil solution under conditions of controlled pH, ionic strength and composition.

Because not all acid soils are the same, different acid soils may not respond similarly to improved germplasm. In the soil chemical context, properties such as P availability and Al toxicity can vary greatly from one soil to the next, largely as a function of differences in soil mineralogy and chemistry. Agro-ecological factors such as climate, soil water holding capacity, the position of the soil in the landscape, and other factors also can influence plant response to the proposed plant intervention mechanisms. To understand the impact of the proposed plant intervention mechanisms, such as enhanced low-molecular weight organic acid exudation by roots, we must understand both the soil chemical context of the root-soil environment, as well as the broader agro-ecological context into which enhanced germplasm is likely to be introduced. There is need to develop a comprehensive knowledge and adequate database of the character (the relationship among physical, chemical, mineralogical and agro-ecological properties), suitability, and limitations of these soils for sustainable crop production. To establish key similarities and differences among these soils for effective management, qualitative and quantitative evaluation of key soil properties is necessary. Some of the key indicators commonly used in tracking major alterations in soil chemical and mineral composition include ion exchange characteristics, phosphorus sorption properties, and elemental and mineralogical composition. Agro-ecological factors can only be assessed in the field.

1.3. Research objectives

The research objectives are as follows:

1. Evaluate the availability of essential plant nutrients (N, P, Ca, K and Mg) in selected Kenyan acid soils.
2. Investigate the relationships among selected soil properties (pH, organic matter content, cation exchange capacity, soil solution composition) of selected Kenyan acid soils.
3. Evaluate phosphorus sorption characteristics of selected Kenyan acid soils and to identify soil properties that are associated with phosphorus sorption.
4. Gain knowledge of the mineralogical composition of selected Kenyan acid soils.
5. Compare key properties of selected Kenyan acid soils to acid soils of central Brazil (where much of the previous plant breeding to develop acid-tolerant varietieshas occurred).

1.4. Literature Review

1.4.1. Causes and types of soil acidity

Decline in soil fertility and subsequent soil acidification is a result of complex interactions between biophysical and socioeconomic factors (Kamprath and Foy, 1985). Many soils are acidic because either their parent materials are acidic and initially low in basic cations, or because they have been exposed to long periods of weathering (Rao et al.*,* 1993). In humid climates, acidification of soil is a natural process. The main factor in producing acid soils is continued leaching by rain, which is both a good solvent and slightly acidic (Schwab et al., 1989; Barak et al., 1997; Bouman et al., 1995; Sanchez and Logan, 1992; Baligar and Fagaria, 1997). The cation exchange sites vacated by the leached nutrients are gradually replaced by Al and H^+, gradually dissolving most primary and secondary minerals and subsequently reducing cation exchange capacity (CEC). Consequently, the 2:1 phyllosilicate minerals weather away, resulting in insufficient amounts of exchangeable bases. The advanced stage of weathering is commonly associated with the soil minerals kaolinite, gibbsite, and Fe-oxides (Sanchez, 1976; Muggler et al.*,* 2001; Ritcher and Babber, 1991; Mauricio and Ildeu, 2005). This natural process is often intensified by agricultural practices such as annual crop removal (with minimal or no nutrient replenishment) and some fertilization practices.

Numerous studies have shown that excessive fertilization of some agricultural soils induces soil acidification and other negative changes to agricultural land (Rasmussen and Rohde, 1989; Bolan et al., 1991; Bouman et al., 1995; Porter et al., 1995; Barak et al., 1997; Fageria and Baligar, 2001). Applications of NH_4^+ producing fertilizers (e.g., urea, anhydrous NH_3, $(NH_4)_2SO_4$) can acidify soils through a biological reaction by which NH_4^+ is oxidized to NO_3^- and H^+. In many industrialized areas, the atmospheric deposition of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) is a major source of acid rain and subsequent acidification of soils with low buffering capacities (Paces, 1985; van Breemen et al., 1984).

Coleman and Thomas (1967) observed that there are two definitions for an acid soil: (i) the pH is < 7; and (ii) the effective CEC is not countered by the basic cations. Acid soils vary considerably due to differences in climate, parent material and vegetation. FAO (2000) identifies three major types of acid soils: (1) Strongly acid soils with pH (H_2O) < 5 and $> 60\%$ Al saturation of the cation exchange capacity, which are more likely to suffer from Al toxicity. (2) Moderately acid soils without aluminum toxicity (pH > 5 and < 6.5). In this group, there are no principal differences with regard to the pH demands of crops if aluminum toxicity is excluded. Even crops that are known to demand more neutral soil conditions may give reasonable yields on moderately acid soils if appropriate nutrient and water supply and favorable rooting conditions are ensured. A special case of acid soils with aluminum toxicity are acid sulfate soils (3) which have a sulfuric horizon in the upper soil horizons. If these soils are drained, oxidation processes result in extremely acid soil conditions.

The main forms of soil acidity in mineral soils are associated with Al, which can be exchangeable or non-exchangeable (Sparks, 2003). Large quantities of exchangeable H^+ are likely to be found in very acid soils with pH < 4 and in soils high in organic matter. Evans and Kamprath, (1970) found less exchangeable Al in organic soils than in mineral soils, even when the pH of the organic soil was lower. Mineral soils high in montmorillonite tend to have greater amounts of exchangeable acidity than soils high in kaolinite due to the greater CEC of the montmorillonitic soils and the predominance of constant charge (Coleman et al., 1959).

1.4.2. Aluminum toxicity

Aluminum is the third most abundant element in the Earth's crust, and is a major constituent of mineral soils (Huang et al., 2002). Most of the Al in soils occurs in combination with Si in primary and secondary minerals in soils. Feldspars, micas, and clay minerals, are the most common primary and secondary minerals in soils (McLean, 1965). Other sources of aluminum include aluminum oxides and hydroxides. Gibbsite ($Al(OH)_3$) is the most common crystalline form of Al found in soils (McBride, 1994). Gibbsite is common in soils of hot climates, both humid and dry. Aluminum also can be found in soils as organic complexes, noncrystalline coatings on soil constituents, discrete amorphous phases, and as hydroxy polymeric compounds occupying the interlayer spaces of 2:1 clay minerals and thus can be partially exchangeable or totally non-exchangeable with other cations.

The typical range of aluminum in soils is from 1% to 30% (10,000 to 300,000 mg Al kg^{-1}) (Lindsay, 1979). Lindsay (1979) used an average of 7.1% (71,000 mg Al kg^{-1}) as an arbitrary aluminum reference concentration for all soils. Weathering and subsequent release of aluminum from 2:1 layer silicates in soils is enhanced by inputs of acids from the natural decomposition of organic matter and minerals and from pollution (McBride, 1994). Though weak, carbonic acid can significantly enhance the weathering of minerals such as calcium carbonate (limestone).

Aluminum can easily replace exchangeable cations such as Ca^{2+}, Mg^{2+}, or K^+ bound to negatively charged clay surfaces by electrostatic forces. The concentration charge rule and thermodynamic principles provide reasonable explanations as to why aluminum has relatively higher affinity for the exchange sites compared to low valent cations. The concentration charge rule applies to all cations involved in cation exchange as long as their ionic charges are different and the solution is sufficiently dilute. The higher charged cation will always be the one that is preferentially adsorbed (McBride, 1994). Thermodynamically, adsorption of high-charge cations occurs favorably because of an entropy gain and not because of lowering of the energy in the water-clay system adsorbed, when the geometry of the multivalent cation is considered (McBride, 1994). The increased entropy, which results when a high-charge cation displaces low-charge cations from the exchange surface into the solution, could arise from increased disorder of either cations or water molecules in the exchange system. The more hydrated cations (multivalent) may have greater mobility at the surface of the clays (more entropy) and hence greater tendency to form ion pairs with the exchange sites.

Chemically active (soluble and exchangeable) soil Al can occur in a variety of forms that are controlled primarily by the pH, mineralogy, organic matter, concentration of other cations, anions and total salts, and plant species (Foy, 1984; Kamprath and Foy, 1985). Aluminum is toxic for many plants when the soil solution concentration is greater than 2-3 ppm with soil pH < 5.5 (Balsberg Pahlsson, 1990).

Several different solid phases have been proposed to control Al solubility in soils. A number of studies (Bloom et al., 1979; Cronan et al., 1986 and Walker et al., 1990) attributed Al solubility control in organic soil horizons to exchange reactions between H and Al with soil organic matter. Walker et al. (1990) found that equilibrium solubility was attained within hours and increased with decreasing pH and increasing degree of saturation of soil organic matter with Al. From results of a leaching experiment, Mulder et al. (1989) concluded that even in acid mineral soil horizons, Al solubility can be controlled by complexation with soil organic matter. This finding was confirmed by soil solution data obtained from acid brown forest soils in The Netherlands (Mulder and Stein, 1994). Berggren and Mulder (1995) attributed Al solubility in acid mineral soil horizons from southern Sweden with pH < 4.1 to complexation reactions with soil organic matter, and, at higher pH values, to an $Al(OH)_3$ phase with a higher solubility than gibbsite. David and Discroll (1984) found that solutions from two Spodosol B horizons were often close to equilibrium with synthetic gibbsite. Dahlgren et al. (1989) observed a fast equilibrium in a Spodosol Bs horizon with $Al(OH)_3$ from both conditions of undersaturation and oversaturation in a laboratory study. They attributed the control of Al solubility to hydroxy-Al interlayers of expansible 2:1 layer silicates, since (i) no or only trace quantities of gibbsite could be detected in the soil samples; and (ii) Al activities were oversaturated with respect to gibbsite. Similar results were reported by Dahlgren and Walker (1993). Turner and Brydon (1965, 1967), using smectites, also showed that hydroxy-Al interlayers are less stable than gibbsite.

In slightly acid soil solutions and natural waters, hexa-aqua Al ions, $Al(H_2O)_6^{3+}$ are the predominant species formed when Al^{3+} is released from Al-bearing minerals. The $Al(H_2O)_6^{3+}$ is acidic and undergoes hydrolysis to form a number of soluble hydrolysis species (Huang et al., 2002) that influence the subsequent solid phases. The hydroxy species may be comprised of simple monomeric ions, polynuclear species of various sizes and degrees of bacicity or, more probably, of a complex admixture of both. Some of these hydrolysis species are toxic to plants and soil organisms (Barnhisel and Bertsch, 1989).

Deleterious effects of Al toxicity on crops include impairment of root development, which is manifested in poor growth and delayed maturity (by interfering with cell division in plant roots); fixation of phosphorus in less available forms in the soil and plant roots; reduction in root respiration; interference with the activity of many enzymes; increased cell wall rigidity (cross-linking pectins) and interference with the uptake and transport of essential nutrients (Ca, Mg, K, P) and water to plants (Yamoah et al., 1996; Kochian, 2000; Foy, 1984; 1992; Nichol and Oliveira, 1995). Aluminum not only inhibits uptake and translocation of phosphate, but also inhibits the functions of metabolically incorporated phosphate. Bennet et al., (1985) observed nutrient disorders involving the uptake and transport of Ca, Mg, K, and P in maize. Phosphorus transport between roots and shoots diminished with increased Al concentration in the roots. Ohki (1987) also reported positive correlation of P and Al in the roots of sorghum. The degree of Al toxicity depends on the plant species (Foy, 1984; Foy, 1988; Anderson, 1988; Roy et al., 1988) and the Al species (Foy, 1984). For example, maize growth was reduced when Al concentration in the solution was 3.6 mg/L (Evans and Kamprath, 1970). In a similar experiment, soybean growth was reduced when Al concentration in the solution was only 1.8 mg L^{-1}.

The symptoms of Al toxicity may be difficult to identify due to their similarity with deficiency symptoms of P and Ca (Foy, 1984). Foliar symptoms similar to P deficiency include overall stunting, delayed maturity, purpling of leaves and stems, and death of leaf tips. Symptoms resembling Ca deficiency include curling and rolling of leaves. Damage to the root systems due to Al toxicity is often characterized by poorly branched and necrotic roots, with little or no root hair development (Kochian, 2000) resulting in drought susceptibility. Aluminum interference with P uptake also might result in P deficiency in plants grown in acid soils or in nutrient solutions (Jan and Pettersson, 1989).

1.4.3. Soil phosphorus bioavailability

Phosphorus is one of the key substrates in energy metabolism and biosynthesis of nucleic acids and membranes. It also plays an important role in photosynthesis, respiration, and regulation of a number of enzymes. Among the essential nutrients required by plants, P is the most important element to significantly affect plant growth and metabolism (Raghothama, 1999). Depending on the type of soil, the organic P content may constitute a considerable fraction (20-80%) of the total P content (Jungk et al., 1993) in forms such as humus and biological residues. Naturally occurring, inorganic phosphorus originates from apatite-rich (rock phosphate) parent material. During pedogenesis, mineral P weathers, slowly releasing phosphate ions to the soil solution. Other direct inputs include fertilizers, plant and animal residues, municipal wastewater treatment effluent, and runoff from industrial sources. Secondary minerals such as vivianite and strengite (iron-phosphates) and wavellite and variscite (aluminum-phosphates) form when solution P reacts with cations (Al, Fe, Ca) in the soil. Orthophosphate ions ($H_2PO_4^-$and HPO_4^{2-}) are the predominant forms in most soil solutions available for immediate biological (plant and microbial) uptake.

Soil phosphorus bioavailability is controlled by processes such as leaching, erosion, plant uptake, adsorption/precipitation, desorption/dissolution, and reactions with other ions. Orthophosphate ions also may be sorbed, desorbed, or fixed by clay minerals and iron and aluminum oxides. All of these chemical and physical processes are linked and complicated by biological activity; there is a constant conversion from organic to inorganic P through mineralization and immobilization reactions.

Phosphorus bioavailability is of particular concern in highly weathered or volcanic soils of the humid tropics and subtropics, and in many sandy soils of the semiarid tropics (Sanchez et al., 1997; Vitousek, 1984). Soils may contain several hundred to several thousand pounds of phosphate per acre. However, the active P pool (P that can be released into solution) is generally small in comparison to the fixed P. Phosphorus is particularly problematic due to low inputs from primary minerals, formation of low solubility Fe- and Al-phosphates, and the occlusion in secondary Fe minerals (Sanchez, 1976; Hsu, 1982).

In response to low levels of P availability in the rhizosphere, plants have developed morphological, physiological, biochemical, and molecular mechanisms to acquire and utilize P from the environment. Some of the morphological responses include increased root: shoot ratio, changes in root morphology and architecture, increased root hair proliferation, root hair elongation, accumulation of anthocyanin pigment, and increased association with mycorryzal fungi (Barber, 1984; Raghothama, 1999). Anthocyanin is a class of flavonoid pigments derived from photosynthetically produced carbohydrates via enzyme catalyzed reactions. This pigment is sparked by a net starch accumulation brought on by less leaf growth and continued photosynthesis.

Physiological adaptation includes enhanced P uptake, reduced P efflux, increased P use efficiency, and secretion of organic acids, protons, and chelators. Biochemical and molecular responses include activation of key enzymes and genes (Raghothama, 1999). Plants can change the soil solution chemistry of the rhizophere (e.g pH and redox) and affect the pool of disequilibrium desorbable P by secretion of low molecular weight organic acids (LMWOA) such as oxalate, citrate and malate. Root respiration promotes the bicarbonate anion in solution to produce ligands that have greater affinity for the soil surface than does phosphate. These mechanisms combine to form a ligand desorbable pool of bioavailable P (Sato and Comerford, 2006).

1.4.4. Phosphorus sorption

Sorption is one of the most important chemical processes in soils because it affects the fate and mobility of nutrients and contaminants. Sorption is a general term referring to processes such as adsorption, surface precipitation, co-precipitation, and diffusion into crystals, and is used only when the retention mechanism at the surface is unknown. Adsorption refers to the "accumulation of a substance or material at an interface between the solid surface and bathing solution" (Sparks, 2003). It is strictly a two-dimensional process and does not include three-dimensional processes such as surface precipitation, co-precipitation, and diffusion into the crystal (Scheidegger and Sparks, 1996). Desorption on the other hand is the release of the sorbate (sorbed material) to the sorptive solution.

Numerous studies have investigated various aspects of sorption of plant nutrients and environmental contaminants based on macroscopic approaches. In such studies, mathematical functions, kinetic models and equilibrium-based isotherms are used to manipulate sorption data to extrapolate bonding information and reaction rates. Many of these studies used empirical and semi-empirical equations (e.g Langmuir, Freundlich), and surface complexation models (e.g constant capacitance, triple layer) to describe adsorption. Equilibrium based isotherms rely on bond strengths, charge properties, and concentration-distribution relationships. At best, these models are purely descriptions of macroscopic data and do not definitively prove a particular reaction mechanism. Thus, it is difficult to differentiate between adsorption and other sorption processes.

A classic example is an attempt by Muljadi, et al. (1966a, 1966b, 1966c) to define three distinct regions (I, II, III) of phosphate adsorption isotherms. The observations were based on the ease with which sorption to kaolinite and aluminum oxides (gibbsite and pseudoboehmite) were reversed due to changes in solution P concentration, pH and temperature. The authors assumed that regions I and II are governed by Langmuir isothgerms, while region III is determined by a linear isotherm. They suggested that these regions were related to the affinity of phosphate for the three energetically different sorption sites. For the adsorbents studied, region I had the greatest binding affinity followed by region II. Regions I and II represent chemisorption of P (only reversible with increased pH) at surface/edge hydroxyl or water sites (ligand exchange). Region III, on the other hand represents more physically sorbed P, which has penetrated into more amorphous regions of the clay, but is the most reversible. The equilibrium dependent regions (I, II, and III) are analogous to "compartments" A, B, and C defined by the kinetic approach of Barrow and Shaw (1974), representing short-term and long-term supply of phosphorus to the soil solution (region III being equivalent to compartment B) (Ryden and Syers, 1977). Others studies suggest that at low concentrations phosphate undergoes ligand exchange (Parfitt, 1978); whereas at high concentrations, it seems that some destruction of the sorbent can occur; creating new sorption sites (Rajan and Perrott, 1975) or probably due to interparticle diffussion.

Although the rate of sorption/desorption reactions can provide significant information on possible mechanisms, to ascertain precise sorption/release mechanisms, approaches which yield atomic/molecular information have been employed. Spectroscopic and microscopic techniques have been employed to observe and investigate the local bonding environment of phosphate with clays and metal oxide surfaces (Parfitt and Russell, 1977; Parfitt et al., 1975; Parfitt, 1989; Breeuwsma and Lyklema, 1973; Russell et al*.,* 1974; Goldsberg and Sposito, 1984; Persson et al., 1996). With the use of infrared (IR) absorption, Russell et al. (1974) showed that hydroxyl groups are lost from the goethite surface when P is adsorbed. This confirms that ligand exchange is the mechanism by which phosphate attaches to iron oxides, forming an inner-sphere complex, much like arsenate (Goldberg and Johnston, 2001). With this understanding of the binding mechanism, further studies using IR techniques defined the surface complex by which phosphate was held: a bidentate, binuclear bridging complex with Fe (III) on crystalline and amorphous iron oxide surfaces (Parfitt and Russell, 1977; Parfitt et al., 1975) and on the edge sites of Al oxides (Parfitt et al., 1977). Based on the knowledge gained from ideal, well defined surfaces, it is now possible to investigate the mechanisms of phosphate fixation by more complex and heterogeneous systems, like soils, because P sorption properties of soils are similar to those of iron and Al oxides.

Phosphorus sorption and release may be controlled by any combination of factors: pH, Al saturation, and composition of any given soil (mineralogy and organic matter content) (Sanchez and Uehara, 1980). Crystalline and non-crystalline oxides of Fe and Al are considered the main sorbents (Schwertmann and Taylor, 1977; Prafitt and Smart 1978; Ballard and Pritchett, 1974; Ballard and Fiskell, 1974; Maguire et al., 2001a). Using chemical speciation of each species in solution to interpret the adsorption envelopes, Cabrera et al. (1977) concluded that Al oxides are more reactive with phosphate than iron oxides of similar surface area. Maximum adsorption on such surfaces occurs at slightly below pH 5, and decreases with increased pH. At pH near five, amorphous Al phosphates control the solution equilibrium because they are most stable (Lookman et al., 1997), but above pH 5.5 calcium phosphates predominate (White and Taylor, 1977a). Discreet Al- and Si-bearing precipitates also have been found in soils (Pierzynski et al., 1990a, 1990b).

Bidentate complexes of phosphate on iron-bearing surfaces are directly dependent upon loading levels and pH. At higher loading and lower pH they are not present (Parfitt and Russell, 1977), possibly because monodentate complexes form (Persson et al*.,* 1996) so that more sites are available. Adsorption reactions are usually more rapid on clay surfaces such as kaolinite and oxides than on clay surfaces such as mica and vermiculite (Scheidegger and Sparks, 1996). Under high initial concentrations, phosphate binds weakly (physically) to the surface, and with increasing time migrates to a chemically bound form which is more recalcitrant to desorption.

There is a strong relationship between the incubation time and the strength with which phosphate is held in the soil (Barrow and Shaw, 1975; Ryden et al., 1977a, 1977b; 1977c; White and Taylor, 1977b). With time, as P sorption sites become occupied, the buffering ability of the soil decreases, leading to decreased P adsorption (Barrow, 1974; 1985; Parfitt et al., 1975; Zhou et al., 1997). The inorganic P that remains in the soil is released into the soil solution through desorption from the soil surface and dissolution of relatively soluble P compounds (Wolf and London, 1994).

1.4.4.1. Sorption isotherms

A common way to measure P sorption capacity is by construction of sorption isotherms. Sorption isotherms are usually made by equilibrating soils with solutions containing known amounts of P (batch process). After equilibration, the soil and solution are separated by centrifugation and/or filtration. Phosphorus in the solution is measured and the difference between initial and final P concentration and P in the equilibrium solution is assumed to be sorbed or desorbed P by the soil.

Quantitative descriptions of P sorption by soils often have been made with the Langmuir, Freundlich, and Temkin equations. Although these equations were originally derived to describe the adsorption of gases by solids, in many cases these models were able to provide adequate mathematical descriptions of P sorption in soils. By far, the most widely used model is the Langmuir equation (Cabrera et al., 1977; Rajan and Perrott, 1975; Ryden and Syers, 1977; Ryden et al., 1977b, 1977c). The Langmuir equation implies that sorption takes place in a monolayer on the soil surface and that a further increase in P concentration above P sorption maximum will not result in an increased sorption. This equation is based on the assumption that the energy of absorption does not vary with surface coverage. The distinct advantage of the Langmuir over the Freundlich and Temkin equations is that the Langmuir equation allows estimation of a sorption maximum and a constant that is related to the P binding strength. The sorption maximum derived from the Langmuir equation is useful for estimating P sorption capacity and comparing different soils. The Langmuir equation has been used successfully in describing P retention properties of different types of soils (Nair et al., 1999; Zhou et al., 1997; Singh and Gilkes, 1991; Loganathan et al., 1987; Wendt et al., 1993). The Langmuir equation has the form:

$$q = \frac{k_d q_{\max} C}{1 + k_d C} \qquad \text{Eq. 1.1}$$

Where C is the concentration of P in the equilibrium solution (mg P L^{-1}), q is the amount of P sorbed (mg kg^{-1}), q_{max} is the Langmuir sorption maximum (mg kg^{-1}), and k_d is a constant related to bonding energy (L kg^{-1}) (Barrow, 1978; Parfitt, 1978). The plot of C/q against C gives a straight line with slope equal to q_{max}^{-1} and the intercept $(k_d q_{max})^{-1}$. The linear form of Langmuir equation is given below:

$$\frac{C}{q} = \frac{C}{q_{\max}} + \frac{1}{k_d q_{\max}} \qquad \text{Eq. 1.2}$$

However, the Langmuir plots are only approximately linear over a limited concentration range (0.5 x 10^{-5} M to 5 x 10^{-4} M) (Bache and Williams, 1971). Over wider concentration ranges, the plots tend to be curved, indicating that the bonding energy is, in fact, not constant, and that there is no well defined constant. The possible explanation for this, according to Bache and Williams is (1971) is that sorbed phosphate migrates to the sub-surface layers.

The Freundlich equation was first introduced as a purely empirical equation, which implies that the energy of adsorption decreases exponentially with increasing saturation of the surface. The Freundlich equation has the form:

$$q = a\, C^{1/n} \qquad \text{Eq. 1.3}$$

Where q and C have the same meaning as in the Langmuir equation and *a* and *n* are empirical parameters. The Freundlich equation often is used in logarithmic form:

$$\log q = \log a + 1/n \log C \qquad \text{Eq. 1.4}$$

The Freundlich equation does not give a maximum sorption capacity. The *a* and *n* values are useful for comparison of sorption characteristics of different soils. The *a* parameter represents the amount of P sorbed (mg kg^{-1}) when C is 1 mg L^{-1}. However, these sorption parameters do not provide specific information about the actual mechanism of a sorption process in soils. They are regarded simply as curve-fitting parameters, unless other independent data are presented to support their chemical significance (Sposito, 1982).

1.4.5. Influence of iron and aluminum oxides on phosphorus sorption

Soil test P alone does not give complete information on the likelihood of a soil to release soluble P because it does not give a quantitative indication of the soil's potential to retain P. The nature, amount and distribution of Fe and Al oxides in a soil can significantly affect its properties such as charge characteristics and ion adsorption, particularly phosphate sorption (Torrent, 1987; Torrent et al., 1990). A pedological feature of many highly weathered soils is the abundance of Fe and Al oxides which could be responsible for sorbing large proportions of applied phosphate. The oxides can be divided into three forms according to chemical analyses; (i) dithionate-citrate extractable representing crystalline and amorphous forms, (ii) oxalate extractable representing amorphous forms, and (iii) pyrophosphate extractable representing organic bound oxides (McKeague et al., 1971). Ammonium oxalate often is used to obtain semi-selective dissolution of poorly-crystalline iron and aluminum oxides and organically bound Fe and Al, soil components associated with a high P retention capacity (Borggaard, 1992; Freese et al., 1992; Gerke and Hermann, 1992). Soil saturation indices are preferred to more accurately predict a soil's potential to retain and release soluble P. Degree of phosphorus saturation (DPS) was first developed and used in the Netherlands to evaluate the risk of P leaching from soil (van der Zee et al., 1990). The DPS estimates how close the soil is to saturation and provides possibilities of comparing soils with varying P sorption capacities. Degree of phosphorus saturation is described (van der Zee et al., 1990) as follows:

$$\mathrm{DPS}\,(\%) = \frac{\text{Sorbed P}}{\text{P sorption capacity}} \times 100 \qquad \text{Eq. 1.5}$$

Different methods of estimating sorbed P and P sorption capacity can be combined to determine DPS. Acid ammonium oxalate extractable P (P_{ox}) has been used as an estimate of sorbed P while Fe and Al in the same extract (Fe_{ox} and Al_{ox}) are used to estimate sorption capacity (Schoumans, 2000; van der Zee and van Riemsdijk, 1988):

$$\mathrm{DPS_{ox}}\ (\%) = \frac{\mathrm{P}_{ox}}{\alpha(\mathrm{Fe}_{ox} + \mathrm{Al}_{ox})} \times 100 \qquad \text{Eq. 1.6}$$

Where (Al_{ox} + Fe_{ox}) is taken to represent P sorption capacity (PSC) and P_{ox}, Al_{ox}, and Fe_{ox} are expressed in mmol kg^{-1}: The parameter α is a scaling factor which is experimentally determined for a given soil type and is time and concentration dependent (van der Zee and van Riemsdijk, 1988).

1.4.6. Ion exchange phenomena in acid soils

Cation exchange sites are found primarily on soil mineral and organic matter (OM) surfaces (Johnston and Tombácz, 2002). The cation exchange capacity (CEC) of a soil is a measure of the quantity of sites on soil surfaces that can retain positively charged ions, while the anion exchange capacity (AEC) is a measure of the quantity of sites on soil surfaces that can retain negatively charged ions by electrostatic forces. Cations retained electrostatically are easily exchangeable with other cations in the soil solution and are thus readily available for plant uptake. Thus, CEC is important for maintaining adequate quantities of plant available Ca^{2+}, Mg^{2+} and K^+ in soils. Under acidic conditions ($pH < 5.5$), Al^{3+} also may be present as an exchangeable cation. While a soil with a higher CEC may not necessarily be more fertile, when combined with other measures of soil fertility, CEC is a good indicator of soil quality and productivity.

The beneficial effects of soil organic matter management in the tropics have been amply documented. Besides nutrient release (nitrogen and phosphorus in particular) (Nziguheba et al., 2000), soil organic matter also is known to contribute to total charge of a soil, a charge that is mostly pH-dependent. Empirical relationships exist that predict soil cation exchange capacity (CEC) based on organic matter content. Soil organic matter will develop a greater CEC at near-neutral pH than under acidic conditions (Manrique et al., 1991; Asadu et al., 1997, Krogh et al., 2000). Additions of organic materials are likely to increase the soil's CEC above that derived from the soil mineral component. Addition of organic matter can increase CEC from as low as 1 $\mathrm{cmol_c\ kg^{-1}}$ to 4-6 $\mathrm{cmol_c\ kg^{-1}}$ (Gallez et al., 1976; Oades et al., 1989). Soil CEC also may decrease with time through acidification and organic matter decomposition.

There are numerous methods for determining CEC and many will give quite different results. Older methods used extractants buffered at high pH, e.g. pH 7 ammonium acetate and pH 8.2 barium chloride-triethanolamine. “Exchangeable acidity" measured in this fashion was really a measure of pH buffering capacity. Because of the differing methods to estimate CEC, it is important to know the intended use of the data. If a pH-buffered CEC measurement is needed, the pH 7.0 ammonium acetate procedure of Chapman (1965) or modified versions are recommended. The pH 7.0 ammonium acetate CEC method has been widely used in the U.S. for decades. Consequently, a large data base exists for soil CEC by this method. Soil classification (Soil Taxonomy) traditionally requires CEC to be measured by this procedure. The main problem with this method is that it buffers soil pH at 7.0 causing large overestimates of CEC for acid soils (Sumner and Miller, 1996).

1.5. Management of acid soils

Choice of the best approach for amelioration of soil acidity is governed by economic considerations and is also strongly soil dependent. Although liming of acid soils as practiced in developed countries can ameliorate soil acidity, this is neither an economic option for poor farmers nor an effective strategy for alleviating subsoil acidity (Pandey et al., 1994), especially in developing countries. Subsoil usually remains unaffected by liming because deep liming is technically difficult and expensive. In addition, application of high rates of lime in highly weathered tropical soils is often detrimental to soil structure as well as availability of P and several micronutrients such as Zn (Foy, 1992).

A low input management strategy involving adapting plants to the soil's limitation rather than the traditional approach of adapting the soils to meet the crop requirements would be relevant to tropical regions with low capital (Sanchez and Uehara, 1980). Combining more efficient P fertilization practices such as use of cheaper sources of P with crop cultivars more resistant to biotic stresses and more responsive to soil improvements would probably be the most logical strategy for increasing food production in tropical acid soils. A concerted effort is now being made to combine high yield and quality with high tolerances to soil-related stresses. Development of cultivars more tolerant to low levels of available P and toxic levels of Al seems to be a promising alternative to supplement liming and other agronomic practices, and is likely to result in more efficient use of P fertilizer. This rationale has been effective especially in the "Cerrados" of Brazil (Yamada, 2005).

CHAPTER 2. AGRO-ECOLOGY AND GEOMORPHOLOGY

2.1. Introduction

This chapter is intended to provide an overview of the agro-ecological and physiographic background relevant for interpretation of the soil properties discussed in the subsequent chapters. Soil characteristics result from the combined action of soil forming factors (climate, geomorphology, age, parent material and vegetation). Variability in soil fertility management at different scales also may be due biophysical and soci-economic factors. Variability at the regional scale is determined by climate. The variability between farm types within a village is associated with the soilscape, such as the location along a catenary sequence (Deckers, 2002) and with differences in soil fertility management. An understanding of soil in the context of these factors, together with the influence of human activities, can aid in interpretation of key soil properties.

To facilitate the transfer of efficient nutrient management technologies, nutrient management recommendations should be specific for well-defined Agro-Ecological environments. FAO (1987) defined an Agro-Ecological Zone (AEZ) by its relevant agro-climatic factors, differentiated by soil pattern, and having a specific range of potentials and constraints for land use, with soil moisture and temperature regimes determining the crops grown. Land use systems on the other hand, are characterized by nutrient inputs (mineral fertilizer, manure, atmospheric deposition, biological nitrogen fixation, sedimentation) and nutrient outputs (removal of harvested crop parts and residues, leaching, denitrification, erosion), and the balance between the two. The landscapes and agro-ecological conditions in which Kenyan farming systems have evolved are very diverse in terms of physical attributes and the history of use and management. Sombroek et al. (1982) recognized that the soil pattern in Kenya is very intricate because of the striking differences in altitude, landforms (their shape, stability, and age), geology, and climate (including past climates). Watershed, upland and bottomland areas provide contrasting soils, slopes, patterns of drainage, and crop growing conditions and, hence are managed differently by farmers.

2.2. Brazilian Cerrado soils

Geomorphology and agro-ecological information about the Brazilian Cerrado soils used in this study are described elsewhere by Marques (2000) and Marques et al. (2004a; 2004b). In summary, soils fo the Brazilian Cerrado have been weathering for many million years, as long as 72 million years, in some places. As a result, Cerrado soils have been considered marginal for a long time. In the past, the vast Cerrado region was mainly used for pasture and cattle grazing. In recent years however, appropriate use of fertilizers and improved crop varieties have significantly boosted the productivity of these soils. The achievements have partly been attributed to the fact that much of the landscape is suitable for mechanization. The Kenyan situation is different however because the majority of subsistence farming is still under smallholdings, particularly in the densely populated highlands.

The Brazilian samples were collected from three main regions of central Brazil: (1) eastern Goiás (G1 and G2), (2) northeastern Goiás (N1, N2 and N5), and (3) the Triângulo Mineiro (T1, T2, T4 and T5) area of western Minas Gerais. These soils were developed on clayey sediments of unknown origin and are underlain by sandstone, except for soils T4 and T5 which were developed on basalt. In addition, soils T4 and T5 are the most inherently fertile, and are used for high-input agriculture (Marques et al., 2004a). The majority of the Brazilian soils used in this study have simililar properties as those of EMBRAPA's current maize and sorghum breeding of locations.

2.3. Site melection and field methods in Kenya

Site selection was geared towards being representative as well as covering a wide range of agro-ecological environments and farming systems in the rain-fed agricultural regions of Kenya. The site selection procedure was based on a careful evaluation of soil and climate maps for Kenya. The exploratory soil and agro-climatic zone maps of Kenya (Sombroek et al., 1982) were used to identify potential fertility "hot spots" of the country. Fertility hot spots were recognized as croplands with symptomatic 'low fertility patches'. Low soil fertility patches result from continuous cropping of land without addition of external nutrient sources (Woomer et al., 1997). A diagnostic survey in parts of Western Kenya (Vihiga, Busia and Bungoma districts) showed that such low fertility patches occupy between 10% and 30% of farm land and that the soil test parameters (pH, C, N and available P) were lower in these patches as compared to the same parameters for adjacent soils where crops grew vigorously (Nekesa et al., 1999). The fields furthest from homesteads rarely receive nutrient inputs, but these fields also are cropped continuously (Okalebo et al., 1992). These fertility-depleted patches persist because farmers have little opportunity to reverse nutrient depletion trends due to poor access to markets and restricted availability of modern farm inputs (Woomer et al*.,* 1998).

Eleven different districts in Kenya, representing a wide range of soils, climate, and socioeconomic and ethnic settings were selected for field survey (Figure 2.1). For each site, land use type/farming systems were described. These sites also represent major maize growing areas with acid soils (Kanyanjua et al., 2002). The study sites were grouped into three major geomorphic provinces for ease of comparison, namely;

1. The Uasin Gishu plateau and lower level upland plains west of the Rift Valley (Kuinet, Chepkoilel (both near Eldoret), Ikholomani, Vihiga, Bumala and Siaya).

   The high level structural plains (Uasin Gishu plateau hereby represented by the two sites in Eldoret) are included in this geomorphic province because they are relatively flat. These areas are underlain by horizontal or slightly inclined strata of unequal resistance to weathering, with inclusions of bottomlands.

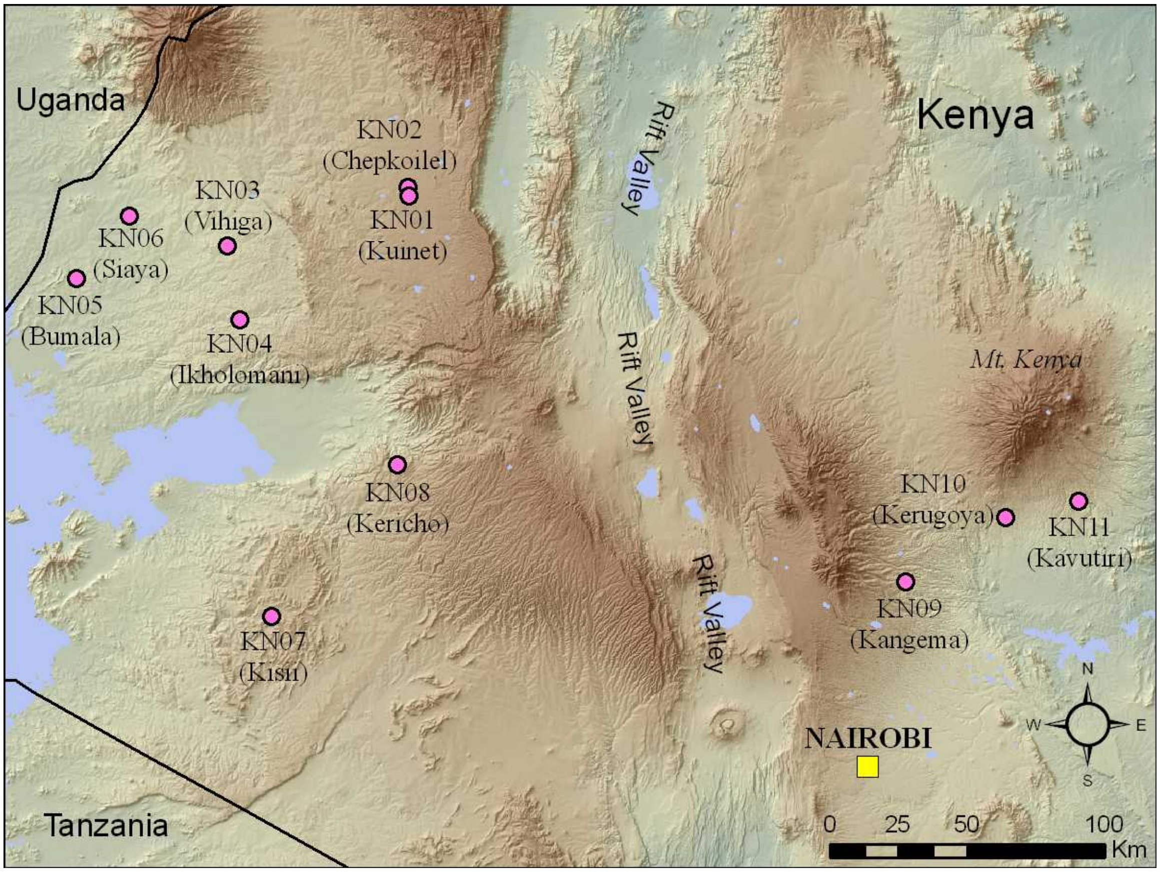

Figure 2.1 A section of the map of Kenya showing the soil sampling locations and major physiographic features.

2. The Western Kenya highlands comprises: Kericho (volcanic foot ridges) and Kisii (lower middle-level uplands) highlands are typically soils formed from old volcanoes. The uplands are usually undulating: attitude 3500 -6500 feet above sea level; about 1500 feet above local base level.
3. The volcanic foot ridges east of the Rift Valley (Kangema, Kerugoya and Embu) –a landform that consists of broad parallel, rather convex interfluves alternating with deeply incised valleys, often with convex slopes and with a narrow valley bottom.

The Kenyan rift valley is a sector of the rift system of eastern Africa which is marked by volcanic activity throughout its history from Miocene time. Activity is not confined to the rift zone, but extends for distances of 200 km or more both to the east and west and is broadly centered on the Kenya 'dome', to the east and west, a topographic culmination in the course of the rift (King et al., 1972). King et al., (1972) and Crossley (1979) outlined the chronology of events leading to the formation of the present Kenyan rift system. The oldest volcanoes are members of the melanephelinitic association, which were erupted onto metamorphic basement topography from central volcanoes and fissures situated mainly in the down-warped area within which rift faulting subsequently developed. The onset of volcanism within the rift is reported to have occurred during the middle Miocene (15-12 million years ago) which is significantly younger than the onset of volcanism in the northern section of the rift (~30-20 million years ago). A period of major faulting (most of it post-0.6 million years ago) created much of the present rift topography. Mount Kenya is an extinct volcano, 50 km in diameter at the base, and is located on the eastern side of the Kenyan rift valley system. It is a result of massive, successive and intermittent volcanic eruptions approximately 3.2 to 2.8 million years ago (MCK, 2006).

Additional landscape, land use and morphological information were obtained from field surveys. Pits were opened in each site, described and sampled by horizon for laboratory analysis. Detailed pedon descriptions are located in Appendix A. Geographical location, major landforms/relief, slopes, parent materials and major land use associated with each sampling site are provided in Table 2.1. The volcanic rocks range in composition from acidic to basic. There are giant nephelinite volcanoes extending from central volcanoes of eastern Uganda, including Mt. Elgon, and western Kenya; and the giant phonolitic-trachyte or basalt-phonolite-trachyte volcanoes of Mt. Kenya. Key characteristics of the various parent materials associated with each pedon are summarized in Table 2.2. The parent materials are various types of igneous rocks (intermediate, basic and Tertiary igneous rocks) whose chemical composition varies significantly in terms of silica and alkali composition and relative ease of weathering. The properties of soils in the region around Mt. Kenya are influenced, to a large extent, by the relatively less weathered, porous volcanic ash deposits. On the other hand, hard igneous and relatively older volcanic deposits on the plateaus and highlands neighboring the Kenyan rift valley system to the west largely affect the properties of soils formed in that region.

Generally, land use in Kenya varies depending on the prevailing agro-ecological conditions, particularly rainfall. The annual rainfall distribution exhibits marked spatial variation because of the complicated nature of the local topography and elevation.

Table 2.1 Site characteristics and locations of pedons in Kenya

Pedon	Location[‡]: Latitude and longitude	Elevation[‡] (m asl) [†]	Geomorphic* position	Slope*	Land use at the site	Soil Classification (FAO-UNESCO)*
Highlands and upland plains west of the Rift valley: Soils developed on intermediate igneous rocks (syenites, trachytes, phonolites etc)						
KN01 Kuinet	N 0° 36.781″ E 35° 18.280″	2127	Plateau, high level structural plain (Uasin Gishu plateau)	Flat to gently undulating slopes, nearly level; < 8% slopes.	Maize and wheat production, dairy farming.	Rhodic Ferralsols, petroferric phase
KN02 Chepkoilel	N 0° 34.997″ E 35° 18.561″	2148	Plateau, high level structural plain.	Flat to gently undulating slopes; < 8% slopes.	Soil fertility field experimentation: maize and wheat and dairy farming.	Rhodic Ferralsols, petroferric phase
KN03 Vihiga	N 0° 02.524″ E 34° 42.854″	1651	Plateau, high level structural plain.	Flat to gently undulating slopes; Backslope ~3% slopes.	Initially under equatorial forest but has been settled for a long time. Maize, beans, napier grass and sesbania (mixed farming).	Rhodic Ferralsols, petroferric phase
KN04 Ikholom-ani	N 0° 10.614″ E 34° 45.225″	1600	Upper-level uplands.	Undulating to rolling.	Initially under forest but has been settled: maize, beans, tea and mixed farming.	Mollic Nitosol

Table 2.1 Continued

Pedon	Location[‡]: Latitude and longitude	Elevation[‡] (m asl) [†]	Geomorphic position	Slope	Land use	Soil Classification (FAO-UNESCO)
KN05 Bumala	N 0° 18.910″ E 34° 13.231″	1200	Lower-level uplands.	Undulating to rolling.	Subsistence farming; maize, beans. Soil fertility trial site	Rhodic Ferralsols, petroferric phase
KN06 Siaya	N 0° 03.112″ E 34° 23.658″	1399	Lower level upland.	Undulating to rolling.	Originally open woodland, shrubs. Later settled, currently under subsistence farming. Soil fertility trial site.	Dystic Nitosol with orthic Ferralsols, petroferric phase
Highland west of the Rift valley: Soils developed on tertiary basic igneous rocks (olivines, basalts, phonolites, older basic tufts, nepheline etc)						
KN07 Kisii	S 0° 47.574″ E 34° 51.446″	1830	Lower midland level upland. Undulating to mountains.	Lower 1/3 of a long linear back slope. 16% slope.	Originally under woodlot. Recently cultivated; mixed intensive framing.	Mollic Nitosol
KN08 Kericho	S 0° 17.773″ E 35° 16.350″	1904	Volcanic foot ridges, dissected lower slopes of older volcanoes and mountains).	Undulating to hilly.	Mixed cropping and dairy farming; Tea vegetables, maize and fodder.	Humic Nitosol

Table 2.1 Continued

Pedon	Location[‡]: Latitude and longitude	Elevation[‡] (m asl) [†]	Geomorphic position	Slope	Land use	Soil Classification (FAO-UNESCO)
Highlands east of Rift valley: Soils developed on tertiary basic igneous rocks (olivines, basalts, nepheline etc)						
KN09 Kangema	S 0° 40.883″ E 36° 56.097″	1920	Volcanic foot ridges, undulating to hilly	~ 20-40% slopes	Mixed farming; maize, bananas, beans, vegetables fodder, tea, and dairy farming	Ando-humic Nitosol / Humic Andosol
KN10 Kerugoya	S 0° 28.181″ E 37°15.752″	1702	Volcanic foot ridges, undulating to hilly	~ 20-40% slopes	Mixed farming; maize bananas, beans, vegetables fodder tea and dairy farming	Ando-humic Nitosol / Humic Andosol
KN11 Kavutiri	S 0° 25.004″ E 37° 30.062″	1810	Volcanic foot ridges, undulating to hilly	~ 20-40% slopes		Humic Andosol

[†] meters above sea level [‡] Latitude, longitude and elevation from GPS, WGS 84 map datum

* Geomorphic descriptions, slope descriptions and soil classifications from Sombroek et al. (1982).

Table 2.2 Parent materials and properties of key mineral constituents

Site	Rock type^1	Properties^2
Kuinet (KN01) Chepkoilel (KN02)	Intermediate igneous rocks e.g. Syenites, trachytes, phonolytes	Syenites (alkali-rich feldspar - $KAlSi_3O_8$) - found in dark colored rocks - formed when magma is cooled at moderate depths and relatively fast - Silica-poor minerals (high in dark colored minerals) Trachytes (alkali-rich feldspar- $(K,NaSi_3O_8)$ - found in extrusive igneous rocks like sanidine - cooled quickly from an initially high temperature of eruption Phonolite - volcanic equivalent of nepheline syenite and thus poorer in silica than trachyte - contains feldspathoids (orthoclase or sanidine)
Vihiga (KN03)	Granites	Granite ($NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O) - granular (plutonic) rock of light color and even texure - consists chiefly of feldspar and quartz and sometimes a small amount (about 8%) of biotite mica and hornblende)
Siaya (KN06)	Intermediate igneous rocks e.g. Basalt	Basalt - dark colored, fine-grained rock, the volcanic equivalent of gabbro - contains mostly labradorite feldspars, calcic plagioclase, and sometimes brown hornblendes and brown biotite
Bumala (KN05)	Basic igneous rocks e.g. Basalt	
Kisii (KN07)		

Table 2.2 Continued

Site	Rock type[1]	Properties[2]
Kakamega (KN04) Kericho(KN08) Kangema (KN09) Kerugoya (KN10) Embu(KN11)	Tertiary basic igneous rocks e.g. basalts, olivine, nepheline, phonolites, older basic tufts	Olivine $(Mg,Fe)_2SiO_4$ - found in dark colored igneous rocks such as gabbro, basalt, peridotite - formed from silica-poor magma Nepheline $(NaAlSiO_4)$ - rock forming mineral found in silica-deficient intrusive and extrusive rocks. - contains 21.8 Na_2O_8, 35.9 Al_2O_3, 42.3 SiO_2 and 3-12% by weight K_2O Phonolite Tuff - fragmental igneous material ejected during volcanic activity - Consists mainly of volcanic ash and dust

[1] Rock types are summarized from Sombroek et al. (1982) [2] Rock properties are summarized from Klein and Hurlbut, (1997).

Greater annual precipitation and cooler temperatures are more common in the highlands than the neighboring warmer and drier medium altitude lands. Consequently, the majority of the best rain-fed agricultural lands are found in the highland areas, in spite of the prevailing hilly terrain and declining soil fertility. The Kenyan highlands generally comprise areas with elevations ≥ 1000 m above sea level, mean annual temperatures of 10–18° C and a bimodal rainfall pattern, often > 800 mm annually (Jaetzold and Schmidt, 1983). Among the selected study sites, elevation ranges from about 1300 m in the western upland plains, to 2200 m in Uasin Gisu plateau. The annual bimodal distributions are classified based on "rainfall seasons", namely: 1) long-rains which fall between March- May, and 2) short-rains which fall between July-August or October-December, depending on the region. Although there is spatial variation of the rainfall during the short rain over many parts of west-central Kenya, short rains make an important contribution to the yearly total precipitation (up to 33 per cent) (Davies et al., 1985). Up to 85 percent of the national annual maize output is obtained from the long-rains season (FEWS NET, 2002). The three geomorphic provinces described previously fall within the high and medium potential land, and are mainly used for intensive cropping and livestock production.

2.4. Kenyan Agriculture

Agriculture plays a major role in the Kenyan economy as it provides livelihood to over 85% of the population and contributes over 65% of foreign exchange earnings (World Bank, 1991). The contribution of the agricultural sector to the gross domestic product (GDP) has progressively declined from 37% of GDP in the early 1970’s to about 25% at the end of 2000 (GOK, 2002). The majority of farmers are smallholders who produce for subsistence and have low purchasing power. Due to population pressure, more people have moved from high potential areas to settle in more fragile environments without corresponding appropriate technologies for utilizing resources in such areas. Most of the original vegetation in many parts of the Kenyan highlands has been cleared for agricultural use, and farms have been sub-divided into smaller units. In such areas, cultivation has become more intensive.

The most important food crops are maize, beans, sorghum, millet, potatoes and cassava. Important cash crops include tea, coffee, wheat, pyrethrum and sugarcane. Maize is Kenya’s staple food crop. Most of the lands of high or medium potential for farming are in Western, Rift Valley, Central and Nyanza provinces. The arable areas of the Rift Valley Province are commonly referred to as the ‘grain-basket’ of Kenya. It is the leading producer of maize, beans, wheat, tea, and pyrethrum (CIA, 2003). Rift Valley province alone, accounts for more than 50 percent of the national long-rains maize output and close to 45 percent of total national annual maize output (FEWS NET, 2002). The Northern and southern regions (Eastern, North Eastern and parts of Coast province) do not have a climate suitable for agriculture. The Eastern province produces approximately 12 % of the total national annual maize output (CIA, 2003).

The common farming systems are mainly subsistence mixed farming. Traditional farming practices are no longer capable of meeting the country’s food demands. In the bulk of the growing areas of Kenya, maize yield without fertilizers or manure ranges between 1.1 and 2.5 t ha^{-1} (17.5 and 39.8 bu $acre^{-1}$)) (Wokabi, 1999). Under smaller holdings, the relative proportions of family land under food crop production is frequently greater than the proportion under non food crop cover such as pasture and fodder, woodlots, or tree fallows, and cash crops such as tea and coffee. Most food crops are grown both during the long and short rain seasons. In some areas, fodder and pasture are grown besides other region-specific crops such as wheat, bananas, tobacco, sugarcane, tea and coffee, particularly in areas where dairy farming is practiced. Tea is the dominant cash crop, particularly in the highlands, while wheat is grown within the Uasin Gishu plateau and its neighboring districts.

Save for the commercial farms, where mineral fertilizers are used, most of the farmers hardly use fertilizers due to low capital endowment. Kenya imports all her fertilizer requirements and this has been supplied to the farmers at subsidized prices for a long time. With structural adjustment policies, these subsidies were largely abolished in 1992 and the subsequent increase in fertilizer prices has discouraged farmers from using mineral fertilizers (Heisey and Mwangi, 1996). In the Kenyan market, however, there are several fertilizer grades. Nitrogen-based fertility resources include mineral fertilizers, organic resources, and rhizobuim inoculums for legumes. The commonly used P-fertilizers are; Single Super Phosphate (SSP, 8% P_2O_5), Triple Super Phosphate (TSP, 46% P_2O_5) Mono-Ammonium phosphate (MAP, 11-52-0) and Diamonium Phosphate (DAP, 18-46-0). Potassium fertilization has been limited to specific needs (commonly high value crops). For a long time, K was believed to be adequate in most soils in the country (FURP, 1987) and this was attributed to feldspar- and mica-rich parent materials. Recent studies however, suggest that potassium is becoming deficient in some Kenyan soils (Kanayanjua et al., 2006). Similarly, mechanization of farming operations in large parts of the study areas is largely hindered by hilly topography, smaller land holdings, and lack of capital, with the exception of the Uasin Gishu plateau and its neighboring districts where wheat and maize farming is largely mechanized.

CHAPTER 3. SOIL PYHSICAL AND CHEMICAL PROPRTIES

3.1. Introduction

Soils are highly variable and complex, especially from the chemical and biological standpoint, and soil properties exert a strong influence on land use. This chapter describes and evaluates key physical and chemical properties of selected Kenyan acid soils and their influence on the availability of essential plant nutrients. It also attempts to investigate relationships among selected soil properties (pH, organic matter content, cation exchange capacity, and various forms of Fe and Al oxides) of selected Kenyan acid soils. Where data are available, an attempt has been made to compare key properties of Kenyan acid soils with representative Brazilian Cerrado soils.

3.2. Sample Preparation and Preservation

All bulk samples from each horizon of all the pedons located in Kuinet (KN01), Chepkoilel (KN02), Vihiga (KN03), Ikholomani (KN04), Bumala (KN05), Siaya (KN06), Kisii (KN07) and Kericho (KN08) were air dried, hand-ground in a porcelain mortar to pass through a 2-mm sieve, and then stored in polypropylene bags until analysis. The samples from the Mt. Kenya region (Keruygoya -KN09, Kangema -KN10 and Embu -KN11) which were thought to be halloysitic were each divided into two portions and one portion of each preserved field-moist in a sealed glass container, while the other portions were air-dried and sieved to pass through a 2 mm sieve and stored with the rest. Air-dried samples were used in all laboratory analyses except for mineralogical analysis where field moist samples for the three pedons from Mt. Kenya region were used.

3.3. Physical properties

Particle size distribution (sand, silt and clay) was determined by the hydrometer method (Gee and Bauder, 1986). Also, the results of the fractionation procedure (Jackson, 1969) for mineralogical analysis were used to estimate the distribution of the major particle size fractions. In summary, 7 g of < 2 mm soil was placed into a 250 mL polypropylene centrifuge bottle. The samples were saturated with Na by 3 washings with pH 5 1M sodium acetate (NaOAc). Organic matter was removed by 3 additions of 10 mL of 30 % (w/v) H_2O_2 in 1M NaOAc, heated to about $100^{\circ}C$ in a water bath. The samples were then centrifuge-washed with deonized water and centrifuged until dispersion of clay occurred. After dispersion, the samples were sonicated for 10 minutes using a Branson model 450 sonifier with a ½ inch probe with replaceable tip). The suspension was adjusted to pH 8 with a few drops of 0.02 M NaOH. The sand (> 50μm) fraction was separated by wet sieving through a 270 mesh sieve. The coarse (20-50μm), medium (5-20 μm), and fine (2-5 μm) silt fractions were separated by sedimentation technique. The coarse (0.2-2 μm) and fine (< 0.2 μm) clay fractions were separated by centrifugation.

Moisture content was determined by oven-drying at 105° C. All results are expressed on an oven-dry weight basis. Bulk density was determined by measurement of the volume of field moist soil and oven dry mass (Blake and Hartge, 1986) using undisturbed core samples taken at different depths from all the pedons. The samples were oven-dried at 110° C and weighed. Soil bulk density was calculated as the ratio of the mass of dry solids to the bulk volume of the soil (solids and pore space).

3.4. Chemical Analyses

Soil pH was measured using a 1:1 soil:water/solution ratio (Thomas, 1996) with a standard glass combination electrode immersed in the solution above the soil, in H_2O, 1 M KCl and 0.01M $CaCl_2$. Delta pH was computed as pH (H_2O) pH (KCl) -.

A Leco automatic analyzer (Leco CHN - 2000) was used to determine the total nitrogen and carbon in the samples. This analytical method quantitatively determines the total amount of nitrogen, hydrogen and carbon in all forms in the soil using a dynamic flash combustion system coupled with a gas chromatographic (GC) separation system and thermal conductivity detection (TCD) system. Loss on ignition (LOI) (Nelson and Sommers, 1996) also was used to estimate the organic matter content of soils by measurement of the weight loss on sample ignition. This method quantifies the amount of organic matter that is lost when the sample is heated at 400° C in a muffle furnace overnight. However, the weight loss during heating may also be due to dehydroxylation of inorganic constituents such as gibbsite, which dehydroxylates at 300° C and other poorly crystalline or amorphous inorganic materials.

Extractable phosphorus was estimated by the 0.5 N $NaHCO_3$ procedure (Olsen and Sommers, 1982). This procedure is commonly used in many soil analyses laboratories in Kenya. Phosphorus in the extract was determined by the ascorbic acid reduction procedure of Murphy and Riley (1962). Bray-1, Bray-2 (Bray and Kurtz, 1945) and bicarbonate P contents of the surface and subsurface samples were determined by A & L Great Lakes Laboratory, Inc. Fort Wayne, IN according to standard procedures.

Exchangeable cations (K, Mg, Ca and Na) and extractable Al and cation exchange capacity (CEC) were determined by the unbuffered salt solution method (Sumner and Miller, 1996); 0.2M NH_4Cl_2 saturating solution, 0.04 M NH_4Cl_2 equilibrating solution and 0.2 M KNO_3 extracting solution. The exchangeable cations were determined by atomic absorption spectroscopy (AAS) (AA-6800 atomic absorption spectrometer, Shimadzu Corporation, Kyoto, Japan) with a C_2H_2 flame. Extractable Al was determined by graphite furnace AAS after adjusting the pH of the extracts to 2 with dilute HCl to inhibit re-precipitation of Al ions in the solution. The CEC and AEC of the extracts were estimated using a Lachat automatic ion analyzer (Zellweger Analytics, Inc., Lachat Instruments division, Milwaukee, WI). QuikChem Method 10-07-06-2-J was used for ammonium (for CEC estimation) and 10-117-07-1-B for chloride (for AEC estimation) determination by flow injection analysis. Effective cation exchange capacity (ECEC) was calculated as the sum of exchangeable K, Mg, Ca and extractable Al. Aluminum saturation percentage (ASP) was calculated in relation to the effective CEC. All elemental analytical results were reported on oven-dry basis.

3.4.1. Oxalate extractable Fe, Al, and P

Oxalate-extractable P (P_{ox}), aluminum (Al_{ox}) and iron (Fe_{ox}) were determined by variations of an acid ammonium oxalate extraction (Schwertmann, 1964; McKeague and Day, 1966) procedure as described by Loeppert and Inskeep (1996). The extraction was performed with a buffered solution of 0.175 M ammonium oxalate [$(NH_4)_2C_2O_4$] and 0.1 M oxalic acid ($H_2C_2O_4$) adjusted to pH 3. The extraction procedure involved mixing 0.500 g of soil and 30 mL of the ammonium oxalate solution in 50-ml centrifuge tubes. The tubes were immediately placed in a box covered with aluminum foil to eliminate light, and shaken on a horizontal reciprocating shaker for 2 hours (Parfitt, 1989) at 154 excursions per minute. The extract was centrifuged for 15 minutes at 810 ×g and filtered through Whatman® #1 (Whatman Chemical Separation, Inc., Clifton, NJ) filter paper. Iron and aluminum concentrations in the soil extracts were determined by AAS after 10 or 12.5 fold dilution of the extracts. For Al, a N_2O-C_2H_2 flame was used while Fe was detected with a C_2H_2-air flame. The extracts were prepared for phosphorus determination according to the procedure used by Wang et al. (1991) and Guo and Yost (1999). An aliquot (1 mL) of the extract was evaporated to dryness in a heated oven. The residues were then ashed at 500°C in a muffle furnace for 1 hour, and re-dissolved in 1 mL of

1 M HCl. After dilution to 10 mL volume with deionized water, P in the extract was determined colorimetrically by the modified Murphy and Riley (1962) method. The assay total volume was 4 mL; 2 ml of filtrate and 2 mL assay reagent (1 volume 3M H_2SO_4, 1 volume 0.02M ammonium molybdate, 1 volume 10 % (v/v) ascorbic acid, and 2 volumes ultra pure water) and was left for 1 hour at room temperature to develop a blue color and analyzed on a colorimeter at 880 nm wavelength.

The phosphorus saturation index (PSI) was calculated for all the topsoils according to equation 3.1:

$$\mathrm{PSI} = \frac{\mathrm{P}_{ox}}{\mathrm{Fe}_{ox} + \mathrm{Al}_{ox}} \times 100 \qquad \text{Eq.3.1}$$

Where P_{ox} is oxalate extractable P, Fe_{ox} is oxalate extractable Fe and Al_{ox} is oxalate extractable Al (in mmol kg^{-1}).

3.4.2. Dithionate-Citrate-Bicarbonate (DCB) extractable Fe and Al

The modified Dithionate-Citrate-Bicarbonate (DCB) procedure (Mehra and Jackson, 1960; Jackson et al., 1986) described by Loppert and Inskeep (1996) was used to extract aluminum (Al_d) and iron (Fe_d) oxides. The major modification of this procedure involved shaking the samples instead of heating to accelerate the rate of reaction. The samples were ground to pass 140-mesh sieve, and weighed (one gram) into centrifuge tubes. The samples were first treated with citrate-bicarbonate buffer (a mixture of 35 mL of 0.3 M sodium citrate and 5 mL of 1 M sodium bicarbonate solutions) to remove possible Al adsorbed prior to dissolution, and shaken on a horizontal reciprocating shaker at 154 excursions per minute for six hours before adding one g of dithionate to each tube and stirring briefly. The samples were then shaken overnight for 12 hours before adding the second gram of dithionate, stirred and shaken for another six hours before adding 10 mL saturated NaCl solution to promote flocculation. The samples were centrifuged at 1822 ×g for 10 minutes and the extracts were decanted and filtered into 125 mL flasks. The extraction procedure was repeated a second time for all the samples and the extracts combined with the previous. Iron and Al in the extracts were determined by AAS after dilution as described earlier.

The difference between Al_d and Al_{ox} was assumed to be the Al substituted for Fe^{3+} in the crystalline Fe oxides. Indices based on DCB and ammonium oxalate extractable Fe and Al were calculated according to the following equations:

$$\text{Ratio of amorphous to total oxides} = \frac{\mathrm{Fe}_{ox} + \mathrm{Al}_{ox}}{\mathrm{Fe}_{d} + \mathrm{Al}_{d}} \qquad \text{Eq. 3.2}$$

$$\text{Mole \% Al substitution} = \frac{(\mathrm{Al}_{d} - \mathrm{Al}_{ox})}{(\mathrm{Fe}_{d} + \mathrm{Al}_{d}) - (\mathrm{Fe}_{ox} + \mathrm{Al}_{ox})} \times 100 \qquad \text{Eq. 3.3}$$

Where Fe_{ox} is oxalate extractable Fe, Al_{ox} is oxalate extractable Al, Fe_d is DCB extractable Fe, and Al_d is DCB extractable Al (mmol kg^{-1}).

3.5. Data analysis

Statistical analysis was performed using the Statistical Analysis System (SAS, 2002) software package (SAS Institute, Inc., Cary, NC, USA); as described below:

a) Classical descriptive statistics (including means, standard errors, minimum and maximum), and correlation coefficients among different chemical characteristics were determined. Analysis of variance (ANOVA) using general linear models (GLM) was done to compare the properties (variables) of the eleven Kenyan sites hereby represented by pedons. To compare sites, the pedons were considered fixed effects while the sampling depths (4-5) within each pedon were considered random effects (replicates within each pedon). Two different sources of variation for each variable were considered since it was not appropriate to pool the error term for most variables. Where necessary, Box-Cox transformations (Box and Cox, 1964) were applied before analysis to obtain approximately multivariate normally distributed values. Heterogeneity of variance components among some variables necessitated various types of variance stabilizing transformations: - 1) For variables whose values are expressed in percentages; aluminum saturation percentage (ASP), N, C, and loss on ignition (LOI), an arcsin transformation was considered appropriate; 2) a square root transformation was appropriate on exchangeable Ca; and 3) a log transformation was considered appropriate on exchangeable K, AEC. No transformation was necessary on the soil pH, CEC, ECEC, extractable Al and exchangeable Na. The ANOVA results are located in Appendix F.   Mean separation for the pedons were computed by

SAS using the least significant differences at α level of 0.05 ($\text{LSD}0_{.05}$). A similarity matrix was developed based on p-values associated with the least-square means as an attempt to group the pedons.

b) Comparison of sampling depth within each pedon: - due to lack of field replicate samples within each sampling depth; it was not possible to use ANOVA to test the differences within pedons (sampling depths). The laboratory replicates were therefore considered as independent observations for each sampling depth. Student t-tests (pair wise comparisons) were performed on all variables and pedons as shown in the matrix below;

$$\begin{matrix} A & B & C & D & E \\ B & C & D & E & A \\ C & D & E & A & B \\ D & E & A & B & C \\ E & A & B & C & D \end{matrix}$$

It is important to note that the letters used to represent the different sampling depths do not necessarily imply the standard nomenclature used to describe soils in the field. These letters were conveniently used to designate different sampling depths progressively from the surface (A) to the bottom (D/E). It is also worth noting that the sampling depths were non-uniform, for example the thickness of A in one profile does not necessarily correspond to the thickness of A in another profile.

3.6. Results and Discussion

Profile Descriptions

The major soil units (FAO-UNESCO legend) identified from the Exploratory Soil Map of Kenya (Sombroek et al., 1982) were mainly; Ferralsols and Nitisols in the upland plains west of the Rift Valley; Nitisols in the highland west of the Rift Valley; and Andisols in the highlands east of the Rift Valley. Their morphological characteristics were approximately uniform for each geomorphic region, reflecting similar degree of weathering and influence of parent materials. Largely, properties of these soils matched those of the Ultisols, Oxisols, and Andisols soil orders of the US Soil Taxonomy.

Detailed morphological descriptions of the Kenyan pedons are presented in Appendix A. The profiles were all well drained. Solum thickness ranged from 60 cm to >160 cm. Besides the soil's ability to supply nutrients required for plant growth, rooting conditions which permit plants to develop to their full biological potential are desirable. In general, most of the profiles studied were generally deep without any limiting horizon, except pedon KN01 which had an effective depth of 60 cm. In this profile, a limiting layer consisting of laterite may limit the depth that plant roots can explore for nutrients and water.

The hues of the topsoils varied from 2.5YR in Kuinet, Chepkoilel, Bumala, Kangema and Kerugoya; 7.5 YR in Embu (2.5 YR the rest of the profile); 5 R in Siaya and Kericho; and 10 R in Vihiga, Kakamega and Kisii, all of which tended to be the same throughout the profile, but with minor variations in a few profiles in lower depths. Low values and chroma describe profiles that are dark in color. In general, most of the surface horizons (Ap) had both chroma and values ≤ 4 except for Kerugoya (2.5YR 5/2) and Embu (7.5YR 5/6). All the pedons had very friable or friable moist consistency in both surface and sub-surface horizons.

Textures of the Kenyan soils determined by different methods were variable. Based on the hydrometer method, the soils were predominantly sandy, especially in the upper parts of the pedon (Figure 3.1 and Appendix C). But the fractionation results indicated that the top and the lower sampling depths in all the geomorphic units were generally clayey, > 40% clay (Figure 3.2 and Appendix C). This is in agreement with the textural distribution obtained in the field (by feel) indicating that the surface soils were predominantly clayey in most of the pedons except for Kuinet (very fine sandy loam), Chepkoilel (fine sandy loam) and Vihiga (sandy clay loam). The lower clay content obtained by the hydrometer method can be attributed to clay coatings and cementation by iron oxides on sand particles. Kunze and Dixon (1986) observed that iron-containing Oxisols and some Ultisols were particularly very difficult to disperse unless the free iron oxides are removed. The aggregation effect, however, varies from soil to soil due to the variation in the amount and nature of the coatings and cements (Schwertmann and Taylor, 1989).

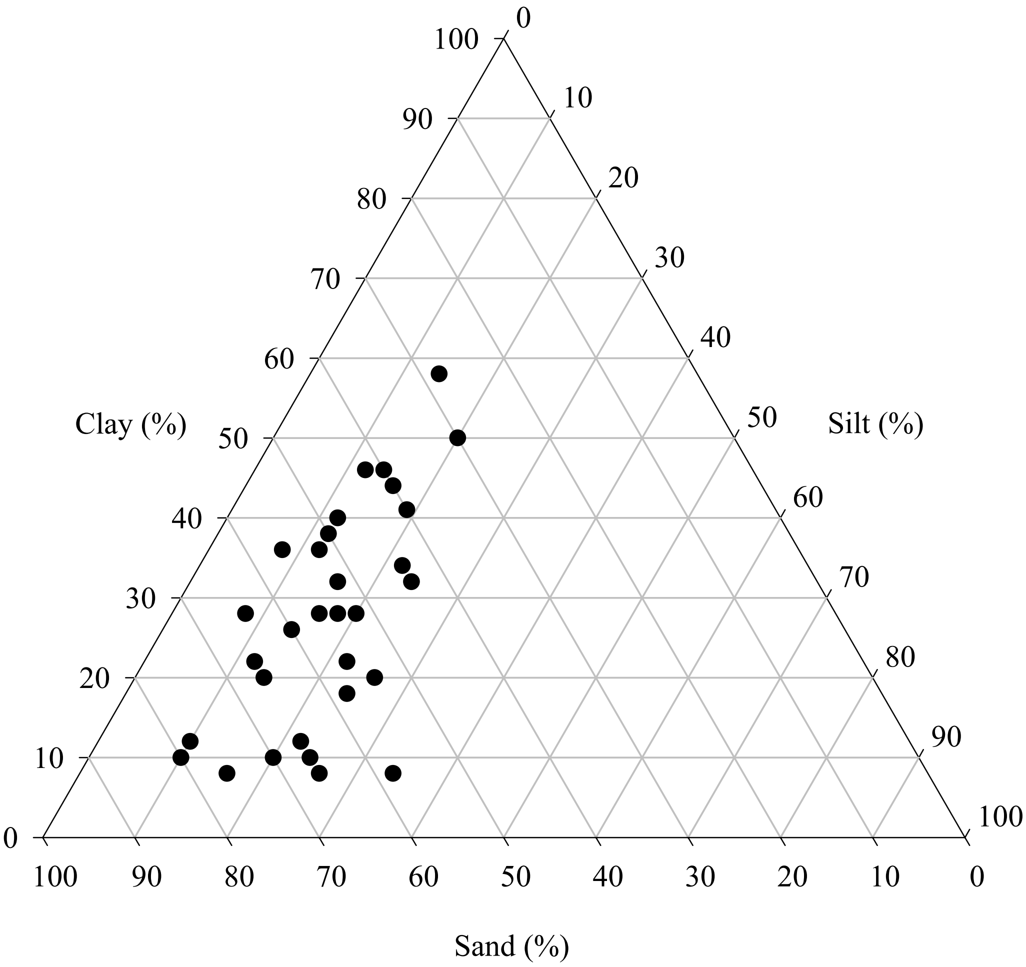

Figure 3.1 Ternary plot showing textural composition of Kenyan soils by the hydrometer method (all horizons for most pedons except KN03 and KN11.

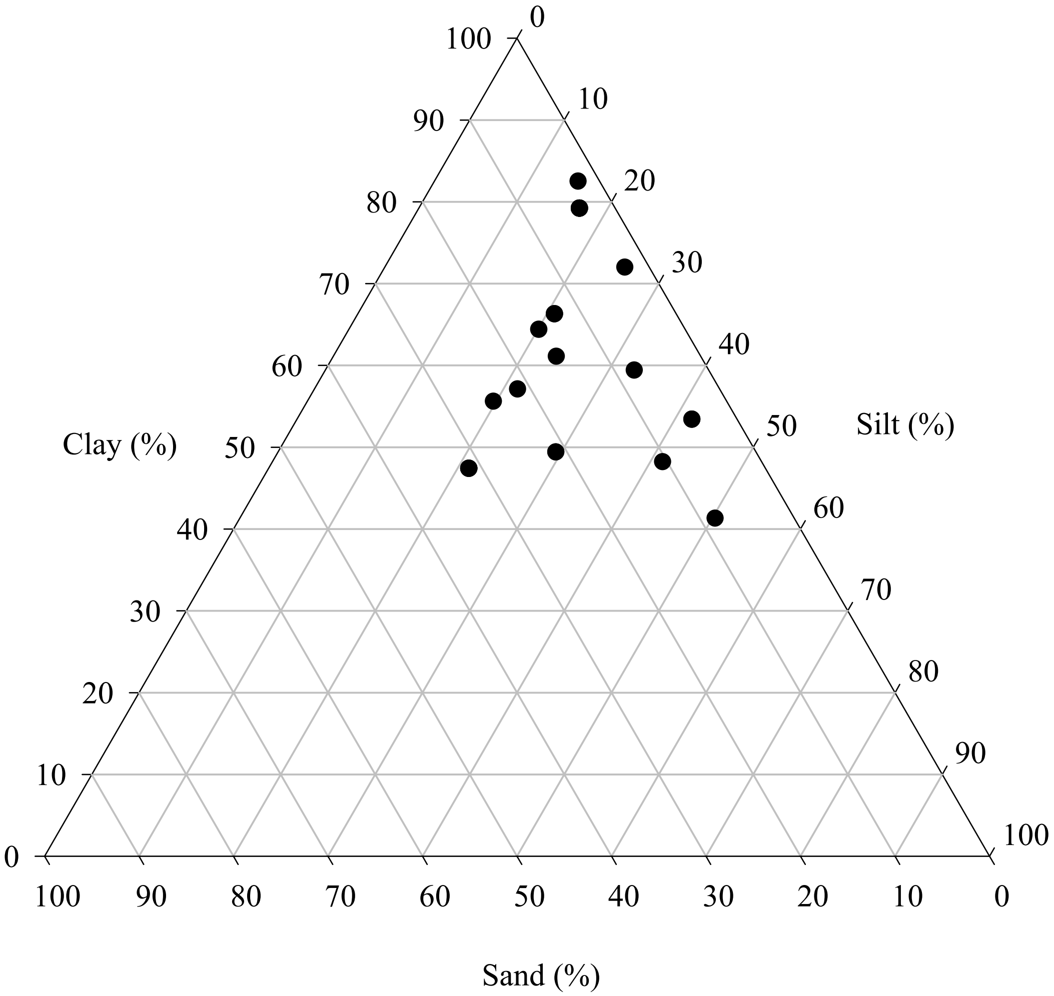

Figure 3.2 Ternary plot showing textural composition of Kenyan soils (surface and lower depths) by the fractionation method.

This effect can therefore be reflected in the charge characteristic and chemical behavior of the bulk soil. On the other hand, the possibility of overestimation of clay content during fractionation cannot be ruled out. In particular, there is a possibility of disintegration of sand particles during the sonication procedure. Sonication, was necessary, however to keep these samples dispersed during fractionation.

The particle size distribution of the Brazilian Cerrado soils analyzed by Marques, (2000) were used for comparison in the subsequent sections is presented in Figure 3.3. The particle size distribution of these samples was determined according to the Brazilian standard procedure described by EMBRAPA (1997). Like the Kenyan soils, most of the Brazilian soils also were clayey, except for a few pedons formed from sandstone parent material. While the Kenyan soils tended to plot along the clay-silt axis, the Brazilian soils tended to plot along the clay-sand axis. Silt content of the Brazilian Cerrado soils was generally very low. However, clay content in the subsurface was generally greater than in the surface horizons of both the Kenyan and Brazilian soils, probably due to: (1) clay eluviation; (2) selective erosion of fine particles; and (3) underestimation of clay in the surface horizon due to aggregation effect of soil organic matter (Marques, 2000). Though there is a wide variation in texture, it seems not to be a limiting factor for the intensive agricultural utilization of both the Kenyan and Brazilian Cerrrado soils. The very sandy Brazilian soils are used for pasture, but not row crops. The bulk density (Table 3.1) of Kenyan soils ranged from 0.80 g cm^{-3} within 50 cm depth in Kangema to 1.60 g cm^{-3} within 100 cm depth in Siaya.

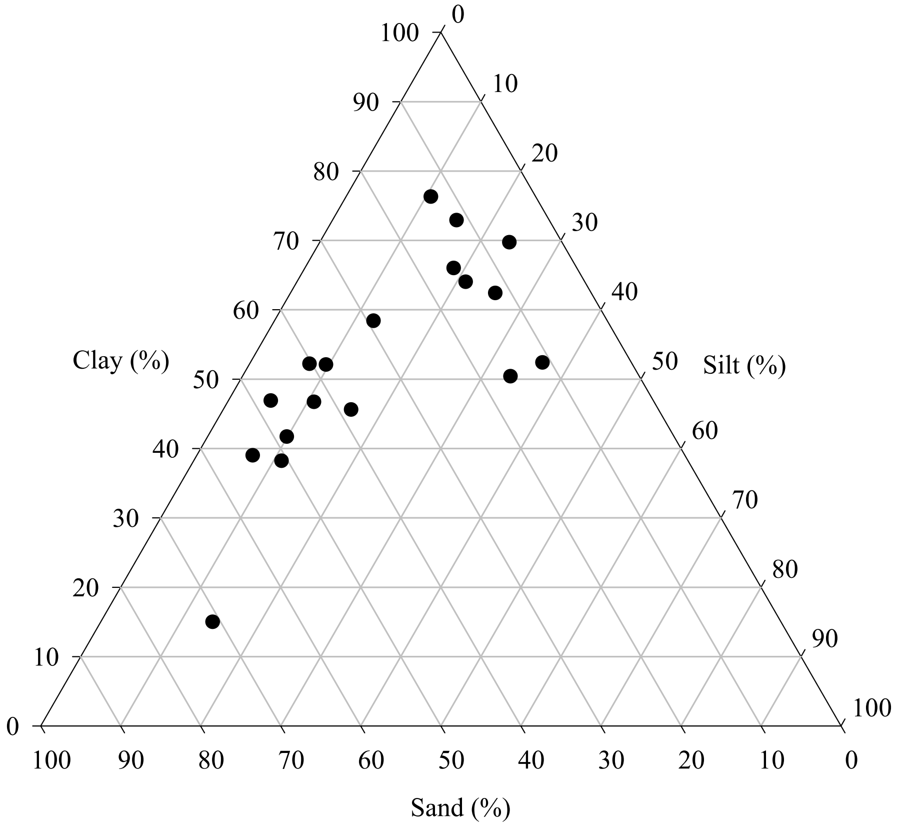

Figure 3.3 Ternary plot showing textural composition of Brazilian soils (0-20 and 20-100 cm depths (data from Marques, 2000).

Table 3.1 Bulk densities of Kenyan soils

Site	Sample ID	Depth[1] (cm)	Bulk density (g cm^{-3})	Site	Sample ID	Depth[1] (cm)	Bulk density (g cm^{-3})
Kuinet	KN01	5	1.23	Kisii	KN07	3	1.19
	KN01	35	1.34		KN07	15	1.31
	KN01	65-75	1.54		KN07	53	1.33
Chepkoilel	KN02	8	1.51	Ainamoi	KN08	10	1.41
	KN02	23	1.42		KN08	50	1.31
	KN02	85	1.42		KN08	98	1.32
Vihiga	KN03	9	1.47	Kangema	KN09	10	0.98
	KN03	31	1.30		KN09	48	0.93
	KN03	100	1.36		KN09	124	1.02
Ikholomani	KN04	12	1.30	Kerugoya	KN10	9	0.88
	KN04	34	1.43		KN10	50	0.80
	KN04	100	1.62		KN10	130	1.14
Bumala	KN05	5	1.25	Kavutiri	KN11	2	1.05
	KN05	30	1.34		KN11	22	1.06
	KN05	50	1.18		KN11	78	1.00
Siaya	KN06	5	1.41				
	KN06	26	1.50				
	KN06	55	1.51				
	KN06	110	1.60				

[1] Lower depth.

Variation in bulk density is attributable to differences in the relative proportion and specific gravity of solid organic and inorganic particles and to the porosity of the soils. Most mineral soils have bulk densities between 1.0 and 2.0.

One of the key requirements for andic soil property is bulk density of 0.90 or less at 33 kPa within 30 cm (Soil Survey Staff, 1999). Although all soils from the Mt. Kenya region (KN09, KN10 and KN11) have lower bulk densities than the other Kenyan soils, only KN10 (within 50 cm) fulfills this key requirement. All three soils however, fulfill other key requirements for andic properties described in USDA Soil Taxonomy (Soil Survey Staff 1999) and the World Reference Base for Soil Resources (FAO/ISRIC/ISSS 1998) including high acid-oxalate extractable aluminum and iron percentages, high phosphate retention, less than 25% organic carbon by weight, and the presence of volcanic glass. The primary control of the andic soil properties is the volcanic parent material, especially ash that is active or has been active during the Holocene period (Buol et al*.,* 2003) and are attributable to the presence of significant amounts of short-range-order compounds such as allophane, imogolite, ferrihydrite or aluminum-humus complexes in soils. Besides parent materials, time is another key factor which influences soil formation and subsequent properties. Slight deviations may therefore be explained by the fact that as soils progress through the development stages, older soils often have mineral suites dominated by crystalline aluminosilicates produced by soil-forming processes or extensive weathering. As mentioned earlier, Mt. Kenya last erupted ~3 million years ago. This period is long enough for the volcanic materials to have been altered by the chemical and physical agents of weathering. These soils have been weathering much longer than Andisols in parts of the Pacific Northwest of the US, in Japan, and Newzwaland.

Chemical properties

Basic chemical properties are presented in Table 3.2 for the Kenyan soils. Chemical properties of Brazilain Cerrado soils are located in Appendix D. Levels of certain elements, where applicable, will be compared to soil test values suggested by Okalebo et al., (1993) for crop production in a range of Kenyan soils, and Landon, (1984) for tropical soils. The results of statistical analyses are located in the following Appendices: analysis of variance (ANOVA) in Appendix E; least-squares mean separation in Appendix F; t-test comparison of horizon means in Appendix G; and correlation coefficients of soil properties are located in Appendix H.

Soil pH

In Table 3.2, pH_{H2O}, pH_{CaCl2}, and pH_{KCl} are presented for all the Kenyan soils. Soil pH_{H2O} of Kenyan soils ranged from 4.30 to 6.20, with a mean for the topsoils of 5.37 ± 0.20. Although soil pH increased with depth, both in water and electrolyte for all the Kenyan pedons, subsoil acidity is also eminent in most of these soils. In all cases, pH_{CaCl2}, and pH_{KCl} were lower than pH_{H2O} indicating that the natural pH of these soils is greater than the point zero salt effect (PZSE). One of the reasons for using calcium chloride is to give a pH believed to be more closely related to the root environment, where the soil solution has soluble salts present rather than pure water.

Table 3.2 Chemical properties of Kenyan soils

Sample ID[1]	Depth[2]	…………..pH………..			ΔpH	N	C	LOI	Bray-1 P	Bray-2 P	Bicarbonate P
	(cm)	Water	KCl	$CaCl_2$		(g kg^{-1})		(%)	………… (mg kg^{-1})……………..		
KN01A	15	4.3	3.5	4.0	0.8	1.7	22.2	7.0	5	12	11
KN01B	25	4.5	3.8	4.1	0.7	1.6	15.6	6.3	3	4	4
KN01C	43	4.7	4.1	4.5	0.6	0.8	13.9	6.4			
KN01D	60	5.1	4.2	4.3	0.9	1.0	13.0	6.2			
KN01E	> 60	5.1	4.1	4.4	1.0	1.3	12.1	6.3			
KN02A	20	5.0	3.9	4.3	1.1	1.6	20.0	7.0	8	15	18
KN02B	40	5.0	4.2	4.5	0.8	0.7	13.5	6.1	1	3	6
KN02C	60	5.1	4.1	4.4	1.0	0.6	12.1	6.2			
KN02D	120	5.3	4.2	4.4	1.1	0.5	10.0	5.4			
KN03A	25	5.3	3.9	4.3	1.4	1.5	19.9	4.7	3	6	10
KN03B	42	5.7	4.4	4.8	1.3	1.5	20.6	4.7	1	3	4
KN03C	82	5.9	4.7	5.1	1.2	1.6	10.5	4.1			
KN03D	120	6.0	4.9	5.2	1.1	0.4	6.4	3.5			
KN04A	24	6.2	4.9	5.2	1.3	1.9	25.4	6.5	3	6	7
KN04B	50	6.2	5.0	5.4	1.2	2.0	20	6.7	1	2	5
KN04C	85	6.6	5.3	5.6	1.3	1.2	6.9	3.8			
KN04D	>140	6.5	5.3	5.7	1.2	0.1	4.8	3.9			

Table 3.2 Continued

Sample ID[1]	Depth[2]	………….pH……… …			ΔpH	N	C	LOI	Bray-1 P	Bray-2 P	Bicarbonate P
	(cm)	Water	KCl	$CaCl_2$		(g kg^{-1})		(%)	………… (mg kg^{-1})……………..		
KN05A	11	5.6	4.2	4.5	1.4	1.9	31.6	7.7	3	5	5
KN05B	40	5.4	4.2	4.3	1.2	1.8	19.5	6.5	2	3	4
KN05C	65	5.5	3.9	4.1	1.6	0.8	16.2	5.8			
KN05D	78	5.6	4.1	4.3	1.5	0.7	12.5	5.4			
KN05E	95	5.5	4.2	4.3	1.3	0.5	11.5	0.0			
KN06A	18	5.1	3.8	4.2	1.3	1.6	17.3	4.8	3	4	4
KN06B	33	5.3	4.0	4.3	1.3	0.9	13.6	4.4	2	3	4
KN06C	68	5.7	4.4	4.7	1.3	0.6	8.0	4.4			
KN06D	106	5.8	4.8	4.8	1.0	0.4	5.6	3.6			
KN06E	120	6.0	4.7	4.9	1.3	0.0	2.4	0.0			
KN07A	11	6.0	4.9	5.2	1.1	2.8	26.9	7.8	5	8	14
KN07B	27	6.0	4.8	5.2	1.2	1.5	19.5	6.6	1	3	5
KN07C	45	5.9	4.7	5.2	1.2	0.9	14.1	6.0			
KN07D	66	6.0	5.2	5.2	0.8	0.7	9.6	5.5			
KN07E	>120	6.0	4.9	5.6	1.1	0.6	6.3	5.1			
KN08A	20	5.5	4.3	4.9	1.2	2.7	39.5	11.5	9	14	20
KN08B	38	5.6	4.4	5.0	1.2	1.1	23.9	8.8	1	4	6
KN08C	60	5.9	4.4	4.8	1.5	1.0	18.8	7.7			
KN08D	90	5.9	4.8	5.1	1.1	0.5	11.5	6.6			
KN08E	>120	6.1	4.9	5.2	1.2	0.2	7.7	6.0			

Table 3.2 Continued

Sample ID[1]	Depth [2]	………….pH………..			ΔpH	N	C	LOI	Bray-1 P	Bray-2 P	Bicarbonate P
	(cm)	Water	KCl	$CaCl_2$		(g kg^{-1})		(%)	………… (mg kg^{-1})………………..		
KN09A	20	4.6	3.7	3.7	0.9	3.8	57.4	16.8	6	8	10
KN09B	40	4.7	3.7	4.0	1.0	2.4	39.6	13.4	1	5	12
KN09C	70	4.9	4.0	4.0	0.9	1.7	30.1	11.8			
KN09D	112	4.9	4.1	4.0	0.8	1.7	22.2	11.0			
KN09E	160	5.0	4.1	4.2	0.9	1.0	16.1	10.6			
KN10A	20	4.6	3.6	3.9	1.0	3.2	31.3	10.9	46	46	144
KN10B	65	5.1	3.8	4.1	1.3	1.8	21.1	9.1	10	10	72
KN10C	110	5.1	4.0	4.2	1.1	1.7	14.7	8.1			
KN10D	130	5.0	4.1	4.1	0.9	1.9	12.4	7.6			
KN11A	12	4.7	3.8	3.9	0.9	3.5	42.5	12.8	16	16	29
KN11B	32	4.8	3.9	3.8	0.9	2.3	32.2	11.3	6	2	6
KN11C	50	4.7	3.8	3.8	0.9	1.7	24.6	10.3			
KN11D	95	4.5	3.8	3.8	0.7	1.4	19.2	9.3			
KN11E	130	4.5	3.8	3.8	0.7	1.0	15.0	8.7			

[1] Alphabet letters do not represent the standard USDA (Soil taxonomy) horizon designation;

[2] Lower depths

The mean charge pH (ΔpH calculated as pH_{H2O}-pH_{KCl}) of the entire set of Kenyan pedons was 1.11, indicating the predominance of net negative charge in all the soils at their natural pH. Also, their mean pH_{CaCl2} was lower than pH_{H2O} by 0.85 pH units. Based on soil pH_{H2O}, the Kenyan soils can be broadly grouped into; (1) moderately acidic soils, represented by those from the western highlands, and (2) strongly acidic soils occurring in the Uasin Gishu plateau and eastern highlands (Mt. Kenya region). For the Brazilian soils, pH_{H2O} was always greater or equal to pH_{KCl}. However, the difference between the pH_{H2O} and pH_{KCl} tended to be smaller in the subsoils than in the surface horizons. Although it is not appropriate to directly compare the soil pH of Kenyan and Brazilian soils because the soil: solution ratios were different, theses values give an idea of general trends.

Although pH *per se* has no direct effect on plant growth, at pH values less than 4.2, the hydrogen ion concentration may stop or even reverse cation uptake by roots (Sanchez, 1976). More importantly, soil pH provides information on the solubility, and thus potential availability or phytotoxicity of some plant nutrients and nonessential elements, and the relative biological activity of plants and microorganisms (Sims, 2000). The solubility of micronutrients and several nonessential trace elements is highly pH dependent. For most elements, the solubility increases as the soil becomes more acidic; exceptions include P, which is most available at pH 5.5-7.5 and Ca and Mo, which are more available at pH >7.0 (Sims, 2000). At pH values < 5.5, solubility and toxicity of Al and Mn increases (Landon, 1984).

Total carbon, nitrogen and loss on ignition (LOI)

Organic carbon content is often taken as a measure of the quantity of organic matter in soils, which in turn is taken as a crude measure of fertility status. Soil total C content of Kenyan soils varied significantly with site, and tended to decline progressively with depth. Soil C content of Kenyan topsoils ranged from 17.3 to 57.4 g kg^{-1}. As a group, the soils from the western plateau and neighboring upland plains had lower organic C content compared to their counterparts from the relatively cooler highlands. As the soils did not contain carbonates, all the soil carbon is assumed to be derived from soil organic matter. The soil organic carbon content of the Kenyan topsoils was highly correlated to the aluminum saturation percentage (R 0.972^{***}), anion exchange capacity ($R = 0.736^{***}$) and loss on ignition ($R = 0.513^{***}$), among others.

Similarly, the total N content of the Kenyan pedons also declined with depth, ranging from 1.5 to 3.8 g kg^{-1} with a median of 1.9 g kg^{-1} in the topsoils. The nitrogen content of most of these soils would be rated as medium or adequate. Due to the dynamic nature of soil N, soil testing for N in humid regions is not an accurate predictor of N availability to plants. Therefore, most fertilizer N recommendations are frequently based on field calibration studies to quantify plant responses to N inputs (Sims, 2000). Prediction of plant-available N is complex because high rainfall coupled with warmer temperatures in the humid tropics can cause rapid / seasonal

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*** $p \leq 0.001$

changes in the amount of inorganic N in the profile. Thus the soil test values are merely estimates.

Nitrogen is one of the major nutrients frequently limiting crop production in Kenya, besides phosphorus; particularly in the densely populated western Kenya region. The reason for the widespread deficiency is that most nitrogen is derived from mineralization of organic matter, and some decline in the latter is an inevitable consequence of cultivation in the tropics (Young, 1976). Also, where vegetation is burnt prior to cultivation to facilitate tillage operations, a common practice in large scale wheat and maize farms in areas like Uasin Gishu and the neighboring Trans Nzoia districts (Ndung'u et al., 2003; Okalebo and Woomer, 2003), substantial nitrogen may be lost. The organic matter content of soils in the highlands was within medium range in the western highlands (Kisii and Kericho) and high levels in the eastern (Mt. Kenya) region. Soil organic resources constitute a major source of nutrient inputs to the soil in smallholder tropical production systems. Mineralization and interaction of soil organic constituents with other soil constituents it is largely responsible for much of soil's physical and chemical properties. High population densities in the Kenyan highlands have forced continuous cropping, grain legume intercrops with cereal crops or rotations in smallholder systems. These practices, together with the prevailing agro-climatic conditions (rainfall and temperature), may explain the regional variations in C and N, and hence the organic matter contents of these soils. Relatively lower C content in the western medium-altitude areas may be a result of the higher rate of soil organic matter decomposition, usually associated with warmer temperatures, and the inverse may be true for the higher altitudes. In addition, the influence of the type of vegetative cover and management practices on soil organic matter content could explain the relatively higher C content of some sites. Specifically, two pedons in the cooler western Kenyan highlands were previously under unique vegetation cover. Pedon KN07 (Kisii) was previously under fallow (woodlot with grass under-story) and pedon KN08 (Kericho) was under pasture grass, probably resulting in accumulation of surface litter and below ground root debris in these sites.

With the increased interest in C sequestration, there is need for rapid and inexpensive methods of quantification or prediction of soil C. Schulte and Hopkins (1996) demonstrated that LOI is an accurate, and cost and labor-efficient technique for determination of soil organic carbon (SOC) and soil organic matter (SOM). This approach may particularly be useful for predicting SOC content of soils differing in mineralogy and use.

Loss on ignition (LOI) of Kenyan soils was positively correlated with soil total carbon content ($R^2 = 0.935$; Figure 3.4) of the topsoils. When data for all depths were included, R^2 was 0.769 (Figure 3.5). This relationship suggests that the LOI of the topsoils may largely be due to loss of soil organic constituents. But at greater depths, some proportion of LOI may be due to the dehydroxylation of inorganic constituents.

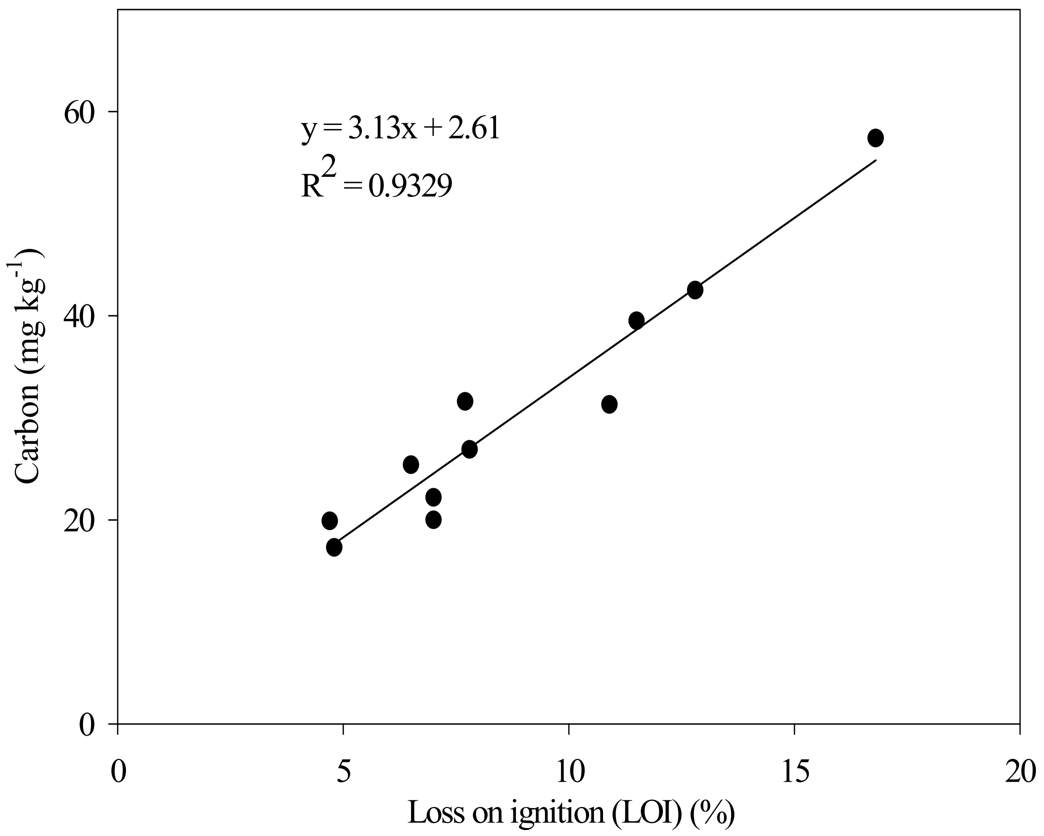


Figure 3.4 Relationship between Loss on ignition at 400° C and soil organic carbon content of the Kenyan topsoils.

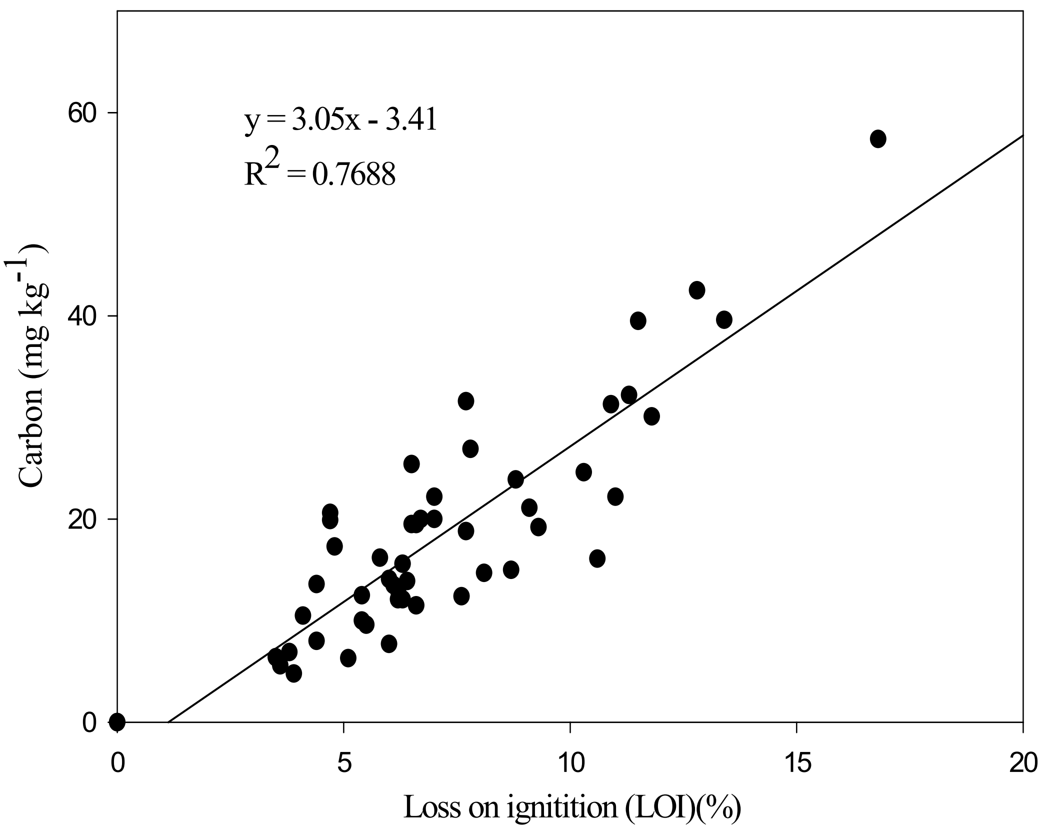


Figure 3.5 Relationship between loss on ignition at 400° C and soil organic carbon content of the entire sampling depth of Kenyan pedons.

For example, the deydroxylation temperature for gibbsite is around 300° C (de Souza Santos et al., 2005), and allophane and imogolite are around 400° C (van der Gaast et al., 1985). The percent loss on ignition therefore was a satisfactory approximation of the organic matter content in the soils, though over-estimation was somewhat likely in lower horizons. The average organic carbon content (27.8 ± 6.0 mg kg^{-1}) and loss on ignition at 400° C (10.1 ± 4.08 %) of Brazilian topsoils were within the 95% confidence interval of the Kenyan soils. On average, topsoils of the Kenyan soils had significantly greater total nitrogen (2.38 ± 0.57 mg kg^{-1}) than the Brazilian soils (1.5 ± 0.50 mg kg^{-1}). The Brazilian soils were sampled under native vegetation.

Extractable phosphorus

Different extractants yield different amounts of extractable phosphorus. Estimates of critical P concentrations in the soils, above which there is no crop response to P applications, also vary with the extractant used (Kamprath and Watson, 1980). The critical P levels are: $\geq$ 10 mg kg^{-1} for Olsen (Olsen et al., 1954), $\geq$ 30 mg kg^{-1} for Bray-1 (Bray and Kurtz, 1945) and $\geq$ 25 mg kg^{-1} for Mehlich-I (Mehlich, 1953) methods. Although the values of P obtained from different methods may be correlated with crop yields, their advantages are to a large extent site (mineralogy) specific (Okalebo et al., 1992).

Despite reasonably high total phosphorus content (Rana, 2007); all but one of the Kenyan soils had very low levels of extractable P determined by different extractants as shown in Table 3.2. Kerugoya (KN10) had exceptionally very high extractable phosphorus estimated by different extractants. However, at the time of site selection and soil sampling, this site (KN10) had the poorest crop growth, with obvious P deficiency symptoms. A reasonable proportion of the total soil phosphorus in this soil is likely to be bound as Fe- and Al-phosphates, or sorbed on the soil matrix, or present as other forms not readily available for immediate plant uptake, but extractable by standard soil tests. In almost of all the Kenyan soils, the Bray-1 & 2, and bicarbonate extractable P levels were negligible compared to the amount of P fixed by the amorphous Fe and Al oxides, or total soil P. This can be illustrated by the high quantities of oxalate extractable phosphorus (P_{ox}) (Table 3.3). Oxalate extractable P includes Fe-, Al-, and Ca- phosphates (Wang, et al., 1991). Because these soils are acidic, Ca-phosphates are therefore unlikely to constitute the P_{ox}. Oxalate extractable P in Kenyan soils varied among pedons and ranged from 187.0 to 4249.3 mg kg^{-1}. Values at the lower end of the range were associated with soils from the western region while values at the higher end were associated with the soils from the eastern region.

Past studies (Okalebo et al., 1992; FURP, 1994; TSBF, 1994) also showed widespread phosphorus deficiency in Kenyan soils. In western Kenya, Obura (2001); Obura et al., (2001); and Waigwa et al., (2000) P deficiencies in soils close to or similar to those used in this study were confirmed. These results indicate that low available phosphorus seems to be a key factor limiting the intensive use of these soils for sustainable crop production. In fact, some of these soils are estimated to have high P sorption capacity (as discussed in chapter 4).

Mehlich-1 and anion exchange resin extractable P contents of all Brazilian soils were low (Appendix D1), except T4 and T5 which had considerably greater in

Mehlich-1 P than the other soils. The parent materials (basalt) of these soils were inherently rich in P. Unlike the rest of the sites which had been under "cerrado vegetation", T4 and T5 were under "forest vegetation". Again, due to differencex in methods used to estimate extractable P, the P data (except oxalate extractable P) can only be used to indicate general trends among the Brazilian and Kenyan soils. However, the oxalate extractable P in the Brazilian soils (Table 3.4) was generally lower than the Kenyan soils, ranging from 83.0 to 885.9 mg kg^{-1}.

The extremely large P_{ox} value of 4249.3 mg kg^{-1} in the Kerugoya (KN10) soil suggests that the observed poor crop growth was probably due to P unavailability, as almost all P in this soil was fixed by Fe and Al oxides. A study of sorption characteristic of productive and adjacent unproductive Niger soils by Wendt et al. (1993) suggests that P deficiency may be the result of high P sorption by oxalate extractable Fe and exchangeable Al. In the same study, they observed that at any rate of fertilization, unproductive soils adsorbed greater levels of applied P than the adjacent productive soils. Yuan and Lavkulich (1994) found that oxalate extractable P represented between 17 and 66% of the total P sorption capacity of 43 Spodosols. The contribution of noncrystalline Fe and Al may even be greater in highly weathered soils such as Oxisols and Ultisols.

Table 3.3 Oxalate and dithionite extractable Fe, Al and P extracted from selected Kenyan acid soils

Sample ID	Pox	Alox	Feox	Ald	Fed	$\frac{Al_{ox}}{Al_d}$	$\frac{Fe_{ox}}{Fe_d}$	mole % Al substitution
	mg kg^{-1}	……………………..……g kg^{-1}…………………………						
KN01A	313.0	4.81	3.36	10.38	93.85	0.464	0.036	11.1
KN01B		5.11	2.11	11.50	93.22	0.444	0.023	13.2
KN01C		5.51	1.90	13.08	87.58	0.421	0.022	15.6
KN01D		6.07	1.75	13.87	85.55	0.437	0.021	16.3
KN01E		6.64	2.80	13.50	91.54	0.492	0.031	14.1
KN02A	330.6	4.70	3.13	12.71	64.87	0.370	0.050	20.8
KN02B		6.58	2.39	15.08	66.50	0.436	0.036	21.5
KN02C		5.61	1.75	16.24	77.62	0.345	0.023	22.4
KN02D		7.47	1.59	17.63	81.47	0.424	0.020	21.2
KN03A	394.1	5.83	3.51	15.60	67.48	0.374	0.052	24.2
KN03B		8.17	1.96	12.22	70.95	0.669	0.027	11.4
KN03C		9.17	2.93	10.68	77.12	0.859	0.038	4.0
KN03D		9.04	2.80	13.80	81.65	0.655	0.034	11.4
KN04A	310.4	9.67	2.49	13.57	83.09	0.712	0.030	8.9
KN04B		9.32	2.29	14.96	75.56	0.623	0.030	13.8
KN04C		7.36	2.01	21.69	89.58	0.339	0.023	25.1
KN04D		7.64	1.71	22.41	88.39	0.341	0.019	25.9

Table 3.3 continued

Sample ID	Pox	Alox	Feox	Ald	Fed	$\frac{Al_{ox}}{Al_d}$	$\frac{Fe_{ox}}{Fe_d}$	mole % Al substitution
	mg kg^{-1}	……………………..……g kg^{-1}…………………………						
KN05A	325.4	7.30	2.10	22.0	105.4	0.331	0.020	23.1
KN05B		7.96	2.05	23.0	101.0	0.347	0.020	23.6
KN05C		13.14	1.96	20.7	106.0	0.636	0.019	12.7
KN05D		13.68	1.76	20.4	113.6	0.672	0.016	11.2
KN05D		13.13	1.54	20.3	119.9	0.648	0.013	
KN06A	187.0	4.41	1.73	13.8	56.9	0.319	0.030	26.2
KN06B		4.13	1.55	25.5	71.2	0.162	0.022	38.8
KN06C		4.17	2.08	23.6	64.6	0.176	0.033	39.5
KN06D		4.57	1.90	21.6	76.2	0.211	0.025	31.9
KN06E		4.98	0.95	18.5	83.8	0.269	0.011	25.6
KN07A	479.6	5.12	4.85	6.3	68.6	0.810	0.070	3.6
KN07B		6.28	5.45	6.9	73.0	0.906	0.074	1.9
KN07C		5.20	3.74	5.8	86.2	0.899	0.044	1.6
KN07D		4.87	3.00	6.9	75.2	0.701	0.039	5.8
KN07E		4.58	3.19	7.6	96.0	0.603	0.033	6.3
KN08A	403.8	7.49	3.88	14.5	89.7	0.518	0.042	14.4
KN08B		7.46	3.15	14.9	94.2	0.501	0.033	14.6
KN08C		6.93	2.74	16.4	104.0	0.423	0.026	16.2
KN08D		6.35	2.77	17.2	103.6	0.369	0.027	18.2
KN08E		4.85	2.30	20.1	102.4	0.241	0.022	23.9

Table 3.3 Continued

Sample ID	Pox	Alox	Feox	Ald	Fed	$\frac{Al_{ox}}{Al_d}$	$\frac{Fe_{ox}}{Fe_d}$	mole % Al substitution
	mg kg^{-1}	……………………..……g kg^{-1}…………………………						
KN09A	500.7	7.23	5.05	18.2	110.1	0.397	0.044	17.8
KN09B		10.57	5.51	16.4	117.0	0.646	0.047	9.3
KN09C		9.45	5.40	16.1	125.0	0.585	0.043	10.4
KN09D		11.30	8.45	14.0	123.4	0.809	0.068	4.6
KN09E		10.45	6.38	16.8	117.9	0.623	0.054	10.9
KN10A	4249.3	14.43	8.78	15.4	103.6	0.938	0.086	1.8
KN10B		13.33	9.99	15.6	92.1	0.857	0.108	5.0
KN10C		12.29	12.38	13.7	89.8	0.898	0.136	4.6
KN10D		8.53	11.25	16.5	85.0	0.516	0.133	18.3
KN11A	511.3	7.35	10.22	15.5	80.8	0.473	0.127	19.8
KN11B		8.93	11.41	12.2	92.0	0.731	0.124	7.7
KN11C		9.11	8.27	9.9	90.3	0.919	0.092	2.8
KN11D		5.57	9.62	8.5	84.8	0.652	0.113	7.5
KN11E		3.71	11.18	14.6	89.1	0.253	0.125	22.5

Table 3.4 Oxalate and dithionite extractable Fe, Al and P extracted from selected Brazilian acid soils.

Sample ID	P_{ox}	Al_{ox}	Fe_{ox}	Al_d	Fe_d	$\frac{Al_{ox}}{Al_d}$	$\frac{Fe_{ox}}{Fe_d}$	mole % Al substitution
	mg kg^{-1}	……………………g kg^{-1}…………………………						
G1A1	105.0	5.07	1.55	19.1	116.0	0.266	0.013	20.2
G1A2		6.26	0.39	13.6	86.1	0.463	0.005	15.6
G2A1	118.3	7.00	1.22	19.3	82.7	0.364	0.015	24.4
G2A2		7.91	3.07	15.1	65.1	0.525	0.047	19.2
N1A1	127.0	5.56	1.67	10.7	78.1	0.523	0.022	12.2
N1A2		5.24	0.31	8.2	77.1	0.638	0.004	7.8
N2A1	87.4	4.95	1.55	10.9	52.2	0.455	0.030	19.6
N2A2		5.56	0.41	12.0	56.0	0.463	0.007	19.4
N5A1	83.0	3.34	0.45	8.5	17.3	0.393	0.026	38.7
N5A2		3.44	0.18	9.3	15.0	0.369	0.013	45.7
T1A1	147.3	5.66	1.56	15.5	63.7	0.366	0.025	24.7
T1A2		3.78	0.51	13.9	75.4	0.273	0.007	22.8
T2A1	107.7	5.71	1.60	17.0	61.6	0.335	0.026	27.8
T2A2		6.16	0.37	19.0	59.3	0.323	0.006	30.6
T4A1	553.6	3.69	3.38	19.2	184.4	0.192	0.018	15.1
T4A2		5.47	1.39	23.8	198.9	0.230	0.007	16.3
T5A1	855.9	8.40	1.40	19.6	187.3	0.429	0.008	11.5
T5A2		3.75	1.42	22.9	294.4	0.164	0.005	11.9

It is most likely that part of the oxalate extractable P in KN10 was extractable by Bray 1, Bray 2, or bicarbonate extractants, yielding exceptionally high observed values.This is suggested by the correlation between Al_{ox} and Bray-1 P ($R = 0.814$: $p < 0.001$), Bray-2 P ($R=0.767$: $p < 0.001$) and bicarbonate extractable P ($R = 0.826$: $p < 0.001$) among the Kenyan topsoils. Wang et al. (1991) found that noncrystalline P components were more easily extractable by Olsen (0.5 M $NaHCO_3$ pH 8.0) and Mehlich-1 than was P that was associated with crystallized minerals. Although these findings imply that the P associated with noncrystalline oxides becomes available, reversibility or plant availability of P_{ox} may not be predictable in these highly weathered soils.

Oxalate and dithionite extractable Fe and Al

Concentrations of various forms of Fe and Al in the Kenyan soils are also presented in Table 3.3. The amount of Fe and Al extracted by DCB was greater than the oxalate extractable portions. Oxalate extractable Al increased with depth in most Kenyan pedons. Exceptions were pedons KN04 and KN10, in which Al_{ox} decreased with depth and in pedons KN07 and KN11 where Al_{ox} was greatest in the middle part of the profile. Oxalate extractable Fe was relatively greater in the upper horizons in pedons KN01 through KN07, but tended to increase with depth in pedons KN09 through KN11. Oxalate extractable Al was greater than Fe_{ox} in all soils. In all the cases, Al_{ox}/Al_d ratios were much greater than the corresponding values for Fe (Table 3.3). This suggests that Al is largely present in these soils either in poorly crystalline inorganic forms or possibly as Al-organic matter complexes. Although extraction of soils with oxalate and DCB is specific for Fe, the extractants may not necessarily be specific for Al compounds (McKeague et al., 1971). The oxalate extractable Al content of Kenyan soils was positively correlated to P_{ox} and aluminum saturation percentage (ASP), and negatively correlated to ECEC. However, there was no correlation between Al_{ox} and soil organic matter components. Oxalate extractable Fe was positively correlated to pH, LOI, ASP, and negatively correlated to ECEC.

Iron on the other hand, dominated the DCD extractable fractions in both Kenyan and Brazilian soils. Among Kenyan soils, Fe_d increased with soil depth except in pedons KN01, KN09, KN10 and KN11 where it remained relatively constant. The Fe_d content of Brazilian soils was relatively constant with soil depth except in pedons G1and G2 where it was lower in the subsurface and in T5 where it was greater in the subsurface horizon. On average, Fe_d was about three times greater than the Al_d in both Kenyan and Brazilian soils.

The ratio of Fe_{ox}, a selective extractant for removing poorly or amorphous Fe and Al (Schwertmann, 1964) to Fe_d, a selective extractant for removing both crystalline and non crystalline oxides of Fe and Al substituted in crystalline Fe oxides in soils (Mehra and Jackson, 1960; Holmgren, 1967; Torrent, 1987) has been used to assess the degree of crystallinity of Fe oxides in a soil. Low Fe_{ox}/Fe_d ratios indicate a high degree of crystallinity of Fe oxides.

The proportion of DCB extractable iron (Fe_d) that was soluble in ammonium oxalate decreased with depth and ranged from 0.011 to 0.136 and had an overall mean value of 0.048 ± 0.001 for all Kenyan pedons. Values at the lower end of the range were associated with pedons in the western region while values at the upper end were associated with pedons in the Mt. Kenya (eastern) region soils (KN09-KN11). The mean Fe_{ox}/ Fe_d ratio for Mt. Kenya region pedons is comparable to the mean (0.110) reported for other highly weathered soils in Nigeria by Juo et al. (1974). The Fe_{ox}/Fe_d ratio was lower in the Brazilian soils (Table 3.4), ranging from 0.008 to 0.030 with an overall mean of 0.020 ± 0.006. However, Fe_{ox}/Fe_d ratios observed in this study were generally lower than those frequently reported for temperate soils, where Fe_{ox} constitutes about 30-60% of Fe_d (McKeague and Day, 1966; McKeague et al., 1971; Parfitt and Childs, 1988; Yuan and Lavkuvich, 1994; Wang et al, 1987).

Calculated mole % Al substitution among Kenyan soils (Table 3.3) varied significantly among sites and depths. The values ranged from 1.5 to 39.5 with a mean value of 15.16 ± 2.57. Pedon KN07 had the lowest and KN06 had the highest value. The Brazilian soils had significantly greater mole % Al substitution, ranging from 7.78 to 45 with a mean of 21.31 ± 4.84. Trends in these soils suggest that highly weathered soils tend to have greater Al substitution than relatively younger or less weathered soils. Because free ion oxides in soils are rarely pure (Schwertmann and Herbillion, 1992), it is believed that Al_d is reactive amorphous Al occluded in crystalline Fe oxides (Holmgren, 1967) that is isomorphously substituted for Fe^{3+} in iron oxides (Torrent, 1987), although the identity of Al extracted by oxalate or dithionate is not very clear. This has implications for surface reactions and anion retention properties of soils.

Exchange properties

Ion exchange properties of Kenyan soils are presented in Table 3.5. Cation exchange capacity (CEC) was generally low in all soils with a few exceptions. The CEC of Kenyan soils varied significantly with site and depth. Their CECs ranged from 6.4 to 22 $\mathrm{cmol_c\,kg^{-1}}$ with a median of 9.6 $\mathrm{cmol_c\,kg^{-1}}$ and overall mean of 10.65 ± 0.65 $\mathrm{cmol_c\,kg^{-1}}$. Relatively greater CEC values were found in the western highlands; 22.0 $\mathrm{cmol_c\,kg^{-1}}$-soil (KN07) and 18.1 $\mathrm{cmol_c\,kg^{-1}}$-soil (KN08), while lower values were found in the eastern highlands soils (Mt. Kenyan region); 8.5 $\mathrm{cmol_c\,kg^{-1}}$ -soil in the KN11A. Landon (1984), provides the following CEC rating scheme for topsoils: values less than 5 $\mathrm{cmol_c\,kg}$ are considered to be very low, 5-15 $\mathrm{cmol_c\,kg^{-1}}$ low, 15-25 $\mathrm{cmol_c\,kg^{-1}}$ medium, 25-40 $\mathrm{cmol_c\,kg^{-1}}$ high and > 40 $\mathrm{cmol_c\,kg^{-1}}$ very high. Based on this rating scheme, it is clear that the majority of the Kenyan soils have low CEC.

Similarly, ECEC varied with site and depth and was significantly lower than the CEC; ranging from 4.4 $\mathrm{cmol_ckg^{-1}}$ in the top soils in Siaya (KN06A) to 11.0 $\mathrm{cmol_c\,kg^{-1}}$ in the KN08A; and from 4.7 $\mathrm{cmol_c\,kg^{-1}}$-soil in the KN10B to10.4 $\mathrm{cmol_ckg^{-1}}$ in the KN07B. For the Kenyan topsoils, the average ECEC was 6.5 $\mathrm{cmol_ckg^{-1}}$-clay (Appendix C: Table C-2). Buol et al. (1975) and Sanchez (1976) suggested a value of 4 $\mathrm{cmol_ckg^{-1}}$ soil measured by neutral unbuffered salt as the upper limit for a low level of ECEC in fertility classification. The ECEC of most Brazilian samples were lower than the Kenyan soils. The mean CEC at pH 7 of these soils was nearly three times as great as their ECEC, suggesting that most of the CEC was pH dependent (Marques, 2000).

Table 3.3 Exchangeable bases and exchange capacity of Kenyan soils

Site	Sample ID	Depth (cm)	Exchangeable bases ($cmol_c kg^{-1}$)					%Al saturation	ECEC	CEC	AEC
			K	Mg	Ca	Na	Al		($cmol_c kg^{-1}$)		
Kuinet	KN01A	15	0.5	0.6	2.4	0.7	2.3	39.6	5.8	9.5	0.6
	KN01B	25	0.6	0.8	3.0	0.6	2.1	33.0	6.5	9.6	1.5
	KN01C	43	0.2	1.4	2.6	0.6	1.8	30.0	5.9	8.6	3.3
	KN01D	60	0.6	1.3	1.4	0.5	1.9	36.0	5.2	8.4	2.7
	KN01E	>60	0.7	1.2	1.9	0.4	1.1	23.7	5.0	8.4	2.0
Chepkoilel	KN02A	20	1.1	1.4	3.7	0.5	0.8	11.6	7.0	10.5	3.3
	KN02B	40	1.0	1.2	3.6	0.4	1.5	20.4	7.2	12.0	2.2
	KN02C	60	0.4	1.6	3.4	0.3	1.7	24.1	7.2	10.5	1.8
	KN02D	120	0.6	1.6	3.4	0.4	0.5	7.8	6.0	9.3	1.7
Vihiga	KN03A	25	0.2	0.8	3.3	0.5	1.6	27.4	5.8	8.8	1.9
	KN03B	42	0.2	1.0	4.5	0.3	1.4	19.3	7.1	10.2	2.1
	KN03C	82	0.2	1.3	5.1	0.3	0.3	4.1	6.8	8.8	1.7
	KN03D	120	0.3	0.9	5.1	0.2	0.2	3.4	6.4	10.2	1.3
Ikholomani	KN04A	24	0.5	1.6	4.5	0.3	1.1	14.6	7.6	13.7	1.1
	KN04B	50	0.3	0.9	6.9	0.4	1.2	12.7	9.2	12.0	1.2
	KN04C	85	0.2	1.1	6.6	0.4	1.0	11.4	8.9	10.7	1.3
	KN04D	>140	0.2	1.3	5.6	0.4	1.4	17.1	8.5	10.9	1.3

Table 3.5 Continued

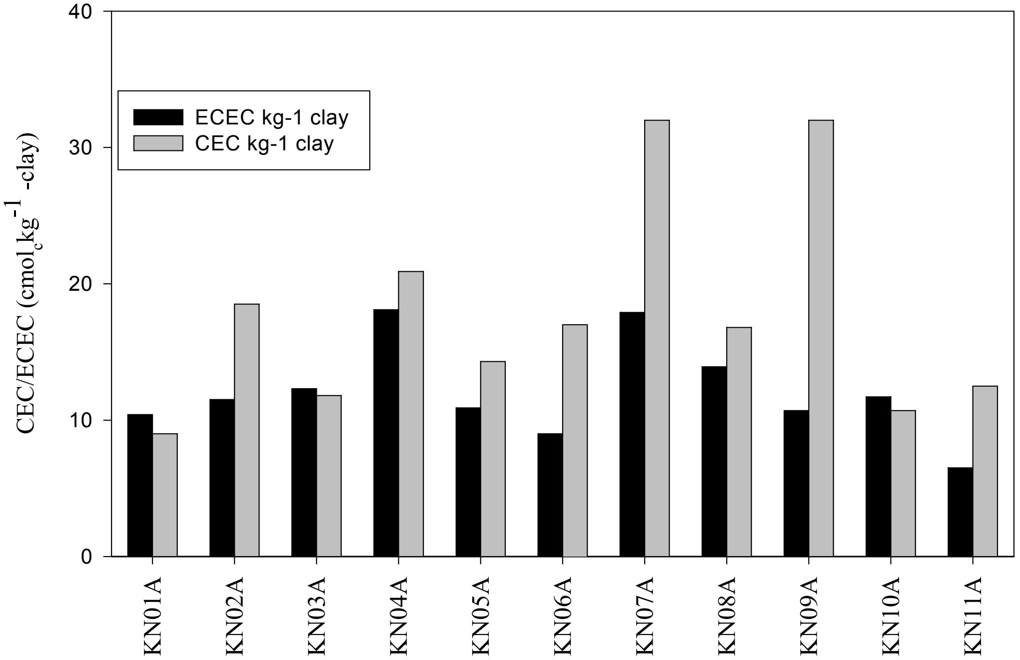
Site	Sample ID	Depth (cm)	Exchangeable bases ($cmol_c kg^{-1}$)					%Al saturation	ECEC	CEC	AEC
			K	Mg	Ca	Na	Al		($cmol_c kg^{-1}$)		
Bumala	KN05A	11	0.4	1.7	3.2	0.3	2.0	26.5	7.2	11.6	1.5
	KN05B	40	0.2	0.9	2.5	0.3	1.9	34.6	5.5	8.5	0.9
	KN05C	65	0.2	0.4	2.7	0.3	1.1	25.2	4.4	8.9	1.1
	KN05D	78	0.2	0.6	2.3	0.2	1.2	27.9	4.4	6.9	0.9
	KN05E	95	0.3	0.3	2.8	0.4	0.2	5.4	3.6	6.4	0.8
Siaya	KN06A	18	0.3	1.1	2.6	0.4	0.4	8.3	4.4	9.3	0.8
	KN06B	33	0.3	1.0	3.6	0.2	0.3	5.1	5.1	9.3	3.7
	KN06C	68	0.2	0.8	3.1	0.4	0.2	5.4	4.3	9.6	1.0
	KN06D	106	0.2	0.6	3.2	0.4	1.6	28.8	5.5	10.0	1.6
	KN06E	120	0.2	1.2	3.6	0.6	1.3	20.8	6.2	9.1	2.6
Kisii	KN07A	11	1.6	3.1	3.6	0.5	0.4	4.3	8.6	22.0	1.1
	KN07B	27	1.0	4.2	4.9	0.4	0.4	3.6	10.4	21.2	1.0
	KN07C	45	1.0	2.9	4.9	0.4	0.1	1.1	8.9	18.1	0.5
	KN07D	66	1.1	3.6	6.7	0.3	3.2	21.7	14.6	16.2	0.9
	KN07E	>120	1.7	3.6	6.0	0.4	1.1	8.4	12.4	15.2	1.7
Kericho	KN08A	20	0.7	1.9	6.3	0.3	2.1	19.0	11.0	18.1	2.2
	KN08B	38	0.3	2.1	5.6	0.4	0.3	3.3	8.8	13.9	0.9
	KN08C	60	0.5	1.7	4.4	0.4	2.0	21.4	9.4	13.4	1.3
	KN08D	90	0.3	2.3	4.3	0.3	1.5	5.2	8.1	11.1	2.1
	KN08E	>120	0.5	2.2	3.1	0.3	1.6	1.1	6.3	10.5	1.6

Table 3.5 Continued

Site	Sample ID	Depth (cm)	Exchangeable bases ($cmol_ckg^{-1}$)					%Al saturation	ECEC	CEC	AEC
			K	Mg	Ca	Na	Al		($cmol_ckg^{-1}$)		
Kangema	KN09A	20	0.3	0.6	1.3	0.3	4.5	58.5	7.7	9.9	1.9
	KN09B	40	0.5	0.3	1.0	0.3	5.5	75.7	7.3	9.6	1.6
	KN09C	70	0.3	0.2	0.9	0.2	5.2	78.9	6.6	8.0	1.8
	KN09D	112	0.2	0.7	1.3	0.3	2.2	53.0	3.9	7.6	1.9
	KN09E	160	0.2	0.5	2.0	0.4	1.4	40.2	3.7	7.0	1.1
Kerugoya	KN10A	20	0.4	1.0	1.6	0.3	2.9	47.6	6.2	10.7	1.1
	KN10B	65	0.3	0.4	1.2	0.3	2.8	60.5	4.7	9.6	1.0
	KN10C	110	0.3	0.3	0.9	0.5	2.3	61.0	3.7	10.4	1.6
	KN10D	130	0.1	0.1	1.1	0.4	1.9	61.7	3.3	10.8	0.9
Kavutiri	KN11A	12	0.4	0.2	1.4	0.3	3.3	60.7	5.3	8.5	2.0
	KN11B	32	0.3	0.1	2.6	0.4	3.7	55.3	6.7	8.0	1.5
	KN11C	50	0.3	0.1	2.0	0.3	3.5	59.4	5.9	7.4	2.2
	KN11D	95	0.2	0.4	1.7	0.3	2.6	52.7	4.8	7.5	1.8
	KN11E	130	0.3	0.3	1.5	0.2	2.2	50.3	4.4	6.6	2.0

A comparison of CEC (pH 7) and ECEC (unbuffered) per kilogram of clay in the Kenyan and Brazilian Cerrado topsoils is presented in Figure 3.6. Most of the Kenyan soils have medium ECECs, and are greater than the mean ECEC for the Brazilian soils. The CEC measurements are commonly made as part of the overall assessment of the potential fertility of a soil. Moreover, the CEC associated with the clay content can sometimes be used as a rough guide to the types of clay mineral constituents (Landon, 1984). In general, high CEC values are always associated with high fertility, high nutrient retention capacity, relatively less weathered and are likely to be dominated by high CEC clay minerals (2:1 phyllosilicates). Low CEC, on the other hand, is generally associated with low fertility, poor nutrient retention capacity, and advanced stages of weathering. In addition, low CEC is usually associated with the disappearance or absence of primary weatherable minerals and accumulation of secondary clay minerals of low activity, resulting from weathering process (Donahue et al., 1983). Examples of such low-charge clay minerals include; kaolinite, gibbsite and iron oxides. These data suggest that these soils are in their ultimate stage of weathering which is characterized by small reserves of plant nutrients. It is therefore critical that any mobile nutrients added to these soils should be retained by the soil matrix for sufficiently long periods to give the plants an adequate opportunity to utilize them efficiently.

The relatively higher levels of ECEC in some of these soils are probably due to; (1) larger proportions of the exchange sites occupied by exchangeable Al as a result of weathering and leaching that has occurred (2) presence of remnants of 2:1 clay minerals, and (3) presence of hydroxy-interlayered minerals.


a) Kenya

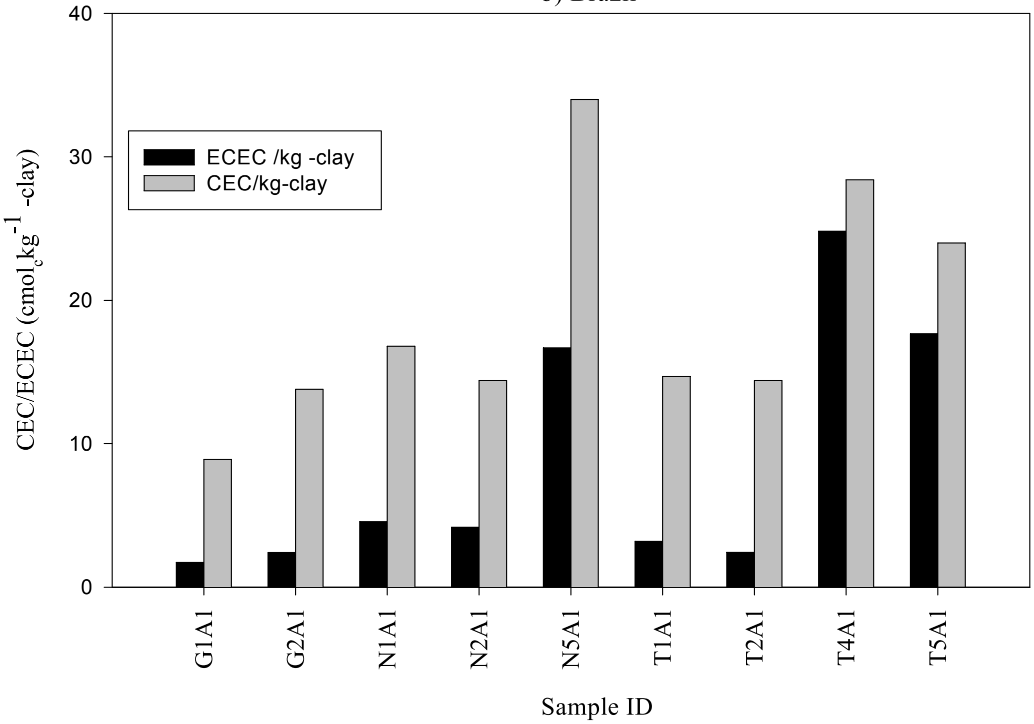

b) Brazil

Figure 3.6 ECEC and CEC kg^{-1} clay of a) Kenyan and b) Brazilian Cerrado topsoils.

Comparing the CEC at pH.7 (ammonium acetate method) of the topsoils, the Brazilian Cerrado soils tended to have much lower CEC values than the Kenyan soils (Figure 3.6; Appendix D). The difference between the CEC/ECEC of Kenyan and Brazilian soils implies that the Brazilian soils are of lower fertility, and probably more weathered than their Kenyan counterparts.

The anion exchange capacity (AEC) of the Kenyan soils ranged from 0.5 to 3.5 with a median value of 1.6 $\text{cmol}_c\ \text{kg}^{-1}$ (Table 3.5). Anion exchange capcity may be greater in the subsoils (Duwig et al., 2003) due to low soil organic matter content, allowing the pristine variable charge surfaces such as those found on gibbsite to be exposed to the soil solution (Huang et al., 2002). A similar trend was expected for these soils. Although there were indications of variation with soil depth, there was no clear trend.

Generally, AEC is a soil property that is less commonly measured during routine soil characterization. Therefore, data for comparison or guidelines for interpretation, particularly for tropical soils is scarce. However, comparing the AEC values found in this experiment with others, these values are significantly greater than those commonly reported for variable charge soils (Hyun et al., 2003; Qafoku and Sumner, 2001; Qafoku et al; 2000). For example, Hyun et al. (2003) reported lower AEC values for four Brazilian Oxisols (within 80-100 cm), three volcanic ash soils from South Korea, one weathered surface soils from Costa Rica and one surface soil from Indiana (USA). Their values ranged from 0.03 to 0.92 $\text{cmol}_c\ \text{kg}^{-1}$. Qafoku and Sumner (2001) found that AEC of selected highly weathered subsoils from the southeastern USA, and other tropical and subtropical areas in Hawaii, South Africa, Australia, Indonesia, New Caledonia, Brazil and Japan ranged from 0.01 to 1.86 $cmol_c$ kg^{-1}. While large AEC is important for retention of nutrients such as nitrates and contaminants, it is particularly undesirable in highly weathered tropical soils (Oxisols and Ultisols), which contain substantial amounts of Fe and Al oxides. Their AEC therefore arises from the variable charge (amphoteric) surfaces of these minerals. Most importantly, anion exchange sites are responsible for the high P sorption capacities of these soils.

Exchangeable bases

Both exchangeable Al and ASP varied significantly with site (Table 3.5), but there was no significant variation with depth in the Kenyan soils. Mean exchangeable Al content of Kenyan pedons ranged from 0.1 to 5.5.$cmol_c$ kg^{-1} with a grand mean value of 1.74 ± 0.35 $cmol_c$ kg^{-1}. The range of exchangeable Al in the topsoils was between 0.4 $cmol_c kg^{-1}$ (Siaya) and 4.5 $cmol_c kg^{-1}$ (Kangema). Exchangeable Al has proved to be a poor indicator of Al-toxic soils and efforts to correlate some measure of plant growth (root length, yield, dry weight, etc.) with components of the soil solution are often hindered by the complex chemistry of Al and the variability of the soils (Delhazie and Ryan, 1995). There are no generally accepted critical levels of exchangeable Al. However, values greater than 2 $cmol_c$ kg^{-1} are generally considered excessive for many crops (Landon, 1984). Most importantly, exchangeable Al data is commonly interpreted in terms of aluminum saturation percentage (ASP), which is a measure of the proportion of the exchange sites occupied by exchangeable Al at the pH of the soil. The aluminum saturation of the exchange complex of topsoils ranged from 4.3 % in KN07A to 60.7 % in KN11A. The yield of aluminum sensitive crops is not much affected in soils with aluminum saturation lower than 30% (Sanchez, 1976: Landon, 1984). The mean Aluminum saturation percentage (ASP) and the corresponding pH_{H2O} of the Kenyan pedons (all depths) are presented in figure 3.7 and the Brazilian topsoils in Figure 3.8. Okalebo et al. (1993) quotes the critical ASP for some of the staple crops in Kenya such as maize and sweet potato as 30%, and sorghum as 15%. Such levels also may be toxic to common bean, *Phaseolus vulgaris*. In Kenya, the dominant types of *Phaseolus*-nodulating rhizobia differed significantly between an acidic soil and a high-pH soil (Anyango et al., 1995), most likely due to Al toxicity.

The soils east of the Rift Valley have significantly greater exchangeable Al, with Al saturation greater than 30% within the rooting depth of most perennial crops. If aluminum occupies more than 60 percent of the exchange complex, large quantities of Al may occur in the soil solution (Nye et al., 1961). The implication of these results are that: (i) sorghum, a common staple crop in the western region (besides the semi-arid regions of the country), and (ii) maize, common beans, and sweet potato which are grown in virtually every arable part of the country, are likely to be affected by the levels of Al observed in most of the study sites. However, some important tropical crops such as tea, cassava, pineapple, and some tropical grasses can tolerate levels as high as 85% (Sanchez, 1976).

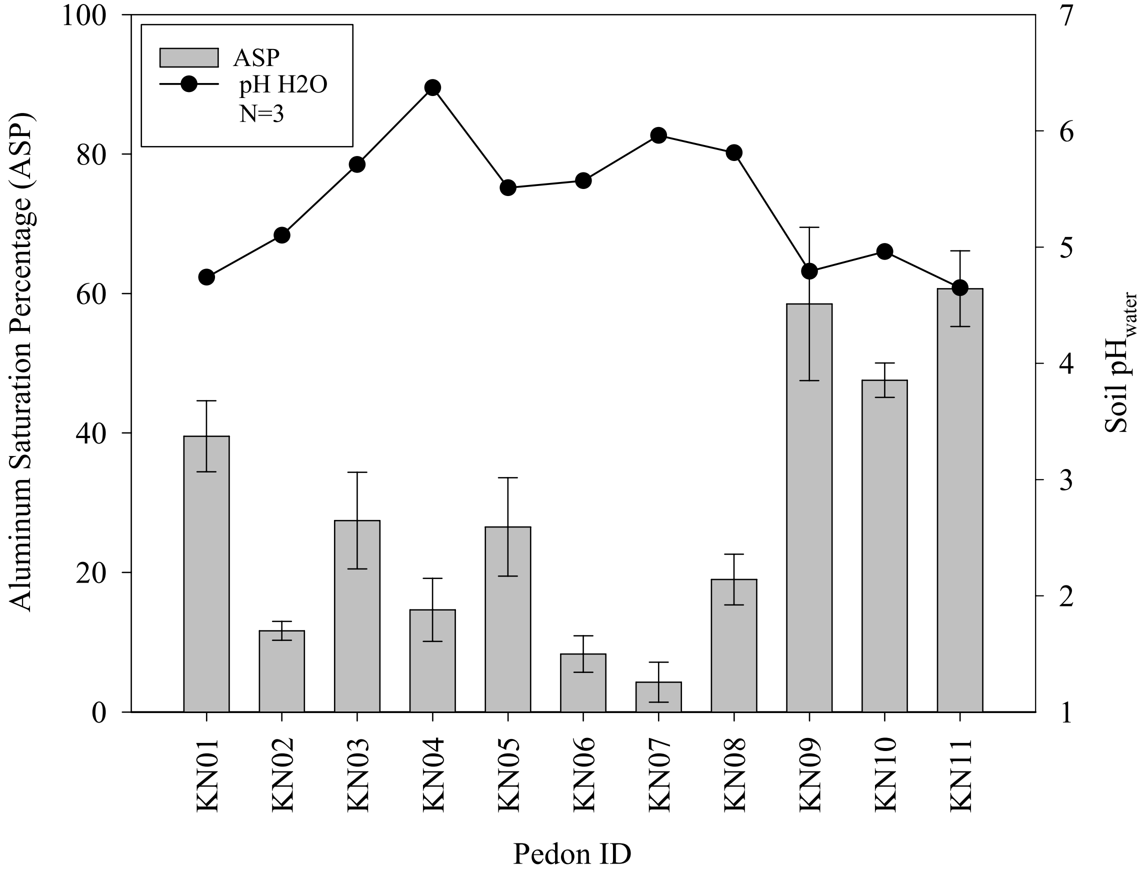


Figure 3.7 Mean Aluminum Saturation Percentage (ASP) and pH (H_2O) of Kenyan Pendons (all depths).

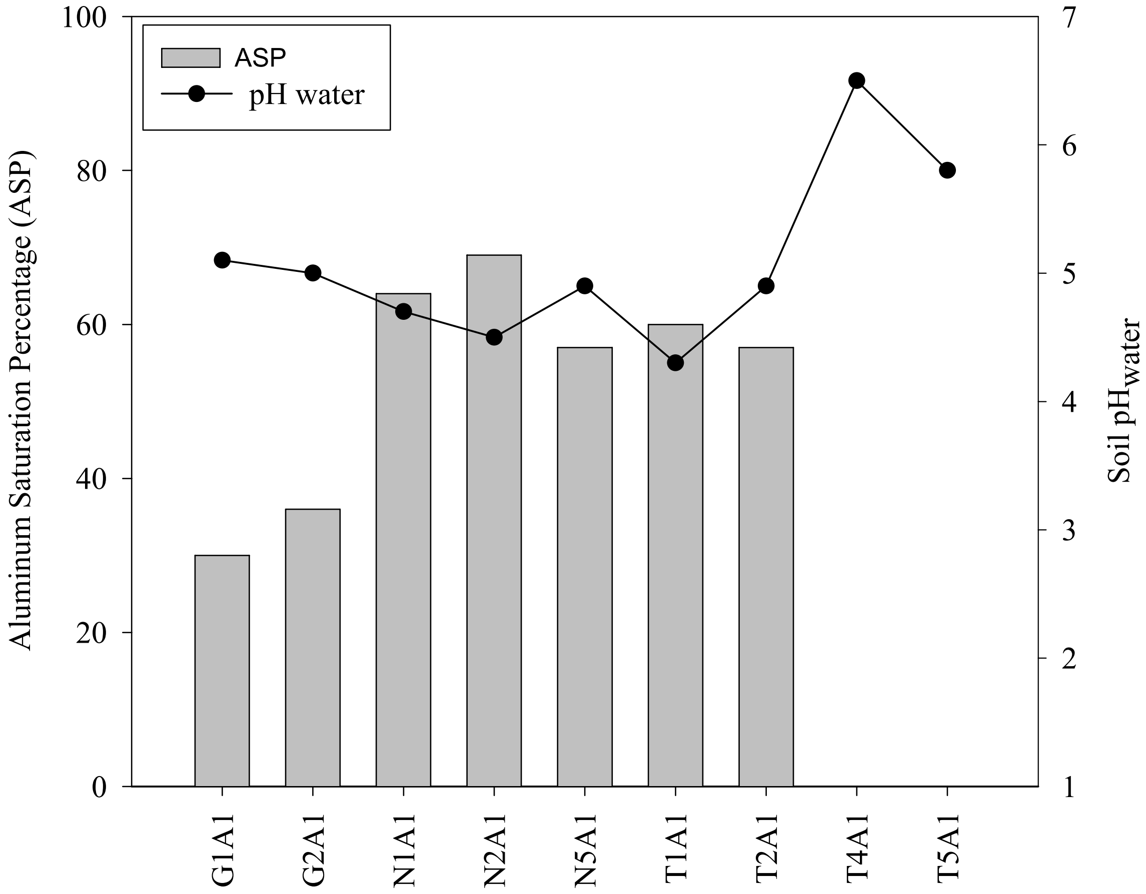


Figure 3.8 Mean Aluminum Saturation Percentage (ASP) and pH $_{H2O}$ of Brazilian topsoils.

These results suggest that not all acid soils studied contain high levels of exchangeable Al^{3+}, and that Al^{3+} may be a function of parent material and mineralogy. It is well known that aluminum toxicity is one of the key factors limiting crop production in acid tropical soils. Poor crop yields can be directly correlated with Al saturation of the effective cation exchange complex (Sanchez, 1976).

The exchangeable Ca, Mg and K were generally low in these soils (Table 3.5 and Appendix D, Table D-2). The exceptions are samples KN07 (Kisii) of Kenya, and T4 and T5 of Brazil. Among the Brazilian soils, exchangeable Al is the most abundant cation on the exchange sites. Exchangeable bases in the Kenyan soils varied significantly with site. Specifically, exchangeable Ca ranged from 1.3- 6.3, Mg ranged from 0.2 to 3.1 $cmol_c kg^{-1}$ and K ranged from 0.2 to 1.6 $cmol_c kg^{-1}$ in the Kenyan topsoils. Exchangeable bases in the pedons east of the Rift Valley (KN09-KN11) were relatively lower compared to the rest of the Kenyan samples. Pedons KN01 (Kuinet), KN02 (Chepkoilel), and KN07 (Kisii) had relatively greater exchangeable K values. Landon (1984) provides the following ratings for exchangeable bases: Exchangeable Ca levels < 4 are considered low and > 10 high. Also, exchangeable Mg levels < 0.5 are considered low and > 4 high and Exchangeable K levels > 0.6 high. He however cautions that these values should not be considered definitive as they are subject to variation dependent on the nature of the soil, the environment, and type of crop. In addition, the balance between these bases is much more significant as they may influence the uptake of one or the other. Adverse cation ratios: notably low Mg: K ratio (> 1:2) may lead to Mg deficiency while Ca: Mg ratios < 1:3 may lead to Ca deficiency, and ≥ 5:1 Mg deficiency and possible P inhibition may occur. An evaluation of the Kenyan topsoils based on these criteria reveal that they are most likely to have Ca deficiency and/or possible P inhibition due to Ca:Mg imbalance (ratios < 3:1); exceptions are pedons KN01, KN03 and KN08 which are within the normal range. Based on Mg:K ratios of the topsoils Mg deficiency is also likely to occur in pedons KN01, KN02 and KN11. The implication of this analysis is that nutrient deficiencies resulting from nutrient imbalances is apparent, and may be one of the reasons for low productivity of these soils. While exchangeable Na levels in the Brazilian soils were undetectable, most of the Kenyan soils had unusually high levels of exchangeable Na, ranging from (0.3-0.7 mg kg^{-1} in the topsoil). Thus Na probably inherited from the Na-rich parent materials.

CHAPTER 4. SOIL PHOSPHORUS SORPTION CHARACTERISTICS

4.1. Introduction

Assessment of the P status and phosphate sorption characteristics is especially important because of the prevalence of P deficiencies in many tropical soils. The prevalence of phosphorus deficiencies in the humid tropics is not only because of limited fertilizer access, but it is particularly acute because these soils are often rich in Fe and Al oxyhydroxides that form strong bonds with phosphate anions (Uehara and Gillman, 1981). The agronomic efficiency of phosphorus fertilizer is strongly dependent on the phosphorus sorption capacity of the soil. Determination of the fertilizer P requirement for plant growth can be made using data from properly calibrated soil tests and past field experiments (Jones and Benson, 1975). Differences in P buffering capacity of soils however, preclude making exact determinations of P fertilizer requirement using this approach. In extreme cases, such as soils with very high P sorption capacities, the P rate needed to achieve maximum yield may be many times greater than the generalized prediction from soil test interpretation guides (Jones and Benson, 1975). Thus, extractable P may be of little use for predicting the amount of fertilizer required to correct such P deficiency (Moody, 1979).

When P sorption capacity is determined by sorption isotherms, it is affected not necessarily by the total P content, but by P already sorbed by the soil (Bache and

Williams, 1971; Barrow, 1974). It is important therefore, to take the P buffering capacity into account in the determination of P fertilizer rate (Beckwith, 1965). In addition, the effectiveness of applied P fertilizer largely depends on P remaining in solution (Olsen and Watanabe, 1963). Beckwith (1965) demonstrated the use of P sorption studies, a technique which relates the P buffering capacity of the soil, or capacity factor, and the P in solution, or intensity factor, to predict P needs of soils. He suggested 0.2 mg P L^{-1} as the standard concentration for comparing soils. He chose this value because, if continuously maintained in solution cultures, this concentration will provide adequate P uptake for many plants. Later studies (Fox and Kamprath, 1970; Juo and Fox, 1977) also concurred that phosphate sorption at this P concentration in solution would provide useful information about phosphate fertilizer requirements. Thus, the standard P-requirement has been defined as the amount of P that must be added to a soil to maintain a concentration of 0.2 mg P L^{-1} soil solution for successful crop growth (Fox and Kamprath, 1970). This equilibrium solution P concentration has traditionally been used in several ways: i) as a point of reference when calculating fertilizer requirements; and ii) to compare soils of varying properties, and it has been found to relate to the threshold above which there is little crop response to P additions for many soils (Kamprath and Watson, 1980).

On the other hand, eutrification in aquatic systems due to phosphorus accumulation in soils and sediments is becoming an environmental concern (Sharpley et al., 1996), particularly in areas where intensive farming is practiced. Because phosphorus is generally the limiting nutrient in surface water systems, even small amounts can have a significant influence on the primary production in these waters

(Correll, 1998). The implication of this is that even small P loses from an agronomic point of view may have serious environmental implications because eutrification depends on the soil solution P concentrations. For most lakes, streams, reservoirs and estuaries, concentrations of 100 μg total P L^{-1} are unacceptably high, and 20 μg total P L^{-1} are often a problem (Correll, 1998). The slope and the x-intercept, at the lowest part of the sorption isotherm ($C \leq 0.1$ mg L^{-1}), which is usually linear, (Hartikainen, 1991) can be calculated. This intercept corresponds to the zero point of P exchange at which no net desorption from or adsorption to soil can occur. This is the equilibrium P concentration (EPC), which the soil can maintain in solution without an additional P supply under the prevailing conditions. This EPC is therefore an estimate of the intensity of P in the soil and it depends on various soil properties, and increases with fertilization (Hartikainen, 1991).

Because the dynamics of P in soils is complex and because it is difficult to establish general rules, it is important to collect local basic data to determine adequate fertilizer practices. Previous research has shown that the P requirement is a function of several quantitative soil properties routinely determined by soil characterization laboratories (Holford, 1977). Besides Fe and Al oxyhydroxides, other soil characteristics such as pH, clay, organic matter content, exchangeable cations, ionic strength, redox potential, and temperature also may influence P sorption (Curtin et al., 1992). If carefully selected, such soil properties can be useful in characterizing the P fertility of soils and predicting P requirement (Holford, 1977; Singh and Gilkes, 1991). Such studies have been carried out in many soil regions, and on different soil types of the humid tropics (Loganathan et al., 1987; Sanyal et al., 1993; Singh and

Gilkes, 1991). So far, little information exists on the P sorption characteristics and the relationship with other soil properties of major soil types of the Kenyan highlands. As mentioned earlier, the Kenyan highlands are very fragile due to intensive utilization; they are of prime agricultural importance to the country. In this respect, it would therefore be useful if P requirements of these soils could be predicted from easily determined soil properties. Therefore, the objectives of this study were: 1) to estimate and compare the P sorption properties of selected Kenyan and Brazilian acid soils; 2) to evaluate the relationship among P sorption parameters and selected soil properties; and 3) to identify soil properties that best predict phosphorus sorption of selected Kenyan and Brazilian acid soils.

4.2. Materials and methods

4.2.1. Short term (24-hour) P sorption isotherms

The topsoils of the 11 Kenyan pedons described in Chapter 2, and 9 topsoils (0 – 20 cm) from the Brazil Cerrado described by Marques (Marques, 2000; Marques et al., 2004a, 2004b) were used. Inorganic P sorption isotherms were determined for each candidate soil with a procedure similar to that of Nair et al. (1984). Duplicate 1.0 g of air-dried soil samples were weighed into 50 mL Nalgene centrifuge tubes and suspended in 30 ml of 0.01M $CaCl_2 . H_2O$ solution containing 0, 2.5, 5, 10, 15, 20, 25, 30 and 40 mg P L^{-1} as KH_2PO_4. Additional concentrations of 50, 60, 70 and 80 mg P L^{-1} were necessary to attain the plateau for samples KN09A, KN10A, and KN11A. A few drops of chloroform were added to each tube to suppress microbial growth.

Equilibration was done in an end-over end shaker for 24 h at room temperature. The samples were centrifuged at 1822 ×g for 15 minutes and the supernatant filtered through Whatman ® #1 filter paper (Whatman Chemical Separation, Inc., Clifton, NJ). The P concentrations in the filtrates were determined colorimetrically by a modified Murphy and Riley (1962) method. The assay total volume was 4 mL; 2 mL of filtrate and 2 mL assay reagent consisting of 1 volume 3M H_2SO_4, 1 volume 0.02M ammonium molybdate, 1 volume 10 % (v/v) ascorbic acid, and 2 volumes ultra pure water. The filtrates were left for 1 hour at room temperature to develop a blue color and analyzed on a colorimeter at 880 nm wavelength. The phosphate sorbed was calculated as the difference between P added and P remaining in the supernatant solution. The P sorption data were fitted to the Langmuir equation. Besides model-specific parameters such as sorption maxima (q_{max}) and binding constants (k_d), phosphorus requirements at two different equilibrium solution concentrations ($EPC_1$and EPC_2) and short-term sorption capacity (PSC) were interpolated from the data. The P requirement at EPC_1 corresponds to P sorption at 0.1 mg L^{-1} and EPC_2 corresponds to P sorption at 0.2 mg L^{-1} equilibrium concentration. The short-term PSCs were calculated as the sum of P already sorbed (P_{ox}) and P sorption maxima (q_{max}) extrapolated form the Langmuir isotherms.

To determine the soil physical and chemical properties affecting P sorption maxima (q_{max}), binding constants (K_d) and P retained at EPC of 0.1 and 0.2 mg L^{-1}, for both Kenyan and Bazilian Cerrado topsoils, a step-wise multiple regression technique and correlation analysis were performed using the Statistical Analysis System (SAS, 2002) software package (SAS Institute, Inc., Cary, NC, USA).

4.3. Results and Discussion

Phosphate sorption isotherms of all the topsoils are shown in Figure 4.1. The P sorption of all the soils was adequately described by simple a Langmuir model. The coefficients of determination (R^2) values > 0.90 were observed for the linear Langmuir fits of all the soils. The Langmuir parameters are shown in Tables 4.1 and the linear Langmuir fits are located in Appendix I. Over all, most of the soils are estimated to have medium to very high P sorption capacity. The sorption maximum of all the topsoils ranged from 426 to 3333 mg P kg^{-1}. Although the Kenyan soils as a group had significantly ($P < 0.05$) greater P sorption maxima (q_{max}) than the Brazilian Cerrado soils, this difference is largely attributable to the soils from the Mt. Kenya region (KN09A, KN10A and KN11A). Among the Kenyan topsoils, the volcanic ash-derived soils, from Mt. Kenya region (KN09A, KN10A and KN11A) exhibited significantly greater capacity to retain P than the rest, as indicated by large sorption maxima, P sorbed at 0.1 and 0.2 mg L^{-1} equilibrium concentrations, and high oxalate extractable P. When these samples are removed however, the P sorption characteristics of the rest of the Kenyan topsoils (from the western region - KN01 to KN08) compared closely with the values observed for the Brazilian topsoils.

Phosphorus requirement at ESC_1 (0.1 mg L^{-1}) ranged from 36 to 871 mg kg^{-1}, and the requirement at ESC_2 (0.2 mg L^{-1}) ranged from 67 to 1380 mg kg^{-1} (Table 4.1).

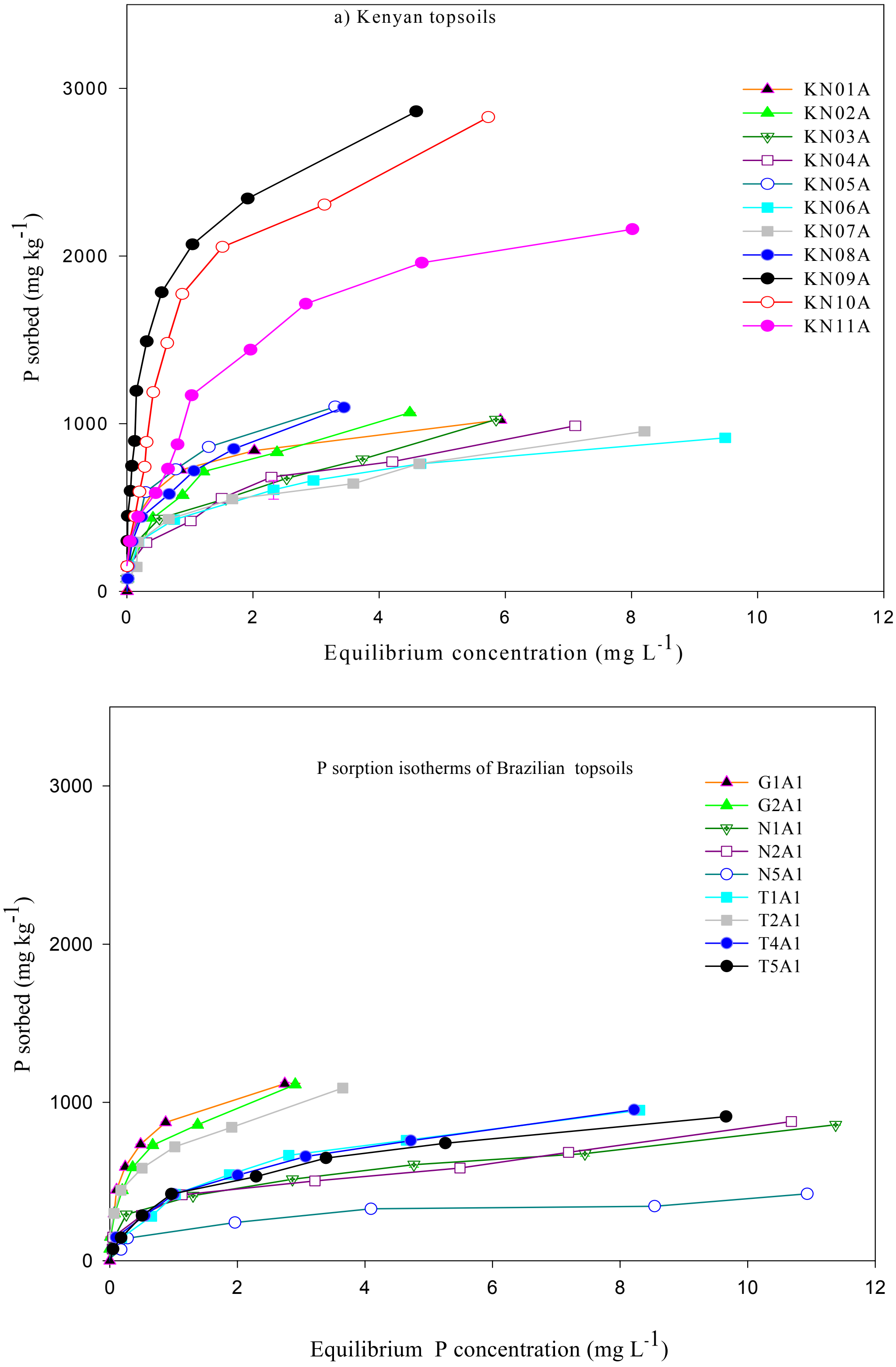


Figure 4.1 Phosphate adsorption isotherms of a) Kenyan and b) Brazilian topsoils

Table 4.1 Short term P sorption properties of selected tropical acid soils derived form the Langmuir model.

Pedon	K_d † (L mg^{-1})	q_{max} ‡ (mg kg^{-1})	P Requirement at 0.1 mg L^{-1} (EPC$_1$)	P Requirement at 0.2 mg L^{-1}(EPC$_2$)
			…...……………..…mg kg	……..…………
KN01A	5.00	1000	333	500
KN02A	1.80	1111	169	294
KN03A	1.67	1000	143	250
KN04A	1.22	1056	113	204
KN05A	2.67	1250	263	435
KN06A	0.86	1056	84	155
KN07A	1.18	1000	106	191
KN08A	3.00	1111	256	417
KN09A	3.54	3333	871	1380
KN10A	1.50	3333	435	769
KN11A	0.73	2500	171	320
G1A1	4.25	1181	351	541
G2A1	4.50	1111	345	526
N1A1	1.65	714	101	177
N2A1	1.81	691	106	184
N5A1	0.93	426	36	67
T1A1	0.63	1056	63	119
T2A1	2.25	1111	204	345
T4A1	0.84	1000	77	144
T5A1	0.77	1000	71	133

† Constant related to sorption affinity (K_d) ‡ sorption maxima (q_{max})

Values of standard P requirement (at 0.2 mg L^{-1}) < 10 are considered to be very low, 10 to 100 low, 100 to 500 medium, 500 to 1000 high and > 1000 very high (Juo and Fox, 1977). The P requirements for the soils of the Mt. Kenya region were more than double the requirement for the rest of the soils in this study. In fact, the soils that had high sorption capacities have both ≥ 35% clay and a high percentage of iron oxides.

Short-term P sorption capacities (PSC) presented in Figure 4.2 were calculated based on the following assumptions: 1) oxalate extractable P (P_{ox}) represents the previously sorbed P, 2) the P sorption maximum derived from the Langmuir equation represents the realized sorption capacity for the duration of the experiment, and 3) unrealized sorption potential is proportional to non crystalline Fe and Al content defined as oxalate extractable Fe and Al (Fe_{ox} +A_{lox}) (Maguire et al., 2001b). Even though P_{ox} in the first assumption may include other forms of phosphate, such as calcium-phosphates (Wang, et al., 1991), this contribution from the acid soils used in this study was expected to be negligible. Moreover, it has been shown that P_{ox} accounts for about 93% of the total P in non-calcareous soils (van der Zee and van Reimsdijk, 1988). In this study, the total short-term P sorption was therefore considered equal to the sum of q_{max} and P_{ox} (Freese et al., 1992). It is apparent that the PSC of the western Kenya soils are comparable to those of the Brazilian Cerrado. The most significant implication of this is that the P management practices that have been successful in the Brazilian Cerrado can therefore be tested for their suitability in western Kenya soils.

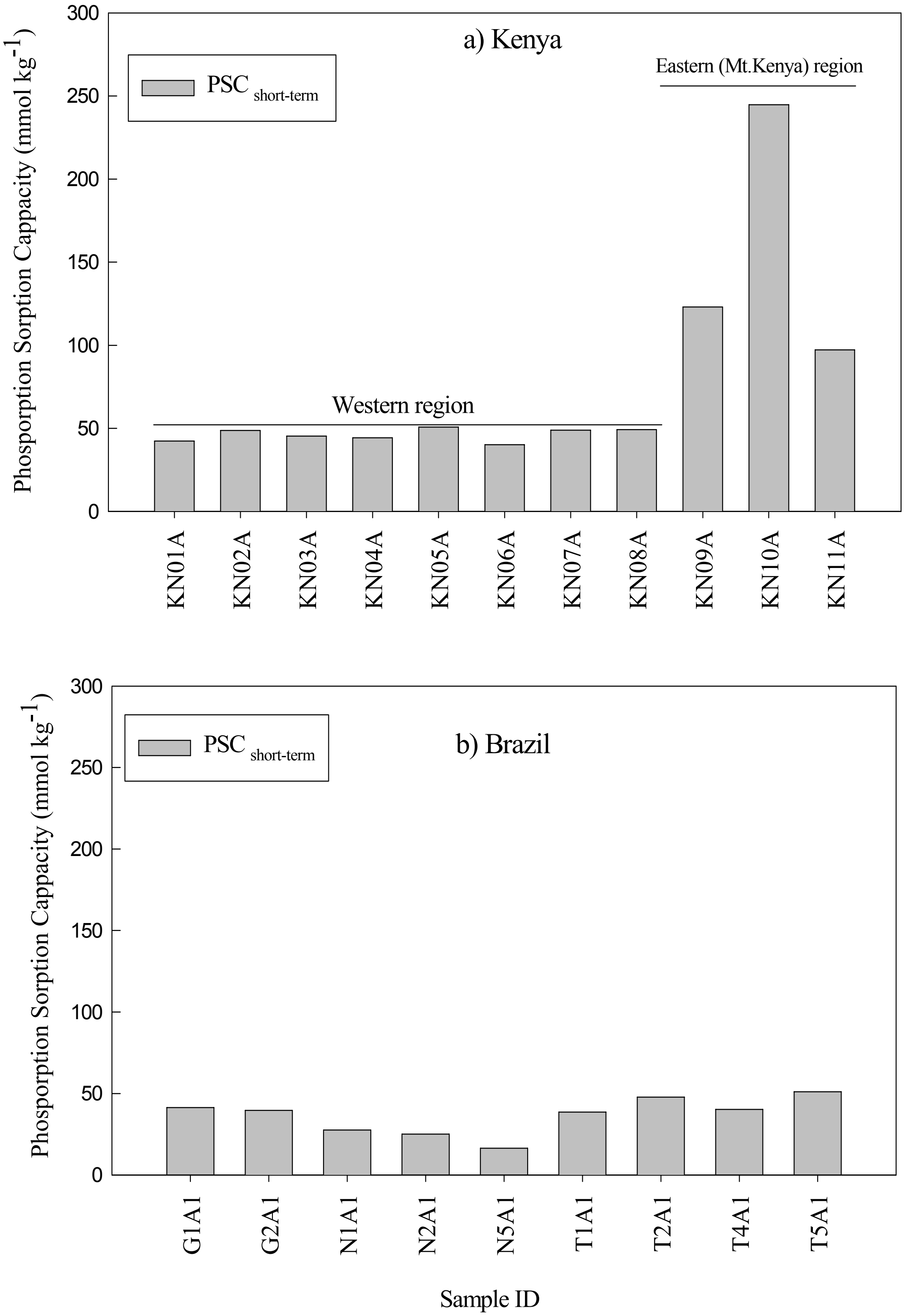


Figure 4.2 Total short-term P sorption capacities of a) Kenyan and b) Brazilian Cerrado topsoils

It is clear from these results that the Mt. Kenya region soils require a special P management regime due to their high P fixation capacity.

To determine the main soil properties affecting P sorption capacity in all the top soils studied, multiple stepwise regression and correlation analyses were performed. Since P is commonly sorbed to Fe and Al oxides and hydroxides, the correlations between different fractions of Fe and Al (Fe_{ox}, Fe_d, Al_{ox}, and Al_d) and the P sorption capacity (q_{max}) were also studied. The results suggest that the soil properties most strongly correlated to phosphate sorption maximum (q_{max}) of the Kenyan topsoils were in the following order: organic matter > exchangeable Al > Loss on Ignition at 400^o C > amorphous Fe and Al oxides (Fe_{ox}+Al_{ox}). For these soils, LOI was positively correlated with soil organic carbon content and hence organic matter content, so a relationship with both factors was therefore expected.

The fact that exchangeable Al and soil organic matter indices (carbon and LOI) were also related to each other and strongly correlated to P sorption suggests either an active participation of soil organic matter constituents or Al-organic matter complexes in P sorption reactions. The role of organic matter in augmenting P sorption in acid soils has often been attributed to the association of organic matter with Fe and Al hydroxides, which provide active sites for P sorption (Sanyal and de Datta, 1991; Holford, 1977; Harter, 1969), besides the contribution of the clay fraction.

In this study, when Fe_{ox} and Al_{ox}, were treated as separate independent variables in the multiple regressions on q_{max}, the relationships were not statistically significant. However, a combination of both amorphous Fe and Al explained about

57% of the total variation in P sorption capacity of these soils. This was not surprising considering the high reactivity of these oxides (van der Zee and van Reidmsjik, 1986; 1988). Although the observed relationship in this study was not as high as expected for tropical soils high in Fe and Al oxides, it is reasonable considering the short equilibration time. Udo and Uzo (1972) and Loganathan et al., (1987) found a positive significant correlation between P adsorption and exch. Al in tropical soils. Similarly, Coleman et al.(1960) also found a significant relationship between exch. Al and P adsorption in temperate soils. Van der Zee and van Reimsdjik (1986; 1988) reported that P sorption in different acid soils from the Netherlands also was linearly related to oxalate extractable Fe and Al. Borggaard et al. (1990) also found that the content of amorphous Fe and Al accounted for P sorption in a range of Danish soils.

For the Kenyan soils, the non-linear equation below best describes the relationship between the sorption capacity and other soil properties:

$$q_{max} = 716.7 + 0.4\ P_{ox} + 117.5\ \text{exch.Al squared.} \qquad \text{Eq. 4.1}$$

Where P_{ox} is expressed in mg kg^{-1} and Exch. Al in $cmol_c\ kg^{-1}$

The initial P contents of soils may vary significantly depending on the previous fertilization practices, as is the case of the soils used in this study. Large P_{ox} values were associated with greater potential for further P sorption, this was unexpected. It was expected that P sorption would be lower in soils which have greater amounts of P already fixed by Fe and Al oxides (P_{ox}) due to slow diffusion of

P further into the hydroxides and precipitation reactions (Barrow, 1974; van Riemsdijk and Lyklema, 1980). For example, Parfitt, (1989) attributed the slow reactions to migration of phosphates to sorption sites of decreasing availability within ferrihydrate aggregates. Parfitt (1989) however, did not observe slow reactions with phosphate on highly crystalline goethite.

For the Brazilian Cerrado topsoils, soil properties most strongly correlated to the phosphate sorption maximum (q_{max}) were in the following order: DCB extractable Al > loss on ignition at 400^{o} C > percent clay. Relative to other forms of Fe and Al, the contribution of crystalline Fe and Al hydrous oxides to P sorption was expected to be minimal since crystalline forms of Fe and Al hydrous oxides sorb less P than their amorphous counterparts. The rather high correlation between DCB extractable Al and P sorption of the Brazilian soils can be attributed to the fact that DCB extracted both amorphous and crystalline Fe and Al oxides (Skjemstad et al., 1989; Boero and Schwertmann, 1989). In addition, LOI was found to be a common predictor of sorption maxima, accounting for up to 68% of total variation in Kenyan topsoils and 81.2% in the Brazilian topsoils. A possible explanation for this relationship is the fact that as much as LOI is an estimate of soil organic matter, dehydroxylation of inorganic soil constituents such as gibbsite, allophane and imogolite can constitute a significant portion of this parameter, but not necessarily in the topsoils rich in organic matter. Considering the andic properties of some Kenyan soils and substantial content of gibbsite in Brazilian soils, it is most likely that these inorganic constituents, though not directly be accounted for, might have a significant contribution to the estimated

LOI and hence P sorption. A summary of the best linear regression equations which best describe the phosphorus sorption maxima of the soils are listed in Table 4.2.

Table 4.2 Selected multiple regression analysis results for q_{max} with soil properties.

Regression equation	R^2
Kenya	
$q_{max} = 284.2\ SOM - 411.7$	0.703**
$q_{max} = 611.0\ exch.\ Al + 425.0$	0.680**
$q_{max} = 206.6\ LOI - 217.8$	0.650**
$q_{max} = 5.1(Fe+Al)_{ox}-134.0$	0.553**
Brazil	
$q_{max} = 1.4\ Al_d + 103.5$	0.833**
$q_{max} = 42.9\ LOI + 485.2$	0.812**
$q_{max} =15.0\ clay + 218.5$	0.807**
$q_{max} = 1.6Al_d - 19.3ASP + 29.8$	0.975**
$q_{max} = 396.3\ (Al+H) + 2.6Al_d - 854.9$	0.941**
$q_{max} = 1.5Al_d - 44.2 - ECEC\ 168.0$	0.952**

Regression model is significant at: * $p \leq 0.05$, ** $p \leq 0.01$

There was high correlation between various forms of Al, suggesting that a high concentration of exchangeable Al or Al_d in these two sets of soils may be the main factor to consider when determining the extent of plant availability of added P. The high positive correlation between the P sorption and ECEC is probably due to the dominance of exchangeable Al on the soil exchanges sites, which is expected in highly weathered soils with low pH. In such soils, Al is responsible for the buffering capacity. This is supported by the fact that ECEC was strongly correlated to pH, Al saturation percentage (ASP), exchangeable Al, and Al_d. Although the correlation between soil pH and P sorption capacity was low and insignificant, a model containing other pH related factors such as Al+H, and ECEC of Brazilian soils was significant at the 5% probability level. This is probably due to the effect of pH on exchangeable Al. Under very acidic conditions, the exchange acidity is predominantly due to exchangeable Al.

Although highly significant, the correlation between P sorption capacity and extractable P in the Kenyan soils (Bray-2 P: R = 0.551** and bicarbonate P: R=0.571**) were both positive. Although available P affects the amount of P sorbed (Holford, 1977), a positive relationship was not expected. This is not easy to explain and thus more investigation is necessary to verify this observation. However, neither of these phosphorus availability indices was retained in the regression models. Klages, et al., 1988 found a negative relationship between P sorption and $NaHCO_3$-extractable P.

Phosphorus requirements calculated from the Langmuir model at 0.1 and 0.2 mg L^{-1} were variable (as shown in Table 4-1). The P requirement at 0.1 mg L^{1} for the

Kenyan and Brazilian Cerrado topsoils ranged from 36 to 871 mg kg $^{-1}$. These values represent the minimum and maximum P required for maintaining an equilibrium concentration of 0.1 mg L^{-1} for this set of soils. On the other hand, the P requirement at 0.2 L mg L^{1} derived from the Langmuir equation ranged from 67 to 1380 mg kg $^{-1}$. On average, the minimum P requirement of volcanic ash-derived soils was more than double the values for the rest of the soils. Like most andic soils in other parts of the world, the high P fixation capacity of these soils is probably because they are derived from volcanic ash materials and are high in Fe and Al oxides and organic matter. There was however, no relationship between the phosphorus saturation index (PSI) and phosphorus adsorption maxima, EPC_1 and EPC_2, both in Kenyan and Brazilian topsoils. The phosphorus saturation index (PSI) (not presented) was calculated for each soil according to equation 4.2:

$$PSI_{ox} = \frac{P_{ox}}{Fe_{ox} + Al_{ox}} \times 100 \qquad \text{Eq4.2}$$

Where, P_{ox} is oxalate extractable P, Fe_{ox} is oxalate extractable Fe and Al_{ox} is oxalate extractable Al (mmol kg^{-1}).

The Kenyan soils had a median PSI value of 0.0423 and ranged from 0.025 to 0.198, while the Brazilian soils had a median value of 0.019 and ranged from 0.013 to 0.056. The degree of P saturation has frequently been used to predict the potential of P loss to water (Maguire et al., 2001a), particularly in the developed countries with a long history of heavy fertilization or manure application. Using 19 Indiana soils, Provin (1996) found a significant relationship between this index and P sorption capacity at different equilibrium solution concentrations (ESCs), ranging from 0.1 to 2.0 mg L^{-1}. Limited information is available, however regarding the use of this index in highly weathered soils. In this study, PSI seems not to be relevant since these soils are undersaturated with respect to phosphate. As such, this index should be interpreted cautiously when dealing with P-deficient soils because several other factors, other than Fe and Al oxides (e.g soil texture, soil pH, organic matter content) may influence P-sorption and –desorption and hence bioavailability. Figures 4.3 and 4.4 summarize key relationships observed in this study.

The constant related to binding energy (k_d) ranged from 0.73 to 5.00 L mg^{-1} in the Kenyan topsoils and from 0.77 to 4.50 L mg^{-1} in the Brazilian topsoils (Table 4.1). For the Kenyan topsoils, single parameters were poorly correlated to the binding constant, but a linear regression model containing both oxalate extractable Al and DCB extractable Fe was significant (R^2 =0.726). However, this constant was poorly correlated to LOI with an R^2 value = 0.5749, but the relationship improved significantly (R^2 = 0.8876) when CEC was added to the linear regression model for Brazilian topsoils.

The results of this study have important implications for soil management in the Kenyan highlands: these soils are likely to be phosphate deficient as indicated by low levels of equilibrium P concentrations and high standard P requirements.

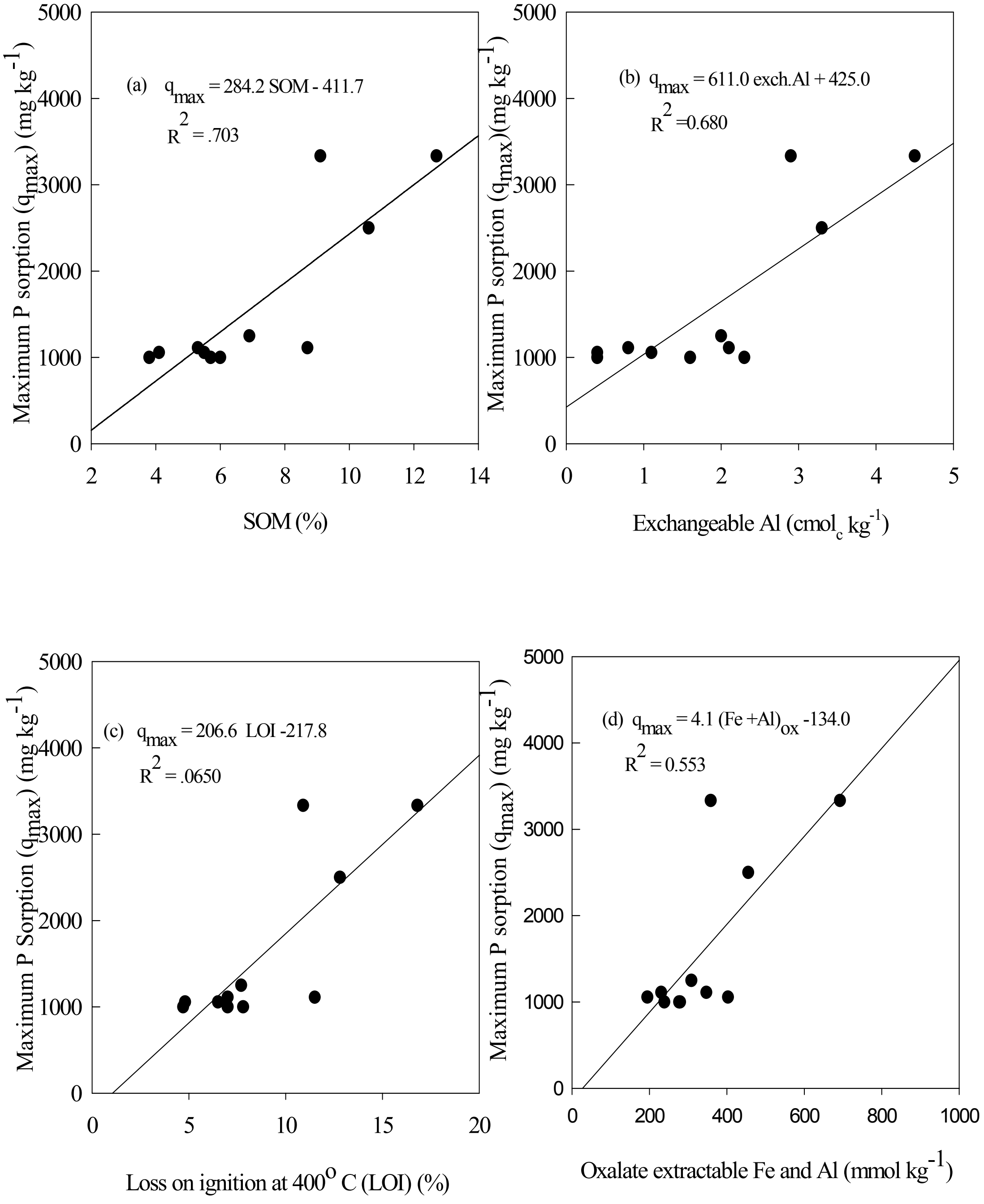


Figure 4.3 Relationship between short-term P sorption maxima of Kenyan soils and a) soil organic matter content, (b) exchangeable Al, (c) loss on ignition, and (d) oxalate extractable Fe and Al.

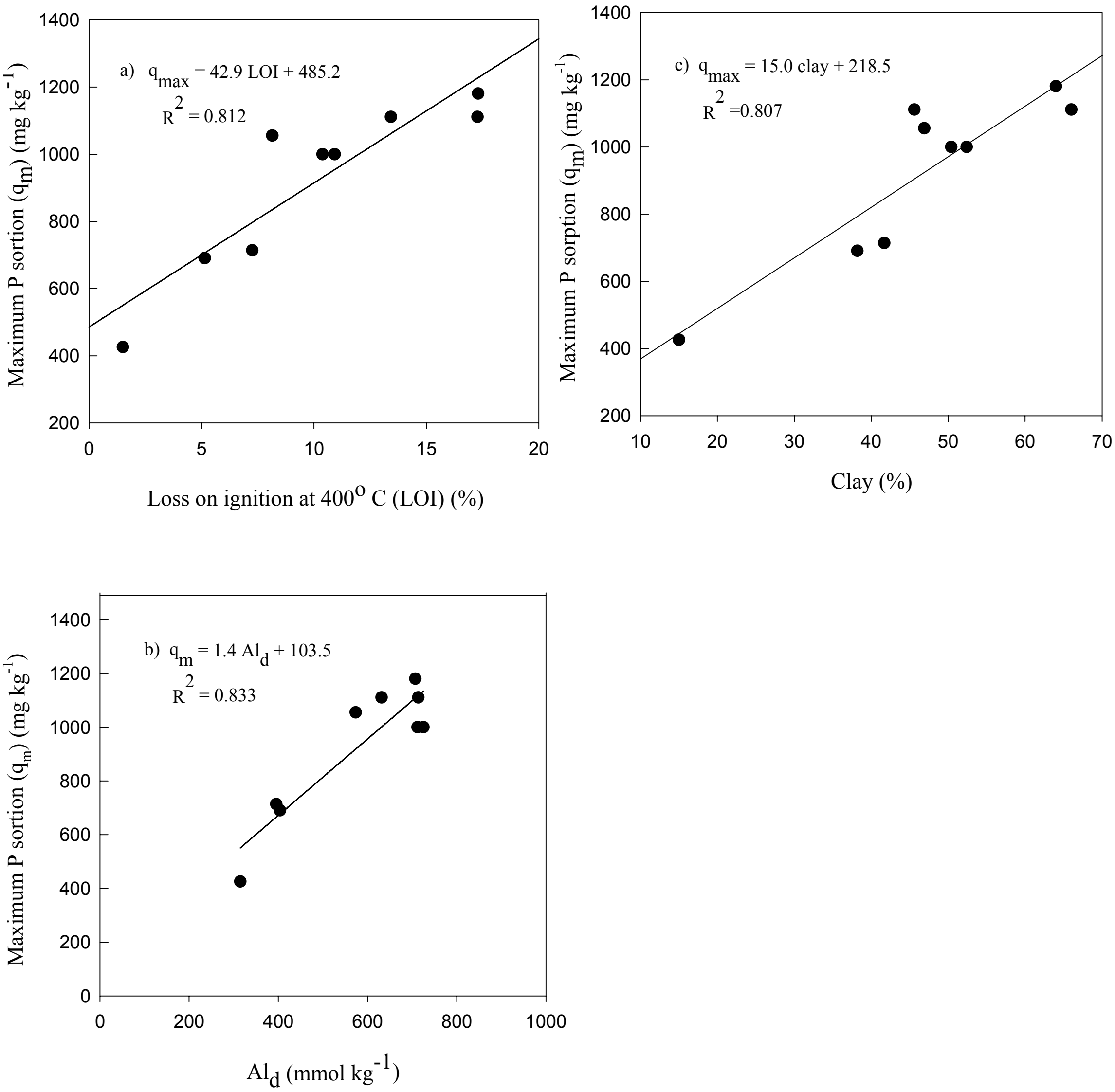


Figure 4.4 Relationships between short-term P sorption maxima of Brazilian topsoils and (a) loss on ignition, (b) DCB extractable Al, and (c) clay content.

CHAPTER 5. SOIL MINERALOGICAL PROPERTIES

The inorganic fraction of most soils consists of a mixture of fine-grained, often poorly-crystalline minerals, frequently with one or more amorphous phases. Since clay mineralogy of a sample is not well quantified by a single analysis, a combination of techniques such as x-ray diffraction, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and thermal analysis were used to investigate the mineralogical composition of soil samples from Kenya (and in some cases, Brazil). In XRD analysis, halloysite and kaolinite may be indicated by a 7 Å peak; therefore separating halloysite from kaolinite by intercalation with organic molecules was necessary. Because the standard XRD results were not conclusive for the Kenyan soils, the dimethylsulfoxide (DMSO) treatment in the x-ray diffraction analysis was used to ascertain the presence of halloysite. The DMSO treatment results in selective intercalation in the halloysite structure, expanding it to 11.4 Å. This expansion facilitates the identification and quantification of kaolinite and halloysite.

This chapter therefore, summarizes the procedures, dominant mineralogical composition of these soils and how their mineralogy may affect their chemical and physical properties.

5.1. X-Ray Diffraction Analysis

Samples from the upper and lower sampling depths of each pedon (Table 1.1) were fractionated for x-ray diffraction analysis (XRD). Pretreatment and fractionation of clays for XRD analyses was done according the procedures described by Jackson (1969). In summary, 7 g of < 2 mm soil was placed into a 250 mL polypropylene centrifuge bottle. The samples were saturated with Na by 3 washings with pH 5 1M sodium acetate (NaOAc). Organic matter was removed by 3 additions of 10 mL of 30 % (w/v) H_2O_2 in 1M NaOAc, heated to about 100° C in a water bath.

Table 5.1 Samples fractionated and used for XRD analyses

Sample ID	Depth (cm)	Sample ID	Depth (cm)	Sample ID	Depth (cm)
KN01A	0-15	KN05A	0-11	KN09A	0-20
KN01D	43-60	KN05C	40-65	KN09C	40-70
KN02A	0-20	KN06A	0-18	KN10A	0-20
KN02C	40-60	KN06B	18-33	KN10C	65-110
KN03A	0-25	KN07A	0-11	KN11A	0-12
KN03C	42-82	KN07D	45-66	KN11D	50-95
KN04A	0-24	KN08A	0-20		
KN04C	50-85	KN08C	38-60		

The samples were then centrifuge-washed with deonized water and centrifuged until dispersion of clay occurred. After dispersion, the samples were sonicated for 10 minutes using a Branson model 450 sonifier with a ½ inch probe with replaceable tip to thoroughly detach clay coatings from sand particles. The suspension was adjusted to pH 8 with a few drops of 0.02 M NaOH. The sand (> 50μm) fraction was separated by wet sieving through a 270 mesh sieve. The coarse (20-50μm), medium (5-20 μm), and fine (2-5 μm) silt fractions were separated by sedimentation technique. The coarse (0.2-2 μm) and fine (< 0.2 μm) clay fractions were separated by centrifugation (IEC PR 7000 centrifuge equipped with an IEC model 949 centrifuge head holding 6 one-liter plastic bottles). The < 0.2 μm clay fractions were flocculated with NaCl, and then dialyzed to remove excess salt. Fractions > 5 μm were oven-dried at 40°C, while fractions < 5 μm were frozen using liquid N_2, then freeze-dried. The freeze-dried fractions were stored in clean polypropylene bottles.

5.1.1. Randomly Oriented Samples

Self-supporting powder mounts of the freeze-dried 2-5, 2-0.2 and < 0.2-μm size fractions were prepared as described by Schulze (1984). First, the samples were gently ground in an agate motor to break large aggregates. Then ~ 200 mg of sample was backfilled into an Al sample holder (15 × 20 mm sample area) and gently pressed against a glass slide underlain by unglazed paper to minimize preferred orientation. After placing the sample holder cover plate onto the samples, the sample holder was carefully flipped over and the glass slide and paper cover carefully removed, exposing a sharp edge flush with the top of the sample holder. The mounted samples which did not appear homogeneous, smooth and almost uniformly flat to the naked eye were remounted.

Diffraction patterns were obtained using a PANalytical X'Pert PRO MPD x-ray diffraction system (PANalytical, Almelo, The Netherlands) equipped with a PW3050/60 θ-θ goniometer and a Co-target x-ray tube operated at 40 KeV and 35 mA. Incident beam optics consisted of an Fe beta filter, 0.04 radian Soller slit, a programmable divergence slit, and a beam mask set to illuminate a 10 x 10 mm sample area. A fixed, 1° anti-scatter slit was used at diffraction angles < 12° 2θ. The diffracted beam optics consisted of a programmable diffracted-beam anti-scatter slit, a 0.04 radian Soller slit, and a PW3015/20 X'Celerator detector configured for an active length of 2.12° 2θ. Powder mounts were prepared in Al sample holders and scanned from 2.1 to 80° 2θ at 0.05° steps with 60 sec measurement time per step. The data were analyzed with the X'Pert High Score Plus^{TM} software package (PANalytical, Almelo, The Netherlands) and were converted to a fixed 1° divergence slit prior to phase analysis and plotting.

5.1.1.1. Porous ceramic tile method for oriented aggregates

The Millipore filter transfer technique (Moore and Reynolds, 1997) was used to prepare oriented clays for x-ray diffraction analyses as described below.

Determination of optimal clay amount for X-ray diffraction analysis: Using the optimum amount of clay ensures that the relative intensities of the sample diffraction peaks are in correct relation to the amount of each mineral in the sample and that no peaks resulting from the supporting medium exist (Rich and Barnhisel, 1977). The optimum amount of clay used in x-ray diffraction analysis was determined using equation 5.1 (Rich and Barnhisel, 1977).

$$\text{mg cm}^{-2} = -500\,[\ln(1-Gx)]\,\sin(2\theta/2)\,/\,\mu^* \qquad [5.1]$$

where;

mg cm^{-2} is the concentration of clay,

Gx is the fraction of the thickness of the sample from which the observed diffraction is produced,

2θ is the angle of diffraction, and

μ^* is the mass absorption coefficient.

The maximum angle of diffraction was chosen to be 50° 2θ. Because the samples were expected to contain different proportions of kaolinite, gibbsite, hematite and goethite, the mass absorption coefficients for each of these minerals were calculated. The mass absorption coefficients were found to be 45.5, for kaolinite, 37.4 for gibbsite, 42.3 for hematite and 39.6 for goethite. The mass absorption coefficient for kaolinite was used for the initial calculation with diffraction intensity (Gx) of 99%, based on an assumption that most of the samples were predominantly kaolinitic, yielding an optimum clay concentration of 21.2 mg/cm^2. The actual clay concentration was then recalculated with 40 (slightly above the average of the four minerals) as the mass absorption coefficient as an additional precaution, just in case an unexpected mineral with a slightly different mass absorption coefficient occurred in the sample. The optimum clay amount was found to be 24.3 mg/cm^2. The filter size was 16.8cm^2 but the effective area for sedimentation of the clay was only 9.62 cm^2; giving the optimum amount of clay required for each sample to be approximately 234 mg, which is the amount of sample used for all the samples.

Cation saturation and sample preparation for XRD

Oriented mounts of the < 0.2 µm size fractions were prepared using the Millipore filtration method (Moore and Reynolds, 1997). Samples were saturated with either K or with Mg saturation plus ethylene glycol solvation prior to x-ray diffraction (Moore and Reynolds 1997). All the saturated sample suspensions were adjusted to pH 8 (and maintained at this pH throughout this procedure) with a few drops of dilute NaOH solution to avoid flocculation. In short, 234 mg of freeze-dried clay was weighed into a 50 mL polypropylene tube. Approximately 10 mL of deionized water was added, and the sample was dispersed by sonification for 30 seconds.

For Mg saturation, approximately 20 mL of 0.5M $MgCl_2$ was added to each smple and mixed for 5 seconds with a vortex mixer to ensure complete saturation with Mg^{2+} cations. The samples were centrifuged (IEC PR-7000) at 204 × g for five minutes, and the supernatant discarded. This step was repeated three more times with the saturating cation solution. After the final cation saturation, the samples were washed with 10 mL deionized water (pH 8), centrifuged, and the clear supernatant was discarded. The washing was also repeated three more times to wash any excess salt from the sample.

Millipore glass microanalysis vacuum filter holders (47 mm) fitted with Millipore 47 mm 0.45 µm filters (Type HVLP) were used (Fisher Scientific). The vacuum filter holder was assembled and rinsed with deionized water (pH 8) to pass through the filter.

The vacuum was released in advance before slowly adding the saturated clay suspension. The vacuum was then turned on slowly so as not to immediately clog the filter pores with the finest clay particles.

For each Mg-saturated sample, one milliliter of five percent ethylene glycol was passed through the filter cake followed by two washes with one milliliter of deionized water (pH 8). After the suspension was completely filtered, the vacuum was removed and the filter containing the sample cake was carefully removed from the holder and the filter placed sample side down onto a clean 29 x 60 mm ceramic tile. After applying the sample cake to the ceramic tile, the back of the filter was smoothed to reduce air bubbles, and the filter was peeled off carefully, leaving the sample on the ceramic tile. Samples with large air bubbles were peeled off and re-suspended. The oriented samples were allowed to dry slowly in a sealed glass container containing a small beaker of 100% ethylene glycol and another beaker of deionized water to slow down the rate of drying and subsequent cracking of samples. The samples remained in the sealed glass container for 3 - 4 days to ensure complete solvation by the ethylene glycol and gradual drying. Ceramic tiles were preferred over glass slides because of reduced cracking and curling, and subsequent peeling off of the samples after complete drying. For K-saturation, the above procedure was repeated, using 1M KCl instead of $MgCl_2$, but the samples were not treated with ethylene glycol. The above procedure was only used for the < 0.2 μm clay fraction. This procedure was later modified by using 30-40 % ethanol in deionized water (pH 8) to wash of the excess salts because use of ethanol was found to reduce cracking and curling of the clays.

Diffraction patterns were obtained using a PANalytical X'Pert PRO MPD x-ray diffraction system as described earlier except the samples were scanned from 2.1 to 50° 2θ. The Mg saturated, ethylene glycol solvated samples were scanned at room temperature, while the K-saturated slides were scanned both at room temperature and after successive heating to 100°C, 300°C and 550°C in a muffle furnace for two hours. Interpretation of diffraction patterns entailed identification of crystalline species from the array of diffraction maxima obtained from the samples. Interpretation of the XRD patterns were done by direct comparison of the observed diffraction patterns of the samples (unknown) with the *d*-spacing and corresponding intensities of known minerals (Whittig and Allardice, 1986; Moore and Reynolds, 1997; Dixon and Schulze, 2002). Further identification of some of the more common clay minerals was accomplished by comparing some of the diffraction maxima obtained for the samples from Mg-saturated, glycerol-solvated, K-saturated and heated samples with the tabulated diagnostic maxima. Mineral phases also were identified using the of X'Pert High- Score Plus ™ software made.

Because of the inherent nature of the clay fractions in the Kenyan samples to crack and peel on drying, the XRD patterns obtained for the samples prepared by the Millipore procedure had irregular peak shifts and broadening whose cause could not be ascertained; whether this was due to experimental conditions or inherent sample properties. Although the Millipore procedure was initially intended to be used for quantification of the various mineral phases in the various fractions, the data obtained were only suitable for mineral phase identification and for comparison (establishment of general trends) of the mineralogical composition of various pedons and sampling depths.

Because of the limitations mentioned above, a quick sedimentation method was used to fractionate the whole clay fraction for further investigation.

5.1.1.2. Quick sedimentation method

Whole clay samples were deposited on 1.27 inch diameter porous disks. These disks are part number 0604DO1.5-B01M 3 from Soil Moisture Equipment Corp., 801 S. Kellog Ave., Goleta, Ca 93117. As received, the disks, made from a high fired alumina body, were 1.625 "diameter x 0.281" thick with a 1 bar air entry value. The diameter of each disk was reduced to 1.25 - 1.27" on a lathe, and the thickness was reduced to about 0.25" by hand grinding on 220 grit wet-or-dry sandpaper placed on a surface plate with water running over it. The face of each disk has a surface area of 7.92 to 8.17 cm^2. An average surface area of 8.0 cm^2 was assumed for subsequent calculations.

The mass of clay needed for 95% theoretical diffraction (based on equation 5.1 above) at 35° 2θ is ~ 11 mg cm^{-2}. Therefore, 88 mg of sample was needed to cover each disk with this mass. The average clay content of Kenyan and Brazilian soil samples was approximately 57% (~ < 2 μm in diameter). Therefore, 0.301 g of whole air-dried soil was considered sufficient to yield ~176 mg material less than 2 μm in diameter (needed for the two disks; Mg and K saturations) for XRD analysis. For moist soils from the Mt. Kenya region, adjustment for moisture content was made, giving ~ 0.360 g whole soil as the starting material.

The samples were weighed into a 50 mL conical bottom centrifuge tube, moistened with deionized water and allowed to re-hydrate overnight. The samples were then washed and the exchange complex was saturated with Na ions by centrifuging 3 times with ~25 mL of 1 M NaCl, discarding the clear supernatant. The samples were then shaken overnight on a reciprocating shaker, with ~25 mL of 1 M NaCl. The centrifuge tubes were filled to the 40 cm mark with deionized water (adjusted to pH 8.0). The suspensions were then shaken thoroughly and centrifuged at 54 × g for 8.2 minutes to obtain the particle size cut off of < 2µm in diameter (based on Stoke's law). This step was repeated 5 more times, collecting the supernatants in labeled plastic beakers.

The clay suspensions collected were divided into two portions (for Mg-glycerol and K-saturation). The supernatants were carefully poured onto the porous disks under suction (over an acrylic block with openings connected to laboratory vacuum) and allowed to uniformly sediment. The samples were then saturated with either K or Mg by slowly pouring 10 mL of either 1M KCl or 0.5 M $MgCl_2$, then washing off the excess salts with deionized water. For Mg saturated samples, 10 mL of 5% glycerol was added drop-wise with a culture pipette. The Mg-glycerol treated samples were allowed to dry gradually (3-4 days) in a sealed glass container containing a beaker of 100% glycerol and another beaker of deionized water. The K-saturated samples were put on paper towels on the laboratory bench, covered at an angle with watch glass and allowed to dry slowly (2 days) before XRD analysis. The XRD analysis and mineral phase identification were done as described earlier.

5.1.2. Intercalation of kaolins

Kaolins are dioctahedral 1:1 phyllosilicate minerals of general structural formula $Al_2Si_2O_5(OH)_4$. Structurally, each layer consists of two sheets: a tetrahedral sheet in which silicon atoms are tetrahedrally coordinated by oxygen atoms; and an octahedral sheet where aluminum atoms are octahedrally coordinated to hydroxyl groups and shared apical oxygens from the silica tetrahedral sheet. One side of each layer presents the siloxane surface arising from the bases of the silica tetrahedral sheet while the other presents the surface of hydroxyl groups from the aluminum octahedral sheet. Consequently, two successive layers are held together by hydrogen bonding (Bish, 1993; White and Dixon, 2002).

Kaolinite exists commonly in platy morphology and typically has a d(001) spacing of 7.2 Å. Halloysite, on the other hand, is the only kaolin mineral occurring naturally as a hydrate (expanded phase with d(001) spacing of 10.0 Å) as a result of the incorporation of water in the interlamellar space ($Al_2Si_2O_5(OH)_4$. $n(H_2O)$; $n = 0$ to 2) (Joussein et al., 2005). The particles of halloysite can adopt several very different morphologies ranging from tubular to spheroidal and sometimes platy (Churchman and Theng, 1984). Studies have suggested the existence of three fundamental hydrated phases, with intermediate spacings resulting from mixed-layering of these three fundamental phases; 10 Å and 8.6 Å hydrates, and the 7 Å dehydrated kaolins (Costanzo and Giese, 1985).

The interlayer water content of halloysite -10 Å is ~12.3 wt. % (Kohyoma et al., 1978) corresponding to two water molecules per formula unit (Joussien et al., 2005). However, a fully hydrated halloysite (10 Å) is very unstable under ambient conditions and rapidly dehydrates if not kept under humid and low temperature conditions (Joussein et al., 2005). Brindley (1961) proposed that the interlayer water molecules in halloysite-10Å form hydrogen bonds with (i) one another, (ii) with oxygens of the siloxane plane, and (iii) with hydroxyls of the (opposite) aluminol plane. Moreover, the water in the interlayer spaces of halloysite (10 Å) and in a synthetic 10 Å kaolinite hydrate has been found to occur in two different environments. One type of water (hole water) is keyed into the ditrigonal holes formed by the tetrahedral oxygens and is strongly bonded to the silicate surface; the other type (associated water) is mobile under ambient temperatures conditions and is weakly bonded to the interlayer surfaces (Costanzo et al., 1982; 1984).

Intercalation, and hence swelling of kaolins, is achieved by using small polar molecules such as dimethyl sulfoxide (DMSO) (Thompson and Cuff, 1985), formamide (Olejnik et al., 1974; Churchman and Theng, 1984; Churchman et al., 1984), hydrazine (Johnston and Stone, 1990), ethylene glycol (Hiller and Ryan, 2002) and sequential treatment with hydrazine followed by water and finally ethylene glycol (HWG) (Churchman, 1990). These molecules are thought to be intercalated directly via hydrogen bonding to the aluminol surface. Among these treatments, the ease of intercalation has been found to decrease in the order: DMSO > HWG > Formamide > (Theng et al., 1984; Churchman, 1990). However, the degree of complex formation may be affected by factors such as structural order, particle size, and reaction time, crystallinity of the kaolins and presence of impurities (Franco and Ruiz Cruz, 2004; Churchman and Theng, 1984).

Intercalation of kaolin minerals leads to layer expansion along the c axis, the process which can be readily observed by XRD (Joussein et al., 2005). This difference in the rate of intercalation is used to identify the presence of halloysite in admixtures with kaolinite (Churchman et al., 1984; Churchman and Theng, 1984). Although the reactivity of the kaolins with DMSO may vary from sample to sample, halloysite almost completely intercalates whereas different kaolins may intercalate to different extents (Churchman, 1990).

Because the XRD patterns of Kenyan clays studied showed broader, less well-defined d(001) peaks of kaolinite, it was therefore necessary to carry out an intercalation experiment to ascertain the existence of halloysite. Since halloysite-10 Å can partially dehydrate during transportation and storage to halloysite 7 Å, the type of kaolin present in these samples was inconclusive, based on the standard XRD analyses preformed. In addition, the curling and peeling of the oriented clay samples on drying during XRD analysis prompted the need for further investigation of possible existence of halloysite in these samples.

Intercalation method

Five representative Kenyan clays and Georgia kaolinite (KGa-1b) from the Source Clays Repository of The Clay Minerals Society (www.clays.org) were intercalated with dimethylsulfoxide (DMSO) according to the modified procedures of Calvert et al. (1984), Heller-Kallai et al. (1991) and Churchman, (1990).

The < 0.2 µm clay fractions were weighed (88 mg) into 25 mL Pyrex tubes, suspended in 10 ml of deionized water and allowed to re-hydrate for 5 hours, then sonicated to disperse the clay. The suspensions were then centrifuged and the supernatant decanted out. The samples were re-suspended in 10 mL of pre-heated DMSO (in a boiling water bath); in two increments of 5 mL. The suspensions were maintained in a hot water bath for 72 hours. Another portion of each sample was treated likewise, but with deionized water instead of DMSO. After cooling the supernatants, they were mounted on porous disks under suction and X-rayed immediately and, after allowing the samples to slowly dry under ambient conditions for 2 and 72 hours. The degree of expansion following complex formation (intercalation) or hydration was assessed by comparing the relative peak heights of the basal reflections for the expanded phases (near 11 Å) and for the unexpanded phases near 7 Å.

5.2. Electron Microspcopy

Five Kenyan samples (four of which were from subsurface horizons) were selected for microscopic analysis. The subsurface clays were selcted because it was already known from XRD analyses that there were no significant diffrences in mineralogy with depth. The other reason for selecting the subsurface clays was to avoid any possible interference from soil organic matter. The only case where the surface clay was used was because there was no sufficient clay in the subsurface sample for all the analyses.

Size and morphology of the crystals were examined by both transmission electron microscopy (TEM) and scanning electron microscopy (SEM). For transmission electron microscopy, a diluted suspension (10 mg clay in 10 mL deionized water) of the < 0.2 and 2-0.2 µm freeze dried clay was prepared. The suspensions were then dispersed by ultrasonic treatment. A drop of each suspension was deposited on 400-mesh carbon-coated formvar grids, which were glow discharged prior to use. The specimens were allowed to dry at room temperature. The specimens were imaged using a Philips CM-100 TEM operated at 100 kV, spot 2, 200 µm condenser aperture and 70 µm objective aperture. Images were captured on Kodak SO-163 electron image film. Magnifications were primarily 8900, 28400 and 39 000 x read-out. The images were digitized at 1200 dpi using Adobe Photoshop software.

The fine sand fraction of the samples was studied using a FEI-NOVA nanoSEM with high resolution under low vacuum detector equipped with OXFORD INCA 250 electron dispersive x-rays.

5.3. Themal Analysis

Thermogravimetric analysis (TGA) of the five representative Kenyan clays (< 0.2 µm) and Georgia kaolinite (KGa-1b) was done using a Mettler TGA/SDTA851^e instrument (Mettler-Toledo, GmbH Analytical, Schwerzenbach, Switzerland) by heating (~18 mg sample) from ambient temperature to 1000°C at 20°C min^{-1} under N_2 atmosphere. The resultant curves were then normalized and first derivatives obtained using the STAR^e evaluation software, version 9.0 x.

5.4. Results and Discussion

XRD patterns of fine clay, coarse clay, and fine silt fractions of Kenyan soils

In general, no distinct differences in clay mineral distribution with depth were observed for any of the pedons studied. Pedons from the same geomorphic province tended to have similar mineral composition. The fine and coarse clay fractions of all horizons in all Kenyan pedons are dominated by kaolinite and/or halloysite as indicated by the first order peak occurring between 7.15-7.28 Å and second order peaks between 4.42-4.45 Å. The peaks between 4.42-4.45 Å may also indicate disordered kaolinite. The broadening of the 7.15-7.28 Å and 4.42-4.45 Å peaks at the base is a common phenomenon in almost all Kenyan soils, strongly suggesting the presence of halloysite or mixed layering. These peaks disappeared at 550°C as kaolinite and halloysite are unstable at this temperature.

Gibbsite, goethite and, hematite also were identified in the clay fractions. In most pedons in the western region the amount of gibbsite is low, and sometimes not detectable. Whenever present in these pedons, gibbsite is indicated by low intensity and broad peaks at 4.86Å in the Mg-ethylene glycol treatment and 25° C K saturation, which disappears after heating to 300° C due to dehydroxylation. Exceptions are for the pedons in the highlands east of the Rift valley (KN09, KN10 and KN11), where gibbsite is relatively abundant. In these pedons, the relative abundance of gibbsite is indicated by well defined peaks at 4.86 Å. Although strongly shadowed by the peaks of the phyllosilicate minerals, goethite and hematite peaks are frequently present in most of the clay fractions from all the pedons. The presence of goethite was indicated by peaks at around 4.12-4.15Å in the Mg-ethylene glycol and 25° C K-saturation. These peaks also disappeared at 300°C due to dehydroxylation of goethite. In the coarse clay fraction of most samples, weak quartz (3.33-3.35Å) and hematite (2.64Å) peaks persistent on heating to 550°C were common.

Although discrete mica particles may not be present in large quantities to show a distinct 10 Å peak in these XRD patterns, its presence is implied in relatively higher intensity peaks around of 3.33 – 3.35 Å in the fine clay fraction of some soils, where quartz is not expected. There is also evidence of mixed layering of mica-kaolinite and/or mica–vermiculite that is prominent in most of the pedons west of the Rift valley. Interlayering of mica with kaolinite is suggested by a broad 4.00-4.44 Å peak, of which most disintegrates when heated to 550°C, leaving a little hump standing out above the baseline near the 10 Å position. The best example of mica-kaolinite interlayering is seen in XRD patterns of KN05A fine clay fraction where the 3.57Å peak of kaolinite collapses on heating to 550°C K saturation and reinforces a mica peak at 3.33Å in its neighborhood, in addition to the emergence of a broad hump in the 14-10 Å region. The presence of hydroxy-interlayered mica/vermiculite in pedons located in the western highland is also suggested by a broad diffraction band around the low angle region (7 – 10, °2θ), measuring between 9.8-14.0 Å with Mg-saturation and ethylene glycol salvation. However, this band was not affected significantly by K saturation or heat treatments. There is however, no evidence of mixed layering in the pedons east of the Rift valley, save for the isolated cases of very low intensity reflections between 10-14 Å.

The quartz peak at 3.35 Å is the strongest peak in the entire fine silt fraction in all the pedons. A small reflection at approximately 10 Å was noticeable above the baseline in the low angle region, both in the Mg-saturation with ethylene glycol salvation and K saturation in the soils west of the Rift valley. This reflection was persistent after heating to 550° C, indicating the presence of micaceous materials.

X-ray diffraction patterns of the whole clay fraction of Kenyan and Brazilian soils

Representative X-ray diffraction patterns (XRD) of the whole clay fraction of the Kenyan soils are shown in Figures 5.1 to 5.4. The rest of the diffraction patterns are located in Appendix K.

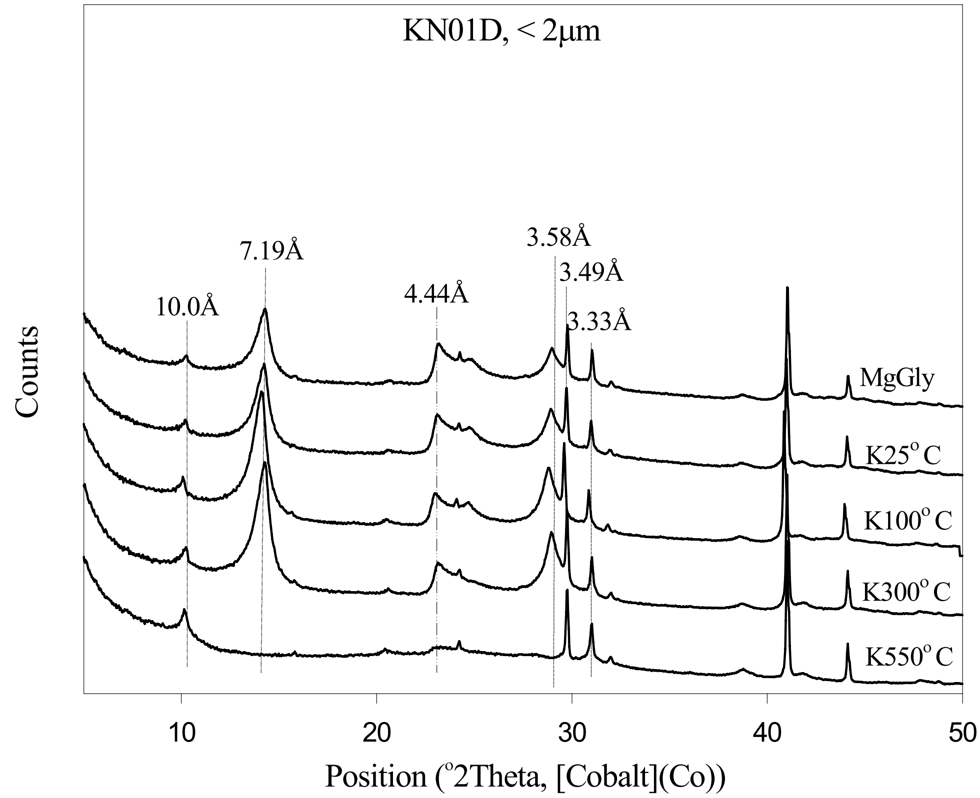


Figure 5.1 X-ray diffraction patterns of Mg-glycerated and 25, 100, 300 and 550° C K-saturated samples of whole clay fractions of KN01D.

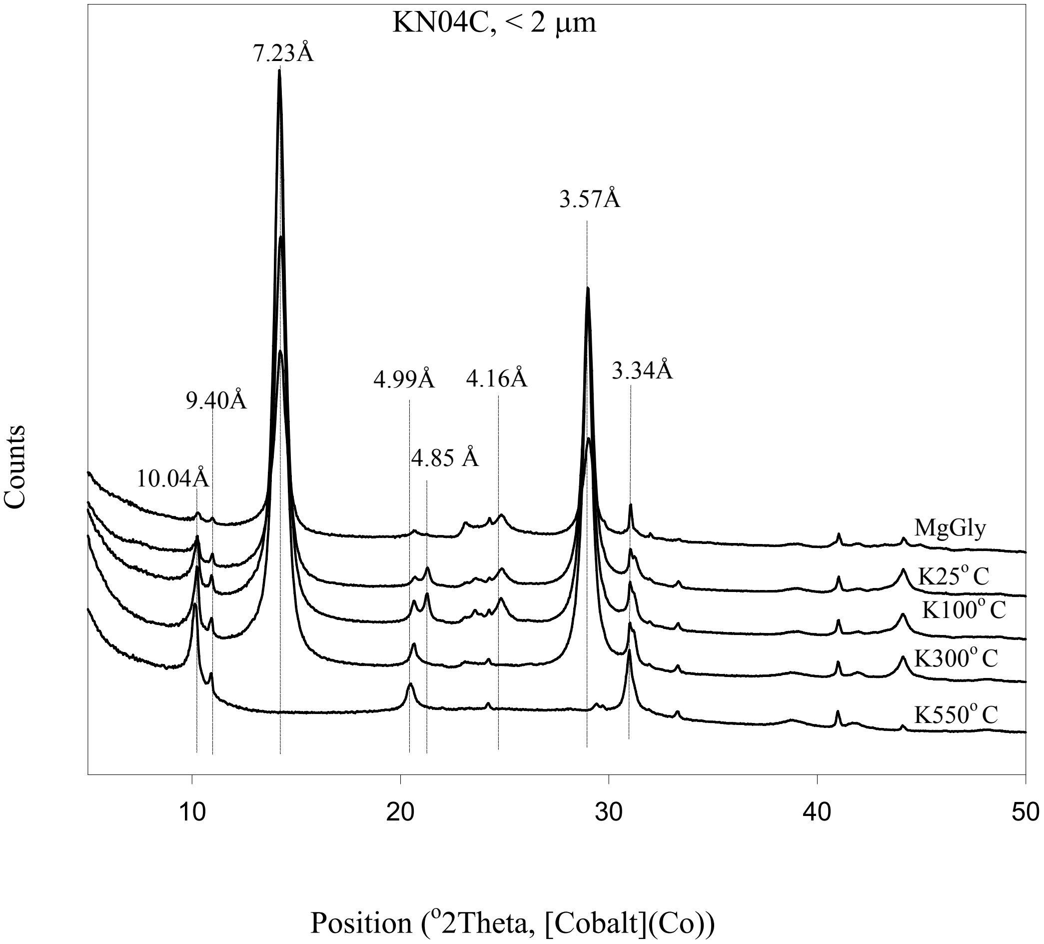


Figure 5.2 X-ray diffraction patterns of Mg-glycerated and 25, 100, 300 and 550° C K-saturated samples of whole clay fractions of KN04C.

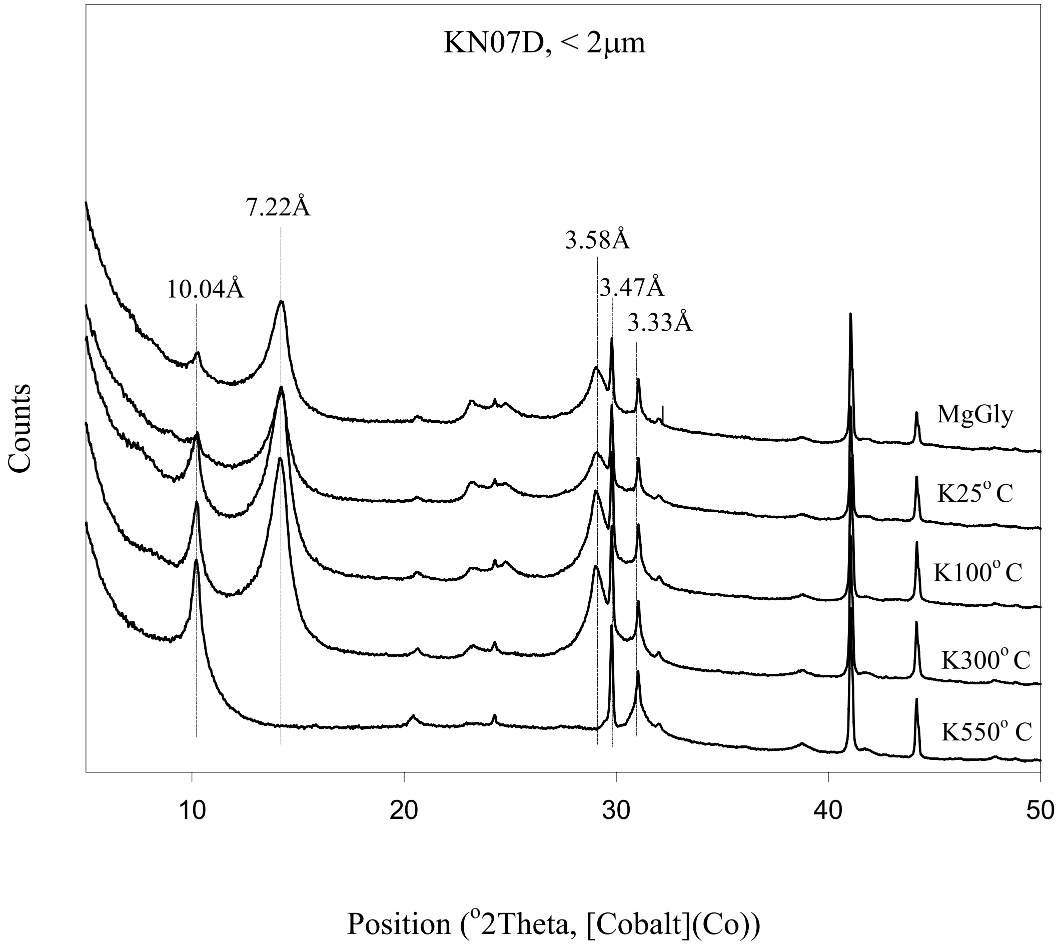


Figure 5.3 X-ray diffraction patterns of Mg-glycerated and 25, 100, 300 and 550°C K-saturated samples of whole clay fractions of KN07D.

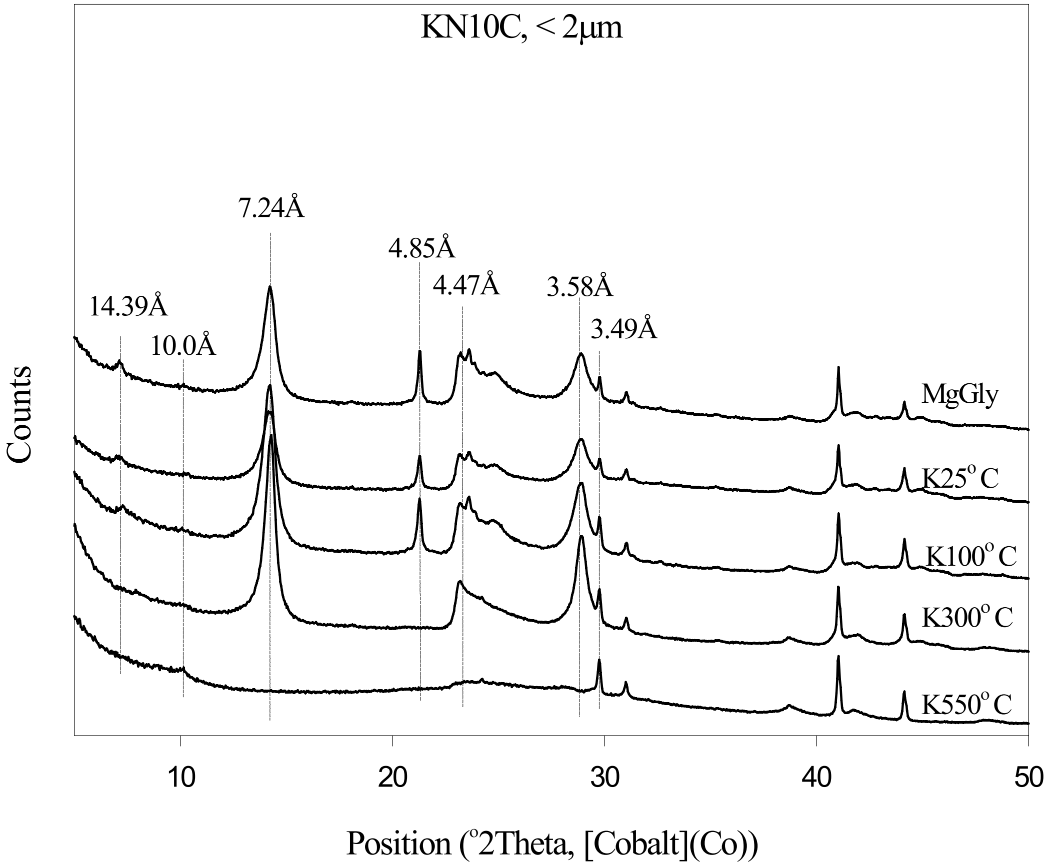


Figure 5.4 X-ray diffraction patterns of Mg-glycerated and 25, 100, 300 and 550°C K-saturated samples of whole clay fractions of KN10C.

The semi-quantitative mineralogical composition was determined based on relative peak intensities (mostly of lower orders). With regards to Kenyan soils, the three geomorphic regions discussed earlier: western uplands, Kisii and Kericho highlands, and eastern highlands (Mt. Kenya region), are represented by XRD patterns of Pedons KN01D KN04C, KN07D, and KN10C. Since there was no significant difference in mineralogical composition with depth, only the XRD patterns of subsurface horizons are shown (Figures 5.1 to 5.4). In general, the whole clay fraction of all Kenyan soils was dominated by broad reflections, probably of poorly crystalline kaolinite/halloysite, indicated by basal peaks at 7.22 and 3.57Å.

Trace quantities of iron oxides (goethite and hematite) were also common in most of the Kenyan pedons, but there were regional differences with respect to the relative proportions of the 2:1 clays and gibbsite. Among the soils in the western uplands hereby represented by KN01D (Figure 5.1), the presence of gibbsite and/or hydroxy-interlayering in the whole clay fraction was not obvious. However, some samples in the same region, represented by KN04C (Figure 5.2), had a weak peak at the 10 Å and 3.33Å regions in the Mg-glycerated samples which were strengthened on heating to 550° C, strongly suggesting the presence of 2:1 phyllosilicates.

Mineralogical composition of the whole clay fractions of Brazilian soils (figures 5.5 to 5.8) was somewhat comparable to most of the Kenyan soils with a few exceptions. Like the Kenyan pedons, there were no significant differences in clay mineralogy of the Brazilian whole clay fractions with sampling depth. Moreover, kaolinite indicated by peaks at 7.17 -7.19 Å and 3.57 -3.59 Å was the dominant clay mineral in all the Brazilian soils.

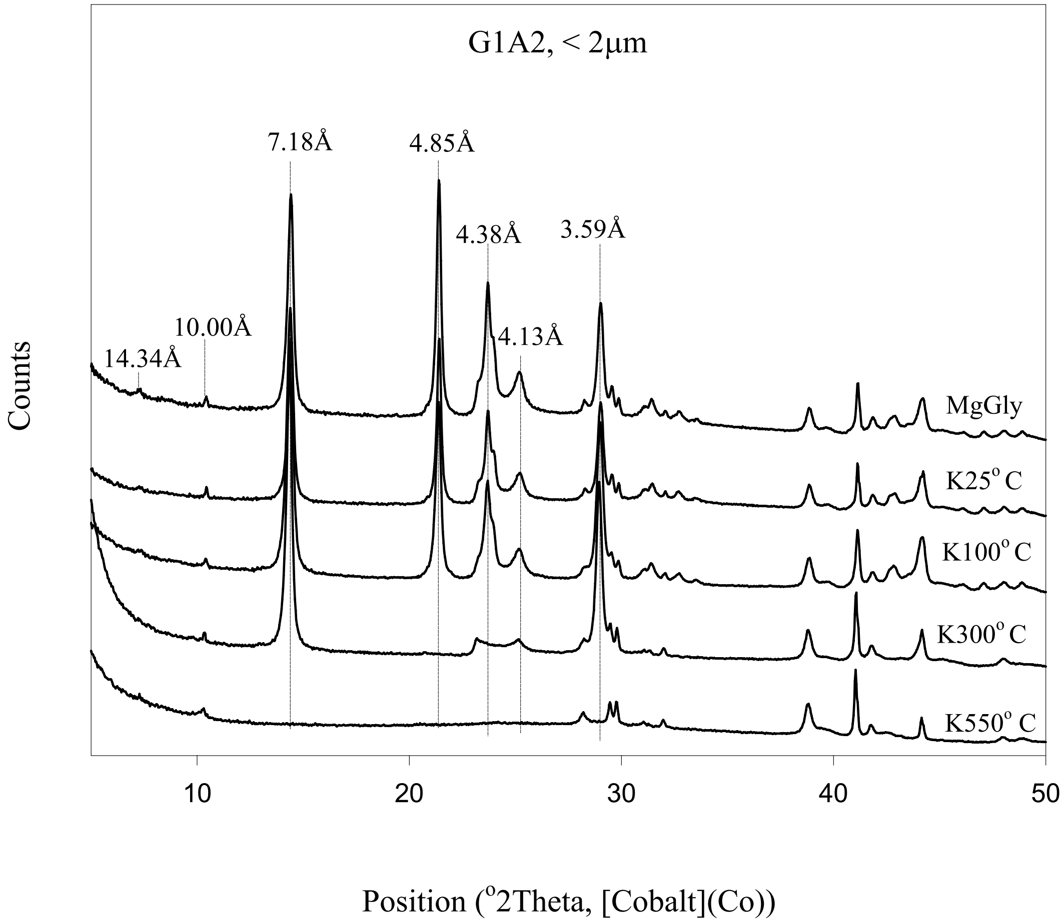


Figure 5.5 X-ray diffraction patterns of Mg-glycerated and 25, 100, 300 and 550° C K-saturated samples of whole clay fractions of G1A2.

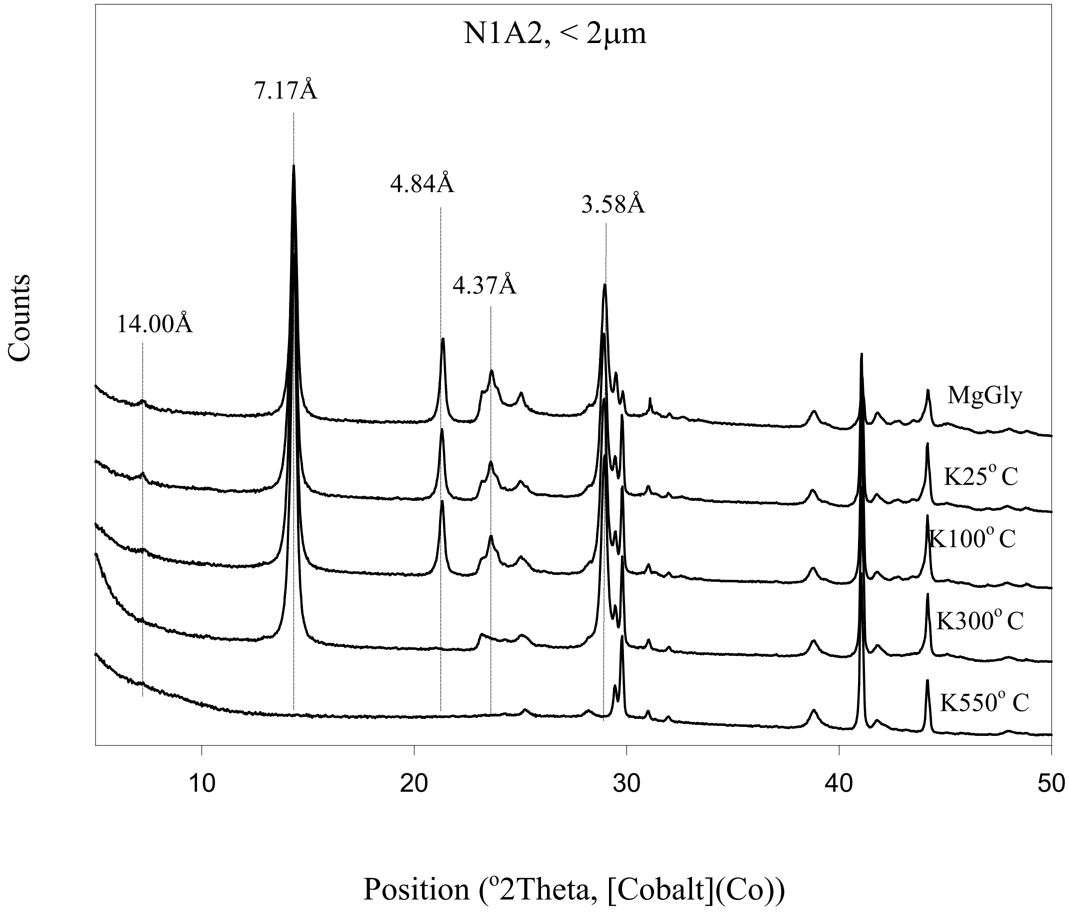


Figure 5.6 X-ray diffraction patterns of Mg-glycerated and 25, 100, 300 and 550° C K-saturated samples of whole clay fractions of N1A2.

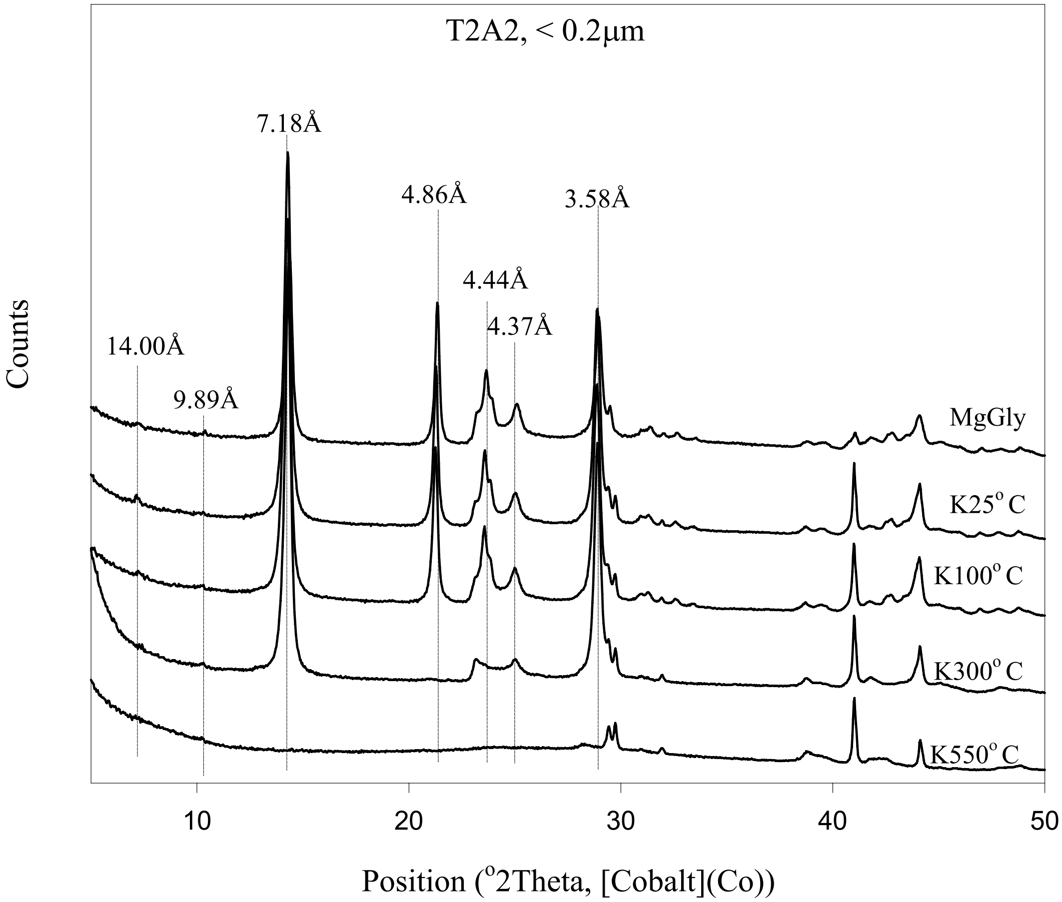


Figure 5.7 X-ray diffraction patterns of Mg-glycerated and 25, 100, 300 and 550°C K-saturated clay fraction of T2A2.

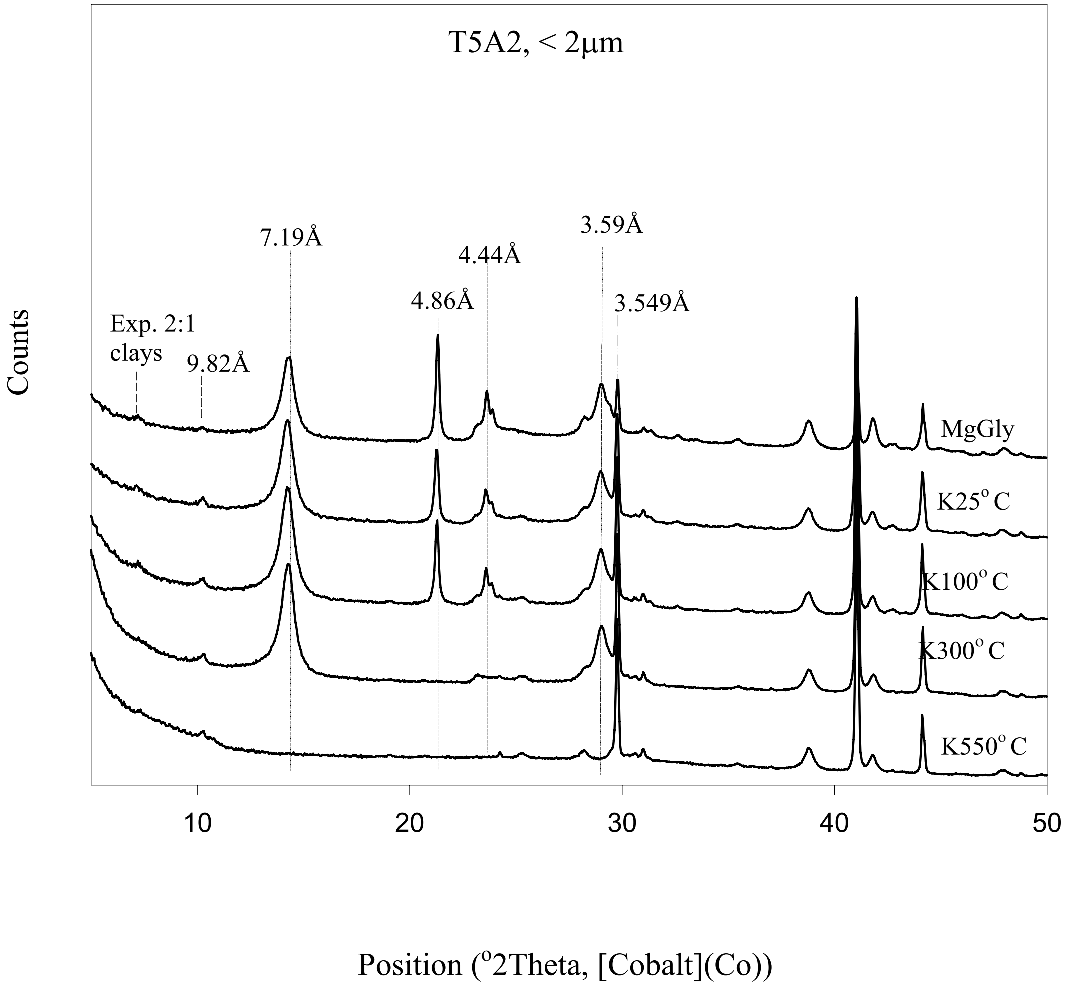


Figure 5.8 X-ray diffraction patterns of Mg-glycerated and 25, 100, 300 and 550° C K-saturated clay fraction of T5A2.

However, kaolinite in the Brazilian samples appeared to be well crystallized as evidenced by the sharpness and intensity of their reflections (Brindley and Brown, 1980). Gibbsite, indicated by 4.84 – 4.86 Å peaks which collapsed on heating to 300°C, was relatively more abundant in all Brazilian pedons, except N5. Among the Brazilian soils, pedon N5 is unique because of relative abundance of 2:1 clay minerals, suggested by 9.82Å and 4.94 Å peaks, both in the Mg-glycerol treatment and K saturation. The 9.82 Å peak was strengthened on heating to 550° C, suggesting the presence of trace amounts of mica.

Although the presence of 2:1 clays and gibbsite in some of the soils studied may be small; they play a significant role in fertility and productivity. For instance, the presence of 2:1 clays corresponded to greater CEC or exchangeable K levels and base saturation in some Kenyan and Brazilian soils. On the other hand, the abundance of gibbsite in some profiles was in agreement with the high Al saturation percentages observed in some of these soils.

XRD–Based Measurements

The XRD patterns were semi-quantitatively evaluated based on the relative abundance of the various clay minerals identified in the samples. An ordinal scale (from 0 to 2 or 3) was used; where 0 corresponds to absence or undetectable levels; and 2 or 3 to the highest levels detectable, as indicated by the relative peak sizes (intensities and area under peak). These numbers were then converted into symbols varying in sizes as a representation of the relative abundance (Table 5.2) of these clay minerals.

Table 5.2 Relative contents of various clay minerals in Kenyan whole clay fraction

Sample ID	2:1 Expandable clays	Mica	Kaolinite /Halloysite	Gibbsite
KN01A		•	•	
D		•	•	
KN02A		•	•	
C		•	•	
KN03A	•	•	●	
C		•	●	
KN04A	●	•	⬤	•
C	●	•	⬤	•
KN05A	•	•	●	
C	•	•	●	
KN06A	•	●	●	
B	•	●	●	
KN07A	•	●	●	
D	•	●	●	
KN08A		•	•	•
C		•	●	•
KN09A	•		•	●
C	•	•	•	●
KN10A	•	•	•	•
C	•		●	●
KN11A	•	•	●	●
D	•		•	•

Table 5.3 Relative contents of various clay minerals in Brazilian whole clay fraction

Sample ID	2:1 Expandable clays	Mica	Kaolinite /Halloysite	Gibbsite
G1A1		•	●	⬤
A2		•	●	⬤
G2A1	•	●	●	⬤
A2		●	●	⬤
N1A1	•	•	⬤	●
A2	•		⬤	●
N2A1	•		⬤	●
A2	•		⬤	●
N5A1	•	●	⬤	
A2	•	●	⬤	
T1A1	•		●	⬤
A2	•		●	⬤
T2A1	•	•	⬤	⬤
A2	•		⬤	⬤
T4A1			•	●
A2	•	•	●	⬤
T5A1	•	•	•	●
A2	•	•	•	●
G1A1		•	●	⬤
A2		•	●	⬤

The d(001) values, full width at half maximum peak height (FWHM) and asymmetry index (AI) for kaolins in the whole clay fraction were also determined. Maximum peak height, full width at half maximum (FWHM) and the position of each d-001 peaks were estimated after normalizing the baseline and correcting for position shifts using corundum as a standard (corundum disks were used as sample holders). Because most of the d(001) peaks were skewed towards the low angle region, the peaks (and hence FWHM) were divided into two parts with reference to the maximum peak height line, normal to the FWHM line. The Asymmetry index was calculated as a ratio of the narrowest to the widest sections of the FWHM line. An asymmetry value of 1 implies perfect symmetry while values other than 1 imply asymmetry. The relationships among these parameters are presented in figures 5.9 and 5.10. The d(001) values varied from 7.18 to 7.26 Å with a mean and median value of 7.20 Å for the Kenyan samples. The d(001) values of kaolins in the Brazilian samples ranged from 7.15 to 7.22 Å with mean and median of 7.17 Å. As a group, the d(001) values of Kenyan soils were statistically different from those of the Brazilian samples ($p < 0.001$).

The FWHM of the Kenyan kaolins ranged between 0.38 and 1.07° 2θ with a mean and median value of 0.77° 2θ. Particularly, kaolins in pedon KN04 had the narrowest peaks and the most intense peaks of all the Kenyan samples. On the other hand, the FWHM of the Brazilian kaolins ranged from 0.30 to 0.76° 2θ with mean and median value of 0.34° 2θ. Over all, the FWHM values of Kenyan samples were statistically greater than the Brazilian set ($p < 0.001$).

Although not statistically significant, the asymmetry index also varied among the samples analyzed, with relatively greater values observed for most of the Kenyan samples. An asymmetry index of 1 was only observed in pedon KN04, suggesting that the kaolins in this pedon may be morphologically different from the others.

A weak linear relationship ($R^2 = 0.436$, $p < 0.001$) was observed between AI and FWHM values of the Kenyan samples, but no relationship of any sort was observed for the Brazilian samples (Figure 5.9). Although FWHM may be inversely related to the size of coherently diffracting domains, variations in the d(001) values may not only be due to small crystal size but also due to interstratification with 2:1 clay minerals (Singh and Gilkes, 1992).

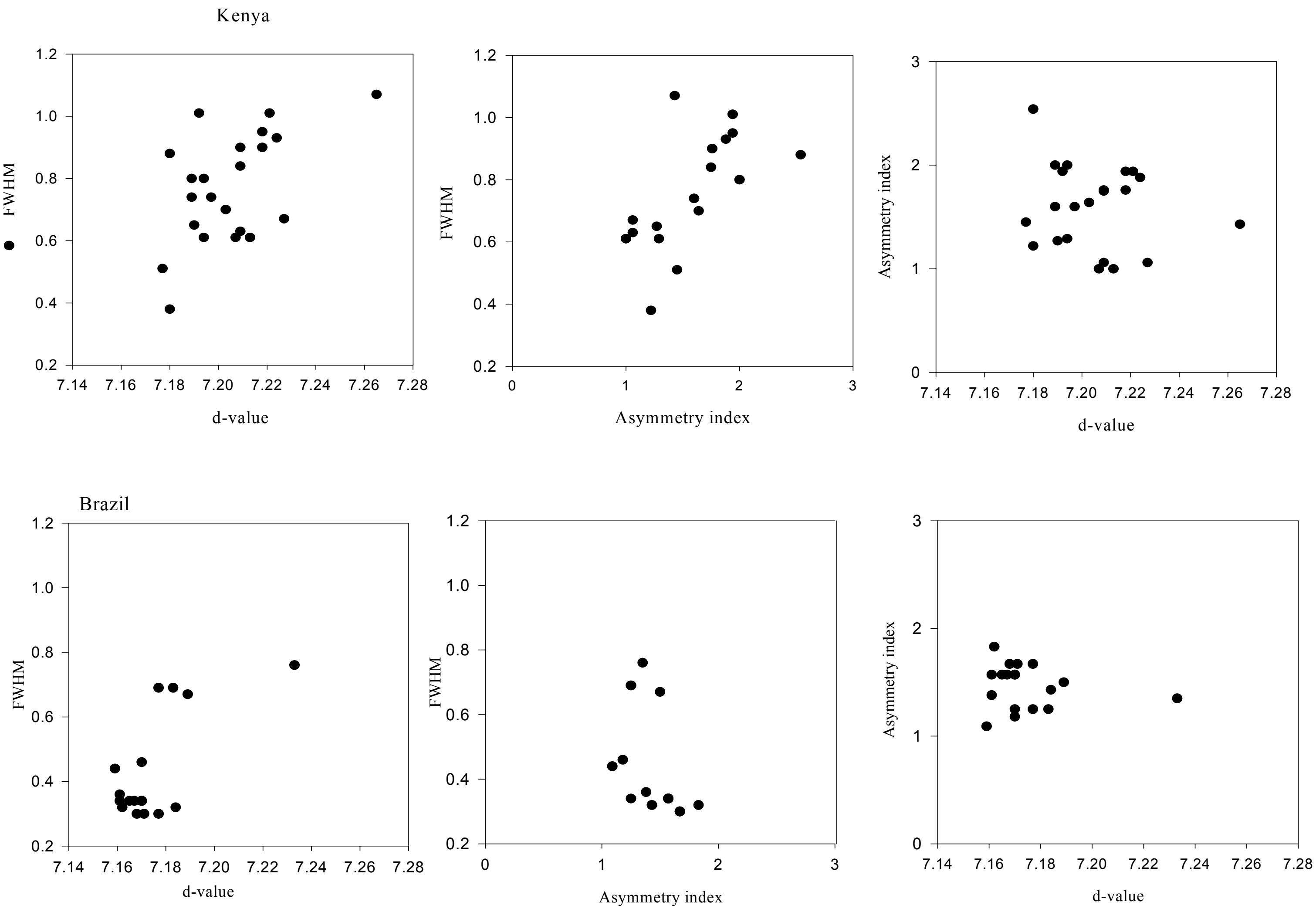


Figure 5.9 Scattergrams of various properties of kaolins in Kenyan and Brazilian whole clay fraction (FWHM in 02θ and 001 d-value in Å).

Intercalated clays

The reactivity of Kenyan kaolins towards DMSO intercalation varied from sample to sample and differred significantly from the standard kaolinite (KGa-1b). The XRD patterns of the DMSO intercalated clays are presented in Figures 5.10-15. Variation due to kinetic factors such as reaction time also was observed; where some samples were only expanded after allowing to dry 72 hours, while others expanded either after a short contact time or after drying for 2 hours. Although the extent of intensification of the 11 Å peaks varied with equilibration time after mounting the samples on the ceramic tiles, relatively more intense peaks might have resulted due to a greater ordering of DMSO in the interlayer or drying off of the excess DMSO in some samples. The effect of reaction time on the rate of intercalation may in turn be related to particle morphology. For example, Georgia (KGA-1b) kaolinite which is relatively pure and is comprised of relatively large crystals was fully expanded at around 11.2 Å immediately following DMSO treatment. In contrast, most of the Kenyan kaolins studied expanded only to a relatively smaller extent under the same conditions. In particular, KN01D did not yield the expected 11 Å reflection, regardless of the treatment time. At the same time; its 7 Å reflection was generally weak and broad.

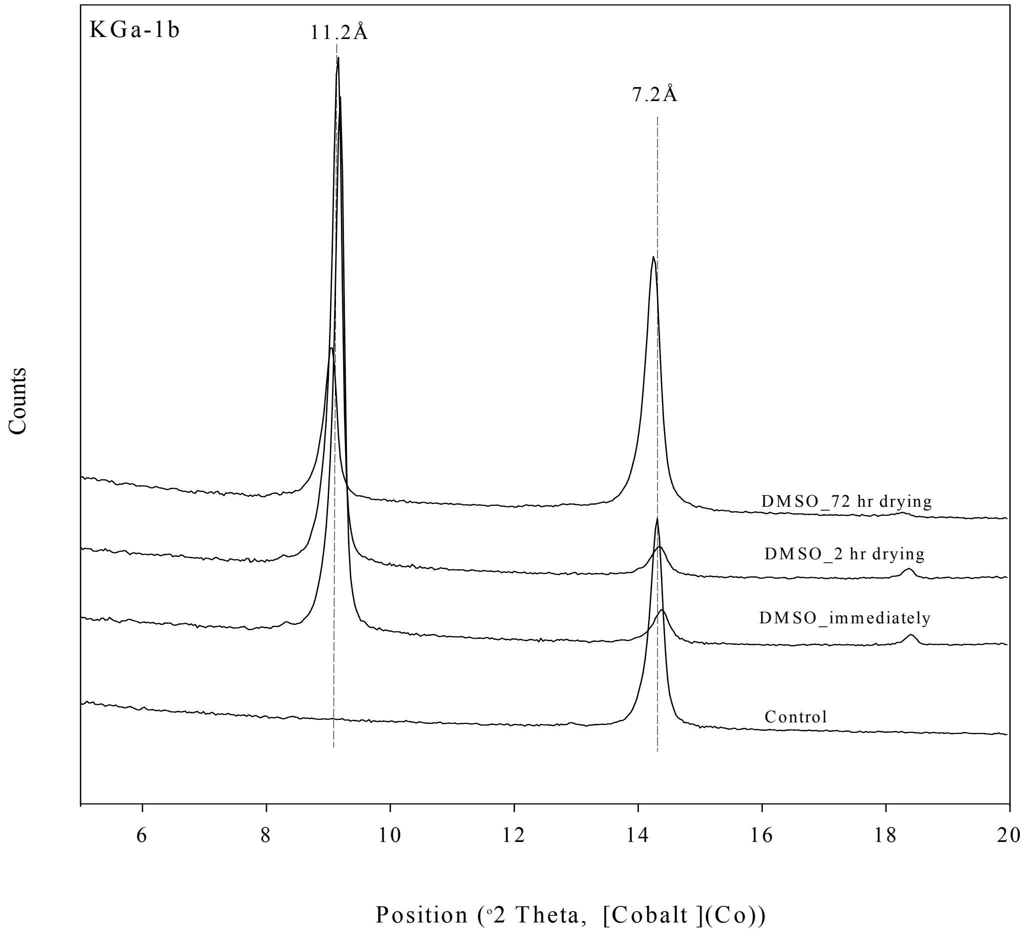


Figure 5.10 XRD patterns of Georgia kaolinite (KGa-1b) treated with DMSO.

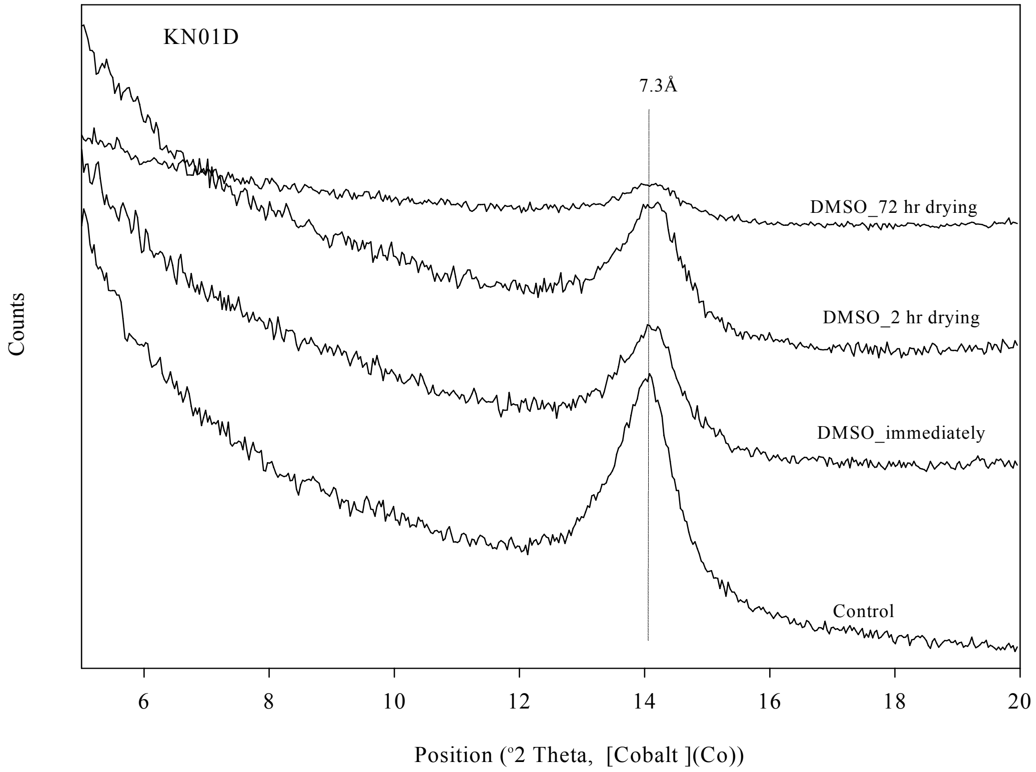


Figure 5.11 XRD patterns of the clay fraction of KN01D treated with DMSO.

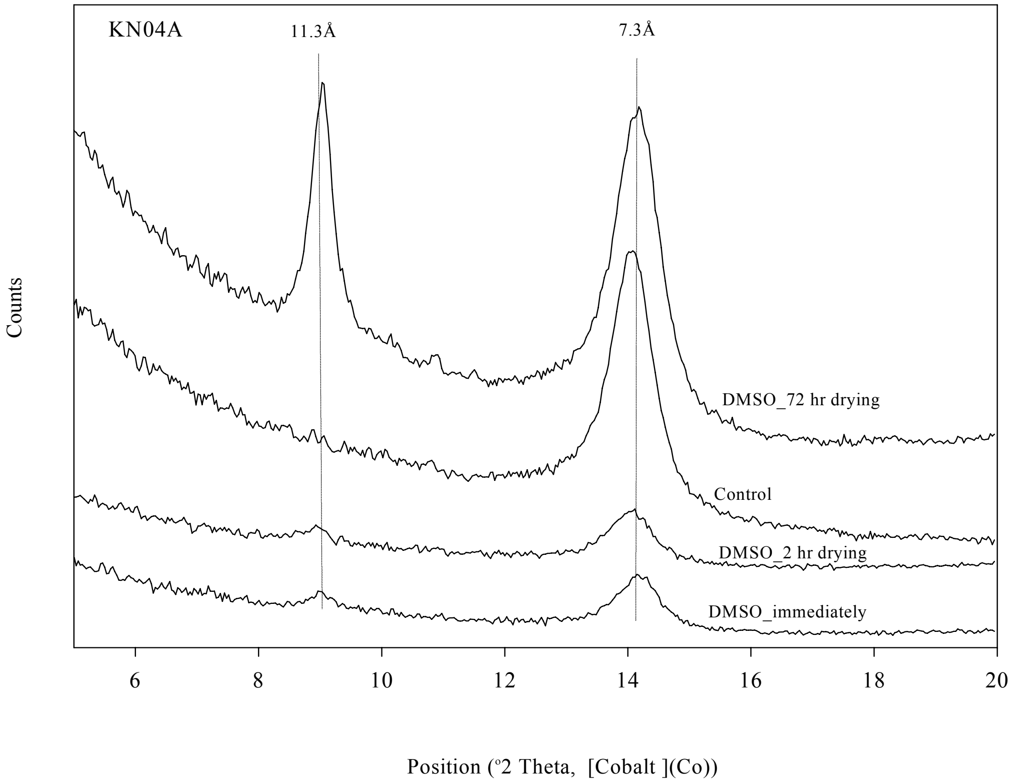


Figure 5.12 XRD patterns of the clay fraction of KN04A treated with DMSO.

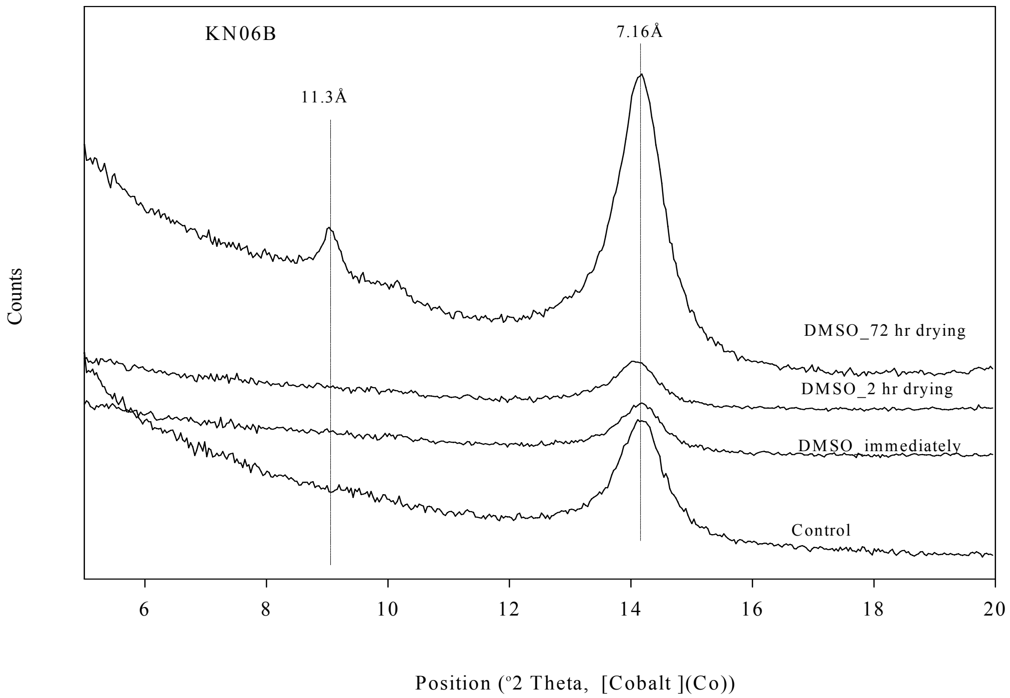


Figure 5.13 XRD patterns of the clay fraction of KN06B treated with DMSO.

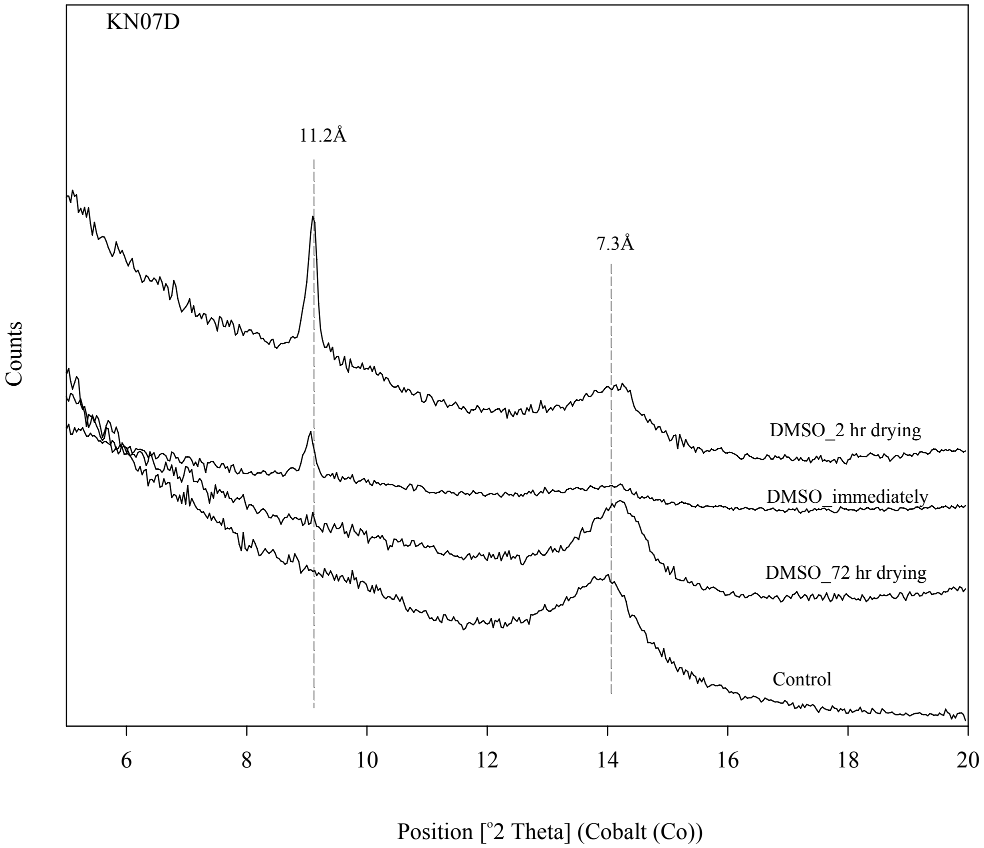


Figure 5.14 XRD patterns of the clay fraction of KN07D treated with DMSO.

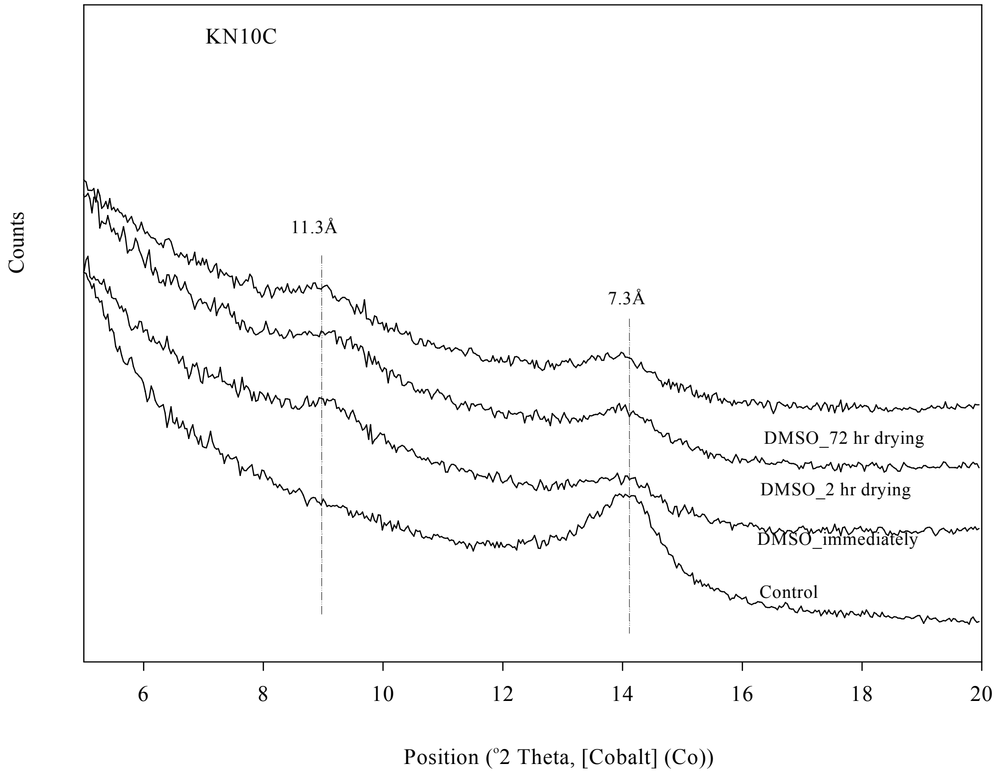


Figure 5.15 XRD patterns of the clay fraction of KN10C treated with DMSO.

On the other hand, a relatively intense 11.3 Å peak was observed only in KN04A after about 72 hours. Although sample KN06B had a relatively intense 7.3 Å peak, the 11.3 Å was weak suggesting perhaps that intercalation was incomplete. Sample KN07D had a very broad 7.3 Å reflection, however, its reflection at 11.3 Å collapsed after 72 hrs, probably due to evaporation of DMSO. For KN10C, there were only broad reflections at 7.3 and 11.3 Å positions, but reaction time did not affect the extent of intercalation.

From these observations, it was particularly difficult to conclusively differentiate samples containing kaolinite and halloysite. The results clearly point out that some other factors may be responsible for the variations in the observations made on these soil kaolins. Some possible factors include existence of an intimate mixture of varying proportions of disodered kaolinite and halloysite in these soils, presence of impurities or other clay minerals (such as allophane, Fe and Al oxides), poor crystallinity, smaller particle size, interstratifications and degree of hydration, among others could be responsible for this uncertainty.

Transmission Electron Microscope of the clay fractions

Transmission electron micrographs of representative Kenyan clays are shown in Figures 5.16-18. These electron micrographs clearly demonstrate the wide range in size and morphology of the crystals present in a single sample. From the micrographs, kaolinite was identified as the dominant clay mineral in all the samples studied.

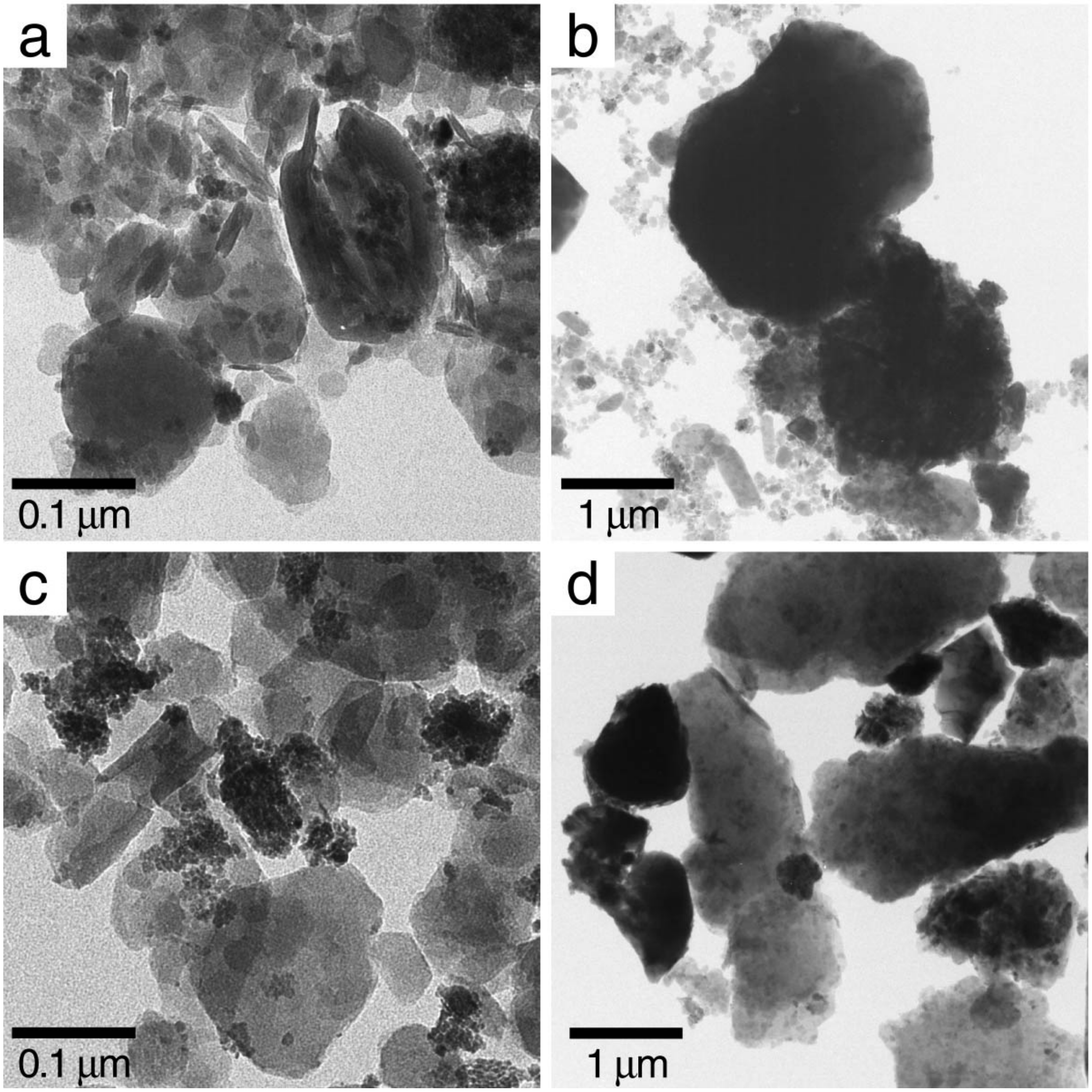


Figure 5.16 Transmission electron microscope (TEM) micrographs of particles from the clay fractions of some representative Kenyan soils: (a) KN01D < 0.2µm (b) KN01D 2-0.2 µm (c) KN04A < 0.2µm (d) KN04A 2-0.2µm.

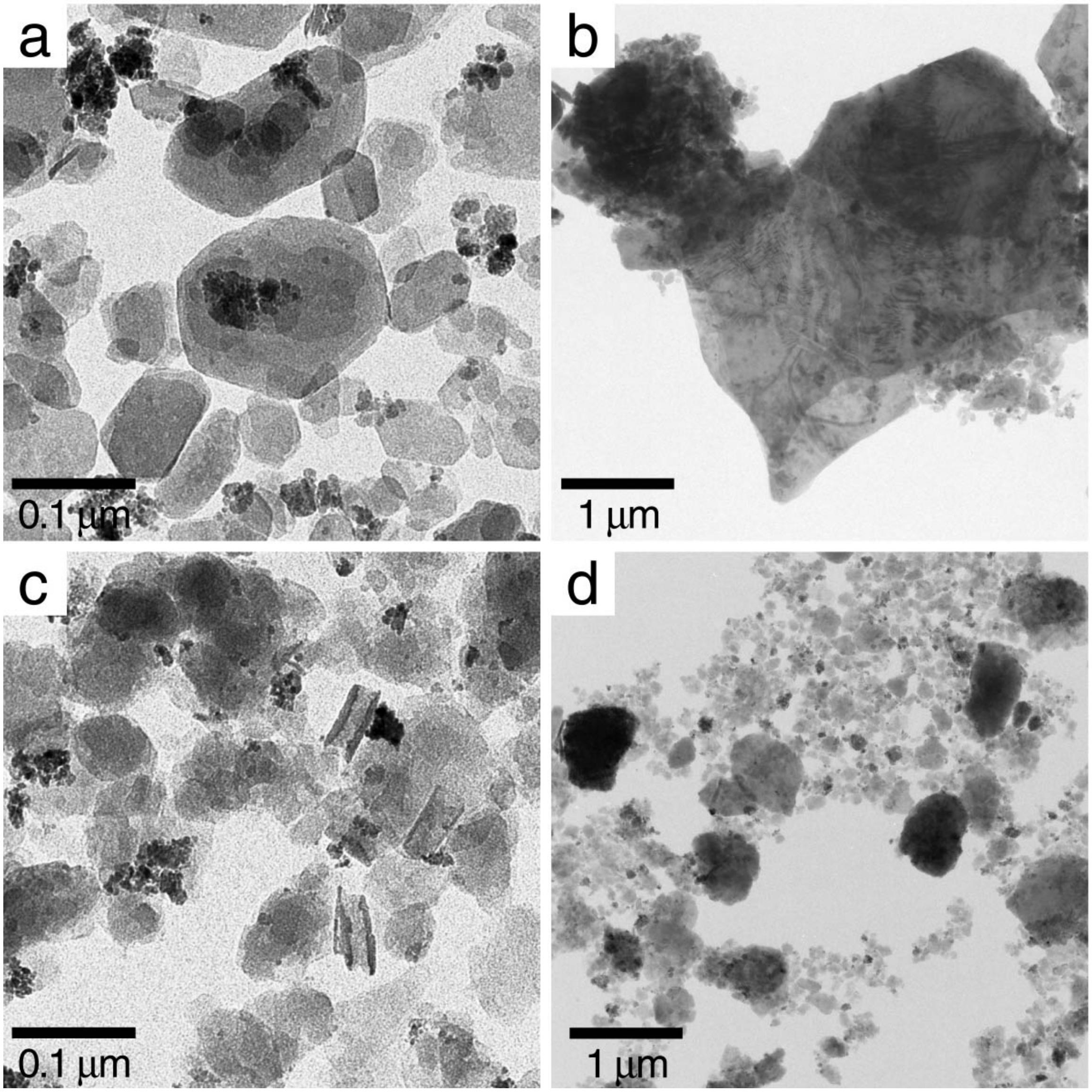


Figure 5.17 Transmission electron microscope (TEM) micrographs of particles from the clay fractions of some representative Kenyan soils: (a) KN06B < 0.2 μm (b) KN06B 2-0.2 μm (c) KN07D < 0.2 μm (d) KN07D 2-0.2μm.

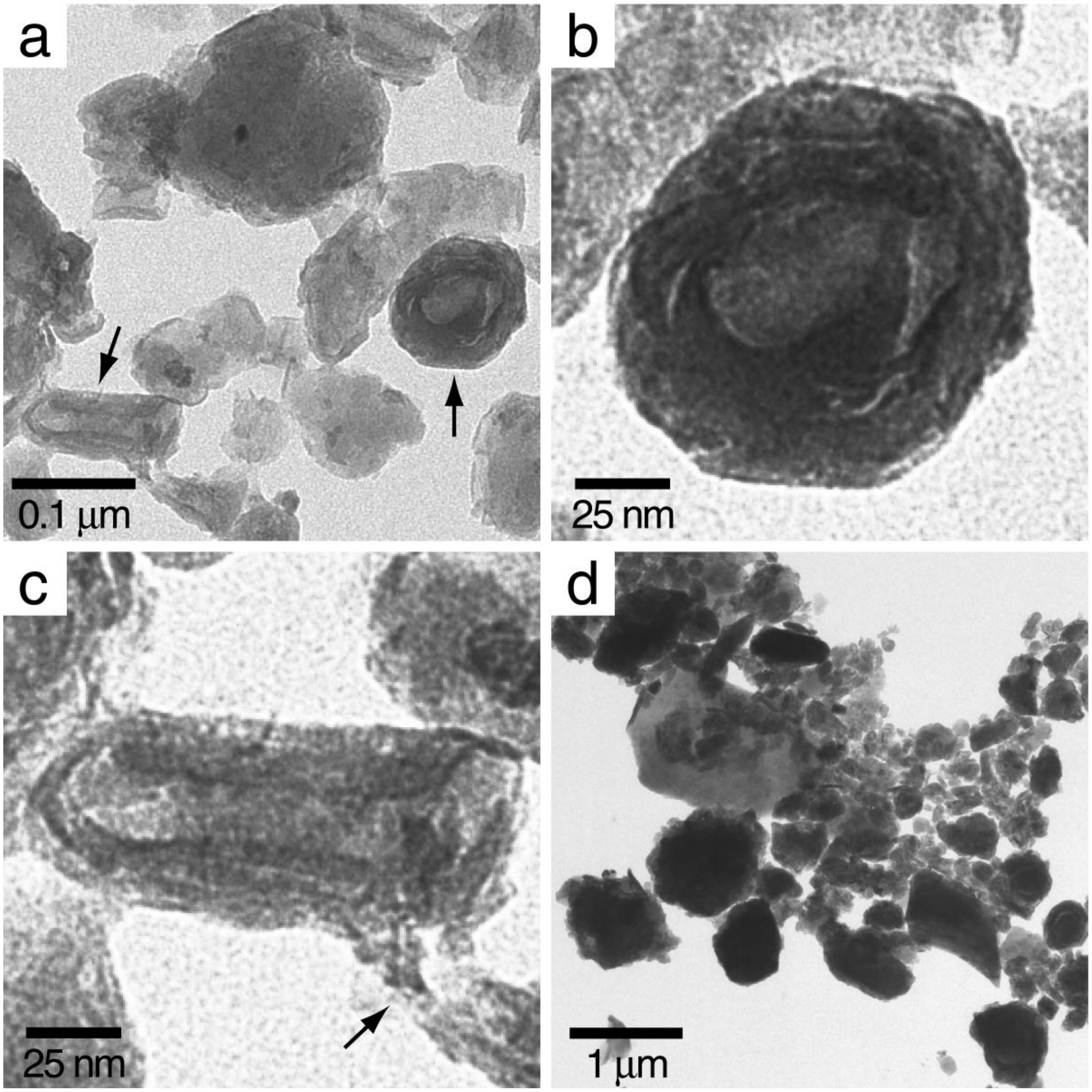


Figure 5.18 Transmission electron microscope (TEM) micrographs of particles from the clay fractions of KN10C (a) < 0.2µm (b) halloysite shaped like cabbage head in KN10C < 0.2µm (c) rolled-up halloysite in KN10C < 0.2µm. Note the amorphous material pointed at by the arrow and (d) KN10C, 2-0.2µm.

However, the clay samples generally consisted of intimate mixtures of various sizes of platy, spherical, tubular, lath or scroll shaped particles identified as kaolinite, halloysite and probably gibbsite. Although XRD analysis showed that gibbsite was present in a number of samples, it was difficult to distinguish gibbsite from kaolinite particles in these mixtures based on particle size and morphology alone. This difficulty arises because both kaolinite and gibbsite particles can sometimes occur as pseudohexagonal plates (de Souza Santos et al., 2005).

The presence of halloysite in these samples was suggested by the presence of laths and several sheets curled up at their edges, like scrolls. The tubular halloysite-like domains co-existing with spheroidal crystals was more peculiar to sample KN10C, which might have weathered from volcanic glass. There also were composite particles, approximately round in shape that appeared to be made up of numerous partly spherical and partly flat segments resembling a cabbage head. Occasionally, their central segment appeared void resembling doughnuts. These were more prominent only in the fine clay fraction of KN10C. In some cases, the smaller kaolinite crystals were generally poorly crystalline. Amorphous materials are present in KN10C are thought to be allophane (Figure 5.18(a) and (c)).

General micromorphology and chemical composition of the sand fraction of representative Kenyan soils (by SEM-EDX)

Scanning electron microscope examination of sand particles showed a wide variation in surface morphology as shown in Figure 5.19. A number of large particles appeared to have numerous etch pits of various sizes. These etch pits provide substantial evidence of aqueous dissolution and alteration of primary minerals like feldspars. The etch pits, which are essentially formed in closed aqueous systems, may be influenced by the soil drainage conditions and the associated geochemical environments.

In addition to etch pits, a number of particles also had coarse, spongy-looking surfaces which appeared like precipitates of secondary minerals or clay coatings. A microscopic examination of some of these surface features revealed what appeared to be continuous layers of weathering products adhering strongly to the surface. There is a possibility that these surface features may be areas of deposition of materials from dissolution and subsequent re-crystallization on the surface of the mineral particle. Alternatively, leaching also could result in such coarse surfaces.

Chemical composition (determined by EDX) of some of these particles which seemed to have coarser surfaces reveal enrichment of Al in some particles and depletion in others as evidenced by the variation in Si:Al ratio, which varied around the typical 1:1 and 2:1. Kaolinite is an example of some of the stable secondary minerals which may form during weathering of silicate materials, and may form surface coatings on sand particles. Luce, et al. (1972) suggested that ferromagnesian (dark colored minerals rich in Fe and Mg) minerals undergo dissolution during weathering by the formation of a protective layer of altered chemical composition on the surface. Figure 5.14(d) shows what appears to be a protective layer beginning to peel off from a particle.

In addition to clay minerals, SEM analysis revealed that pedon KN10C was unique in that it contained very porous, pumice-like and partially weathered glassy materials (Figure 5.20) which are typical constituents of volcanic-ash derived soils. This observation supports the hypothesis that soils around the Mt.Kenya region were formed from porous igneous volcanic rocks, and thus were easily leached, resulting in low soil fertility.

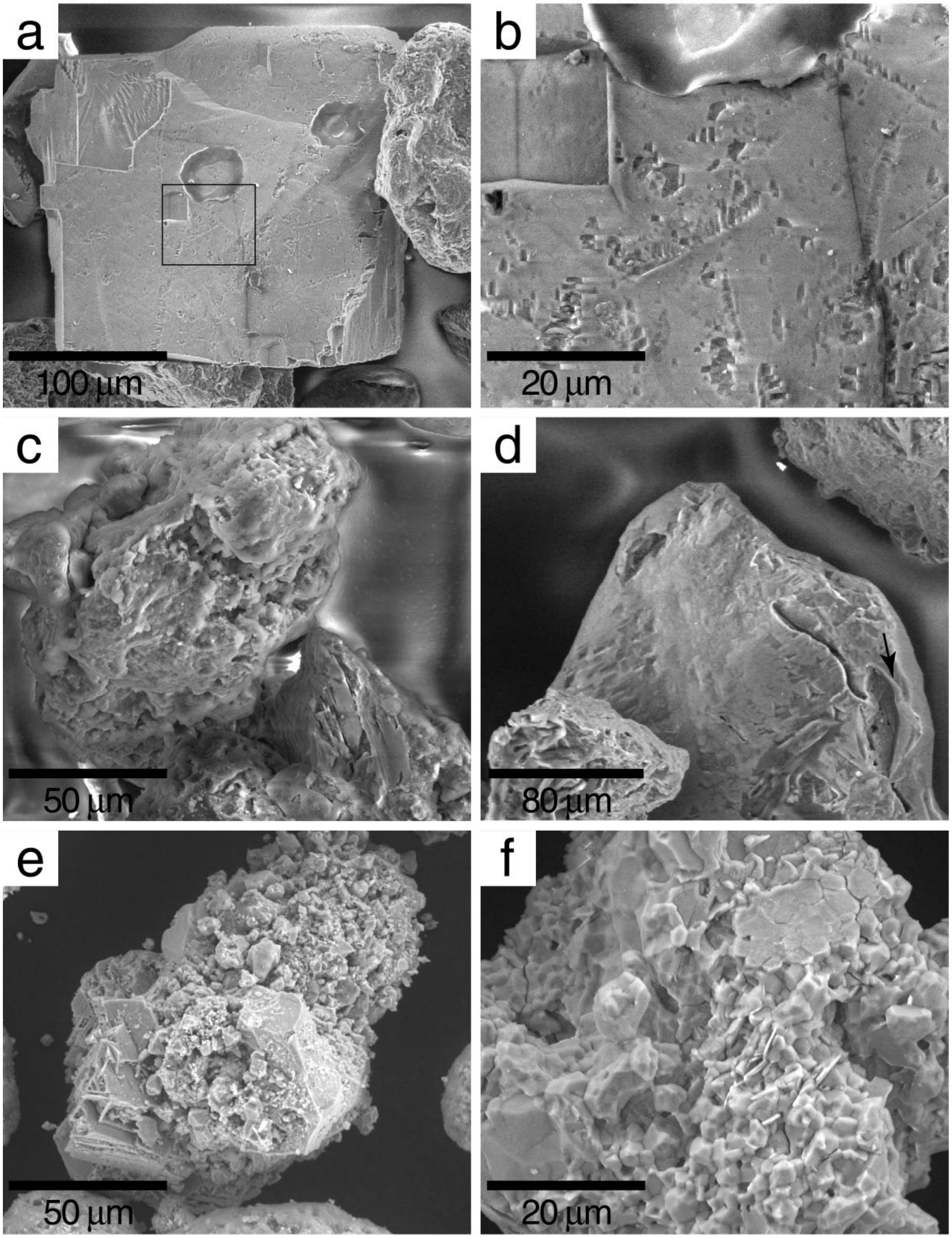


Figure 5.19 SEM photomicrographs (a) etch pits on feldspar in sand fraction of KN01D at 1000 x and (b) 5000 x (c)microscopic particles clinging (looks like crystal growth) on the surface of a Na-rich 1:1 mineral (KN01D), (d) what appears to be a protective layer at the surface is peeling off, (e) Fe- and Ti-rich 1:1 mineral in KN010C, and (f) surface of a Na-rich 1:1 mineral in KN06B.

Further, chemical composition from EDX also indicates the abundance of quartz in the sand fraction of the soils studied. This is in agreement with the XRD analysis of the same soils. Quartz abundance may be explained by the following facts: (1) It is the second most abundant mineral, after feldspars, in the earth's crust, and (2) it is highly resistant to weathering (Allen and Hajek, 1989). Some of the quartz grains also showed signs of etching and pitting on the surface suggesting eventual dissolution under extreme or prolonged weathering conditions; which is likely in older tropical landscapes. Although quartz is mostly inherited from the parent materials, there is evidence of secondary quartz formation. Figure 5.21 is an illustration of the biogenic quartz grain identified in KN01D. An EDX analysis of a section of this particle (Figure 5.21, spectrum a) indicates unusually high carbon content, suggesting that this may be a biological artifact, resulting from Si-cycling by plant roots.

One of the unexpected observations was the presence of substantial amounts of Na in many particles (Figures 5.21 (a), (b) and (d), and 5.22 (KN01D), suggesting either the presence of plagioclase feldspars such as albite or feldspathoids (such as nephelene). In spite of the fact that the parent materials of some of these soils were originally Na-rich, high Na content was not expected since sodium is easily leached and is likely to be lost in the early stages of mineral weathering. Another possible explanation is the substitution of Na for K in the phyllosilicates during mineral weathering as a result of the Na-rich geochemical environment. However, the level of Na determined by EDX is in agreement with the relatively greater exchangeable Na content in this set of soils.

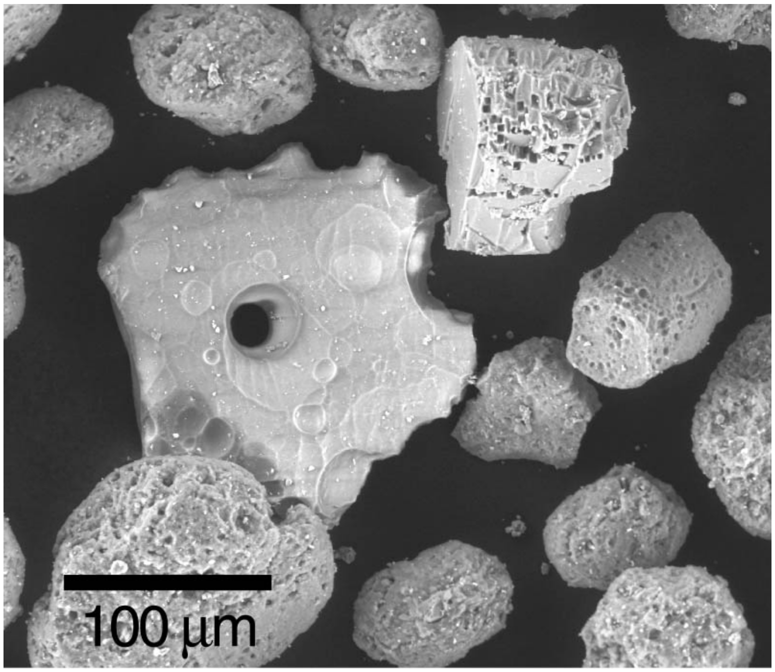


Figure 5.20 SEM photomicrograph of glassy material and pumice-like particles identified in KN10C.

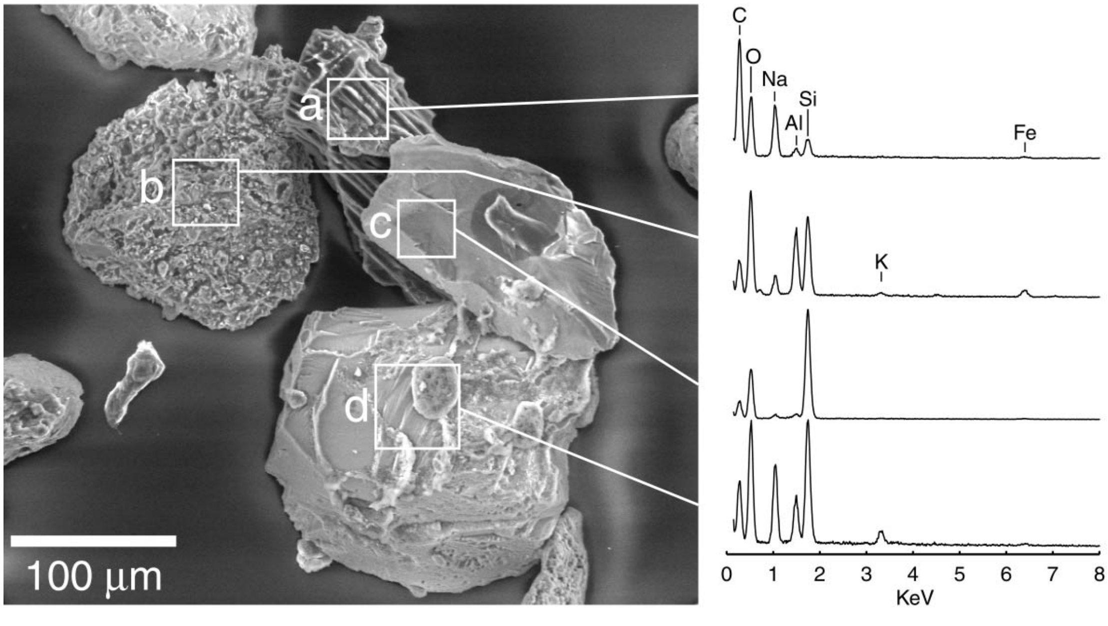


Figure 5.21 SEM photomicrographs of KN01D, showing biogenic quartz particle (a).

A number of samples also had traces of titanium which is usually a key component of accessory minerals like anatase and rutile, which do not have any significant contribution to the productivity of soils.

Although some of the soils also were described as derived from ferromagnesian minerals such as olivine (Chapter 2), there was no indication of any remnant of these minerals in any of the soils studied. This is particularly due to the fact that minerals like olivine are very unstable in pedogenic environments (Jackson and Sherman, 1953). It was therefore not surprising that only traces of Mg and no Ca at all could be detected in these samples by the EDX analyses. This observation is reinforced by the fact that these soils, particularly due to their pedo-climatic environments, have been exposed for long periods to selective dissolution and subsequent chemical leaching loss of Ca and Mg, in addition to plant uptake due to intensive cultivation.

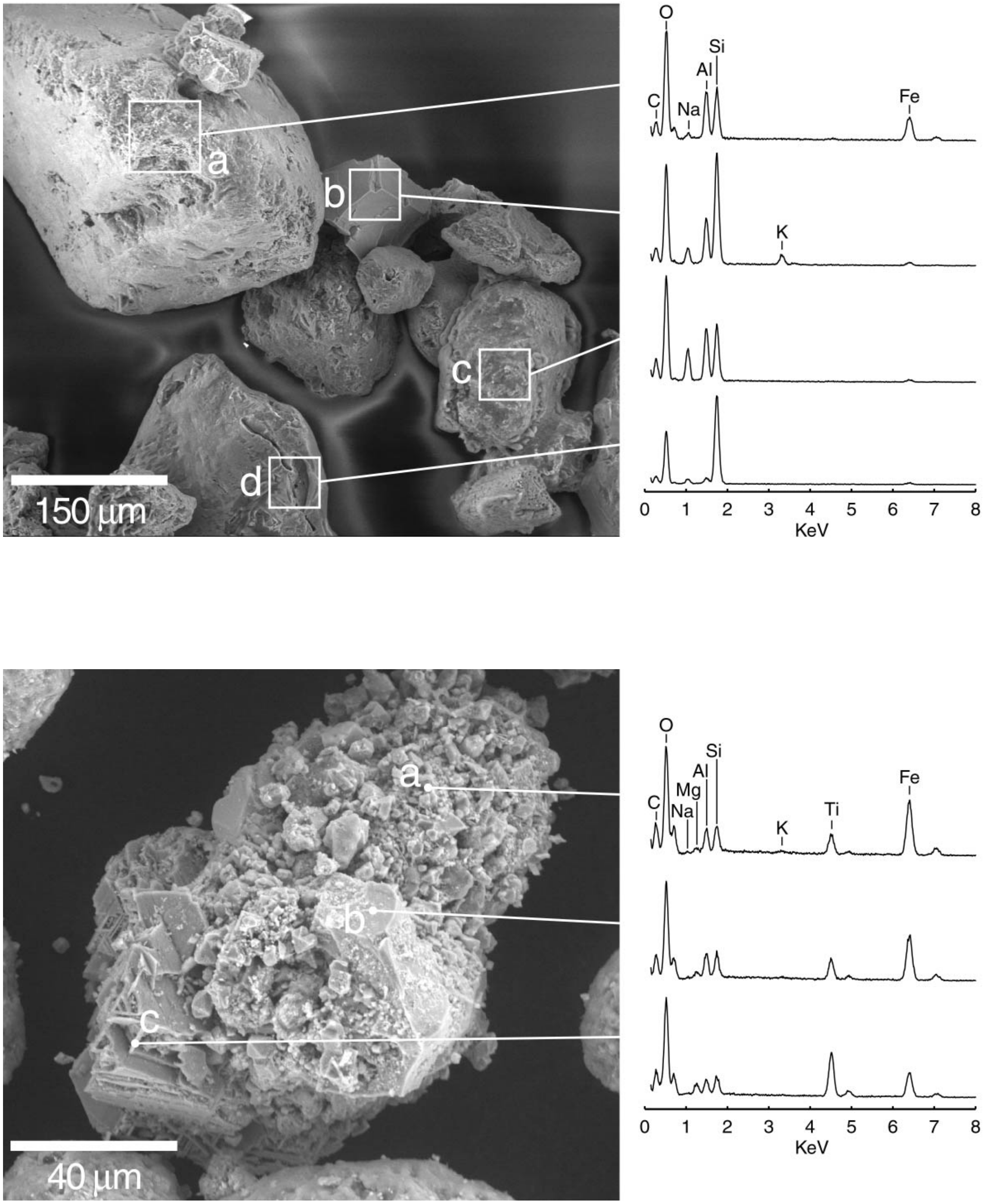


Figure 5.22 SEM images and EDX data of representative Kenyan soils: KN01D (top) and KN10C (bottom).

However, Fe, which is a key constituent of these primary minerals, was relatively abundant in many particles studied suggesting presence of significant amounts of structural iron or iron oxides. Some of the iron could have been released during the weathering of Fe-bearing primary minerals.

Thermo-gravimetric analysis (TGA) of the fine clay

Typical TGA curves of the clay samples are shown in (Figure 5.23). The TGA curves show three distinctive weight loss stages when the samples were heated from 25 to 1000° C. The three weight loss events in the TGA curves and their first derivatives (Appendix L) at 25 - 200° C, 200 - 300° C and 400 - 600° C, yielded total weight loss is in the 12.75 – 17.50 % range. The shape of the TGA curves also show that the Kenyan samples generally experienced weight loss at the same temperatures; however, there are differences in the magnitudes. The extent of weight loss at various temperature ranges are summarized in Table 5.4. Therefore, according to the TGA curves shown in Figure 5.18 and Appendix N, the first endothermic peak is related to the evolution of the physically adsorbed water by the clay particles (molecular water).

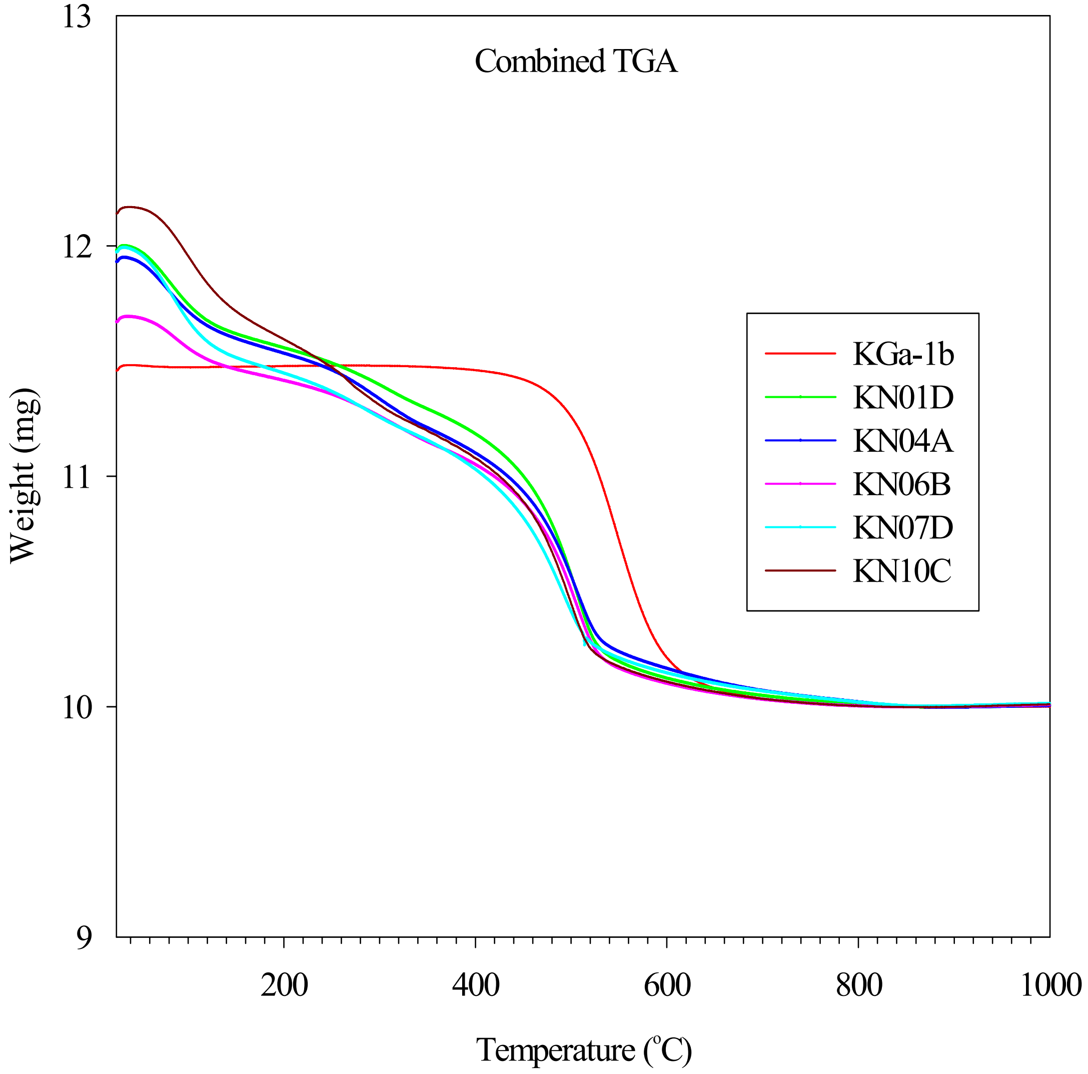


Figure 5.23 Thermal gravimetric analysis (TGA) of representative Kenyan clays and Georgia kaolinite.

Table 5.4 Weight loss during thermal gravimetric analyses of representative Kenyan clays and Georgia kaolinite.

Sample ID	Percentage weight loss at 25-200° C	200-300° C	400-600° C	Total
KGa-1b			12.75	12.75
KN01D	3.67	2.98	9.90	16.55
KN04A	3.44	3.42	9.32	16.18
KN06B	2.11	2.66	9.56	14.33
KN07D	4.42	3.82	8.09	16.33
KN10C	4.43	4.17	8.90	17.50

The second weight loss occurs due to the evolution of water resulting from the dehydration of gibbsite (200-300° C) and its subsequent transformation into a transition alumina phase. The third weight loss (400-600° C) is associated mainly to dehydroxylation of kaolinite (and/or halloysite/metahalloysite, which transforms into metakaolinite. The endothermic event related to the loss of interlayer water in halloysite probably could have overlapped the loss of molecular water in the first endothermic peaks, occurring below 200° C. The amount of moisture lost in this stage was variable among the Kenyan soil clays, but generally negligible for KGa-1b.

On average, kaolinite can loose up to 14 % structural water during thermal analysis (White and Dixon, 2002).

In this study however, the amount of structural water loss was estimated to be ~ 12.75% for Georgia kaolinite. Over all, the Kenyan clays lost more weight on heating than Georgia kaolinite. From these data, it can therefore be concluded that the clay minerals of the studied Kenyan samples consist of a mixture of kaolinite, halloysite and gibbsite with great predominance of kaolinite.

However, differentiation of halloysite from kaolinite in these samples may be subject to uncertainties, due mainly to the fact that the shape, position and area of the dehydroxylation may be affected by a number of factors such as particle size, crystallinity, type of isomorphic substitution, mechanical treatment and impurities such as allophanes (Franco and Ruiz Cruz, 2004). In general, observations from this experiment are consistent with the chemical, X-ray diffraction and TEM results in which kaolinite and/or halloysite were the dominant clay mineral present in all samples, but not easily distinguishable.

Summary of mineralogy

The results presented above demonstrate the diversity of the chemical and morphological properties of the dominant minerals in these soils. This diversity was observed among soils and among size fractions within the same soil. The extent of diversity appears to be related to the parent materials and the prevailing weathering conditions and is reflected in the differences in the chemical and physical properties of these soils as described in previous chapters. The results have shown that kaolinite/halloysite is the dominant clay mineral(s) in the clay fraction of these soils, followed by gibbsite. Quartz is the dominant mineral in the coarser fractions. The presence of smaller proportions of expandable 2:1 clay minerals has been highlighted, as well as the possibility of mixed-layer minerals, though in smaller proportions. With respect to kaolinite, the great morphological diversity, besides very small particle size, poor crystallinity and the presence of structural iron may enhance dissolution process under acidic soil conditions. However, other than chemical analyses, noncrystalline materials and iron oxides were not accounted for in these mineralogical analyses.

The trends within the profiles and physiographic provinces suggest different relative weathering intensities. The presence of kaolinite/ halloysite, gibbsite, and 2:1 phyllosilicates in a decreasing order in these profiles indicates advanced stages of soil development. The soils formed from porous volcanic ash deposits (Mt. Kenya region) were generally greater in gibbsite, again suggesting favorable conditions for continued weathering, neoformation and increasing dominance of kaolins. Favorable environmental conditions are those that would allow leaching of exchangeable bases including silica, leading to re-precipitation of kaolinite and gibbsite. Among the Kenyan soils, high leaching intensity can be attributed to higher precipitation and greater porosity.

CHAPTER 6. SUMMARY AND CONCLUSIONS

Considering the population pressure on land in the Kenyan highlands and the predominance of marginal lands in the rest of the country, research on soil resources for agricultural production under humid and semi-humid environments is a priority. Soils under humid and semi-humid tropical conditions are highly weathered, and most of them are acidic. Although problems associated with soil acidity are many and interrelated, the principle of limiting factor theory implies that crop growth and yield is limited by the nutrient that is in shortest supply. Relative supply of nutrients on the other hand, is particularly complicated by nutrient balance: An excessive supply of one essential nutrient may inhibit plant absorption of another, particularly between the exchangeable bases in non calcareous soils.

In summary the results of this study suggest that soil acidity related problems such as Al-toxicity, phosphorus and exchangeable bases deficiencies, and nutrient imbalances seem to be the major constraints for the sustainable agricultural use of both the Kenyan and Brazilian Cerrado soils. Among the Kenyan soils, nutrient reserves are generally low in the highly leached volcanic soils around the Mt. Kenya area.

Results further suggest that these soils are in their ultimate stage of weathering which is usually characterized by a small reserve of plant nutrients, strongly indicated by their low CEC, ECEC and low base saturation. It is therefore critical that any mobile nutrients added to these soils should be retained by the soil matrix for sufficiently long period to give the plants an adequate opportunity to utilize them efficiently. Given that CEC is essentially a soil property derived from the colloidal fraction of the soil; mainly from clay and soil organic matter, the ability of soils to hold nutrients and other related soil properties can be modified chiefly by; (1) addition of high quality organic matter or, (2) use of lime, if the soil is too acidic, to raise its pH to the range needed for the crops one wishes to grow.

Results of this study also suggest that low available phosphorus is one of the key factors limiting the intensive utilization of most of these soils for sustainable crop production. In fact, some of these soils were estimated to have high P sorption capacity (> 1000 mg kg^{-1} within a period of only 24 hours), and the values are likely to increase with longer equilibration times due to slow reactions. Possible explanations for such high sorption capacities are: the high clay content (> 35% clay), the high percentage of iron and aluminum oxides and organic matter in most of the soils; while high exchangeable aluminum and low phosphorus saturation index (PSI) are probably the major factor in the volcanic ash-derived soils in the Mt.Kenya region.

Although no single soil property can be expected to fully account for the variance in P sorption capacity or requirement because of the multiple-component nature of phosphate adsorption in soil systems (Holford, 1977), the results of this study strongly suggest that their (both Kenyan and Brazilian soils) P requirements may be predicted from a set of soil properties easily determined during routine soil analyses. Moreover, many of the soil properties were found to be correlated to each other. Of importance are the positive correlations found between various forms of Al and the indices of the soil organic component (total C/SOM and LOI) of both Kenyan and Brazilian soils. Although pyrophosphate extractable aluminum was not determined, these relationships further point out that Al may in fact be the dominant factor affecting P sorption in these tropical soils. The pyrophosphate method extracts Fe and Al oxides that are associated with organic matter from soils. Although it dissolves amorphous inorganic oxides only slightly, silicate minerals and crystalline Fe and Al oxides are not attacked to a significant extent (McKeague et al., 1971). The increase in P sorption by high-Al soils, which also happened to have substantial amount of organic matter, can be attributed to greater sorption by Al-organic matter complexes, and/or possibly, the formation of amorphous Al-hydroxy phosphates as suggested by Villapando and Graetz (2001). Thus, the most logical way to avert the effect of Al is by use of Al tolerant plant genotypes or liming to neutralize the exchangeable Al, and to avoid the utilization of large amounts of P fertilizer required to saturate the sorption sites before the added P becomes available for plant uptakes.

However, the effect of oxalate or dithionate citrate bicarbonate extractable iron on P sotption was small and inconsistent. Despite the fact that these soils had significant amounts of clay, the contribution of the clay fraction to P sorption was only statistically significant among the Brazilian soils, probably because of a wider particle size range.

Although the correlation between soil pH and P sorption capacity was low and insignificant, a model containing other pH related factors such as Al+H, and ECEC of Brazilian soils was significant at 5% probability level. Since these factors are essential components of routine laboratory analyses, they can be used to predict P requirements in the respective soils without having to undertake laborious sorption isotherms. These findings therefore are of practical importance, particularly in Kenya, where resources are limited.

Despite their characteristic deficiencies of essential plant nutrients and potential Al-toxicity, the group of soils studied presents a good textual distribution which is a good index for their potential agricultural production if theprevailing chemical limitations are corrected.

The clay size fraction of these soils is dominated by kaolinite /halloysite, gibbsite, iron oxides, and in some cases small amounts of 2:1 clay minerals. Because kaolinite was the dominant clay mineral present in these soils, it was more difficult to identify or quantify the various types of the 2:1 clay minerals whose diffraction peaks were either masked by the amorphous constituents or too broad.

There was regional variation in the relative contents of gibbsite and 2:1 phyllosilicates, and the presence of these minerals seemed to be mutually exclusive. In general, soils developed under tropical acid weathering conditions have been considered highly weathered soils with dominant proportions of kaolin minerals and gibbsite, and often contain insignificant amounts of weatherable minerals. However, the results of this study indicate the presence of appreciable amounts of weatherable minerals. The presence of such weatherable minerals may act as a template for hydroxy-interlayering under acidic conditions (in the presence of Al^{3+}), rendering the formation of gibbsite improbable. This has been referred to as the “anti-gibbsite effect” in the literature (Jackson, 1963a, 1963b).

The presence of large amounts of gibbsite can significantly influence key soil properties. According to Huang et al., (2002), as the proportion of gibbsite relative to kaolinite increases, Oxisols tend toward greater pH values, a higher PZC, positive ΔpH, greater anion sorption capacities, lower CEC, decreasing nutrient retention capacities, lower amounts of exchangeable Al, lower phytotoxicity, and lower lime requirements. However, based on the general trend of the chemical properties of most of the soils in this study, it can be concluded that kaolinite is the dominant clay mineral in these soils.

Two main approaches available to overcome soil acidity related problems discussed herein are: (1) To modify the soil environment to suit the plant, or (2) to breed and select cultivars that are more tolerant to acidic environments. Considering the first alternative, phosphorus fertilization and liming are the traditional methods historically used to overcome this problem. Past studies have demonstrated that phosphorus deficiency in high P sorbing soils may be corrected by (i) high initial P application (Younge and Plucknett, 1966), to quench the fixation needs; (ii) repeated band applications of P; or (iii) a combination of the initial broadcast and repeated band applications (Yost et al., 1979). Theoretically, the same principle of P quenching suggested by Younge and Plucknett (1966) in a Hawaiian Latosol should be applicable to other regions where P fixation is a problem. These authors argue that the extended period over which P quenching is done provides the basis for economic justification of quenching P fixation capacity in the reclamation of such unproductive soils. Moreover, previous work by Slattery et al. (1995) demonstrated the beneficial effects of liming on the soil exchangeable cations of four soil types in northeastern Victoria, Australia. Hammel et al. (1985) also demonstrated that deep incorporation and mixing of lime up to 1 m significantly increased yields of maize and soybean in the highly weathered soils of the southeastern USA. They attributed the yield improvement to deeper root penetration, accompanied by a reduction in exchangeable Al and an increase in exchangeable Ca. In the same study, surface application only increased yields in the second and third year.

However, in Kenya and many other developing countries with such acid soil infertility, the feasibility of such ameliorative treatments in the field remains a challenge. The first approach may therefore not only be technically challenging, but also not economically viable under small holder farming systems. This is particularly considered unviable given the enormous amounts of phosphate fertilizer and lime required, and the fact that a complete mixing of the profile with lime (~1 m depth) is a prerequisite for such impressive results.

While the inherent soil nutrient content is particularly important under traditional, low-technology farming, under commercial agriculture nutrient deficiencies can be remedied by addition of fertilizers and lime. The ability of soils to retain the added nutrients therefore becomes more significant. Although fertilizer application is a necessary condition in the management of such nutrient depleted soils for sustained high yields, it goes hand in hand with other components of improved crop management.

Young (1976) suggested that soil fertility must be assessed within the context of agricultural technology and economic considerations. Farmers do not necessarily adopt agricultural practices as introduced to them by researchers, but select and adjust some components or elements that suit their farming conditions and goals. The dependency on traditional technologies enables farmers to cope with changing environment, which might otherwise not be encompassed in regular research settings. Recommendations for soil fertility managements should therefore provide flexibility in technical options.

Because the smallholder farmers in the developing nations are faced with an array of socioeconomic constraints which do not favor intensive fertilization and liming required for increasing crop production in these soils, other alternatives such as cultivation of cultivars with increased P use efficiency and resistance to toxic levels of Al remains a viable option to be explored. This approach is currently in advanced stages of evaluation by the collaborative crop research project (CCRP) of the McKnight Foundation, both in Kenya and Brazil. So far, this project has achieved significant milestones in the following aspects: (1) identified local landrace maize cultivars (particularly from the acid soils of the western Kenya Corn Belt) with relatively high levels of Al tolerance; and (2) developed and released superior maize cultivars for phosphorus efficiency and tolerance to Al toxicity (McKnight CCRP, 2006). In particular, this project reports a successful release of 44 maize accessions consisting of elite and contrasting germplasm for Al tolerance and phosphorus efficiency from EMBRAPA (Brazil) to Moi University and the Kenya Agricultural Research Institute (KARI) in Kenya. Some of the germplasms evaluated in Kenya has indicated potential for improving the maize varieties and hybrids for Kenyan agriculture.

It is therefore apparent that there have been significant technological developments. It is, however, very important to reiterate that there is no guarantee for adoption of such new technologies, and thus their integration with the more familiar, or rather traditional ones may open up a window for faster adoption. Moreover, hybridization of technologies may cushion the farmer against any unforeseen risk.

In light of the major findings of this study, the western Kenya soils are likely to respond to nutrient management practices that are similar to those already in use in central Brazil, while the soils from the Mt. Kenya region will require crop varieties and management strategies tailored to higher Al toxicity and phosphorus and efficient phosphorus uptake and utilization.

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APPENDICES

Appendix A. Soil profile descriptions

Kuinet - KN01

Kuinet (KN01)

Location: N 0° 36.781″, E 35° 18.280″

Altitude: 2127 m

In a cultivated field containing corn stover from the previous crop. The landscape can be characterized as a broad, very gently rolling plain, nearly level.

KN01A: Ap . 0-15 cm. 2.5YR 3/4; *very fine sandy loam* ; very strong, fine granular structure; loose consistence (dry); few medium Mn nodules; gradual boundary.

KN01B: A. 15-25 cm. 2.5YR 3/3, *very fine sandy loam;* strong, very fine granular structure; very friable (moist); few medium Mn nodules; diffuse boundary.

KN01C : Bo1. 25-43 cm. 2.5YR 3/4; *very fine sandy loam;* strong, very fine granular structure; very friable (moist); few medium Mn nodules; diffuse boundary.

KN01D: Bo2. 43-60 cm. 2.5YR 3/4; *very fine sandy loam;* strong, very fine granular structure; very friable (moist); few medium Mn-nodules; gradual boundary.

KN01E: Bov. 60-100+ cm. Cemented, nodular material that could be dug with a spade with some difficulty down 100 cm depth, but is extremely hard at the bottom of the pit. Loose material filling the voids between indurated material: 2.5YR 3/4; *gravely very fine sandy loam,* with black (N 3/0) concretions 3-10 mm in diameter. When the horizon is cut with a spade, occasional yellowish material (10YR 7/8) is evident. The indurated, Fe-rich material is locally referred to as the "murram" layer.

Corn roots occur throughout the profile down to 60cm, and even into the more loose material in the Bov horizon. The material is believed to have all weathered from igneous rock. The material deeper in the weathering profile is softer and easier to dig than the indurated, nodular material beginning at ~1.0 m below the surface. Some of the soft, light colored material was collected from the spoil pile of the well. A piece of hard rock, with a clear spheroidal weathering rind, was also collected. The interior of the rock may be representative of the original source rock.

From the Kenyan Soils Map:
L - Plateaus and high-level structural plains (flat to gently undulating; slopes in general < 8%)

LI - Soils developed from intermediate igneous rocks (syenites, trachytes, phonolites, etc.)

L24 - Well-drained, moderately deep to deep, dark read, friable clay, over petroplinthite; with inclusions of small bottomland (rhodic Ferralsols, petroferric phase).

Chepkoilel - KN02

Chepkoilel (KN02)

Location: N 0° 34. 997″, E 35° 18.561″

Altitude: 2148 m

Site description: Campus of Moi University, Prof. Gudu's research plot. Bottom of the pit at 102 cm is the top of the indurate material.

KN02A: Ap. 0-20 cm. 2.5YR 3/4; *fine sandy loam* ; very fine granular; slightly hard to hard consistence (dry); this horizon is distinctly compacted by tillage in some areas; gradual boundary.

KN02B: Bo1 20-40 cm. 2.5YR 4/4, *fine sandy loam;* very fine granular structure; very friable (moist); alot of concretions in part of this profile; diffuse boundary.

KN02C: Bo2 40-66 cm. 2.5YR 4/4; *fine sandy loam;* very fine granular structure; very friable (moist); clear boundary.

KN02D: Bov. 60-102+ cm. 2.5YR 4/4; *gravely fine sandy loam;* very fine granular structure; 10Y 2.5/1 black Mn nodules; the Mn-nodules tend to be 5 to 10 mm in diameter. This material is loose and easier to dig than the first (Kuinet) profile.

This is the same soil as the Kuinet site, except that the horizon form 66-102 is more loose than the Kuninet site at the same depth. The bottom of the pit at 102 cm is the top of the indurated material. There is an area of concretions between 27 and 45 cm that could be a filled animal burrow. Numerous mole rat burrows. There roots throughout profile even into concretion horizon. Lower part of the profile is slightly redder than surface material.

From the Kenyan Soils Map:
L - Plateaus and high level structural plains (flat to gently undulating; slopes in general < 8%)

L1 - Soils developed from intermediate igneous rocks (syenites, trachytes, phonolites, etc.)

L24 - Well-drained, moderately deep to deep, dark read, friable clay, over petroplinthite; with inclusions of small bottomland (rhodic Ferralsols, petroferric phase).

Vihiga –KN03

Vihiga (KN03)

Location and: N 0° 02.524″, E 34° 42.854″

Altitude: 1651 m

In a cultivated field previously, planted to corn and Napier grass and sesbania trees in the neighboring field. This area had been equatorial forest, but has been settled for a long time. Farmer with a zero grazing unit. The pedon is located at the Backslope ~ 3 % slope

KN03A: 0-25 cm. 10R 3/4 dry - 10R 3/3 moist; *sandy clay loam*; strong, fine granular structure; friable; few white fertilizer graduals in this horizon; clear boundary.

KN03B: 25-42 cm. 10R 3/2 dry - 10R 3/3 moist, *clay loam*; strong, fine granular structure; friable; large pores, this horizon is probably the original surface; gradual boundary.

KN03C: 42-82 cm. 10R 4/3 moist; *clay loam*; strong, fine granular structure; friable; few medium Mn nodules; diffuse boundary.

KN03D: 2-120 cm. 2.5 3/6 moist; *clay*; strong, fine granular structure; friable

Notes: 3 rd horizon stickier than 4th horizon

From the Kenyan Soils Map:

1 - Uh - upper-level uplands (usually undulating to rolling altitudes 5000-8000 ft; about 2.500 ft above local base level.

2 - Uh7 (UhGah) - soils developed on granites, well-drained very deep, dark red to yellowish red, friable to firm

3 – Sandy clay to clay with an acid, humic topsoil (humic Acrisols).

Kakamega/Ikholomani – KN04

Kakamega (Ikholomani) - KN04

Location: N 0° 18.910″, E 34° 13.231″

Altitude: 1600 m

In the neighborhood of Uasin Gishu at the edge of Kakamega forest, Kakamega district. The pedon is adjacent to old tea bushes. This is very clayey soil, but with many fine pores that conduct water. In the grassy edge of a tea field

KN04B: 24-50 cm. 10R 3/3 moist, *clay*; strong, medium angular block structure; hard dry; many roots; gradual wavy boundary.

KN04C: 50-85 cm. 10R 4/4; *clay*; strong, weak sub-angular blocky structure; slightly hard; diffuse boundary.

KN04D: 85-140+ cm. 2.5YR 4/6; *clay*; weak coarse sub-angular structure; slightly hard; lots of pores.

From the Kenyan Soils Map:

Uh - upper-level uplands (usually undulating to rolling altitudes 5000-8000 ft; about 2.500 ft above local base level.

Uh2- well drained, extremely deep, dark reddish brown, friable clay, with humic topsoil (mollic* Nitisol).

Uh18 – Soils developed on various rocks, well drained, very deep, dusky red to yellowish red, friable firm, clay loam,; in places with an acid humic topsoil (ferralo-chromic*) orthic Acrisol.

Bumala - KN05

Bumala (KN05)

Location: N 0° 18.910″, E 34° 13.231″

Altitude: 1200 m

KN05A: 0-11 cm. 2.5YR 3/3 moist; *clay*; strong fine granular structure; found small earthworm in surface horizon, gradual boundary.

KN05B: 11-40 cm. 2.5YR 3/3, *clay*; massive that; up into strong very fine granular structure; diffuse boundary.

KN05C: 40-65 cm. 10R 4/3 moist; *clay*; strong, very fine granular structure; clear boundary.

KN05D: 65-78 cm. 2.5YR 4/6 moist; *very gravely clay*; soil and nodules loose; clear boundary.

KN05E: 78-95 cm. 2.5YR 4/6 plinthite red black. Continuous hard plinthite.

Notes: There are roots throughout the profile to at least 80 cm. The pedon was dug in the grassy edge of the cultivated field .This is the site of fertility experiments of Prof. Okalebo and Prof Othieno of Moi University.

From the Kenyan Soils Map:

Um- lower middle-level upland. Soils developed on basic igneous rocks (basalt etc).

Um2- (UmBme)- well-drained, very deep, dark red, friable to firm, clay,; in places moderately deep over petroplinthite (cutric Nitisols; with rhodic Frralsols, partly petroferric phase)

L24 – Well drained,, moderately deep to deep, dark red, friable clay over petroplinthite; with inclusions of small bottomland of unit B2 (rhodic Frralsols, petroferric phase).

Siaya – KN06

Siaya (KN06)

Location: N 0° 03.112″, E 34° 23.658″

Altitude: 1399 m

KN06A: 0-18 cm. 5YR 3/3 moist; *clay loam*; moderate, medium, granular structure; gradual boundary; friable (moist) and slightly hard (dry) consistency.

KN06B: 18-33 cm. 5YR 3/3, *clay loamy*; moderate, medium, sub-angular blocky structure; gradual boundary; friable (moist) and slightly hard clay (dry) (moist) consistency.

KN06C: 33-68 cm. 5YR 4/6 moist; gravelly *clay loamy*; weak, large, sub-angular blocky or moderate granular structure; yellowish/black concretions; gradual boundary.

KN06D: 68-106 cm. 5YR 4/6 moist; *gravely clay loam*; weak platy structure; gradual boundary.

KN06E: 106-120 cm. 5YR4/6 (10YR2/1; 10YR7/8) moist, weak platy structure; Saprolite-like material with manganese concretions

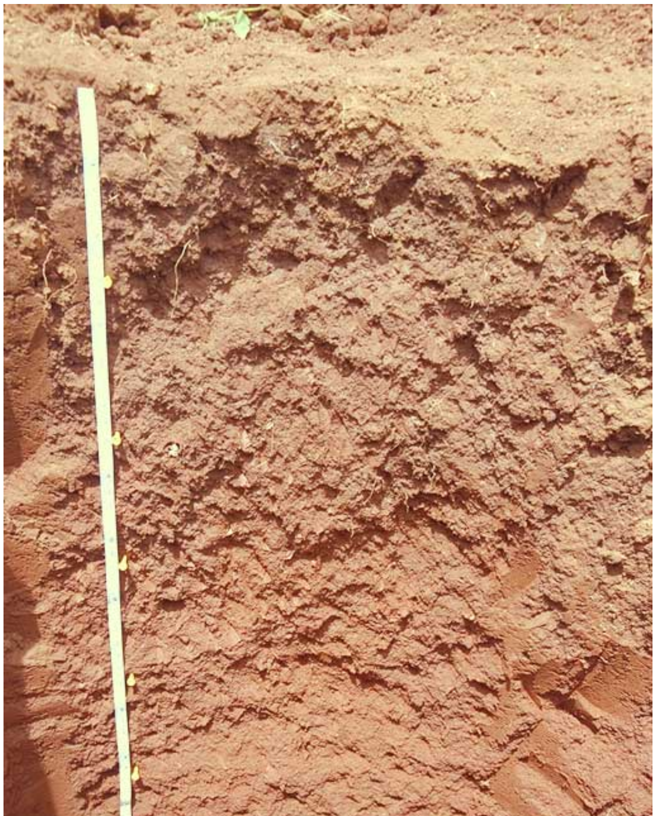
From the Kenyan Soils Map:

UI6- Lower level uplands (usually gently undulating; altitudes 2500-6000 ft above local base level) soils developed on intermediate igneous rocks (basalts, etc) well drained to moderately well drained, shallow, friable, sandy clay loam, over petroplinthite (about 50%); on interfluves (ironstone soils).

Well drained, very deep dark reddish brown to strong brown, friable clay; on valley sides (dystric Nitisols: with orthic Ferralsols)

Notes: This was the site of a soil fertility experiment to test the efficacy of different rock phosphates and *tithonia diversifolia* (Mexican sunflower) (high in N). Before human settlement this area had been wooded open land with a predominance of shrubs plowing is by ox plow.

Kisii - KN07



Kisii (KN07)

Location: S 0° 47.574″, E 34° 5.446″

Altitude: 1830 m

KN07A: 0-11 cm. 10R3/2 moist; *heavy silt loam/clay*; strong, medium, granular structure, friable (moist) and hard (dry) consistency; clear smooth boundary; with a few bits of charcoal.

KN07B: 11-27 cm. 10R4/2 moist; clay; strong, coarse prismatic breaking into strong coarse sub-angular blocky structure; friable (moist) consistency; gradual boundary; with few bits of charcoal.

KN07C: 27-45 cm. 10R3/2 moist, clay, strong, coarse prismatic braking into strong coarse sub-angular blocky structure; friable (moist) consistency; gradual boundary.

KN07D: 45-66 cm. 10R 4/6 moist; *clay*; very weak, prismatic breaking to weak, coarse, sub-angular blocky; friable (moist) consistency; diffuse boundary.

KN07E: 66-120+ cm. 2.5YR 3/6; clay; structureless, massive, breaking into very fine to medium, sub-angular blocky and granular; very friable (moist) consistency; very fine pores and roots downwards.

From the Kenyan Soils Map:

Map unit Um - lower middle level uplands (usually undulating; altitude 3,500-6,500 feet). UmB - soils developed on basic igneous rocks (basalts etc.) Um3 - well drained deep to extremely deep, dark red, friable clay, with thick humic topsoil (Mollic Nitosols with Nitro-luvic phaeozems).

Brazilian class: Terra Roxa Estruturadas (old system) Nitosolos (new).

Notes:

Position: lower 1/3 of a long linear back slope, regional relief is undulating to mountainous.

Kericho (Ainamoi) - KN08

Kericho/Ainamoi (KN08)

Location: S 0° 17.773″, E 35° 16.350″

Altitude: 1904 m

KN08A: 0-20 cm. 5YR 3/2 moist; *clay*; moderate, fine, sub-angular blocky breaking into strong fine granular structure, slightly hard (dry) and friable (moist) consistency, gradual boundary.

KN08B: 20-38 cm. 5YR 3/3; *clay*; weak, fine, sub-angular blocky, breaking into strong fine granular structure;, slightly hard when dry and friable when moist; gradual boundary.

KN08C: 38-60 cm. 5YRR3/3 moist; *clay*; weak, fine, sub-angular blocky, breaking into strong fine granular structure; slightly hard when dry and friable when moist; diffuse boundary.

KN08D: 60-90 cm. 5YR 3/3 moist; *clay*; structureless, massive, breaking into fine granular structure; friable (moist) consistency; diffuse boundary.

KN08E: 90-120+ cm. 2.5YR 4/6 moist; clay; structureless, massive, breaking into fine granular structure; friable (moist) consistency.

From the Kenyan Soils Map:
R - volcanic foot ridges (dissected lower slopes of major older volcanoes and mountains; undulating to hilly)

RB - soils developed on Tertiary basic igneous rocks (olivine basalts, nepheline phonolites; older basic tufts included).

R9 - (Rbnh + bh) association of -well drained, extremely deep, dark reddish brown, friable clay, with on acid humic topsoil.

Kangema – KN09

Kangema (KN09)

Location: S 0° 40.883″, E 36° 56.097″

Altitude: 1920 m

The pit was in a tea field that had been planted 10 years earlier. The farmer used DAP fertilizer 25-5-5-+55 applied in Sept.

KN09A: 0-20 cm, 2.5YR 3/4 moist; *clay*; strong, fine granular structure, very friable, diffuse boundary.

KN09B: 20-40 cm. 2.5YR 3/4; *clay*; strong, fine granular structure; very friable, diffuse boundary.

KN09C: 40-70 cm, 10R 3/3 moist; *clay*; strong, fine, granular structure; very friable, diffuse boundary.

KN09D: 70-112 cm, 2.5YR 3/3 moist; *clay*; soil weak, medium, sub-angular, breaking into strong fine granular structure; friable (moist) consistency; clear boundary.

KN09E: 112 -160+ cm. 5YR 3/4 moist; clay; moderate, medium, sub-angular blocky structure, friable (moist) consistency.

From the Kenyan Soils Map:

R - Volcanic foot ridges (dissected lower slopes of major older volcanoes and mountains; undulating to hilly)

RB – soils developed on tertiary basic igneous rocks (olivine basalts, nephelene phonolites; older basic tufts included)

R2 - Well drained, extremely deep dusky red to dark reddish brown friable clay with and acid top soil humic Nitisols.

Kerugoya – KN10

Kerugoya (KN10)

Location: S 0° 28.181″, E 37° 15.752″

Altitude: 1702 m

The color is absolutely uniform and roots distributed throughout the profile.

KN10A: 0-20 cm. 2.5YR 5/2 moist; *clay*; strong fine granular structure; very friable (moist) consistency; diffuse boundary.

KN10B: 20-65 cm. 2.5YR 3/2, *clay*; strong fine granular structure; very friable (moist) consistency; diffuse boundary.

KN10C: 65-110 cm. 10R 3/2 moist; *clay*; strong fine granular structure; very friable (moist) consistency; diffuse boundary.

KN10D: 110+ cm. 2.5YR 3/2 moist; *clay; weak, medium, sub-angular blocky, breaking into strong, fine granular structure;* friable (moist) consistency.

From the Kenyan Soils Map: From map R - Volcanic foot ridges

RB- Soils developed on Tertiary basic igneous rocks (olivine basalts, nepheline, phonolites, older tufts included.

R1- Well-drained, extremely deep, dark reddish brown to dark brown friable to slightly smeary clay with an acid humic topsoil (ando-humic Nitosols, with humic Andosols).

Embu/Kavutiti - KN11

Embu/ Kavutiri (KN11)

Location: S 0° 25.004″, E 37° 30.062″

Altitude: 1810 m

KN05A: 0-12 cm. 7.5YR 5/6 moist; *clay*; strong fine granular structure; clear boundary; fine roots

KN05B: 12-32 cm. 27.5YR 3/4; *clay*; massive weak, medium, sub-angular structure; soft; diffuse boundary; fine roots

KN05C: 32-50 cm. 2.5 YR 3/6 moist; *clay*; strong, blocky, breaking into strong, fine granular structure; friable (moist); diffuse boundary; fine roots

KN05D: 50-95 cm. 2.5 YR 3/6 moist; *clay*; strong, blocky, breaking into strong, fine granular structure; friable (moist); diffuse boundary: fine roots

KN05E: 95-130+ cm2.5 YR 3/6 moist; *clay*; strong, blocky, breaking into strong, fine granular structure; friable (moist); diffuse boundary: fine roots.

From the Kenyan Soils Map:

From map R - Volcanic foot ridges

RB - Soils developed on Tertiary basic igneous rocks (olivine basalts, nepheline, phonolites, older tufts included, map unit R1 well-drained, extremely deep, dark reddish brown to dark brown friable to slightly smeary clay with an acid humic topsoil (ando-humic Nitosols, with humic Andosols).

R2 - well-drained, extremely deep, dusky red to dark reddish brown, friable clay, with an acid humic topsoil (humic Nitisols).

Appendix B. Soil moisture content

Table B-1 Soil moisture content (air-dried) Kenyan soils

Site	Sample ID	Depth (cm)	Weight (g)			Moisture Content (%)
			Can	can + air dry soil	can + oven dry soil	
Kuinet	KN01A	15	1.61	17.46	17.06	2.52
	KN01B	25	1.58	15.55	15.24	2.22
	KN01C	43	1.58	20.17	19.70	2.53
	KN01D	60	1.58	19.84	19.37	2.57
	KN01E	>60	1.58	13.13	12.84	2.51
Chepkoilel	KN02A	20	1.61	16.01	15.63	2.64
	KN02B	40	1.61	17.18	16.76	2.70
	KN02C	60	1.61	19.61	19.15	2.56
	KN02D	120	1.61	21.81	21.26	2.72
Vihiga	KN03A	25	1.61	18.27	17.93	2.04
	KN03B	42	1.61	17.53	17.19	2.14
	KN03C	82	1.62	19.50	19.10	2.24
	KN03D	120	1.61	18.67	18.27	2.34
Ikholomani	KN04A	24	1.59	15.67	15.36	2.20
	KN04B	50	1.62	20.81	20.37	2.29
	KN04C	85	1.60	20.48	20.10	2.01
	KN04D	>140	1.62	18.53	18.15	2.25
Bumala	KN05A	11	1.59	15.23	14.89	2.49
	KN05B	40	1.60	19.88	19.46	2.30
	KN05C	65	1.62	14.62	14.33	2.23
	KN05D	78	1.62	14.96	14.67	2.17
	KN05E	95	1.61	17.56	17.21	2.19
Siaya	KN06A	18	1.61	20.48	20.11	1.96
	KN06B	33	1.61	18.51	18.18	1.95
	KN06C	68	1.64	21.89	21.49	1.98
	KN06D	66	1.61	22.40	22.07	1.59
	KN06E	120	1.64	21.76	21.42	1.69
Kisii	KN07A	11	1.62	20.97	20.39	3.00
	KN07B	27	1.62	22.24	21.61	3.06
	KN07C	45	1.58	21.53	20.95	2.91
	KN07D	66	1.59	17.38	16.86	3.29
	KN07E	>120	1.58	21.44	20.80	3.22

Table B-1 Continued

Site	Sample ID	Depth (cm)	Weight (g)			Moisture Content (%)
			can	can + air dry soil	can + oven dry soil	
Kericho	KN08A	20	1.58	18.58	17.98	3.53
	KN08B	38	1.60	19.66	19.04	3.43
	KN08C	60	1.58	18.07	17.53	3.27
	KN08D	90	1.60	18.66	17.12	9.03
	KN08E	120	1.58	15.24	14.82	3.07
Kangema	KN09A	20	1.58	11.30	10.90	4.12
	KN09B	40	1.60	15.70	15.10	4.26
	KN09C	70	1.58	11.23	10.90	3.42
	KN09D	112	1.60	14.38	13.96	3.29
	KN09E	160	1.58	19.14	18.54	3.42
Kerugoya	KN10A	20	1.60	10.47	10.04	4.85
	KN10B	65	1.58	15.28	14.61	4.89
	KN10C	110	1.59	19.86	19.11	4.11
	KN10D	130	1.56	20.17	19.41	4.08
Kavutiri	KN11A	12	1.60	15.20	14.75	3.31
	KN11B	32	1.60	12.05	11.73	3.06
	KN11C	50	1.58	16.61	16.18	2.86
	KN11D	95	1.60	19.35	18.89	2.59
	KN11E	130	1.56	24.67	24.06	2.64

Appendix C. Particle size distribution

Table C-1 Particle size distributions of Kenyan soils by the hydrometer method

Site	Depth (cm)	%Sand	%Silt	%Clay	Textural class
Kuinet	0-15	66	14	20	sandy loam
	15-25	66	12	22	sandy loam
	25-43	58	24	18	sandy loam
	43-60	78	10	12	sandy loam
Chepkoilel	0-20	40	16	44	Clay
	0-35.5	56	16	28	sandy clay loam
	35.5-85	42	12	46	Clay
	85-117	52	12	36	sandy clay
Ikholomani	0 - 28.3	44	24	32	Clay loam
	28.3 – 70	44	22	34	Clay loam
	70 – 119	30	20	50	Clay
Bumala	0-11	52	16	32	sandy clay loam
Siaya	0-31.7	52	20	28	sandy clay loam
	31.7-48.3	48	12	40	Loam
	48.3 – 87	56	8	36	sandy clay
	87 - 135.3	60	14	26	sandy clay loam
Kericho	0 - 18.4	40	19	41	Clay
	18. 4 – 57.5	50	12	38	sandy clay
	57. 5 – 116.3	28	14	58	Clay
Kisii	0 – 13	56	22	22	sandy clay loam
	13 - 51.3	54	18	28	sandy clay loam
	51.3 – 129.3	40	14	46	Clay
Kangema	0-20	66	22	12	sandy loam
	20-40	76	16	8	loamy sand
	40-70	54	26	20	sandy loam
Kerugoya	0-20	58	34	8	sandy loam
	20-65	66	26	8	sandy loam
	65-110	70	20	10	loamy sand
	110-130	80	10	10	loamy sand
Kavutiri	0-12	66	24	10	sandy loam
	12 32	64	8	28	sandy clay loam

Table C- 2 Particle size distribution by fractionation, CEC and ECEC per kg clay for selected horizons of Kenyan soils

Sample ID	Depth (cm)	Weight of fraction (g kg^{-1})						Recovery	Clay	CEC	ECEC
		>53	20-50	5-20	2-5	2-02.2	<0.2	g kg^{-1}	%	$coml_c kg^{-1}$ clay	$coml_c kg^{-1}$ clay
		µm									
KN01A	0.5-15.5	83	65	275	261	536	17.7	963	56	17	10.4
KN01D	43-60	78	84	315	220	535	15.6	936	57	15	9.1
KN02A	0-20	84	75	235	305	539	19.4	883	61	17	11.5
KN02C	35-85	74	75	370	258	629	16.7	976	64	16	11.3
KN03A	0-25	73	85	357	110	466	18.8	984	47	19	12.3
KN03C	42-82	138	28	457	56	512	17.1	948	54	16	12.6
KN04A	0-24	181	170	350	38	388	35.3	913	42	32	18.1
KN04C	50-85	190	247	337	64	401	26.7	972	41	26	21.7
KN05A	0-11	58	75	426	148	574	20.3	865	66	18	10.9
KN05C	40-65	71	71	507	158	665	13.4	971	68	13	6.5
KN06A	0-18	105	116	244	227	471	19.7	954	49	19	9.0
KN06B	18-33	94	96	280	247	528	17.6	964	55	17	9.3
KN07A	0-11	173	116	235	219	453	48.5	940	48	46	17.9
KN07D	45-66	199	52	434	140	574	28.2	968	59	27	17.6

Table C-1 Continued

Sample ID	Depth (cm)	Weight of fraction (g kg^{-1})						Recovery	Clay	CEC	ECEC
		>53	20-50	5-20	2-5	2-02.2	<0.2	g kg^{-1}	%	$coml_c kg^{-1}$ clay	$coml_c kg^{-1}$ clay
		µm									
KN08A	0-20	49	79	367	367	735	24.6	927	79	23	13.9
KN08C	38-60	35	57	606	232	838	16	982	85	16	9.5
KN09A	0-20	89	89	485	162	648	15.2	898	72	14	10.7
KN09C	40-70	170	105	490	54	543	14.8	897	61	13	10.8
KN10A	0-20	152	108	205	267	472	22.6	883	53	20	11.7
KN10C	65-110	108	171	171	382	553	18.7	917	60	17	6.2
KN11A	0-12	49	72	642	120	762	11.1	924	82	10	6.5
KN11D	50-95	53	138	598	30	628	11.9	872	72	10	6.7

Appendix D. Chemical properties of Brazilian soils

Table D-1 Soil pH, phosphorus organic C and N levels of Brazilian Cerrado soils

Sample ID	pH[1]		P[1] (mg kg)		LOI (%)	Org. C[1] g kg^{-1}	Leco C	Leco N
	H_2O	KCl	Resin	Melich-1				
G1A1	5.1	4.4	4	1	17.3	19	26	1.1
G1A2	5.5	5.3	4	1	17.0	8	11	0.0
G2A1	5.0	4.5	4	1	17.3	20	35	1.5
G2A2	5.3	5.5	4	1	6.4	7	13	0.2
N1A1	4.7	4.0	4	1	7.3	19	33	1.7
N1A2	5.2	4.5	4	1	5.6	6	9	0.2
N2A1	4.5	4.0	4	1	5.1	17	27	1.3
N2A2	5.1	4.5	4	1	3.2	6	9	0.4
N5A1	4.9	4.9	4	1	1.5	9	9	0.2
N5A2	4.4	4.0	4	1	4.8	4	2	0.2
T1A1	4.3	4.1	5	1	8.1	17	26	1.6
T1A2	5.0	4.8	4	1	11.4	5	8	0.2
T2A1	4.9	4.1	4	1	13.4	18	28	1.4
T2A2	5.2	4.7	4	1	12.4	9	11	0.3
T4A1	6.5	5.9	8	31	10.9	28	34	2.5
T4A2	6.2	5.1	5	1	10.7	8	9	0.1
T5A1	5.8	5.1	4	29	10.4	26	32	2.2
T5A2	5.1	4.4	4	1	17.3	19	26	1.1

[1] Marques (2000)

LOI – Loss on ignition at 400°C

Leco _ Analysed by Leco CHN 2000

Table D-2 Exchangeable cations and exchange properties of Brazilian soils (Marques, 2000)

Sample ID	Exchangeable Cations [1] ($\text{cmo}_c\text{kg}^{-1}$)							Al sat. (%)	Base sat. (%)
	Al	Ca	Mg	K	H+Al [2]	ECEC	CEC[3]		
G1A1	0.3	0.4	0.2	0.08	5.0	1.1	5.7	30	12
G1A2	0.0	0.4	0.2	0.06	2.6	0.7	3.3	0	20
G2A1	0.4	0.4	0.2	0.10	5.6	1.1	6.3	36	11
G2A2	0.0	0.4	0.1	0.04	2.1	0.5	2.6	0	21
N1A1	1.2	0.4	0.2	0.08	6.3	1.9	7.0	64	10
N1A2	0.2	0.6	0.2	0.15	2.3	1.1	3.2	17	29
N2A1	1.1	0.3	0.1	0.10	5.0	1.6	5.5	69	9
N2A2	0.2	0.5	0.2	0.16	2.3	1.1	3.2	19	27
N5A1	1.4	0.8	0.2	0.06	4.0	2.5	5.1	57	21
N5A2	1.2	0.4	0.1	0.01	2.9	1.7	3.4	70	15
T1A1	0.9	0.4	0.1	0.09	6.3	1.5	6.9	60	9
T1A2	0.0	0.4	0.2	0.02	2.6	0.6	3.2	0	19
T2A1	0.9	0.4	0.2	0.09	8.8	1.6	9.5	57	7
T2A2	0.0	0.4	0.2	0.02	3.2	0.6	3.8	0	16
T4A1	0.0	9.8	2.8	0.36	1.9	1.3	14.9	0	87
T4A2	0.0	0.6	0.2	0.39	2.6	1.2	3.8	0	31
T5A1	0.0	5.2	3.3	0.37	3.2	8.9	12.1	0	73
T5A2	0.0	0.8	0.5	0.06	3.2	1.4	4.6	0	30

Appendix E. Analysis of variance

Kenyan soil samples

The GLM Procedure

Class Level Information

Class	Levels	Values
Profile	11	1 2 3 4 5 6 7 8 9 10 11
Depths	5	A B C D E

Dependent Variable: pH_{H2O}

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	44.057516	4.405752	26.55	<.0001
Depth(Profile)	40	6.636923	0.165923	4.48	<.0001
Error: MS(Error)	102	3.777467	0.037034		

Dependent Variable: pH_{KCl}

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	26.534095	2.653409	13.55	<.0001
Depth (Profile)	40	7.830615	0.195765	11.35	<.0001
Error: MS(Error)	102	1.759467	0.017250		

Dependent Variable: pH_{CaCl}

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	39.666562	3.966656	31.79	<.0001
Depth (Profile)	40	4.990577	0.124764	15.32	<.0001
Error: MS(Error)	102	0.830733	0.008144		

Dependent Variable: CEC

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	1420.259078	142.025908	17.22	<.0001
Depth (Profile)	40	329.830333	8.245758	1.97	0.0034
Error: MS(Error)	102	427.080000	4.187059		

Dependent Variable: ECEC

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	571.828140	57.182814	10.06	<.0001
Depth (Profile)	40	227.372450	5.684311	6.44	<.0001
Error: MS(Error)	102	89.976000	0.882118		

Dependent Variable: Log-AEC

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	1.909243	0.190924	2.44	0.0220
Depth (Profile)	40	3.123704	0.078093	7.42	<.0001
Error: MS(Error)	102	1.073425	0.010524		

Dependent Variable: Arcsin-Al saturation percentage (ASP)

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	8.572301	0.857230	16.26	<.0001
Depth (Profile)	40	2.108500	0.052712	7.87	<.0001
Error: MS(Error)	102	0.683433	0.006700		

Dependent Variable: Log-exchangeable K

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	8.140961	0.814096	10.24	<.0001
Depth (Profile)	40	3.179984	0.079500	4.40	<.0001
Error: MS(Error)	102	1.843237	0.018071		

Dependent Variable: Square root- exchangeable Ca

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	30.263670	3.026367	25.58	<.0001
Depth (Profile)	40	4.732167	0.118304	2.40	0.0002
Error: MS(Error)	102	5.020158	0.049217		

Dependent Variable: exchangeable Mg

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	123.914366	12.391437	37.47	<.0001
Depth (Profile)	40	13.227333	0.330683	6.85	<.0001
Error: MS(Error)	102	4.926667	0.048301		

Dependent Variable: exchangeable Na

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	0.690485	0.069049	4.02	0.0007
Depth (Profile)	40	0.687750	0.017194	35.08	<.0001
Error: MS(Error)	51	0.025000	0.000490		

Dependent Variable: exchangeable Al

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	140.817908	14.081791	5.79	<.0001
Depth n(Profile)	40	98.057825	2.451446	8.08	<.0001
Error: MS(Error)	99	30.018783	0.303220		

Dependent Variable: Arcsin-Leco N

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	0.003530	0.000353	1.53	0.1681
Depth (Profile)	38	0.008792	0.000231	46.36	<.0001
Error: MS(Error)	49	0.000245	0.000004991		

Dependent Variable: Arcsin-Leco C

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	0.046235	0.004623	2.08	0.0507
Depth (Profile)	38	0.084298	0.002218	3341.49	<.0001
Error: MS(Error)	49	0.000032531	0.000000664		

Dependent Variable: Arcsin-LOI

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	0.219955	0.021995	16.44	<.0001
Depth (Profile)	38	0.050855	0.001338	84.30	<.0001
Error: MS(Error)	49	0.000778	0.000015875		

Dependent Variable: Sqrt-Ca

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	30.263670	3.026367	25.58	<.0001
Depth (Profile)	40	4.732167	0.118304	2.40	0.0002
Error: MS(Error)	102	5.020158	0.049217		

Dependent Variable: Mg

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Profile	10	123.914366	12.391437	37.47	<.0001
Depth (Profile)	40	13.227333	0.330683	6.85	<.0001
Error: MS(Error)	102	4.926667	0.048301		

Appendix F. Least-square mean separation

Table F-1 Least-Square mean separation of Kenyan Pedons

Soil property	Transformation	Pedon	Values	Transformed	Similarities
pH_H_2O		KN01	4.74	4.741	a
		KN02	5.10	5.103	b
		KN03	5.71	5.713	c
		KN04	6.37	6.370	d
		KN05	5.51	5.514	c e
		KN06	5.57	5.571	c ef
		KN07	5.96	5.960	c g
		KN08	5.81	5.806	c efgh
		KN09	4.79	4.785	ab i
		KN10	4.96	4.965	ab ij
		KN11	4.65	4.650	a ijk
pH_KCl		KN01	3.92	3.919	a
		KN02	4.08	4.076	ab
		KN03	4.46	4.458	c
		KN04	5.14	5.139	d
		KN05	4.12	4.118	abc e
		KN06	4.35	4.349	bc ef
		KN07	4.89	4.894	d g
		KN08	4.58	4.582	c fgh
		KN09	3.91	3.915	ab e i
		KN10	3.86	3.855	ab e ij
		KN11	3.82	3.819	ab e ijk
pH_ $CaCl_2$		KN01	4.26	4.265	a
		KN02	4.41	4.406	ab
		KN03	4.84	4.842	c
		KN04	5.47	5.473	d
		KN05	4.30	4.300	ab e
		KN06	4.57	4.573	bc f
		KN07	5.26	5.255	d g
		KN08	4.97	4.973	c h
		KN09	3.99	3.987	i
		KN10	4.07	4.068	a e ij
		KN11	3.80	3.803	ijk

Table F-1 Continued

Soil property	Transformation	Pedon	Values	Transformed	Similarities
			(%)		
C	Arcsin	KN01	1.52	0.124	a
		KN02	1.36	0.117	ab
		KN03	1.35	0.116	abc
		KN04	1.29	0.114	abcd
		KN05	1.95	0.140	abcde
		KN06	1.08	0.104	abcdef
		KN07	1.43	0.120	abcdefg
		KN08	1.90	0.138	abcdefgh
		KN09	3.16	0.179	e hi
		KN10	1.91	0.139	abcdefghij
		KN11	2.58	0.161	abc e ghijk
			(%)		
N	Arcsin	KN01	0.13	0.036	a
		KN02	0.08	0.028	ab
		KN03	0.12	0.035	abc
		KN04	0.11	0.034	abcd
		KN05	0.13	0.035	abcde
		KN06	0.08	0.029	abcdef
		KN07	0.12	0.035	abcdefg
		KN08	0.09	0.029	abcdefgh
		KN09	0.20	0.045	a cde g i
		KN10	0.21	0.046	a cde g ij
		KN11	0.19	0.043	a cde g ijk
LOI	Arcsin	KN01	6.42	0.256	a
		KN02	6.16	0.251	ab
		KN03	4.22	0.207	c
		KN04	5.14	0.229	abcd
		KN05	6.33	0.254	ab de
		KN06	4.28	0.209	cd f
		KN07	6.14	0.250	ab de g
		KN08	8.00	0.287	a e h
		KN09	12.65	0.364	i
		KN10	8.91	0.303	h j
		KN11	10.42	0.329	jk

Table F-1 Continued

Soil property	Transformation	Pedon	Values	Transformed	Similarities
				($\text{cmol}_c\ \text{kg}^{-1}$)	Transformation
CEC		KN01		8.893	a
		KN02		10.550	ab
		KN03		9.825	abc
		KN04		11.817	bcd
		KN05		8.467	abc e
		KN06		9.447	abc ef
		KN07		18.520	g
		KN08		13.393	d h
		KN09		8.427	Abc ef i
		KN10		10.342	abcdef ij
		KN11		7.607	a c ef i k
ECEC		KN01		5.661	a
		KN02		6.868	ab
		KN03		6.545	abc
		KN04		8.565	b d
		KN05		4.998	a c e
		KN06		5.102	abc ef
		KN07		10.981	g
		KN08		8.709	b d h
		KN09		5.815	abc ef i
		KN10		4.466	a ef ij
		KN11		5.412	abc ef ijk
				($\text{cmol}_c\ \text{kg}^{-1}$)	
AEC	Log	KN01	1.76	0.245	a
		KN02	2.15	0.333	ab
		KN03	1.71	0.233	abc
		KN04	1.18	0.071	a cd
		KN05	1.02	0.008	de
		KN06	1.63	0.212	abcdef
		KN07	0.93	-0.031	de g
		KN08	1.49	0.173	abcdefgh
		KN09	1.59	0.202	abcdef hi
		KN10	1.13	0.053	a cdefghij
		KN11	1.86	0.271	abcd f hijk

Table F-1 Continued

Soil property	Transformation	Pedon	Values	Transformed	Similarities
			($cmol_c kg^{-1}$)		
Ca	Square root	KN01	2.16	1.471	a
		KN02	3.51	1.872	b
		KN03	4.40	2.098	bc
		KN04	5.83	2.415	d
		KN05	2.68	1.636	ab e
		KN06	3.16	1.777	b ef
		KN07	5.14	2.268	cd g
		KN08	5.13	2.266	cd gh
		KN09	1.22	1.106	i
		KN10	1.19	1.092	ij
		KN11	1.80	1.341	a ijk
			($cmol_c\ kg^{-1}$)		
Mg		KN01	1.04		a
		KN02	1.45		ab
		KN03	0.98		abc
		KN04	1.22		abcd
		KN05	0.79		a cde
		KN06	0.93		a cdef
		KN07	3.48		g
		KN08	2.04		h
		KN09	0.45		e i
		KN10	0.43		e ij
		KN11	0.22		ijk
			($cmol_c\ kg^{-1}$)		
K	Log	KN01	0.47	-0.332	a
		KN02	0.70	-0.153	ab
		KN03	0.23	-0.640	c
		KN04	0.25	-0.601	cd
		KN05	0.22	-0.667	cde
		KN06	0.23	-0.632	cdef
		KN07	1.21	0.082	G
		KN08	0.40	-0.393	A d h
		KN09	0.26	-0.587	cdef hi
		KN10	0.25	-0.594	cdef hij
		KN11	0.28	-0.547	cdef hijk

Table F-1 Continued

Soil property	Transformation	Pedon	Values	Transformed	Similarities
			(cmol$_c$ kg^{-1})		
Na		KN01	0.58		GA
		KN02	0.40		B
		KN03	0.31		bc
		KN04	0.38		bcd
		KN05	0.29		bcde
		KN06	0.39		bcdef
		KN07	0.40		bcdefg
		KN08	0.34		bcdefgh
		KN09	0.28		bcdef hi
		KN10	0.37		bcdefghij
		KN11	0.30		bcdefghijk
			(cmolckg-1)		
Al		KN01	1.84		a
		KN02	1.13		ab
		KN03	0.86		abc
		KN04	1.17		abcd
		KN05	1.27		abcde
		KN06	0.74		abcdef
		KN07	1.03		abcdefg
		KN08	1.21		abcdefgh
		KN09	3.76		i
		KN10	2.49		a e ij
		KN11	3.06		ijk
			(cmolc kg-1)		
ASP	Arcsin	KN01	32.18	0.603	a
		KN02	15.44	0.404	b
		KN03	11.56	0.347	bc
		KN04	13.66	0.379	bcd
		KN05	22.61	0.496	abcde
		KN06	12.13	0.356	bcdef
		KN07	6.15	0.251	bcd fg
		KN08	6.84	0.265	bcd fgh
		KN09	61.98	0.906	i
		KN10	57.94	0.865	ij
		KN11	55.67	0.842	ijk

Table F-1 Continued

Soil property	Transformation	Pedon	Transformed	Values	Similarities
				mmol kg^{-1}	
Al_{ox}		KN01		208.6	a
		KN02		225.7	ab
		KN03		298.4	bc
		KN04		314.9	bcd
		KN05		409.3	e
		KN06		165.0	ab f
		KN07		193.1	ab fg
		KN08		245.2	abcdfg
		KN09		363.2	cde i
		KN10		450.2	e j
		KN11		257.0	abcd gh k
AI_d		KN01		462.1	a
		KN02		571.3	ab
		KN03		484.6	abc
		KN04		673.0	b d
		KN05		788.1	de
		KN06		763.9	def
		KN07		248.9	g
		KN08		615.4	b d h
		KN09		603.9	bcd hi
		KN10		566.9	abcd hij
		KN11		450.8	abc jk
Feox	Square root	KN01	6.481	42.0	a
		KN02	6.237	38.9	ab
		KN03	7.043	49.6	abc
		KN04	6.15	37.8	abcd
		KN05	5.797	33.6	ab de
		KN06	5.379	28.9	ab def
		KN07	8.453	71.5	g
		KN08	7.26	52.7	abcd h
		KN09	10.452	109.3	i
		KN10	13.748	189.0	j
		KN11	13.451	180.9	k

Table F-1 Continued

Soil property	Transformation	Pedon	Transformed	Values	Similarities
				mmol kg^{-1}	
Fed		KN01		1617.8	a
		KN02		1300.3	b
		KN03		1330.5	bc
		KN04		1507.0	a cd
		KN05		1954.7	e
		KN06		1262.9	bc f
		KN07		1428.9	bcd fg
		KN08		1768.7	a h
		KN09		2125.6	i
		KN10		1658.6	a d h j
		KN11		1565.0	a d g jk

Table F-2 Least-Square mean separation of Brazilian pedons

Soil property	Transformation	Pedon	Transformed	Values	Similarities
Carbon	Arcsin			(%)	
		G1	0.133	1.769	
		G2	0.151	2.265	
		N1	0.139	1.928	
		N2	0.130	1.679	
		N5	0.070	0.495	
		T1	0.126	1.582	
		T2	0.138	1.881	
		T4	0.139	1.925	
		T5	0.136	1.830	
Nitrogen	Arcsin			(%)	
		G1	0.019	0.035	
		G2	0.026	0.066	
		N1	0.028	0.077	
		N2	0.028	0.076	
		N5	0.008	0.006	
		T1	0.027	0.075	
		T2	0.027	0.073	
		T4	0.028	0.079	
		T5	0.03	0.089	
				(%)	
LOI	Arcsin	G1	0.427	17.1	a
		G2	0.342	11.2	ab
		N1	0.256	6.4	bc
		N2	0.203	4.1	cd
		N5	0.162	2.6	cde
		T1	0.316	9.7	abcd f
		T2	0.367	12.9	abc fg
		T4	0.334	10.7	abc fgh
		T5	0.3	8.8	bcd fghi
				mmol kg^{-1}	
AlOx		G1		209.9	
		G2		276.4	
		N1		200.2	
		N2		194.7	
		N5		125.6	
		T1		174.9	
		T2		219.9	
		T4		169.9	
		T5		225.2	

Table F-2 Continued

Soil property	Transformation	Pedon	Transformed	Values	Similarities
				mmol kg^{-1}	
Ald		G1		604.9	a
		G2		636.2	ab
		N1		350.0	c
		N2		424.2	a cd
		N5		330.2	cde
		T1		544.7	ab d f
		T2		668.4	ab fg
		T4		797.0	b gh
		T5		787.1	ab ghi
				mmol kg^{-1}	
Feox	Square root	G1	3.956	15.7	
		G2	6.05	36.6	
		N1	3.904	15.2	
		N2	3.991	15.9	
		N5	2.309	5.3	
		T1	4.15	17.2	
		T2	3.952	15.6	
		T4	6.385	40.8	
		T5	5.02	25.2	
				mmol kg^{-1}	
Fed		G1		1809.4	a
		G2		1322.7	ab
		N1		1389.8	abc
		N2		968.8	abcd
		N5		289.1	b de
		T1		1245.5	abcdef
		T2		1083.0	abcdefg
		T4		3432.3	h
		T5		4313.1	hi

Appendix G. Sampling depths comparisons by t-test

Table G-1 Significance of T-test of comparison of sampling depths of Kenyan pedons

Pedon	Depth comparison	pH			LOI	C	N
		H_2O	KCl	$CaCl_2$		Leco	Leco
KN01	A B		**	*	*	**	
	A C		**	**	*	**	**
	A D	*	**	**	*	**	*
	A E	*	**	**		**	
	B C		**	**		**	*
	B D		*	**		**	*
	B E		**	**		**	
	C D			**		**	
	C E					**	
	D E					**	
KN02	A B		**	*		*	*
	A C		**	**	*	**	**
	A D		**	**	**	**	**
	B C		*				
	B D						
	C D		**		*	**	**
KN03	A B	*	**	**		**	
	A C	**	**	**		**	
	A D	**	**	**		**	*
	B C		*	**		**	
	B D		**	**	*	**	**
	C D		**			**	**
KN04	A B		**	**		**	
	A C	*	**	**	**	**	**
	A D	*	**	**	**	**	**
	B C	*	**	**	**	**	*
	B D	*	**	**	**	**	**
	C D					**	**

Table G-1 Continued

Pedon	Depth comparison	pH			LOI	C	N
		H_2O	KCl	$CaCl_2$			
KN05	A B			**	**	*	
	A C		**	**	*	**	**
	A D		*	**	**	**	**
	A E			**			
	B C			**			**
	B D			*	*	*	*
	B E			**			
	C D		**	**		**	
	C E		**	**			
	D E			*			
KN06	A B		*	**		**	**
	A C	*	*	**		**	*
	A D	*	**	**		**	*
	A E	**	**	**			
	B C	*	*	**		**	
	B D	*	**	*		**	
	B E	**	**	**			
	C D					**	
	C E			**			
	D E						
KN07	A B				**	**	**
	A C		*	*	**	**	**
	A D		*		**	**	*
	A E			**	**	**	**
	B C				*	**	*
	B D		*		**	**	*
	B E			**	**	**	**
	C D		**	**	*	**	
	C E			**	*	**	
	D E			**		**	
KN08	A B				**	*	**
	A C				**	*	**
	A D	*	*		**	**	**
	A E	*	*		**	*	**
	B C			**	**	**	

Table G-1 Continued

Pedon	Depth comparison	pH			LOI	C	N
		H_2O	KCl	$CaCl_2$			
	B D			*	**	*	
	B E	*		**	**	**	*
	C D		*	**	**	*	
	C E		**	**	**	**	*
KN09	A B			*	**	*	*
	A C		**	**	**	*	**
	A D		**	*	**	**	
	A E	*	**	**	**	**	**
	B C		**		**	**	*
	B D		**		*	**	
	B E		**		*	**	*
	C D		**		*	**	
	C E		**	**		**	*
	D E		**			**	*
KN10	A B	**		**		**	*
	A C	**		**		**	*
	A D	*		**	*	**	
	B C			**	**	**	
	B D		**	**	*	**	
	C D					**	
KN11	A B			*	*	**	**
	A C			*		**	**
	A D			**	**	**	**
	A E			*	**	**	**
	B C					**	*
	B D		**	*	**	**	*
	B E		**		**	**	**
	C D					**	
	C E				*	**	*
	D E				*	**	

Table G-1 Continued

Pedon	Depth comparison	CEC	ECEC	AEC	Al	ASP	Ca	Mg	K	Na
KN01	A B			**						
	A C			**		*		**	**	
	A D			**			**	**	**	
	A E			**	**	*		**		
	B C			**				**	**	
	B D			**			**	**		**
	B E			*	*			**		**
	C D								*	
	C E			*					**	
	D E			*						**
KN02	A B	*			**	*				**
	A C			**		*			**	**
	A D			**	*				*	**
	B C	*							*	**
	B D	**			**	**				
	C D	*			*	**				**
KN03	A B									
	A C				*	*	*			
	A D				**	**	**			
	B C				*	**				
	B D			**	**	**				**
	C D									**
KN04	A B						*	**		**
	A C								*	**
	A D				*					**
	B C									
	B D								**	
	C D				*					
KN05	A B	**								
	A C		*					**		
	A D	**	*					**		**
	A E	**	**			**		**		**
	B C				*					
	B D					*				
	B E	*			**	**				
	C D									**
	C E		*		**	**				**
	D E				**	**		*		**

Table G-1 Continued

Pedon	Depth comparison	CEC	ECEC	AEC	Al	ASP	Ca	Mg	K	Na
KN06	A B			**						
	A C									
	A D			**	**	*		*		
	A E		*	**	*	*	**			
	B C			**						**
	B D			**	**	**		*		**
	B E			*		*				**
	C D				**	**		*		
	C E		*	*	*	*				**
	D E			*				*		**
KN07	A B		*					**	**	**
	A C								*	**
	A D	**	**		*	**	**			**
	A E	**	**				**	*		**
	B C							**		
	B D	*	**		*	**	*			**
	B E	*	*					*	**	
	C D		**		*	*		*		**
	C E		*	*				**	*	
	D E				*	*				**
KN08	A B		*	*	**	**			**	**
	A C									**
	A D	*					*		**	
	A E	*	*		**	**				
	B C				**	**				
	B D			**	*		*			**
	B E			*						**
	C D			*		*		*		**
	C E				*	**		*		**
	D E				*					
KN09	A B								*	**
	A C							**		
	A D		*							**
	A E		*						**	**
	B C								*	**
	B D		*		*			*	**	
	B E		*		*	**			*	**
	C D		*		*			**		**
	C E		*		*	**		*		**
	D E									**

Table G-1 Continued

Pedon	Depth comparison	CEC	ECEC	AEC	Al	ASP	Ca	Mg	K	Na
KN10	A B		*					*		
	A C		**					*		**
	A D		**		**			**	*	**
	B C			*						**
	B D				**				*	**
	C D			**						**
KN11	A B						*	**	*	**
	A C						*			
	A D									
	A E									**
	B C			*						**
	B D									**
	B E		**	*						**
	C D									
	C E									**
	D E									**

Table G-1 Continued

Pedon	Group	AI_{ox},	AI_{d}	Fe_{ox}	Fe_{d}
KN01	A B			**	
	A C		*	**	*
	A D	*		**	*
	A E	*		*	
	B C			*	
	B D			**	
	B E	*		**	
	C D				
	C E			**	*
	D E			**	
KN02	A B	**	*	*	
	A C	*		**	**
	A D	**	*	**	**
	B C	*		**	**
	B D			**	**
	C D	**		**	
KN03	A B	**	*	**	**
	A C	**	*	**	*
	A D	**		**	*
	B C			**	
	B D			**	*
	C D				
KN04	A B			*	**
	A C	**	*	**	*
	A D	**	**	**	
	B C	**	*	**	**
	B D	*	**	**	*
KN05	A B				
	A C	**		*	
	A D	**		**	*
	A E	**	*	**	*
	B C	**			*
	B D	**		**	*
	B E	**	**	**	*
	C D			**	*
	C E			**	**
	D E			**	*

Table G-1 Continued

Pedon	Group	AI_{ox},	AI_d	Fe_{ox}	Fe_d
KN06	A B	*	**	**	**
	A C		**		*
	A D		*	*	**
	A E		**	**	**
	B D			**	*
	B E	*	*	**	**
	C D				*
	C E		*	**	
	D E			**	*
KN07	A B	*		**	*
	A C			**	**
	A D	*		**	*
	A E	**		**	**
	B C		*	**	**
	B D	*		**	
	B E	*		**	**
	C D	**		**	**
	C E	**		**	*
	D E	*		*	**
KN08	A B			**	*
	A C	**		**	
	A D	**	*	**	*
	A E	**	*	**	
	B C			**	*
	B D	**		**	**
	B E	**		**	
	C D	**			
	C E	**	*	**	
	D E	**		**	
KN09	A B	*	*		
	A C	**			*
	A D	**	*	**	*
	A E	**	*	*	
	B C	*		**	
	B D		*	**	
	B E			**	
	C D	**		**	
	C E	*		**	
	D E	*	*	**	

Table G-1 Continued

Pedon	Group	AI_{ox},	AI_d	Fe_{ox}	Fe_d
KN10	A B	**		**	*
	A C	**		**	*
	A D	**		**	
	B C			**	
	B D	**		**	
	C D	**	*	*	
KN11	A B	*			
	AC	*	**	**	
	A D	**	**	**	
	A E	**		**	
	B C		*	*	
	B D	**		**	*
	B E	**			
	C D	**		**	
	C E	**	**	**	
	D E	**	**	**	

Table G-2 Significance of T-test of comparison of sampling depths of Brazilian Pedons

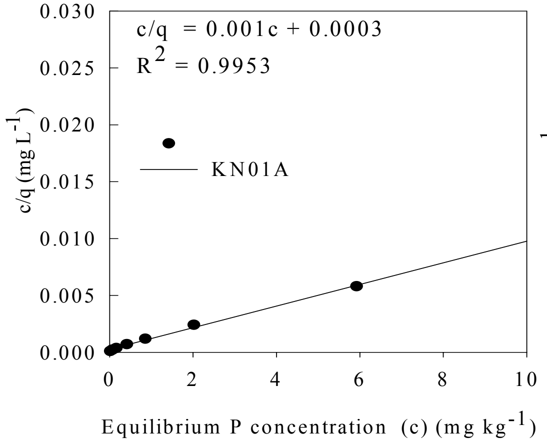
Pedon	Depth Comparison	C (Leco)	N (Leco)	LOI	FeOx	Alox	Fed	Ald	Al Sub	FeAlOx_ FeAlD	Ox FeD
G1	A1A2	**	**	*	**		*	*		**	**
G2	A1A2	**	**	**	**		**	*	*	**	**
N1	A1A2	**	**	**	**						*
N2	A1A2	**	**		**	**					**
N5	A1A2	**			**						
T1	A1A2	**	**		**	**		*		*	*
T2	A1A2	**	**		**						*
T4	A1A2	**	**		**	**		*			**
T5	A1A2	**	**			**	**			**	*

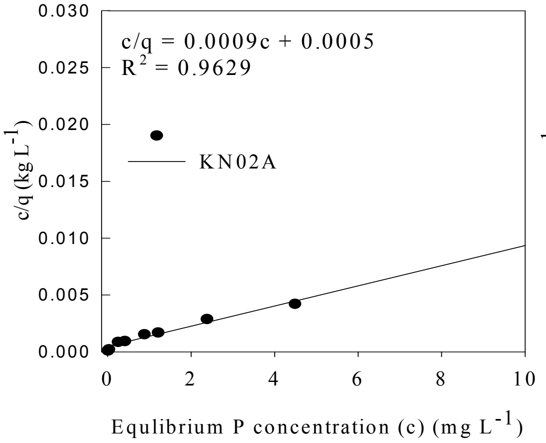
Appendix H. Pearson correlation matrix of chemical properties of Kenyan soils. N = 51

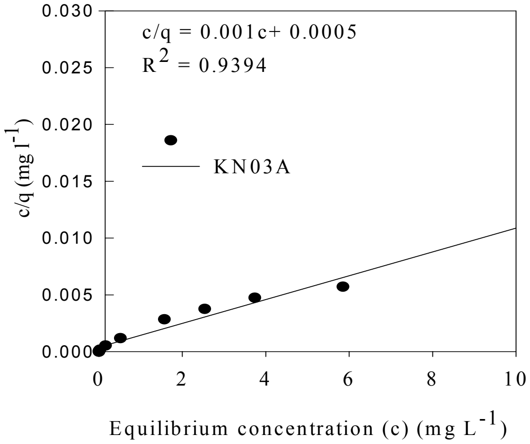
Property	pHwater	N	C	LOI	ASP	ECEC	AEC	Al_{ox}	Fe_{ox}	P_{ox}	Al_d	Fe_d
pH water	1											
N Leco	-0.427 (**)	1										
C Leco	-0.460 (**)	0.888 (**)	1									
LOI	-0.573 (**)	0.753 (**)	0.847 (**)	1								
ASP	-0.707 (**)	0.501 (**)	0.515 (**)	0.693 (**)	1							
ECEC	0.497 (**)	0.017	0.074	0.012	-0.364 (**)	1						
AEC	-0.242	-0.053	0.024	0.038	0.061	-0.079	1					
Al_L	-0.081	0.247	0.227	0.229	0.366 (**)	-0.306 (*)	-.315(*)	1				
Fe_{ox}	-0.515 (**)	0.499 (**)	0.381 (**)	0.616 (**)	0.713 (**)	-.280 (*)	-0.075	0.309 (*)	1			
P_{ox}	-0.313	0.378	0.075	0.232	0.341	-0.107	-0.173	0.839 (**)	0.580	1		
Al_d	0.145	-0.220	-0.113	-0.181	-0.023	-0.394 (**)	0.092	0.168	-0.292 (*)	0.072	1	
Fe_d	-0.198	0.089	0.268	0.391 (**)	0.433 (**)	-0.160	-0.186	0.559 (**)	0.167	0.371	0.236	1

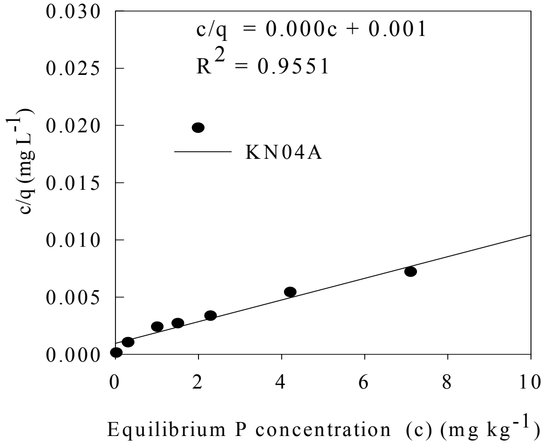
(**) Correlation is significant at the 0.01 level (2-tailed) (*) Correlation is significant at the 0.05 level (2-tailed).

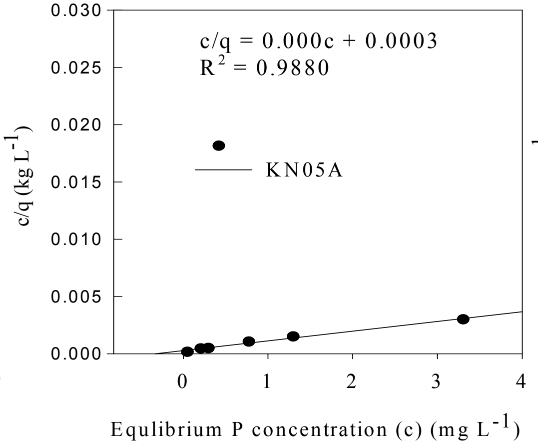
Appendix I. Linear langmuir sorption models of Kenyan and Brazilian topsoils

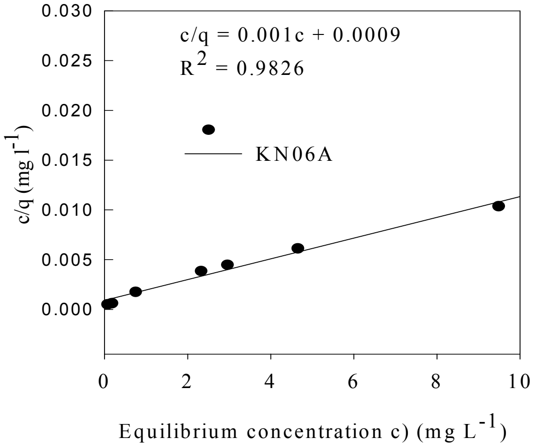


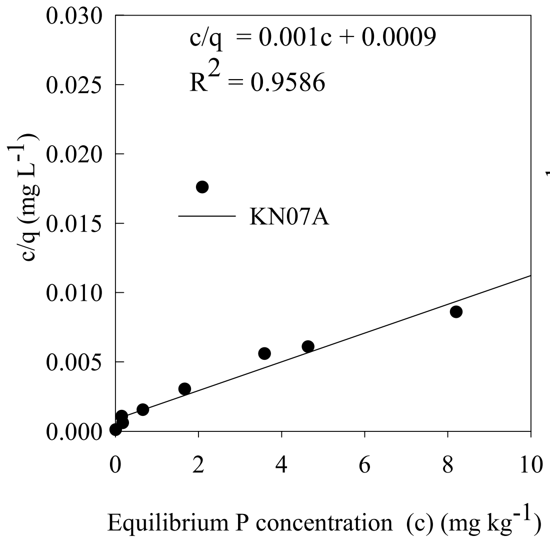


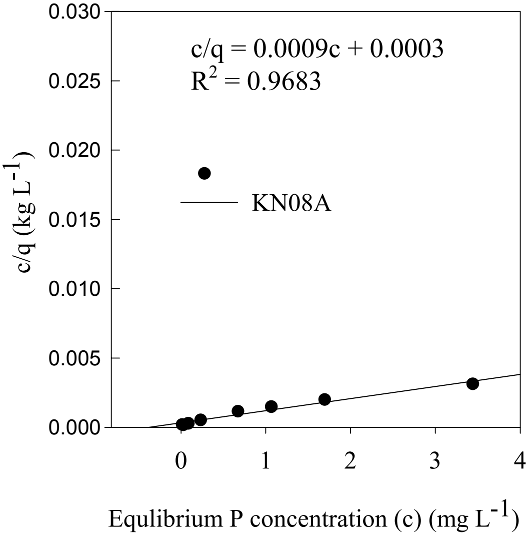


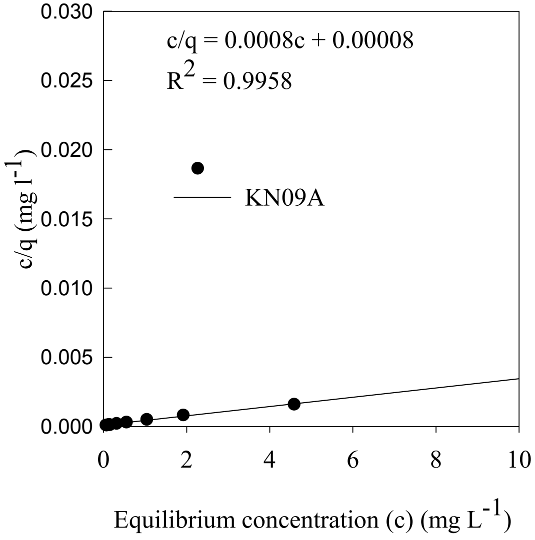


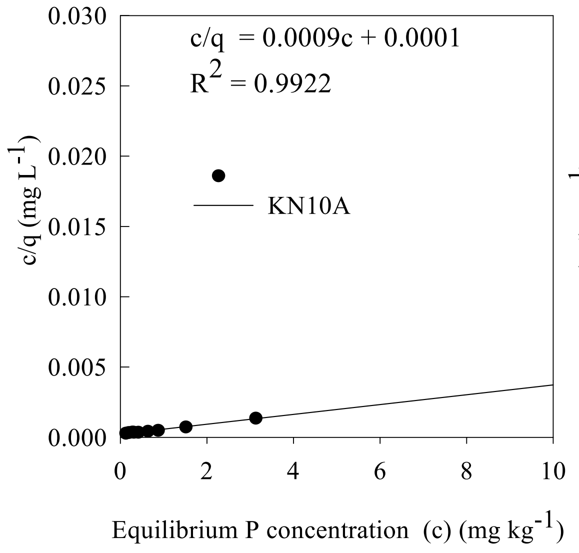


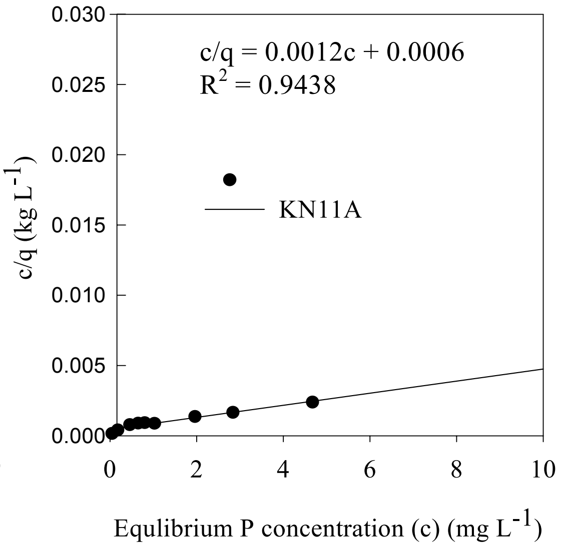


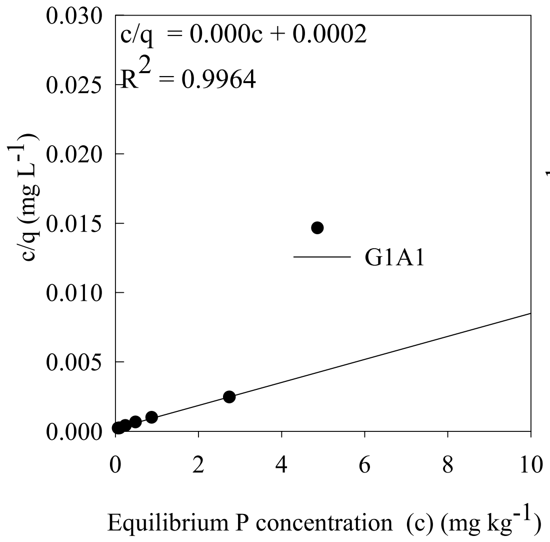

c/q = 0.001c + 0.0009
$R^2 = 0.9586$
KN07A
c/q (mg L^{-1})
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
2
4
6
8
10
Equilibrium P concentration (c) (mg kg^{-1})

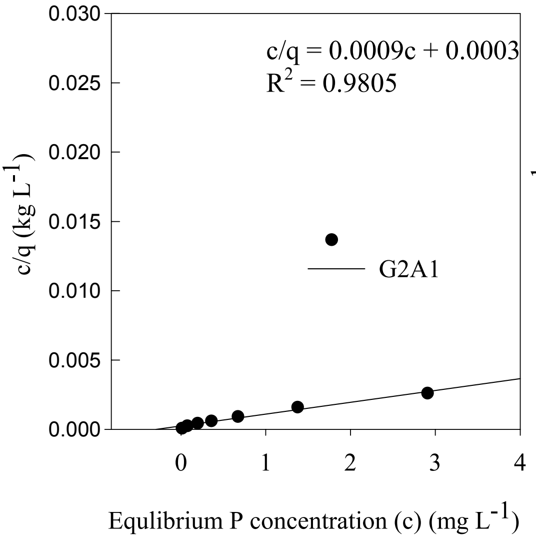

c/q = 0.0009c + 0.0003
$R^2 = 0.9683$
KN08A
c/q (kg L^{-1})
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
1
2
3
4
Equlibrium P concentration (c) (mg L^{-1})

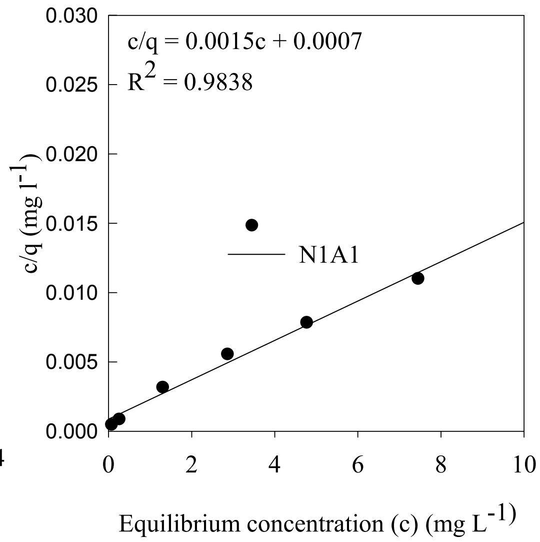

c/q = 0.0008c + 0.00008
$R^2 = 0.9958$
KN09A
c/q (mg l^{-1})
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
2
4
6
8
10
Equilibrium concentration (c) (mg L^{-1})

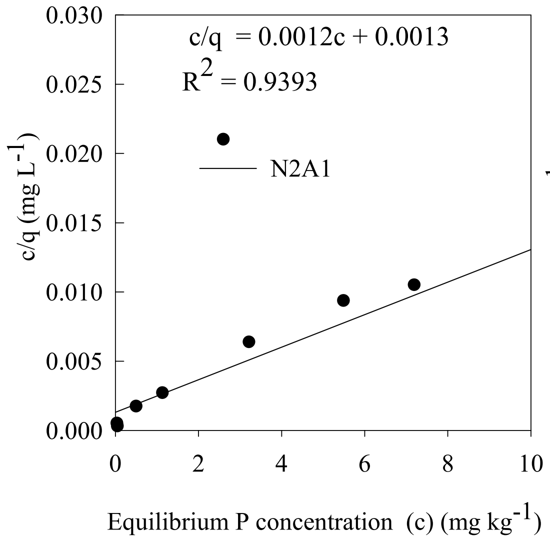

c/q = 0.0009c + 0.0001
$R^2 = 0.9922$
KN10A
c/q (mg L^{-1})
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
2
4
6
8
10
Equilibrium P concentration (c) (mg kg^{-1})

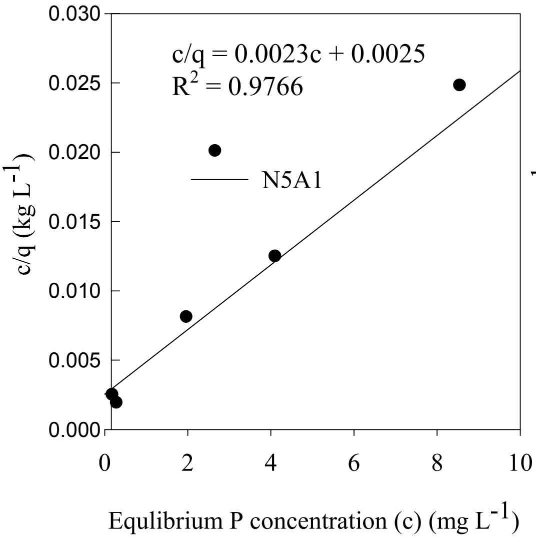

c/q = 0.0012c + 0.0006
$R^2 = 0.9438$
KN11A
c/q (kg L^{-1})
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
2
4
6
8
10
Equlibrium P concentration (c) (mg L^{-1})

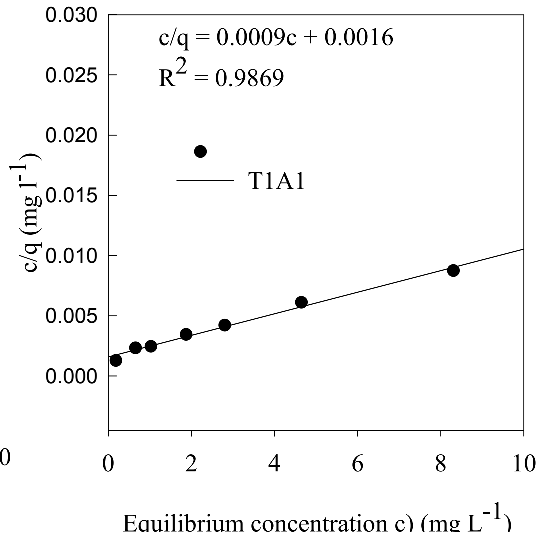

c/q = 0.000c + 0.0002
R^2 = 0.9964
G1A1
c/q (mg L^{-1})
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
2
4
6
8
10
Equilibrium P concentration (c) (mg kg^{-1})

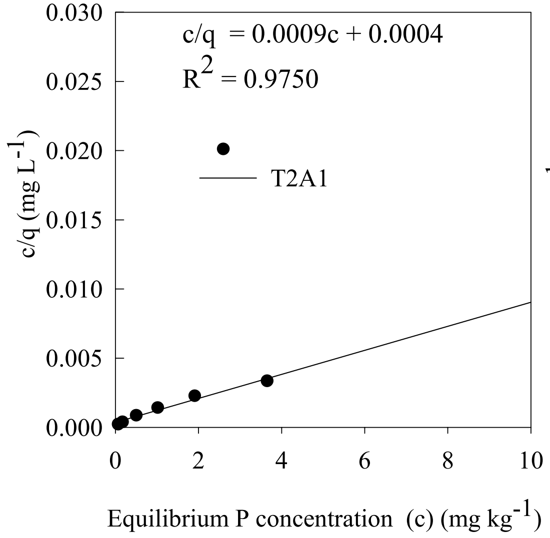

c/q = 0.0009c + 0.0003
R^2 = 0.9805
G2A1
c/q (kg L^{-1})
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
1
2
3
4
Equlibrium P concentration (c) (mg L^{-1})

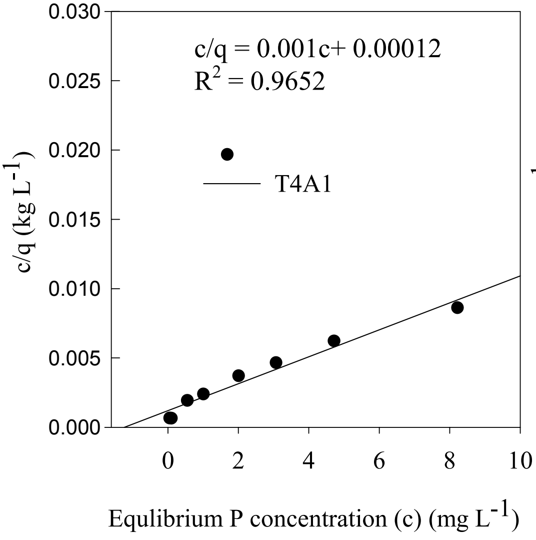

c/q = 0.0015c + 0.0007
R^2 = 0.9838
N1A1
c/q (mg l^{-1})
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
2
4
6
8
10
Equilibrium concentration (c) (mg L^{-1})

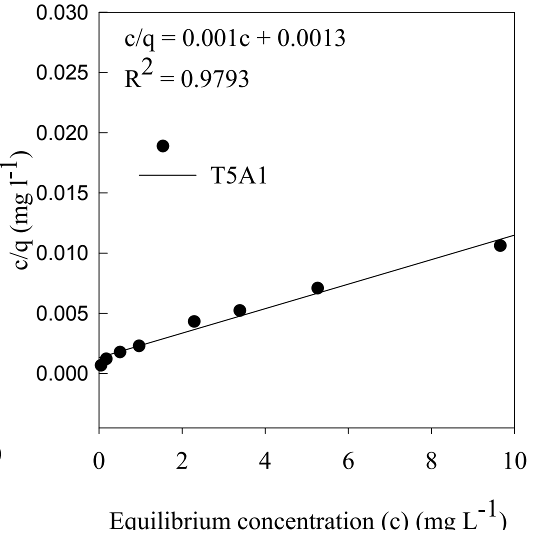

c/q = 0.0012c + 0.0013
R^2 = 0.9393
N2A1
c/q (mg L^{-1})
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
2
4
6
8
10
Equilibrium P concentration (c) (mg kg^{-1})


c/q = 0.0023c + 0.0025
R^2 = 0.9766
N5A1
c/q (kg L^{-1})
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
2
4
6
8
10
Equlibrium P concentration (c) (mg L^{-1})


c/q = 0.0009c + 0.0016
R^2 = 0.9869
T1A1
c/q (mg l^{-1})
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
2
4
6
8
10
Equilibrium concentration c) (mg L^{-1})

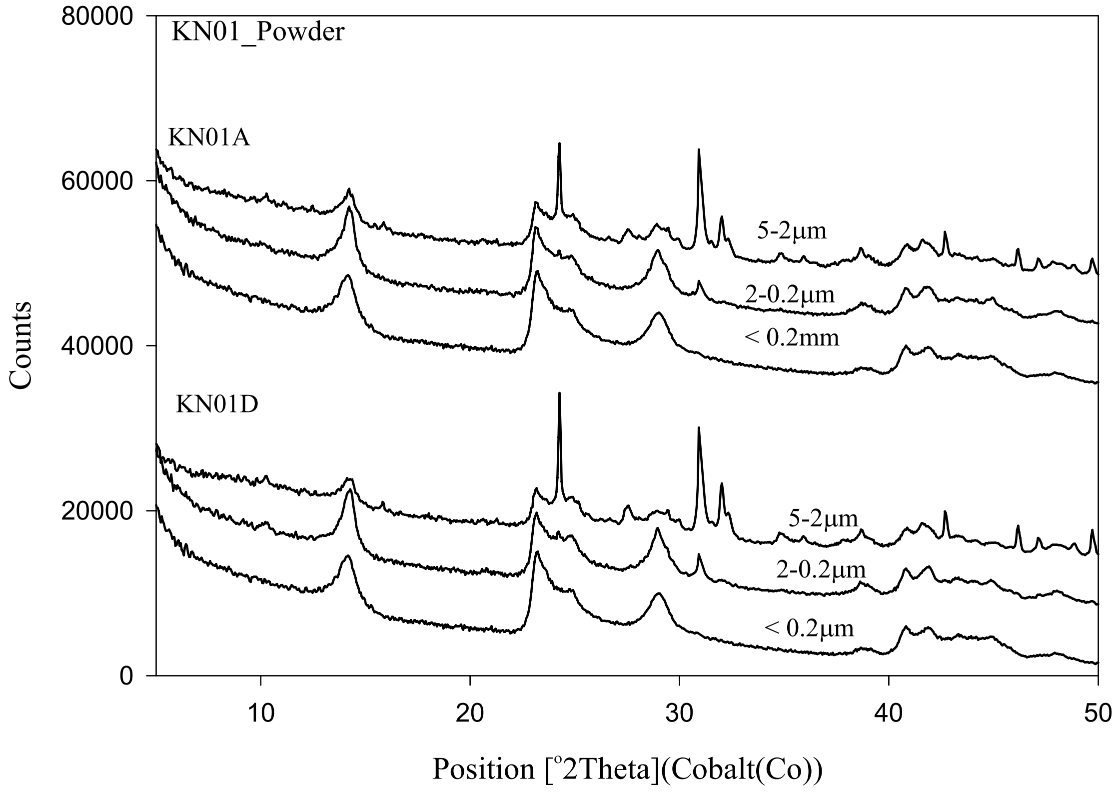


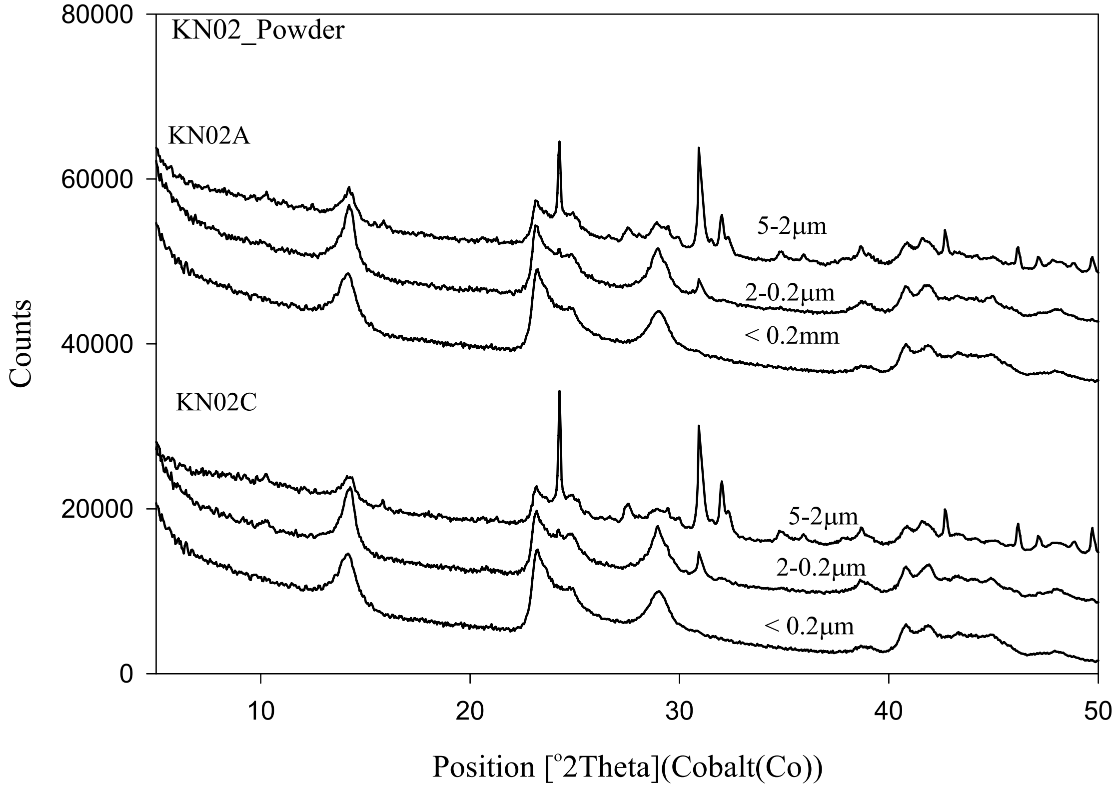


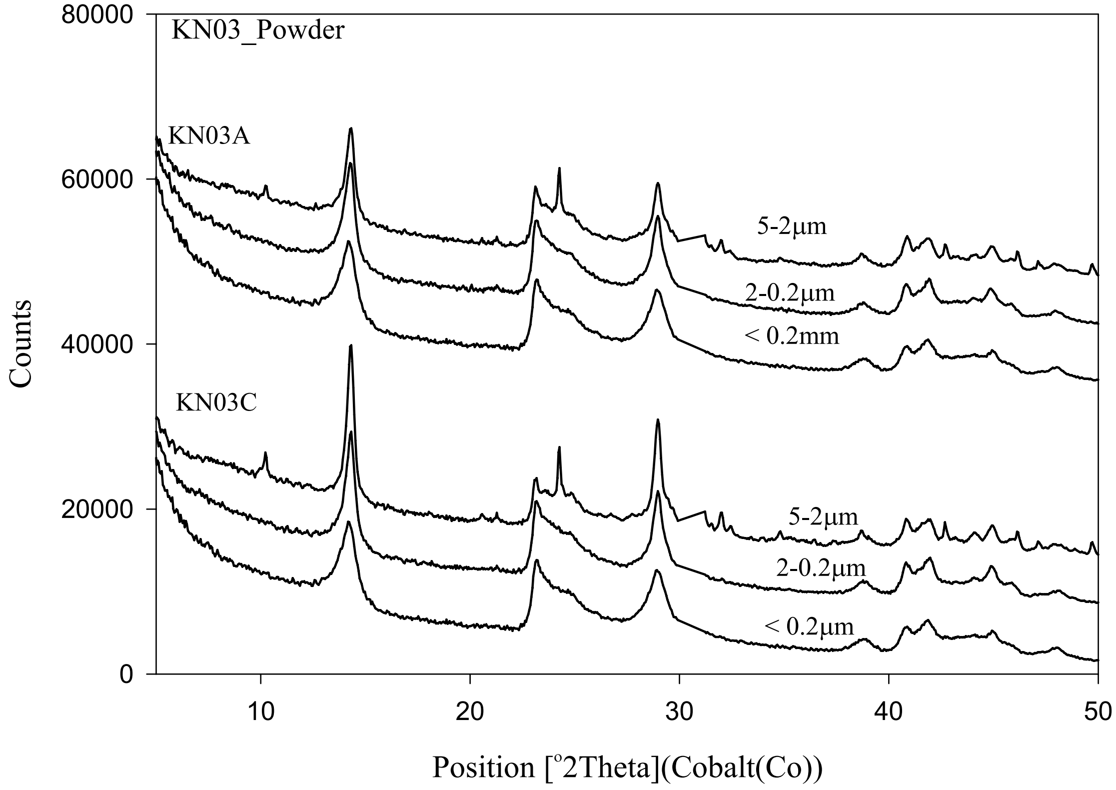


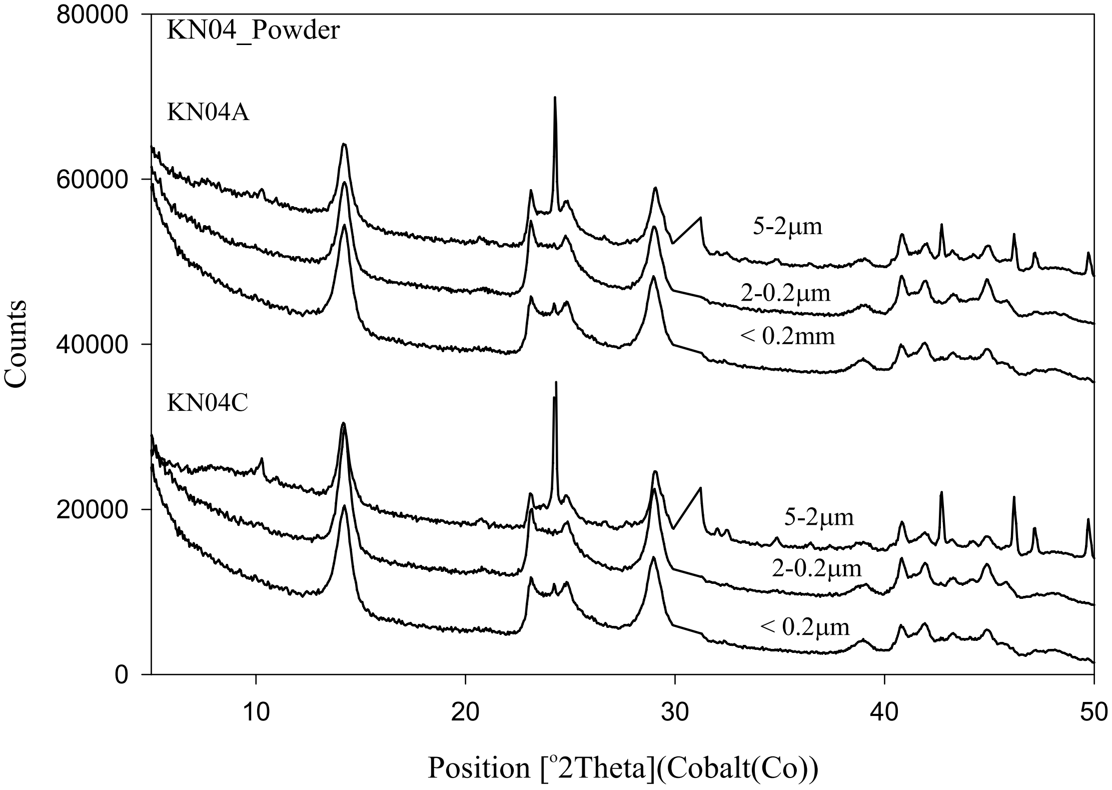
q = P sorbed (mg kg^{-1}).

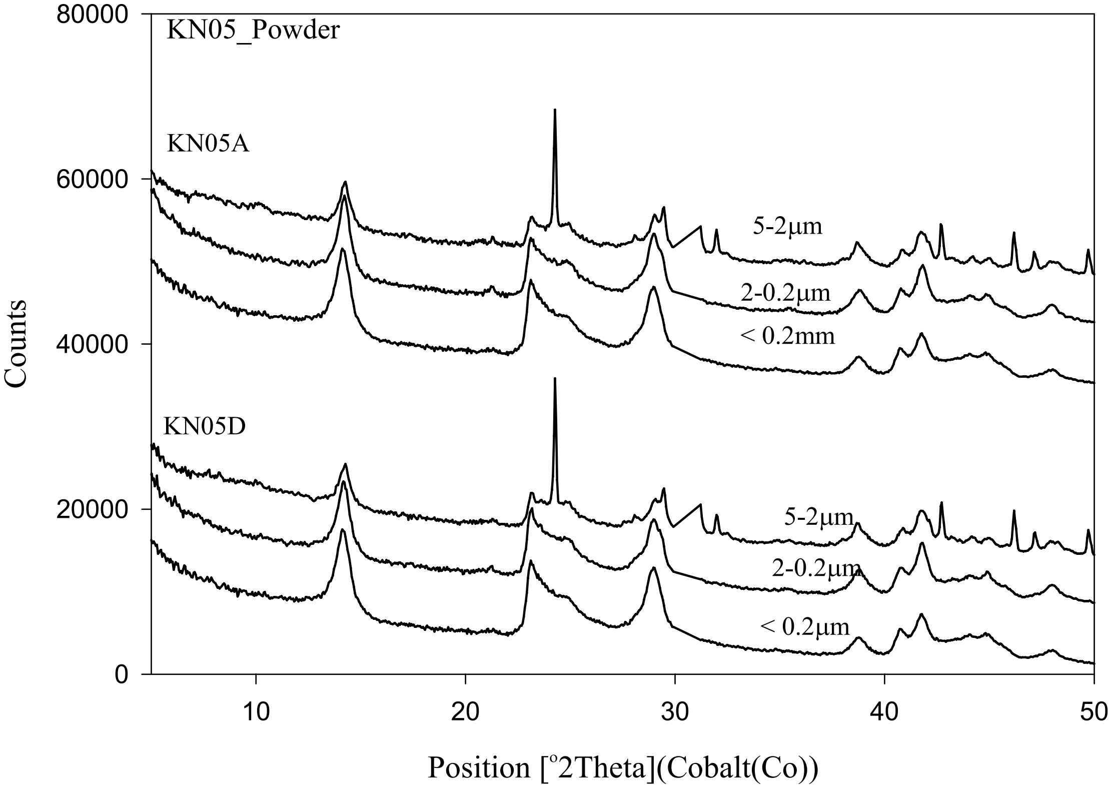
Appendix J. XRD powder diffraction patterns of the Kenyan soils.

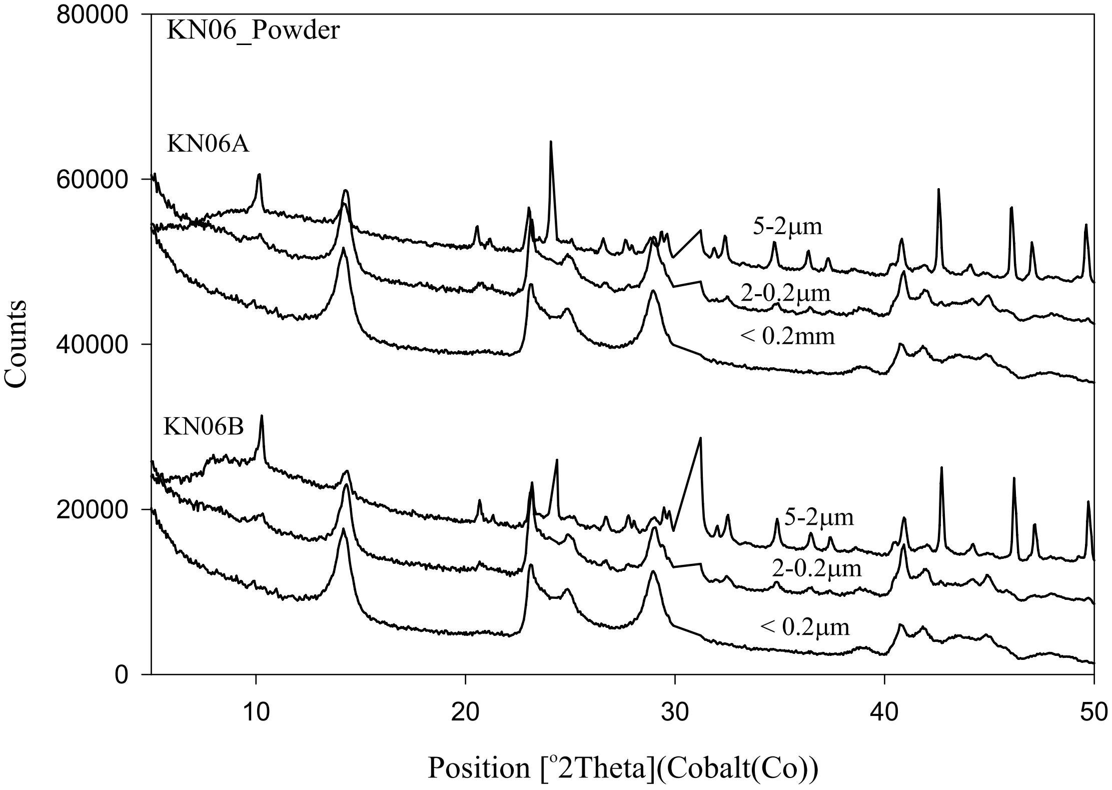


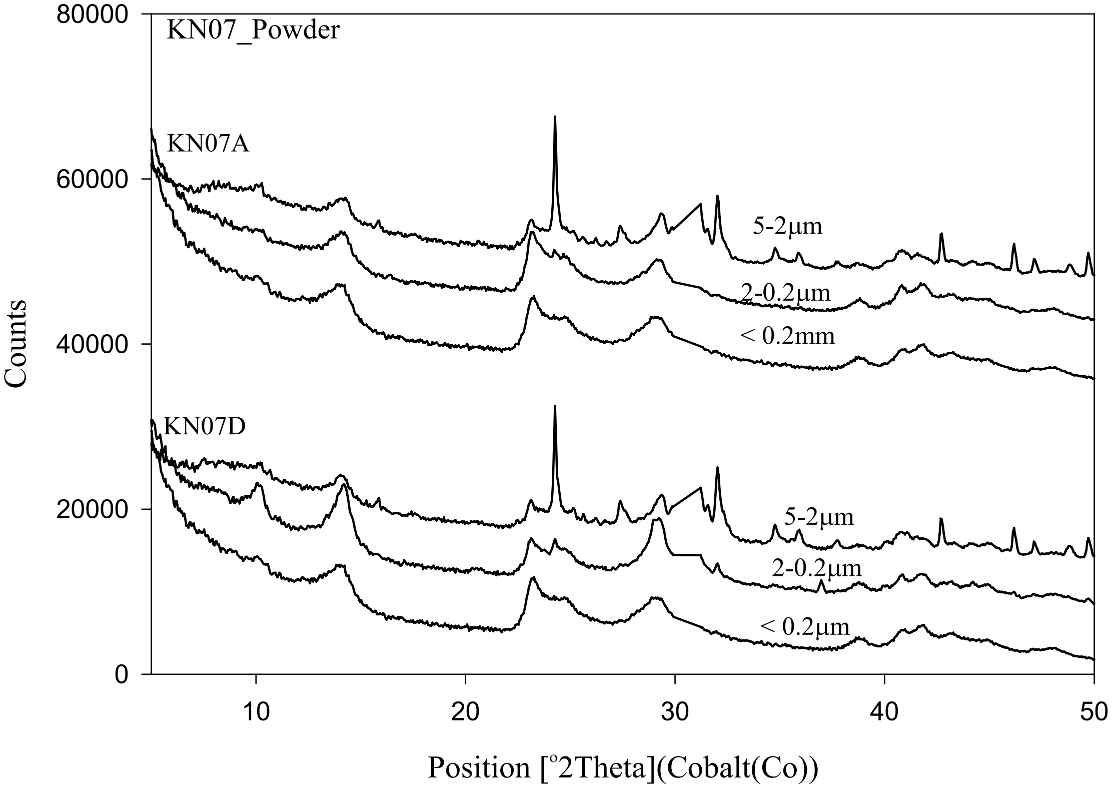

KN02_Powder
KN02A
KN02C
5-2μm
2-0.2μm
< 0.2mm
5-2μm
2-0.2μm
< 0.2μm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position [°2Theta](Cobalt(Co))

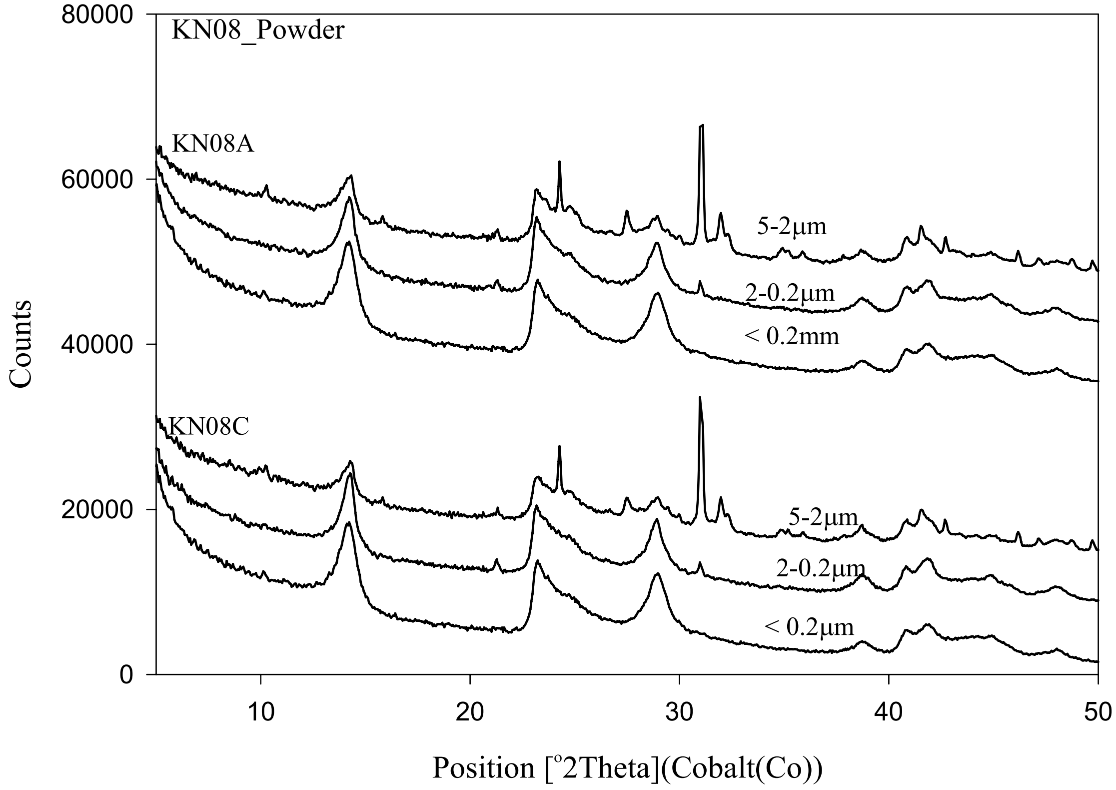

KN03_Powder
KN03A
KN03C
5-2μm
2-0.2μm
< 0.2mm
5-2μm
2-0.2μm
< 0.2μm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position [°2Theta](Cobalt(Co))

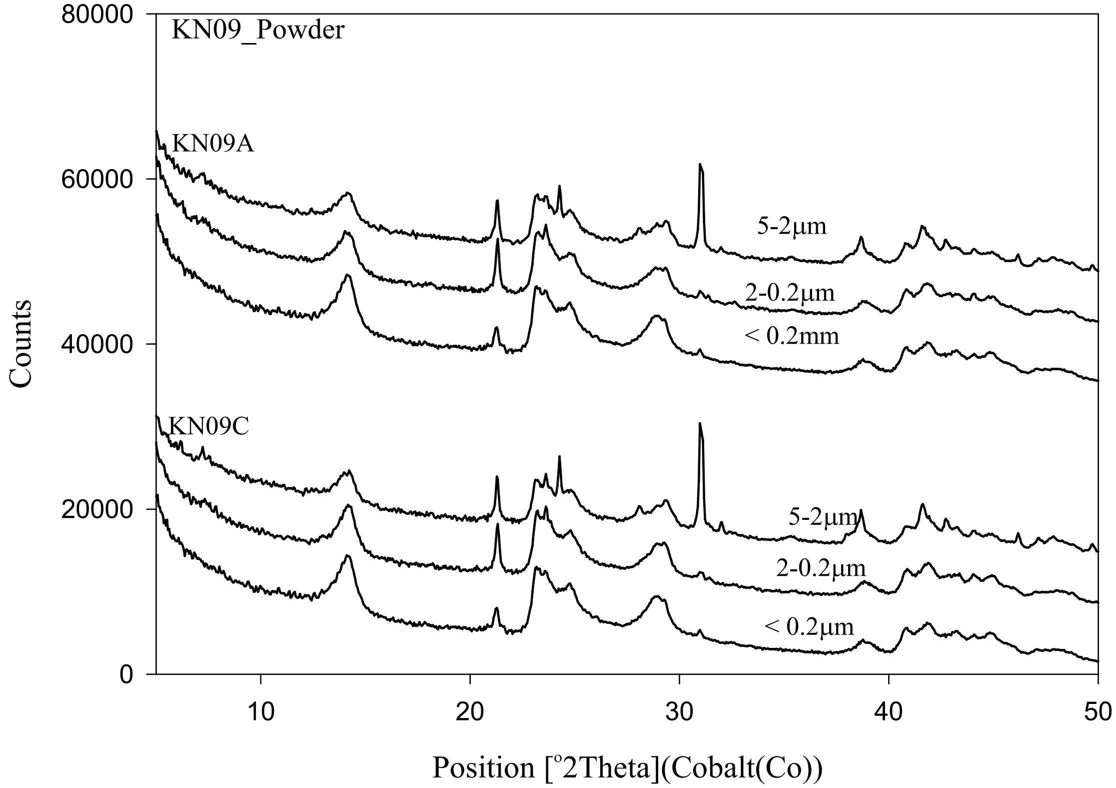

KN04_Powder
KN04A
KN04C
5-2μm
2-0.2μm
< 0.2mm
5-2μm
2-0.2μm
< 0.2μm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position [°2Theta](Cobalt(Co))

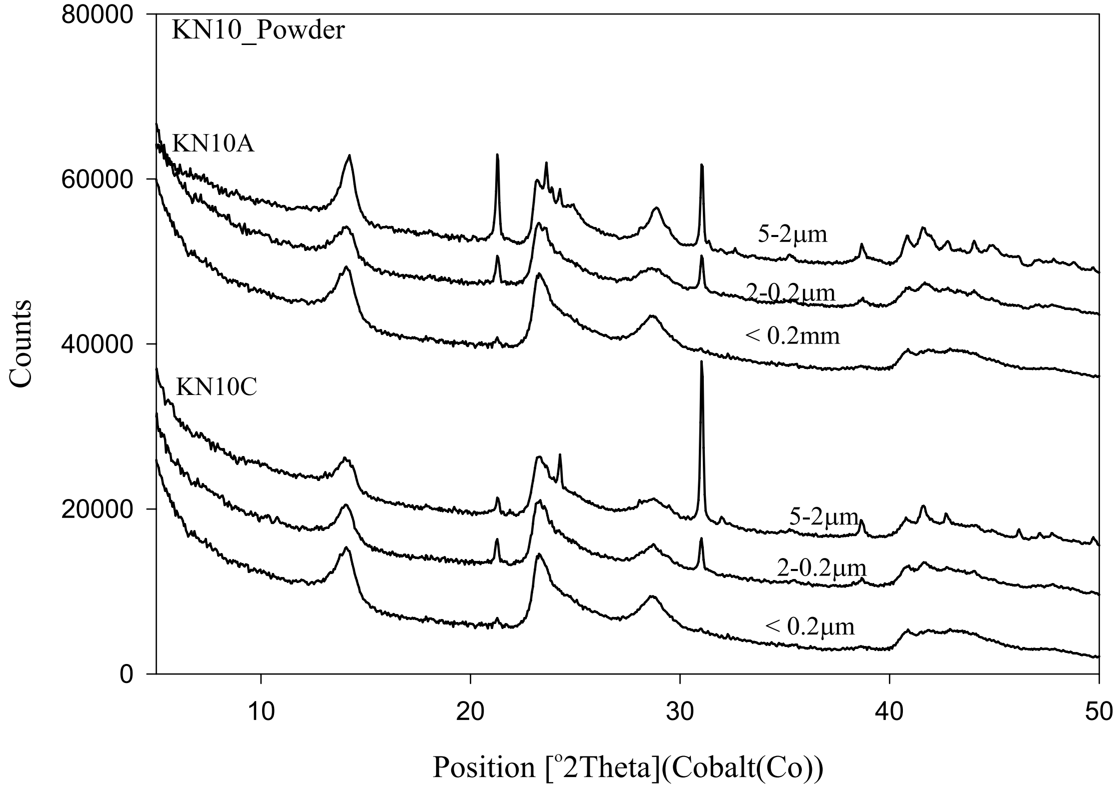

KN05_Powder
KN05A
KN05D
5-2μm
2-0.2μm
< 0.2mm
5-2μm
2-0.2μm
< 0.2μm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position [°2Theta](Cobalt(Co))


KN06_Powder
KN06A
5-2μm
2-0.2μm
< 0.2mm
KN06B
5-2μm
2-0.2μm
< 0.2μm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position [°2Theta](Cobalt(Co))

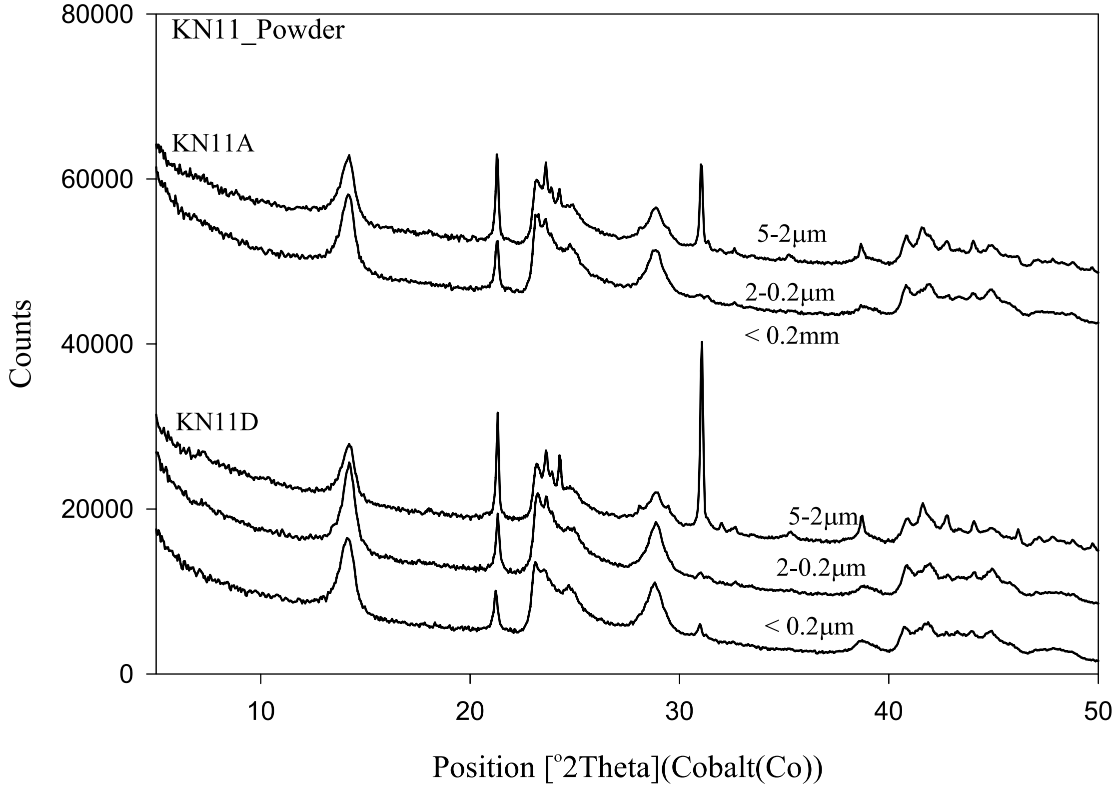

KN07_Powder
KN07A
5-2μm
2-0.2μm
< 0.2mm
KN07D
5-2μm
2-0.2μm
< 0.2μm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position [°2Theta](Cobalt(Co))


KN08_Powder
KN08A
5-2μm
2-0.2μm
< 0.2mm
KN08C
5-2μm
2-0.2μm
< 0.2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position [°2Theta](Cobalt(Co))

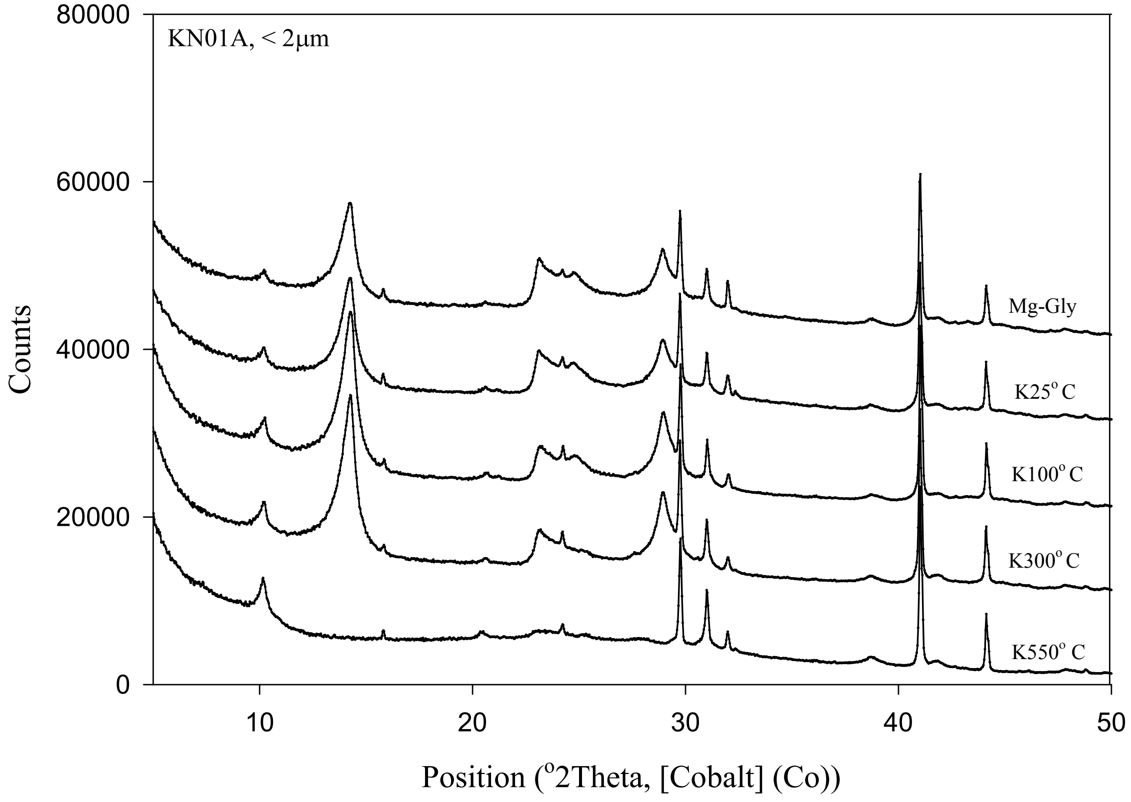

KN09_Powder
KN09A
5-2μm
2-0.2μm
< 0.2mm
KN09C
5-2μm
2-0.2μm
< 0.2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position [°2Theta](Cobalt(Co))

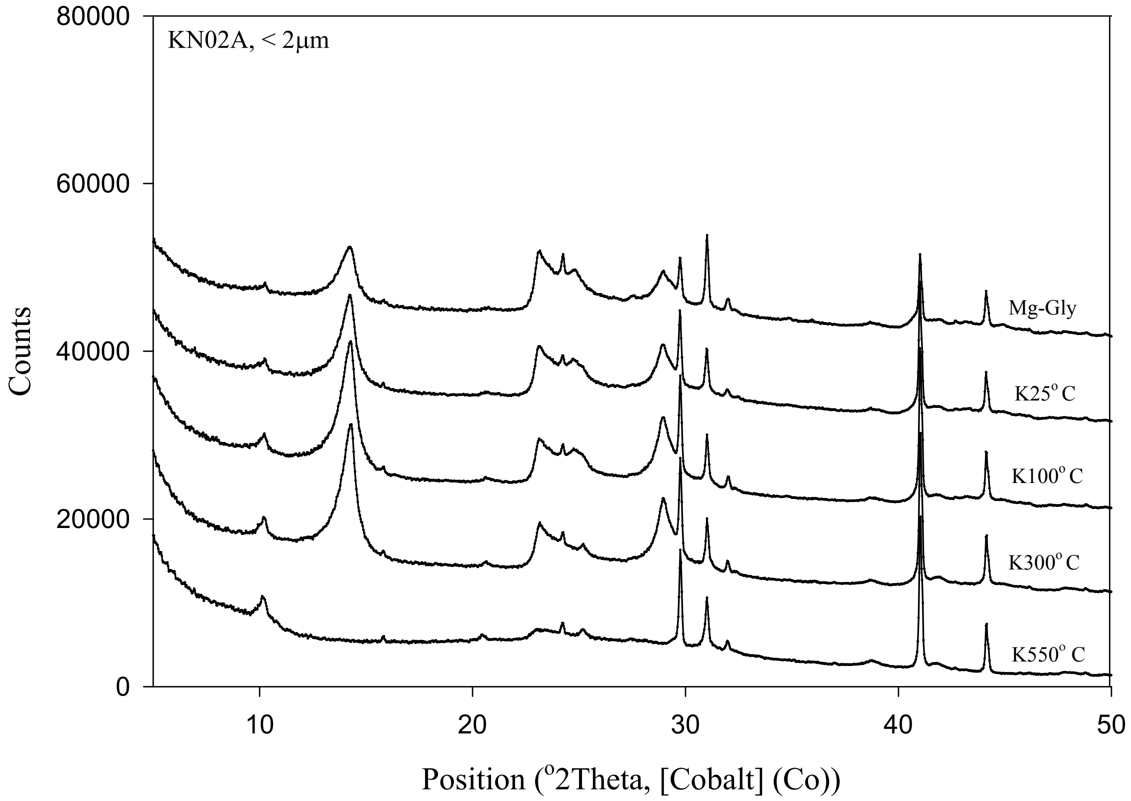


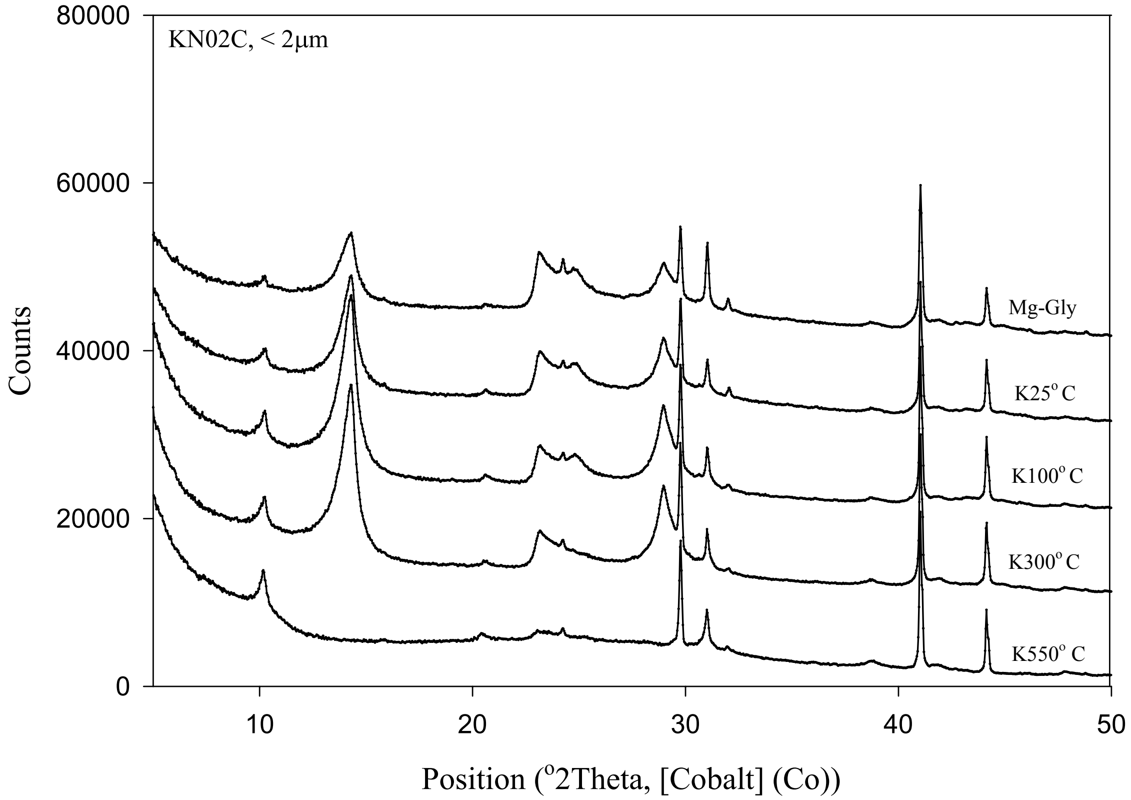
KN10_Powder
KN10A
KN10C
5-2µm
2-0.2µm
< 0.2mm
5-2µm
2-0.2µm
< 0.2µm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position [°2Theta](Cobalt(Co))

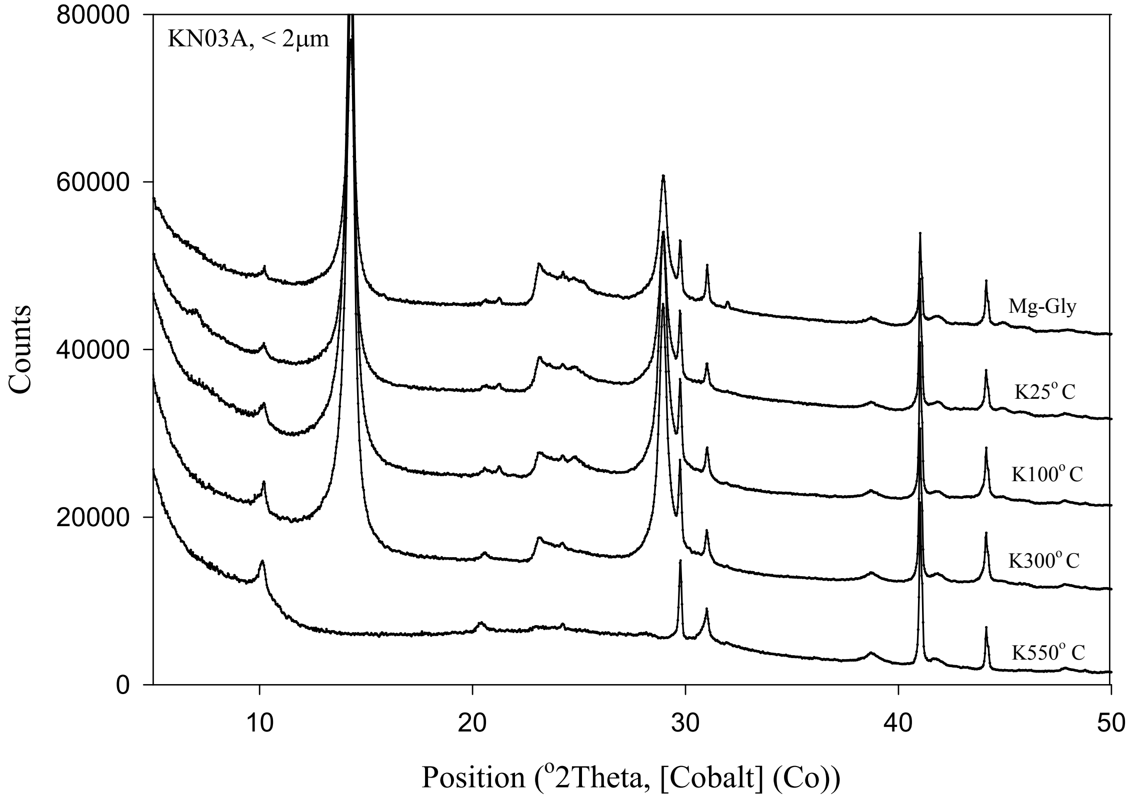

KN11_Powder
KN11A
5-2µm
2-0.2µm
< 0.2mm
KN11D
5-2µm
2-0.2µm
< 0.2µm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position [°2Theta](Cobalt(Co))

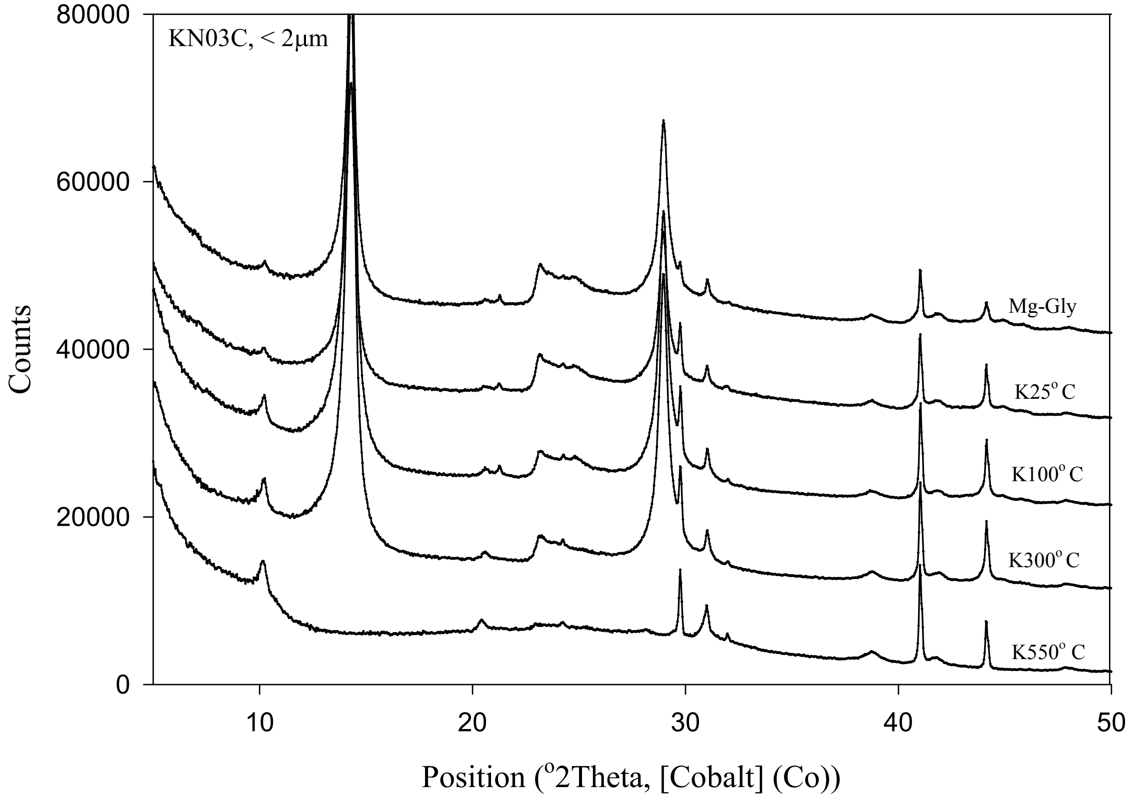
Appendix K. XRD patterns of whole clay fraction of Kenyan and Brazilian soils.

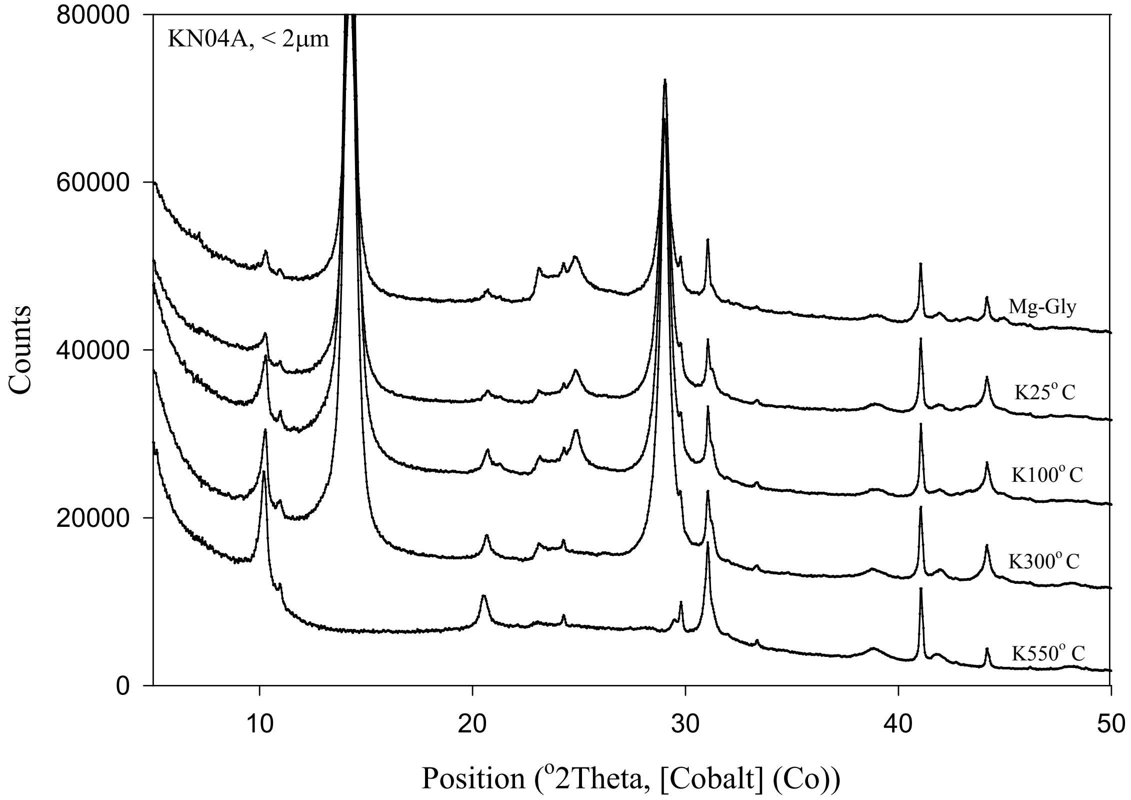


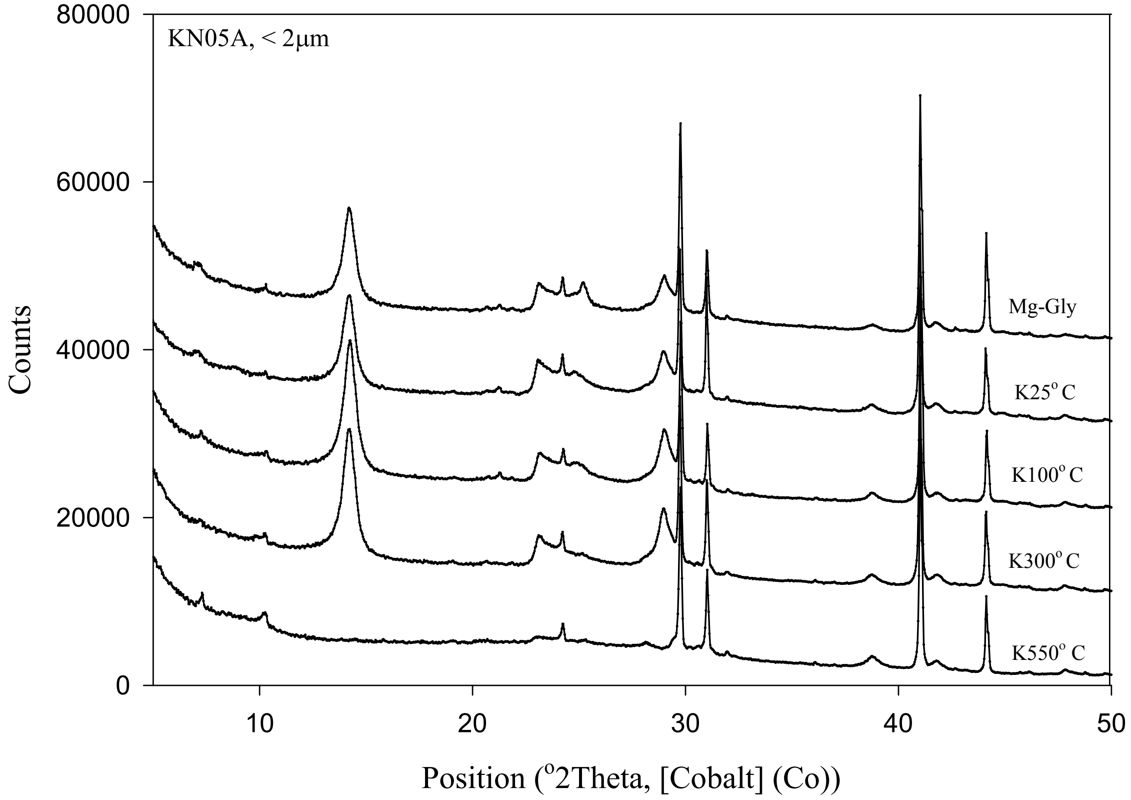

80000
60000
40000
20000
0
Counts
KN02A, < 2μm
Mg-Gly
K25° C
K100° C
K300° C
K550° C
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))

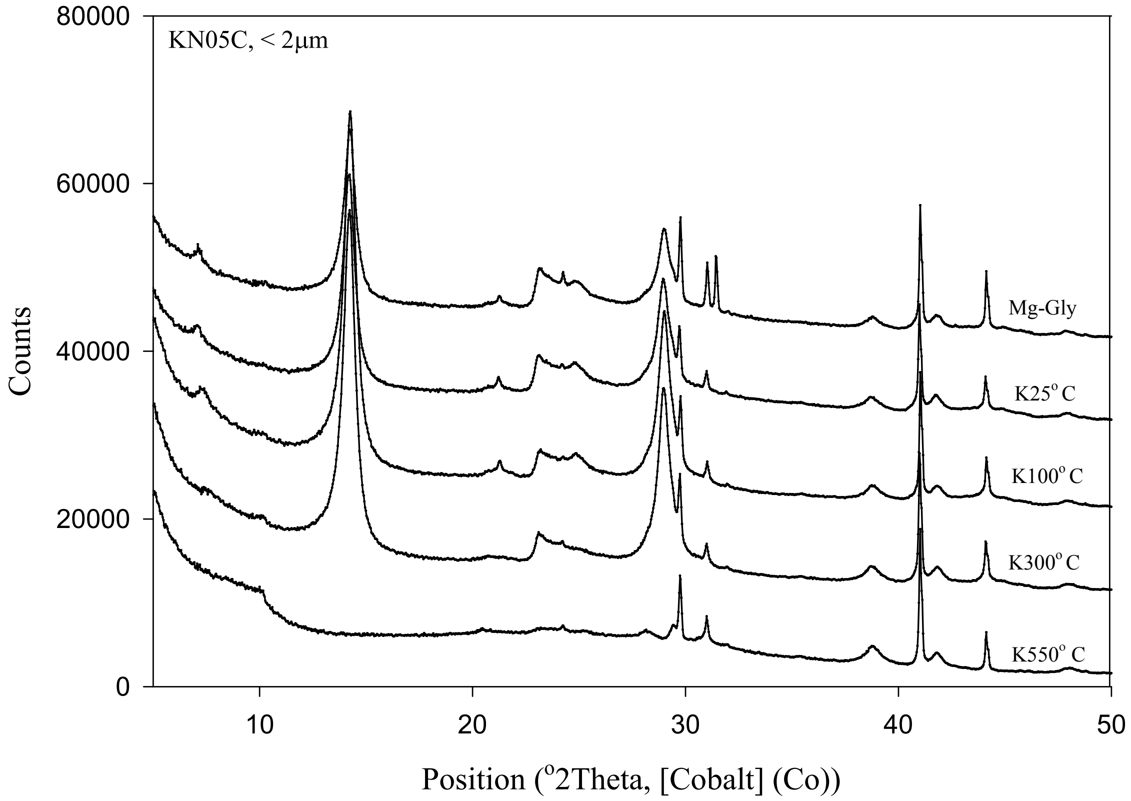

80000
60000
40000
20000
0
Counts
KN02C, < 2μm
Mg-Gly
K25° C
K100° C
K300° C
K550° C
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))

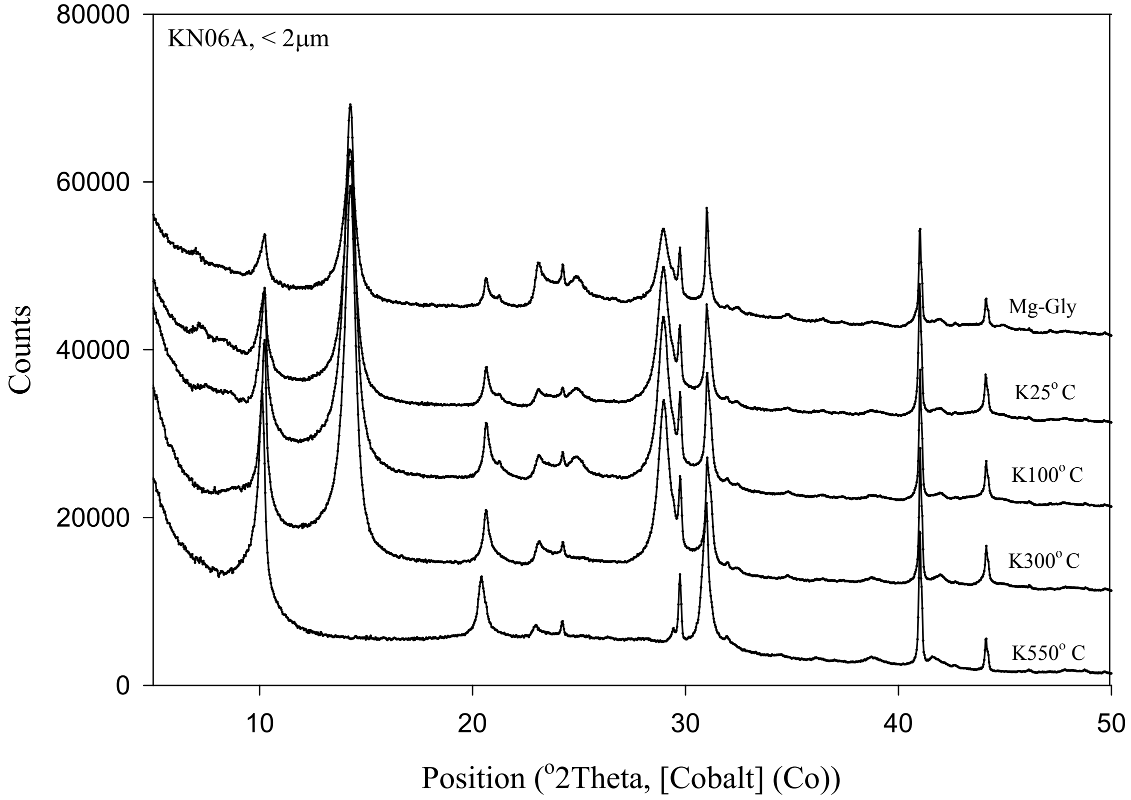

KN03A, < 2μm
Counts
Position (°2Theta, [Cobalt] (Co))
0
20000
40000
60000
80000
10
20
30
40
50
Mg-Gly
K25° C
K100° C
K300° C
K550° C

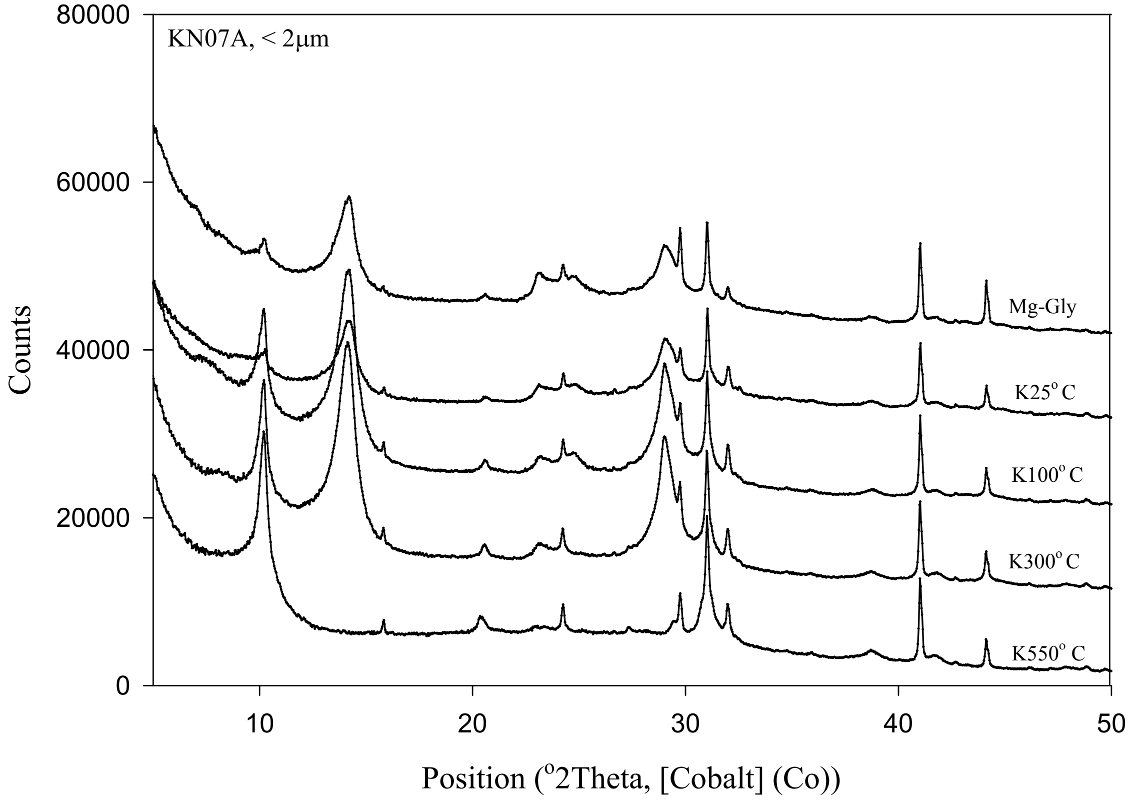

KN03C, < 2μm
Counts
Position (°2Theta, [Cobalt] (Co))
0
20000
40000
60000
80000
10
20
30
40
50
Mg-Gly
K25° C
K100° C
K300° C
K550° C

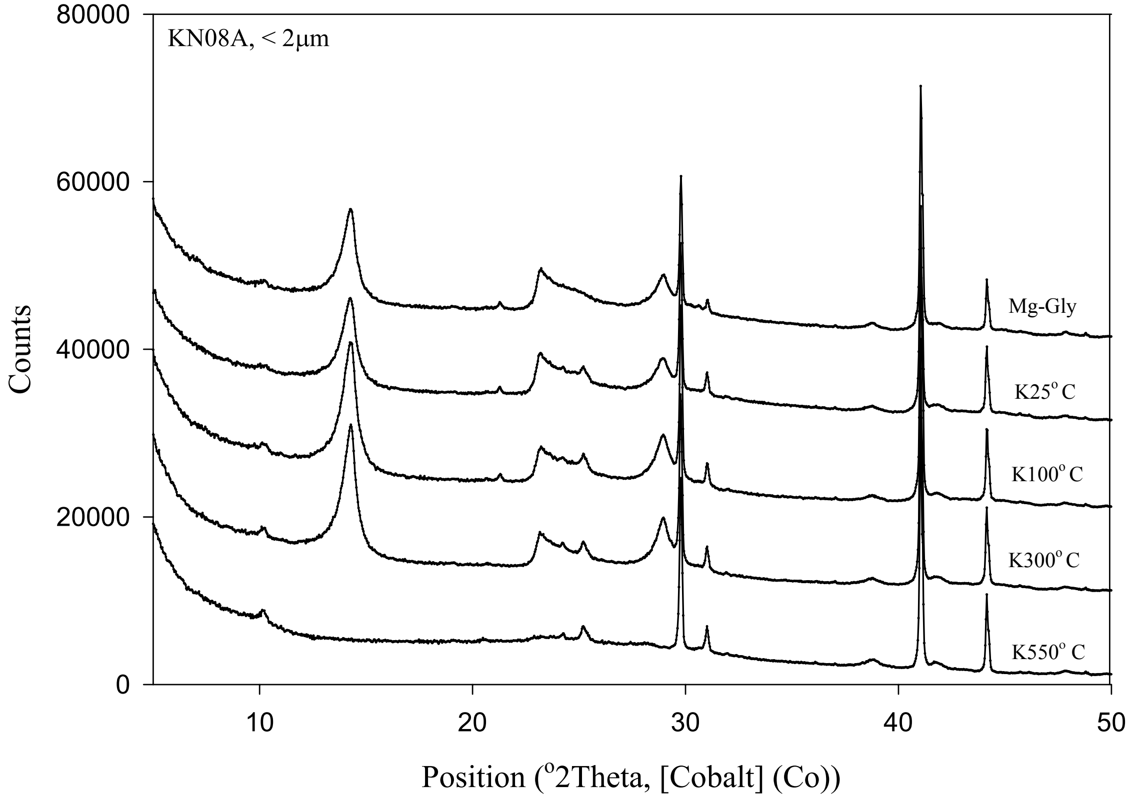

KN04A, < 2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

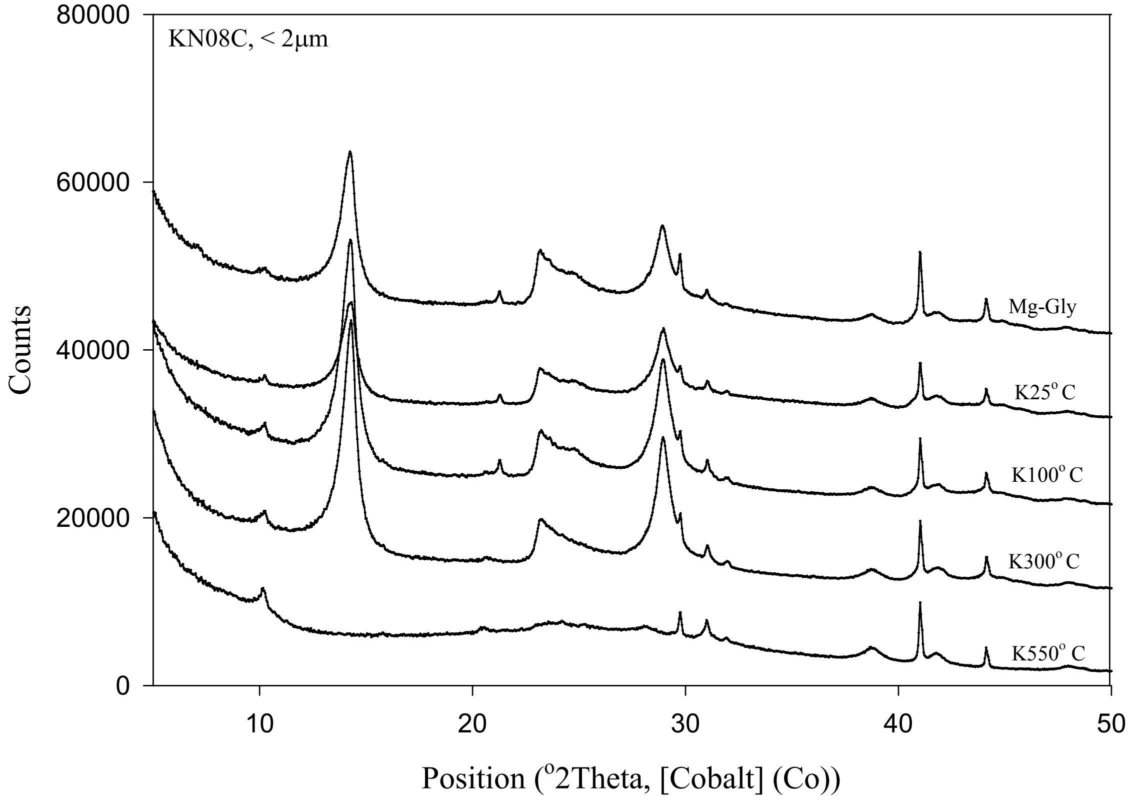

KN05A, < 2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

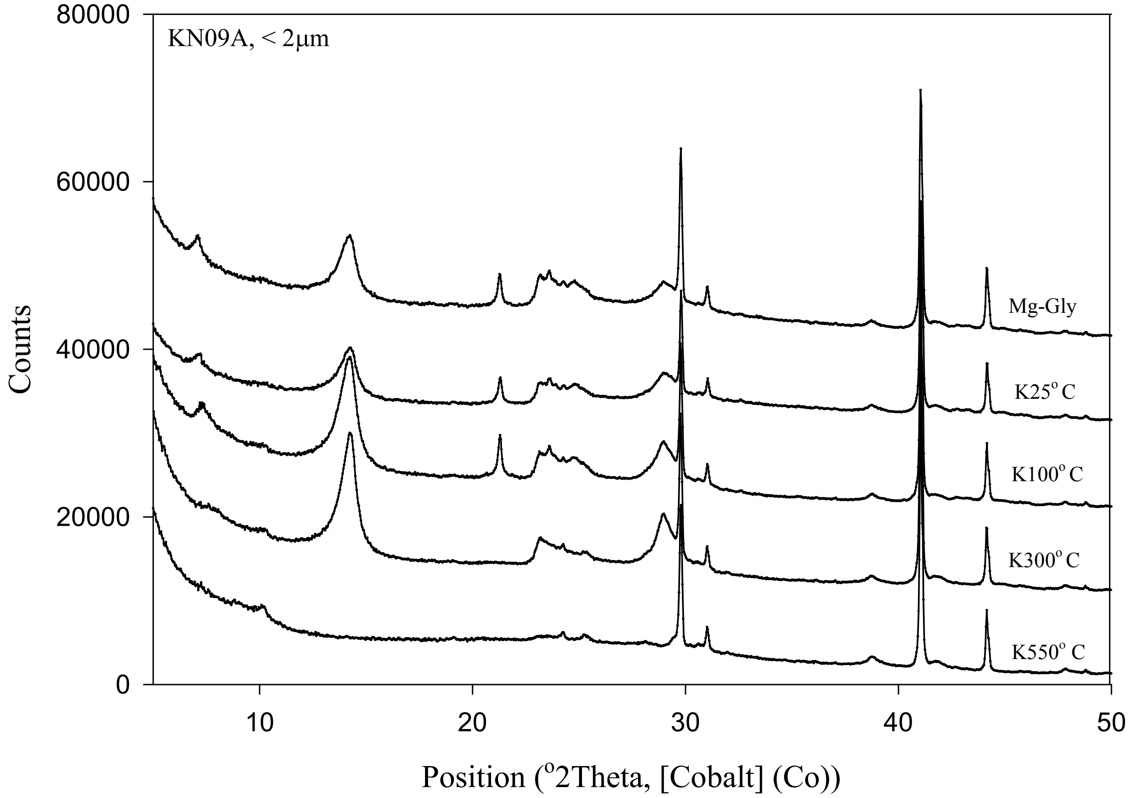

KN05C, < 2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

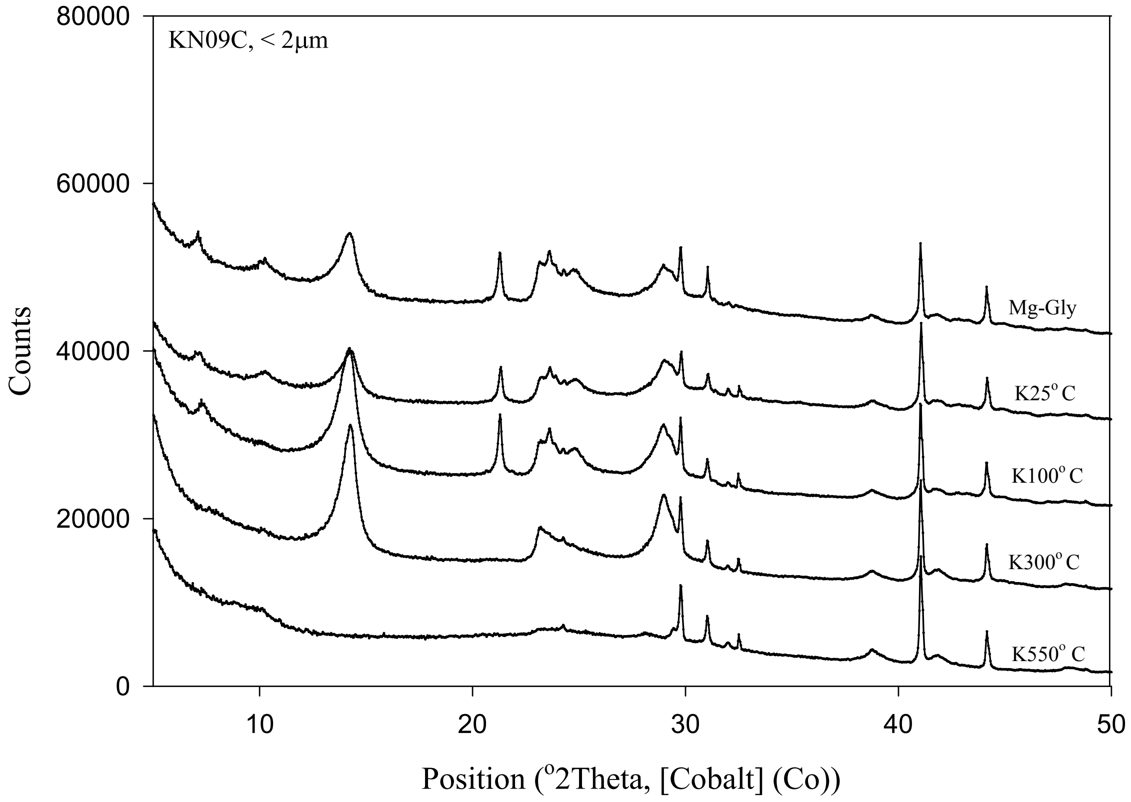

KN06A, < 2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

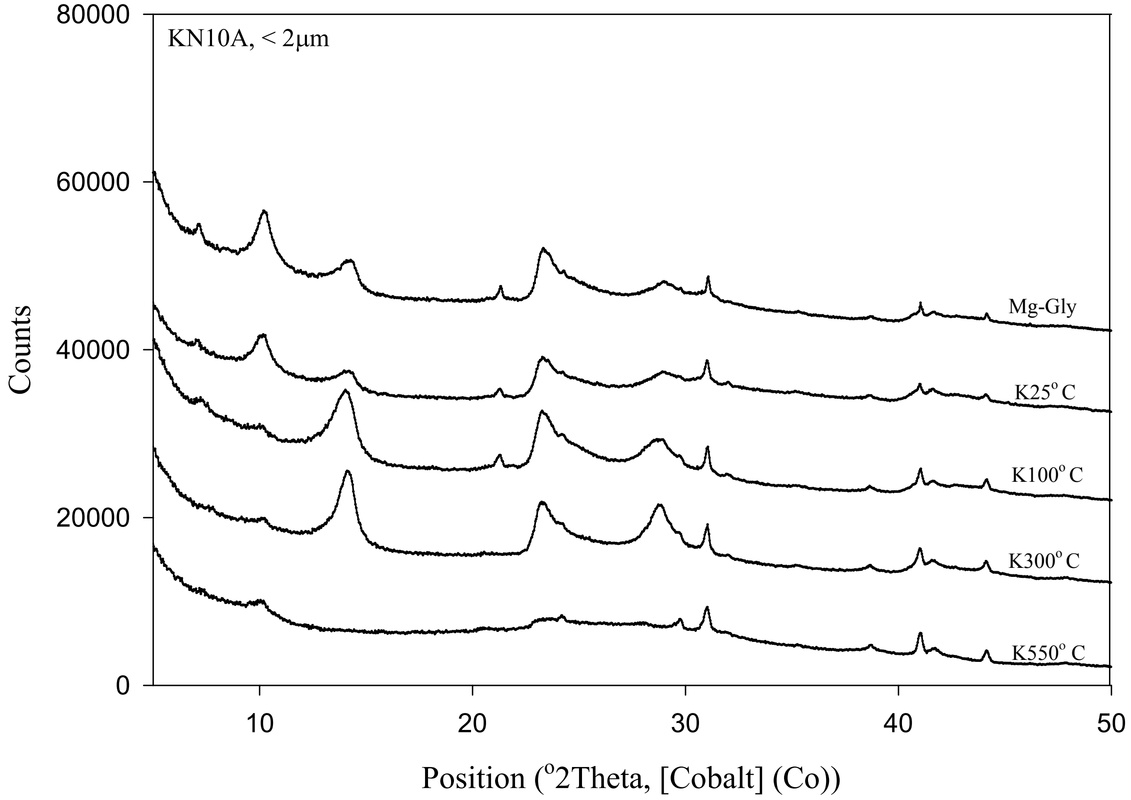

KN07A, < 2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

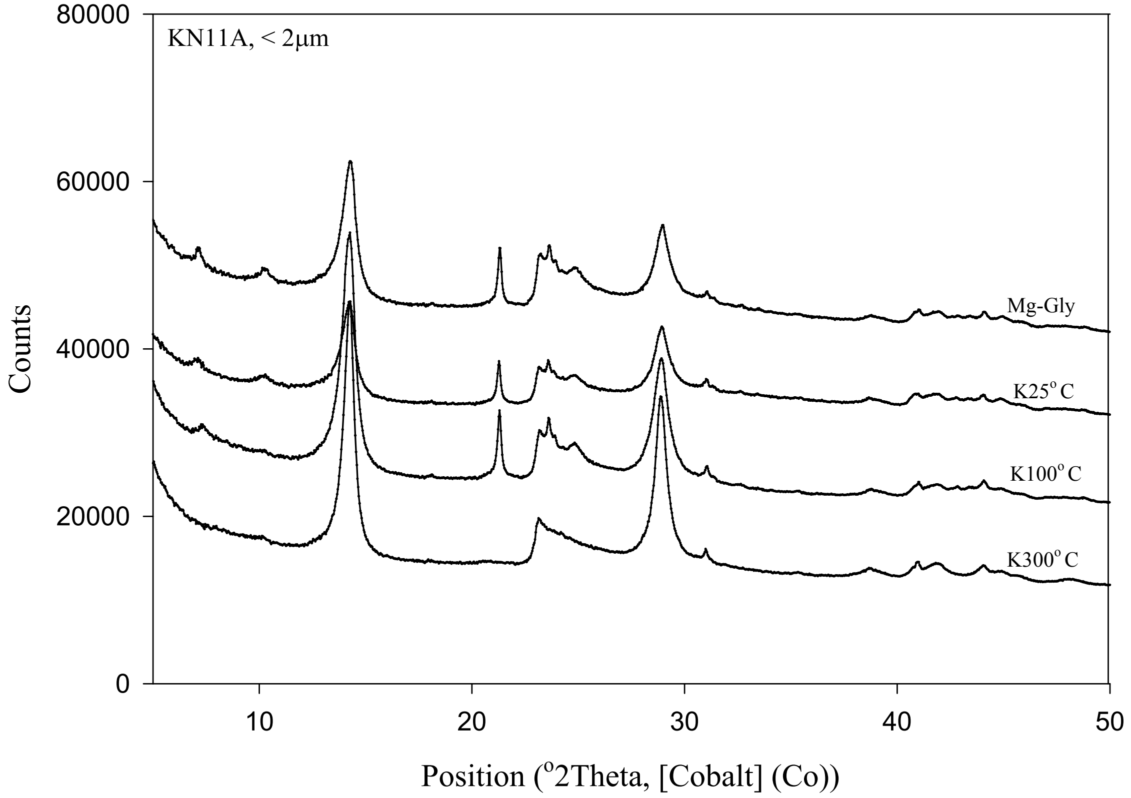

KN08A, < 2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

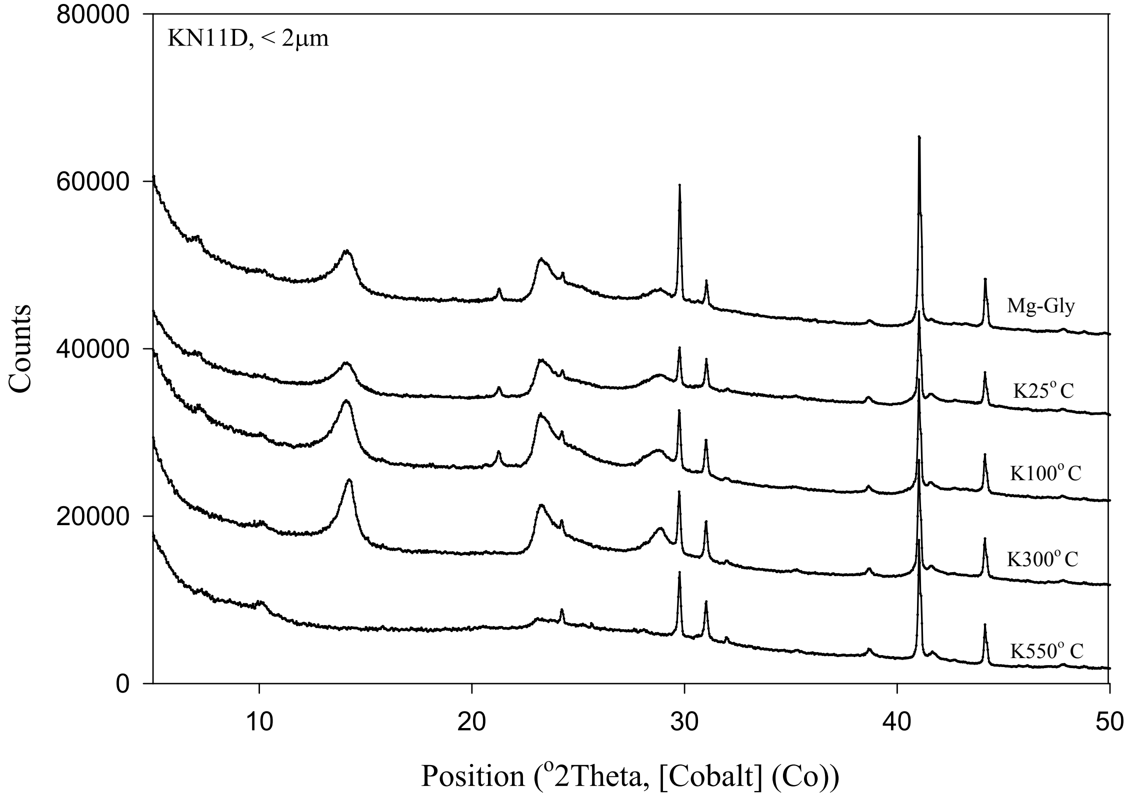

KN08C, < 2μm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

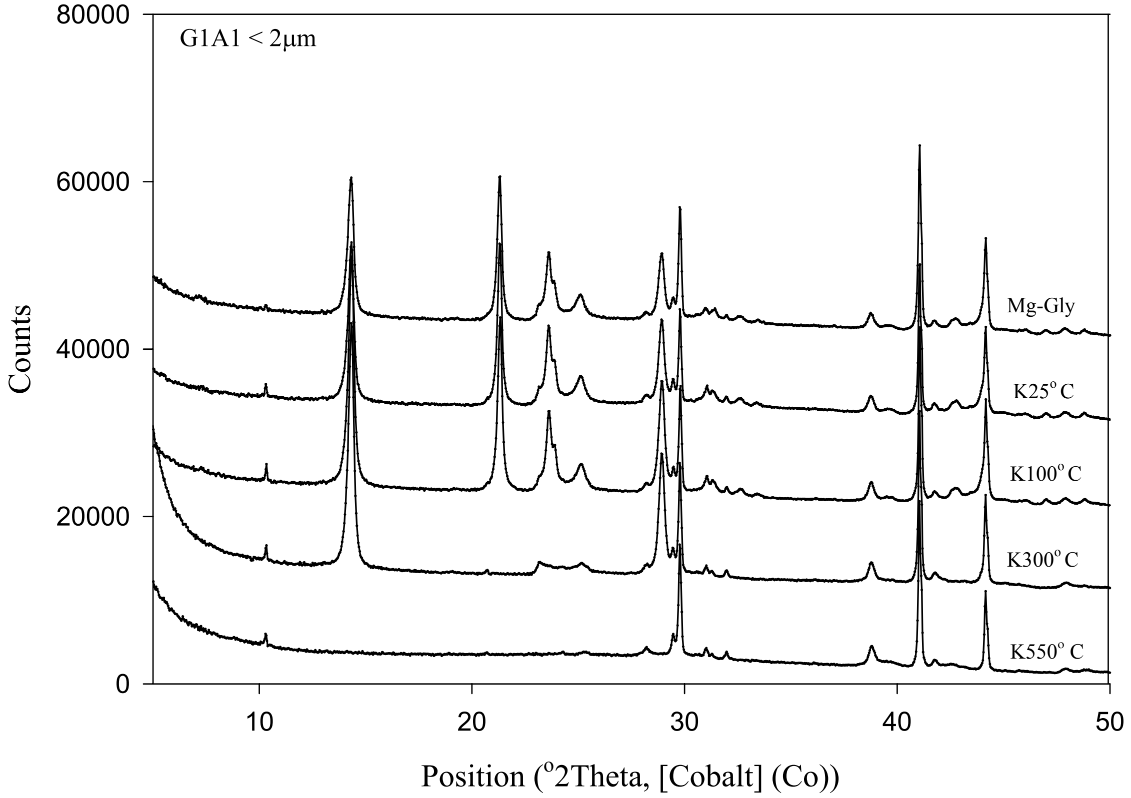

KN09A, < 2μm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

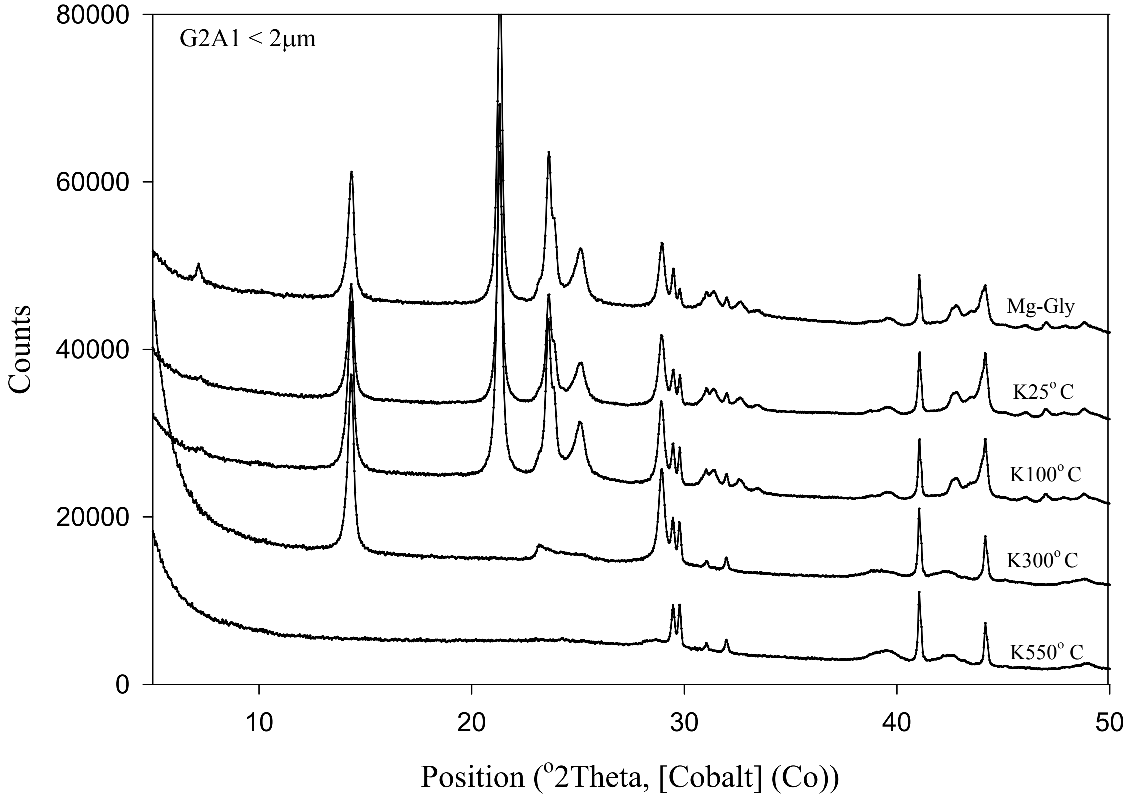

KN09C, < 2µm
Counts
Position (°2Theta, [Cobalt] (Co))
80000
60000
40000
20000
0
10
20
30
40
50
Mg-Gly
K25° C
K100° C
K300° C
K550° C

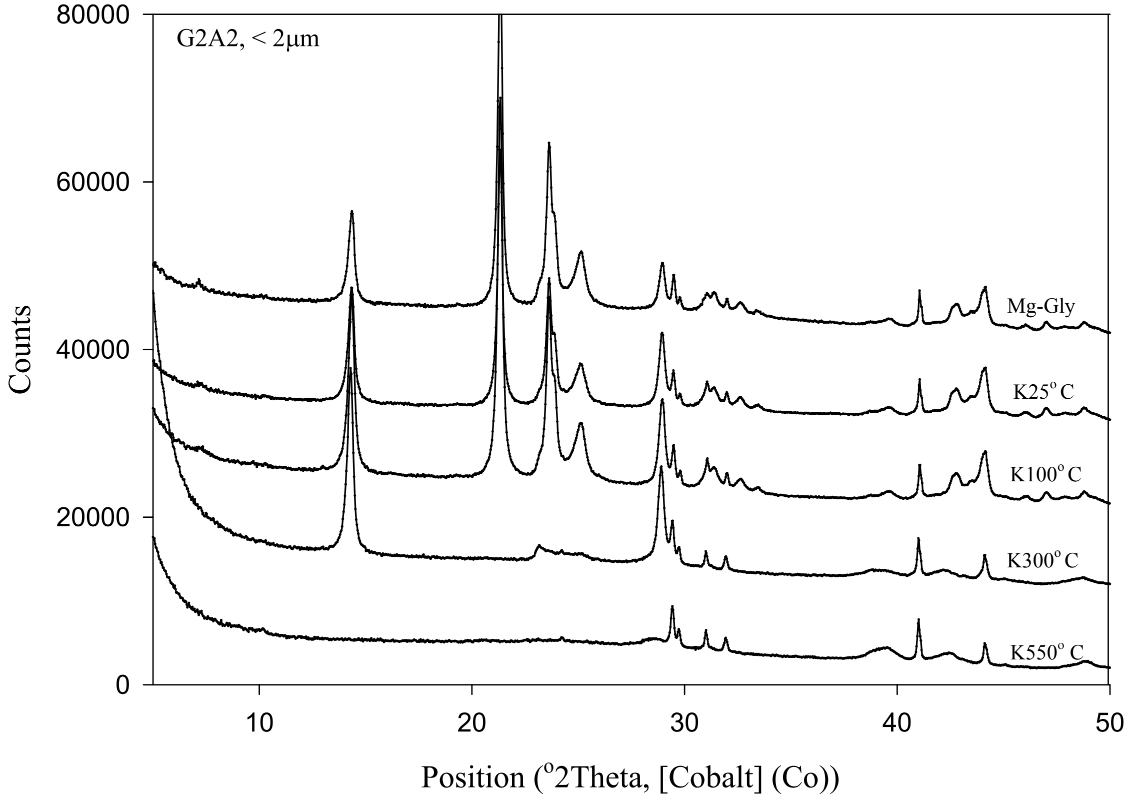

KN10A, < 2µm
Counts
Position (°2Theta, [Cobalt] (Co))
80000
60000
40000
20000
0
10
20
30
40
50
Mg-Gly
K25° C
K100° C
K300° C
K550° C

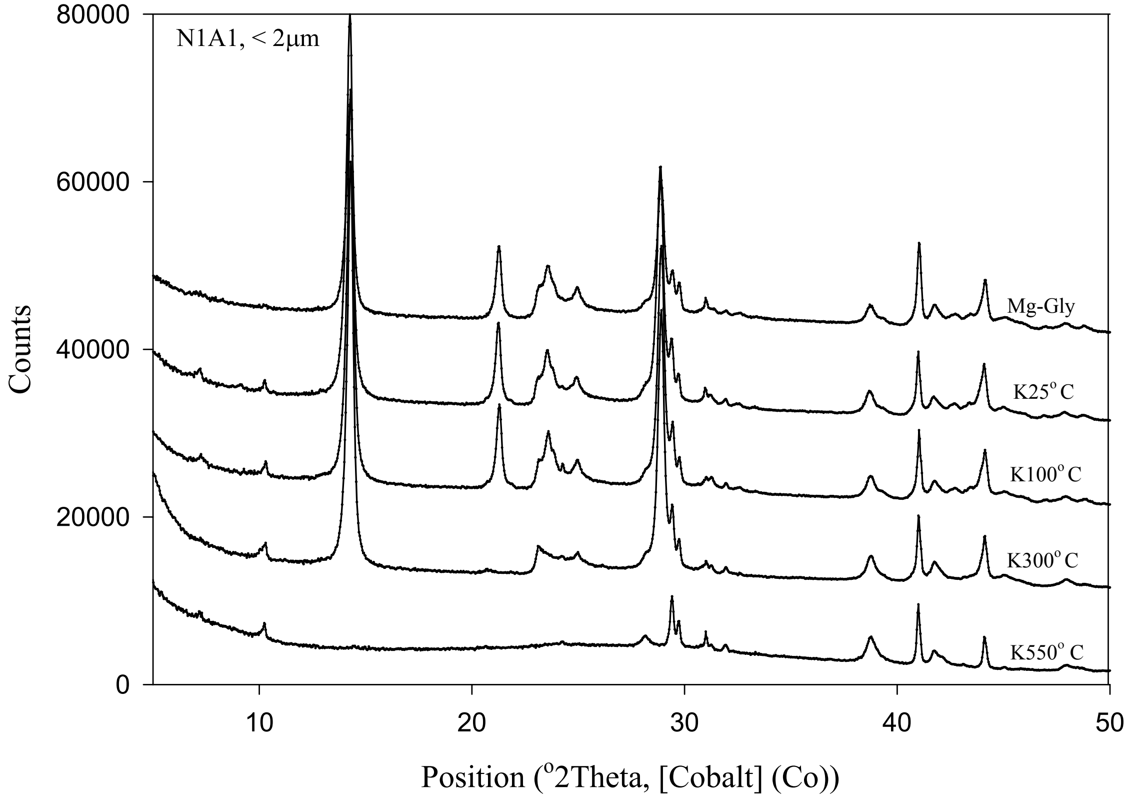

KN11A, < 2µm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C

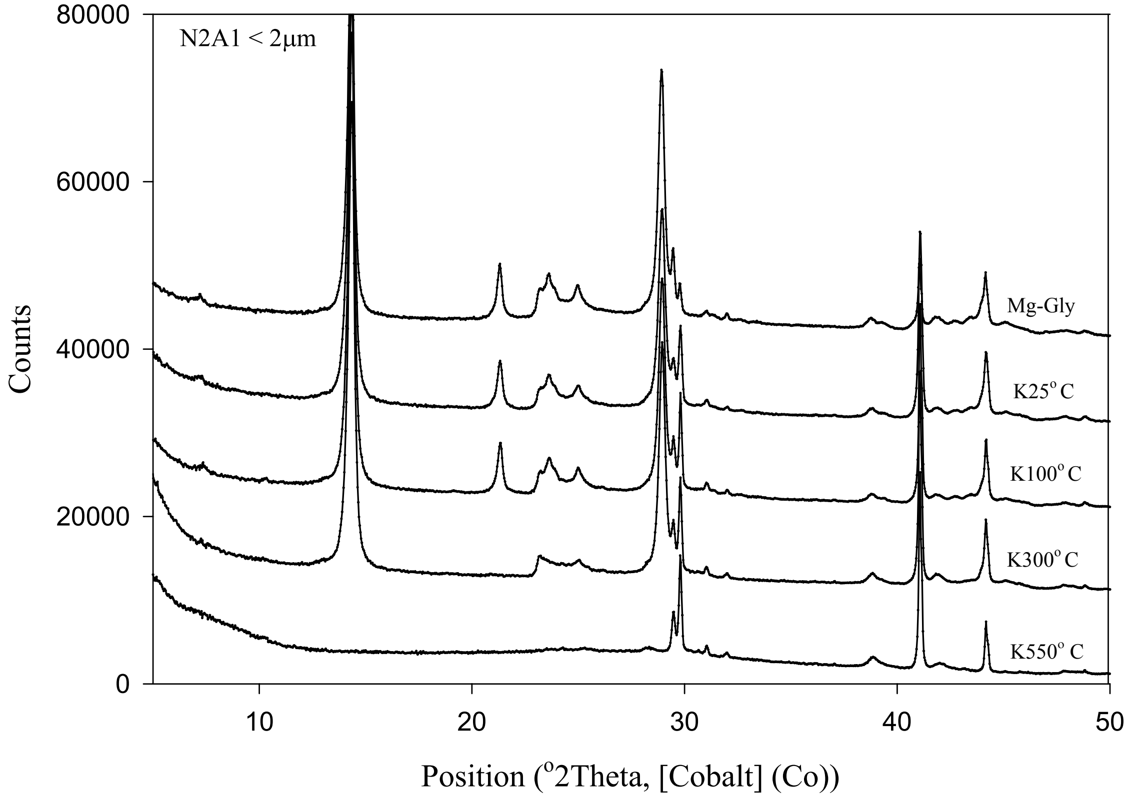

KN11D, < 2µm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

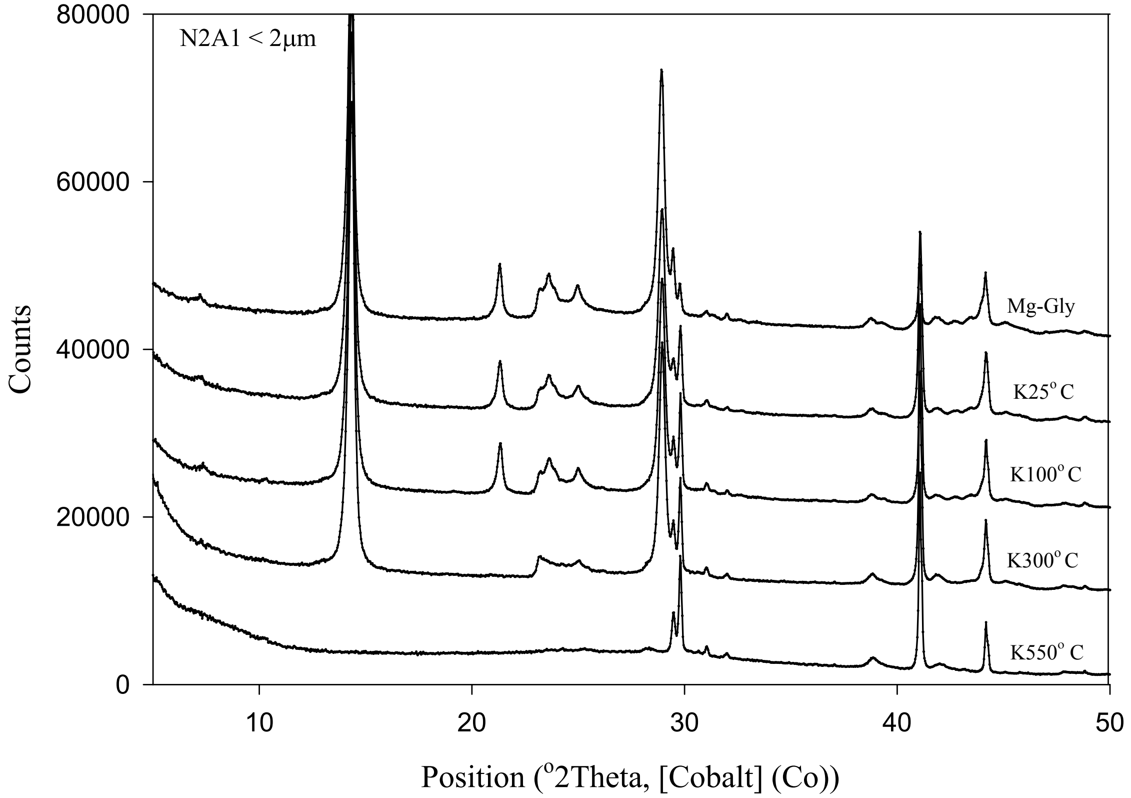

G1A1 < 2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

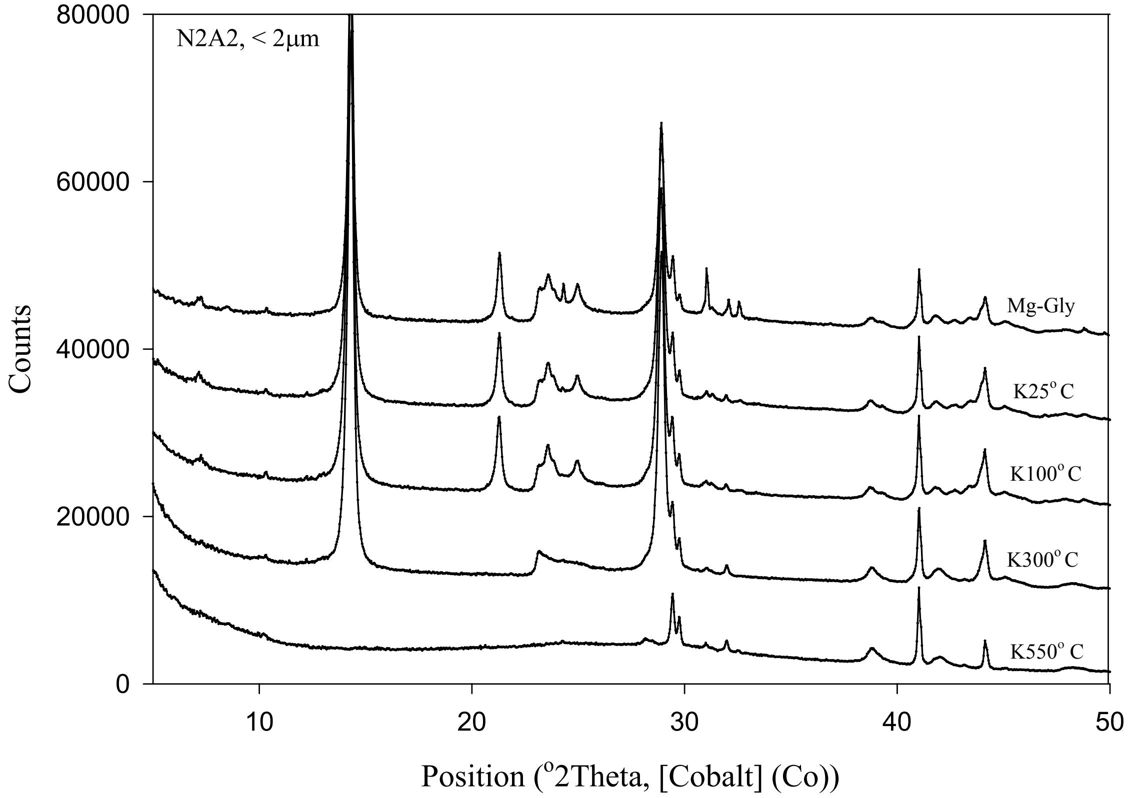

G2A1 < 2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

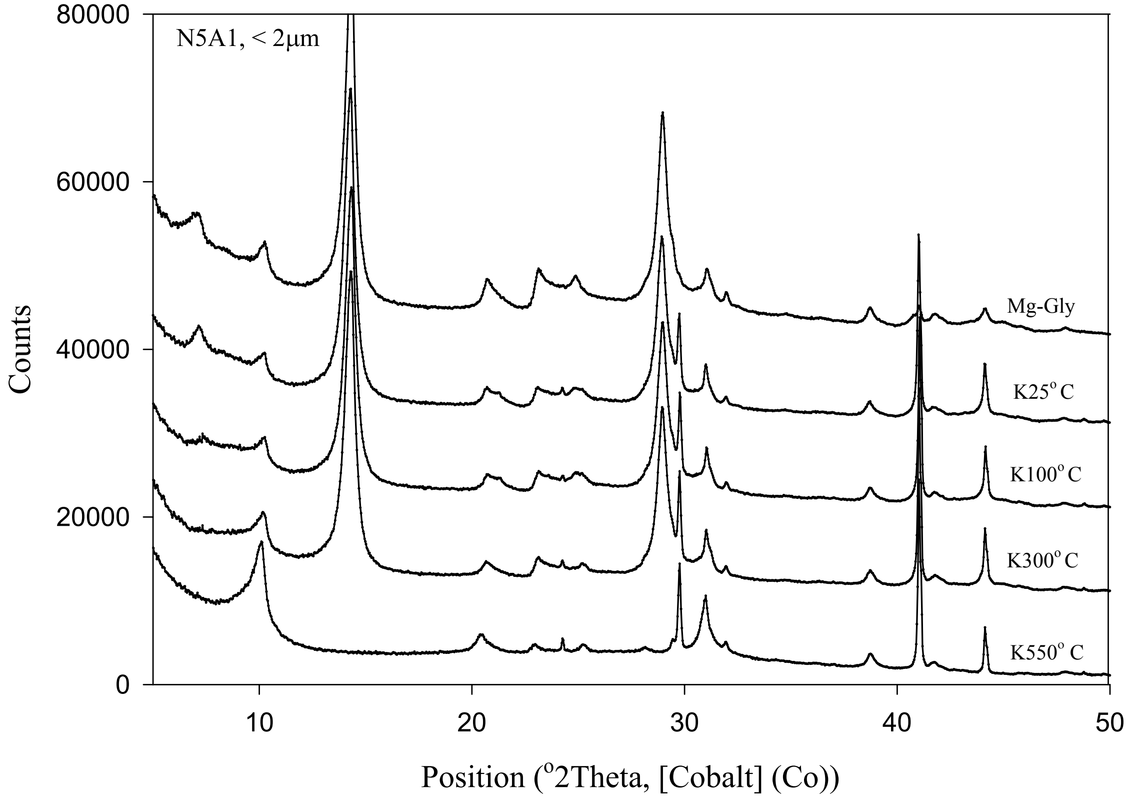

G2A2, < 2µm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

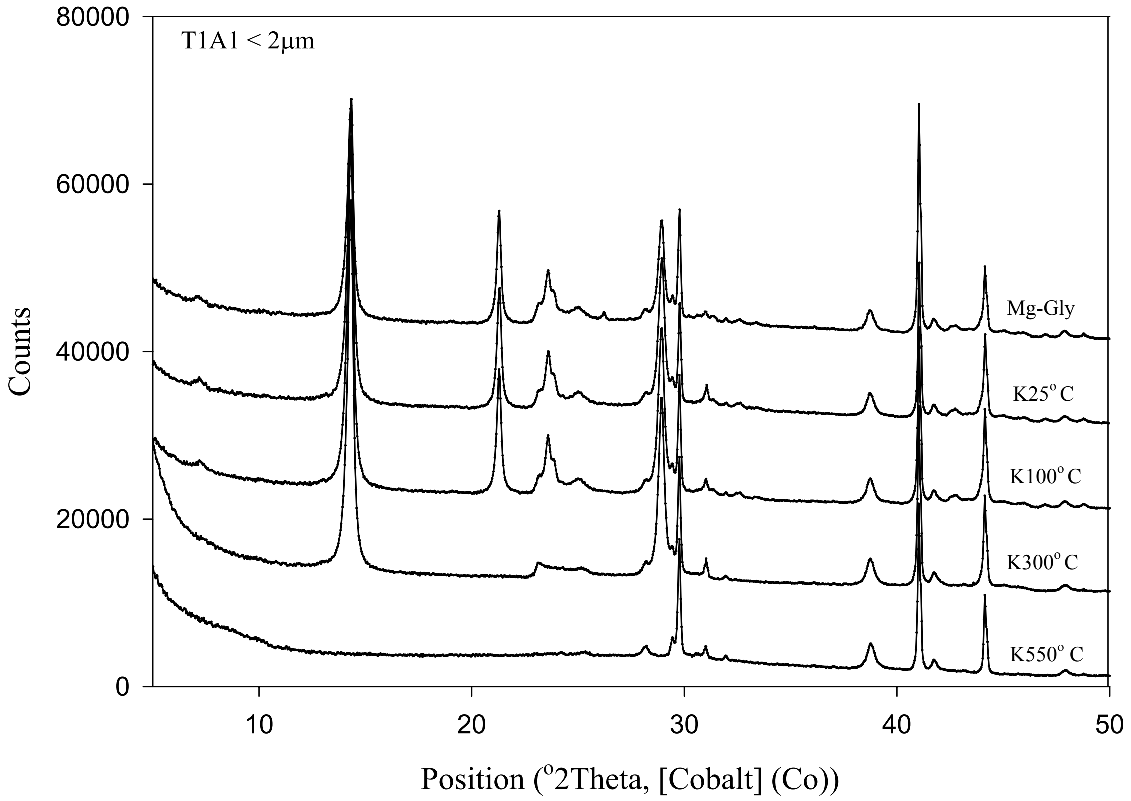

N1A1, < 2µm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

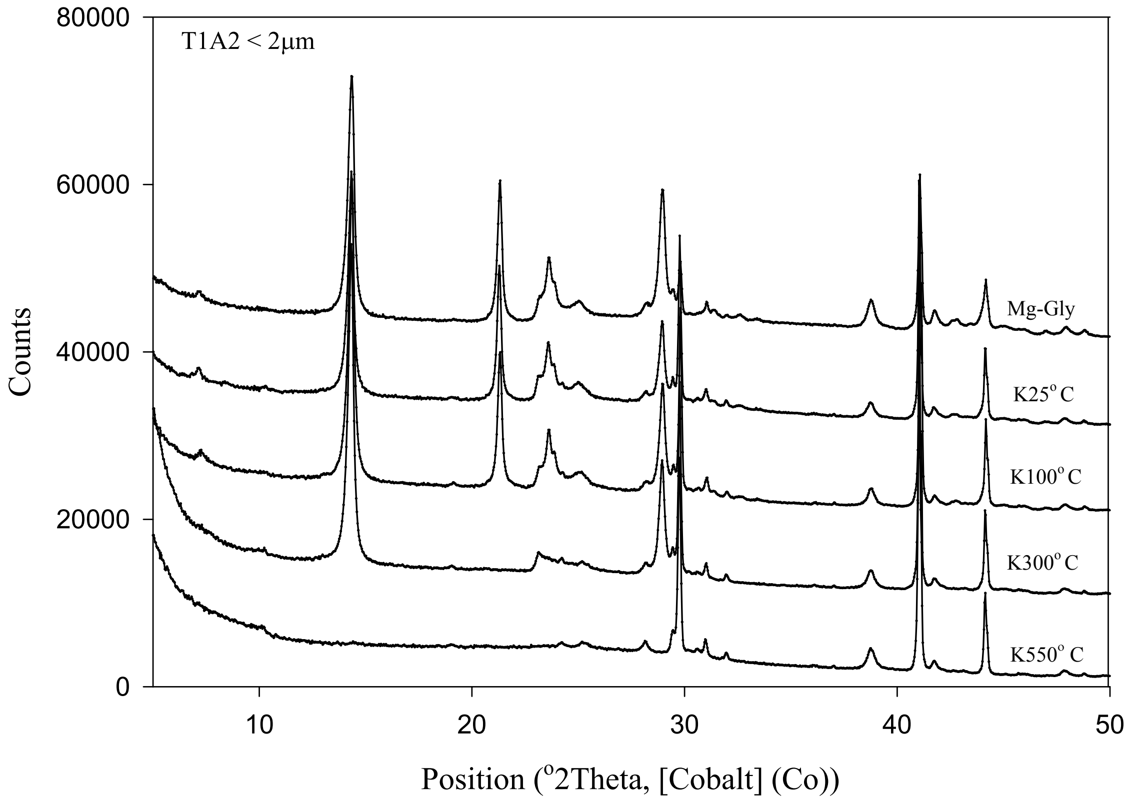

N2A1 < 2μm
Counts
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C
0
20000
40000
60000
80000
10
20
30
40
50

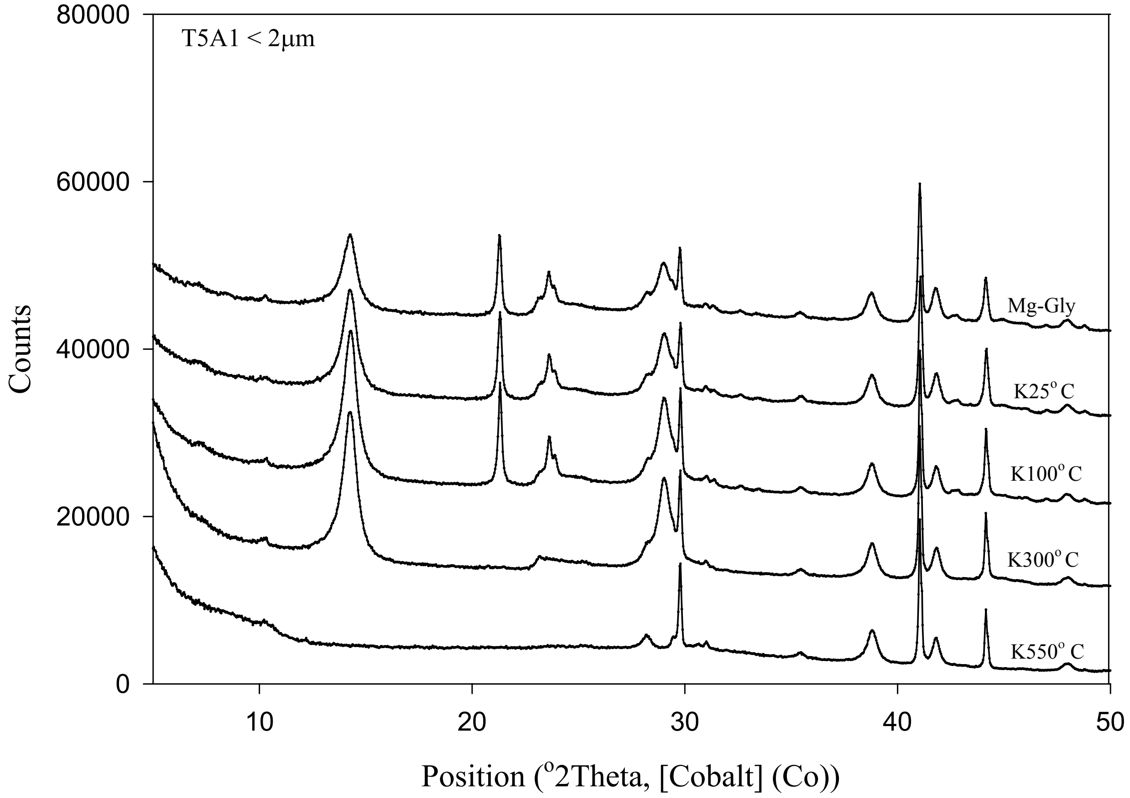

N2A1 < 2μm
Counts
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C
0
20000
40000
60000
80000
10
20
30
40
50

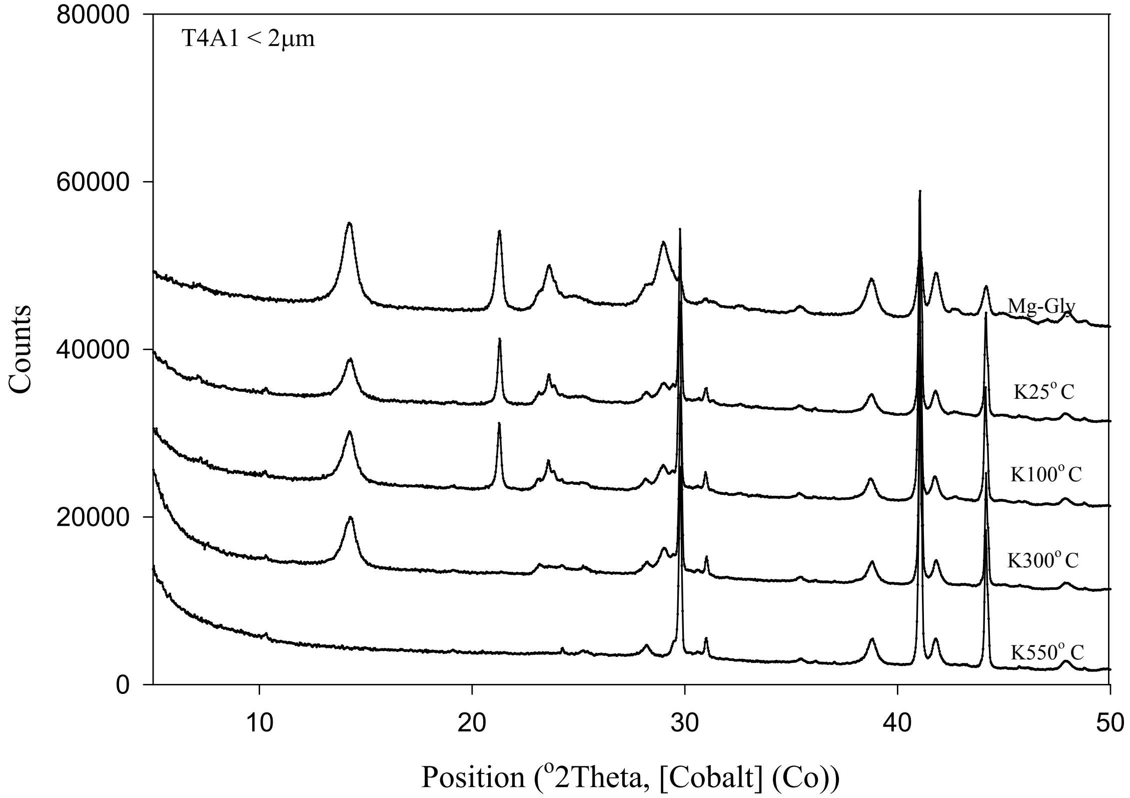

N2A2, < 2µm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

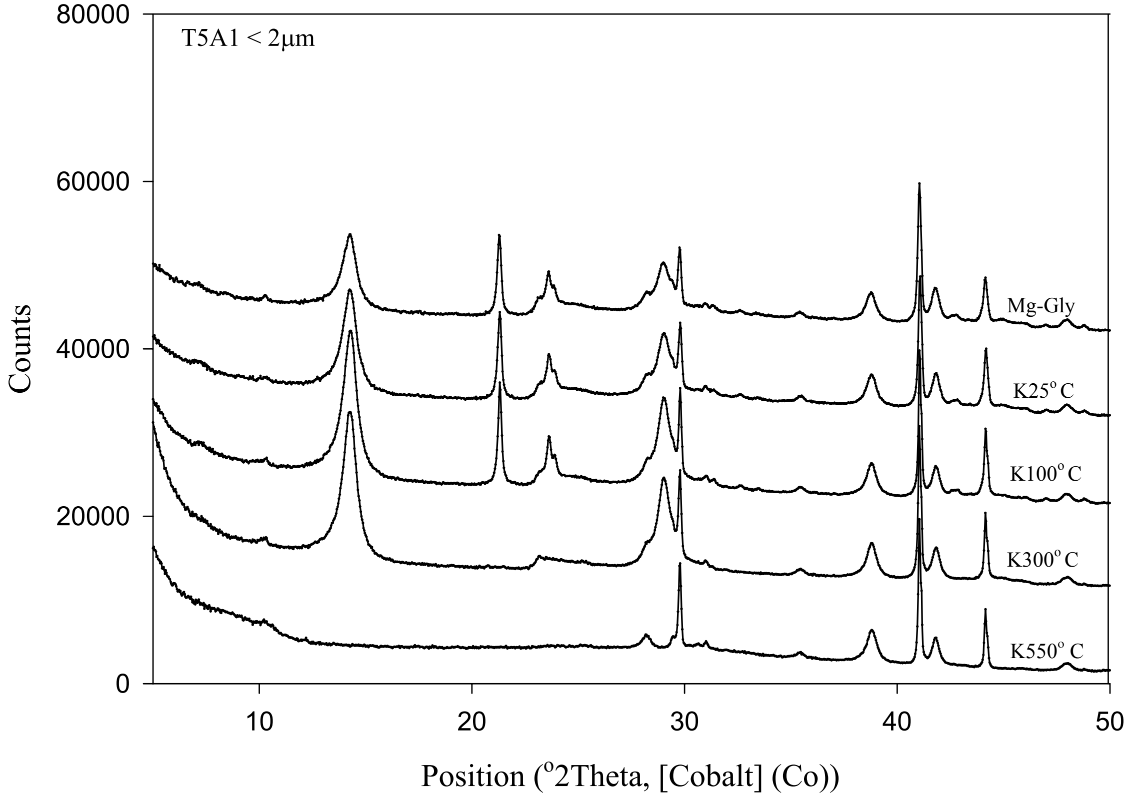

N5A1, < 2µm
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C


T1A1 < 2μm
Counts
Position (°2Theta, [Cobalt] (Co))
0
20000
40000
60000
80000
10
20
30
40
50
Mg-Gly
K25° C
K100° C
K300° C
K550° C

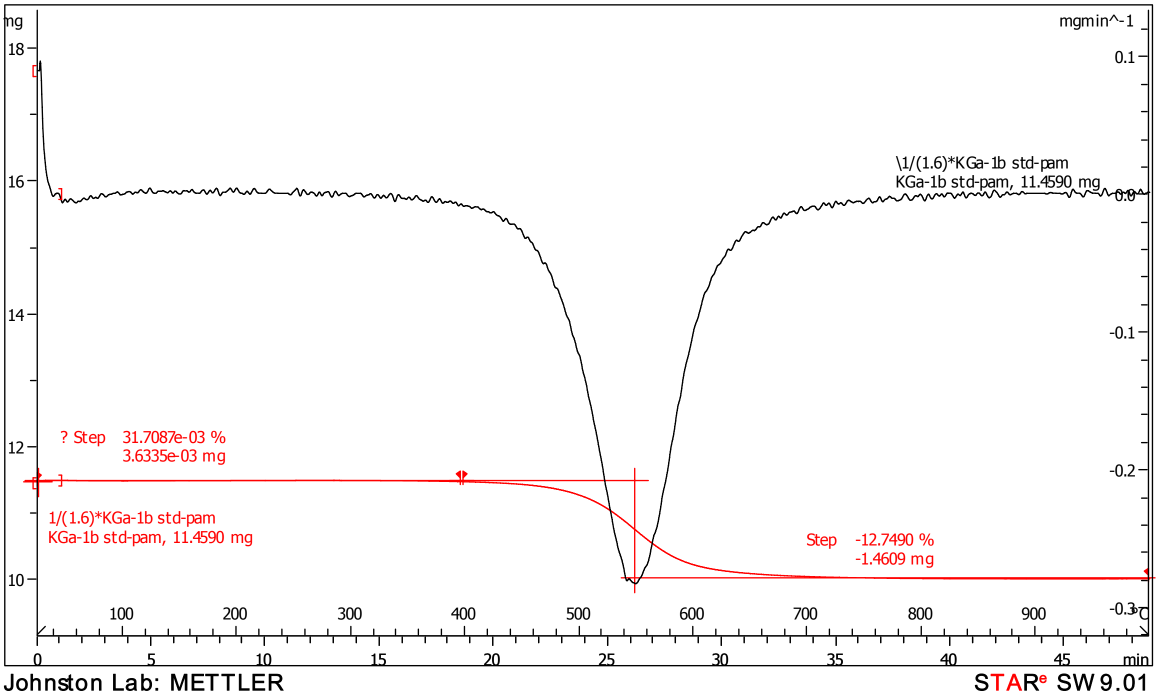

T1A2 < 2μm
Counts
Position (°2Theta, [Cobalt] (Co))
0
20000
40000
60000
80000
10
20
30
40
50
Mg-Gly
K25° C
K100° C
K300° C
K550° C


T5A1 < 2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C

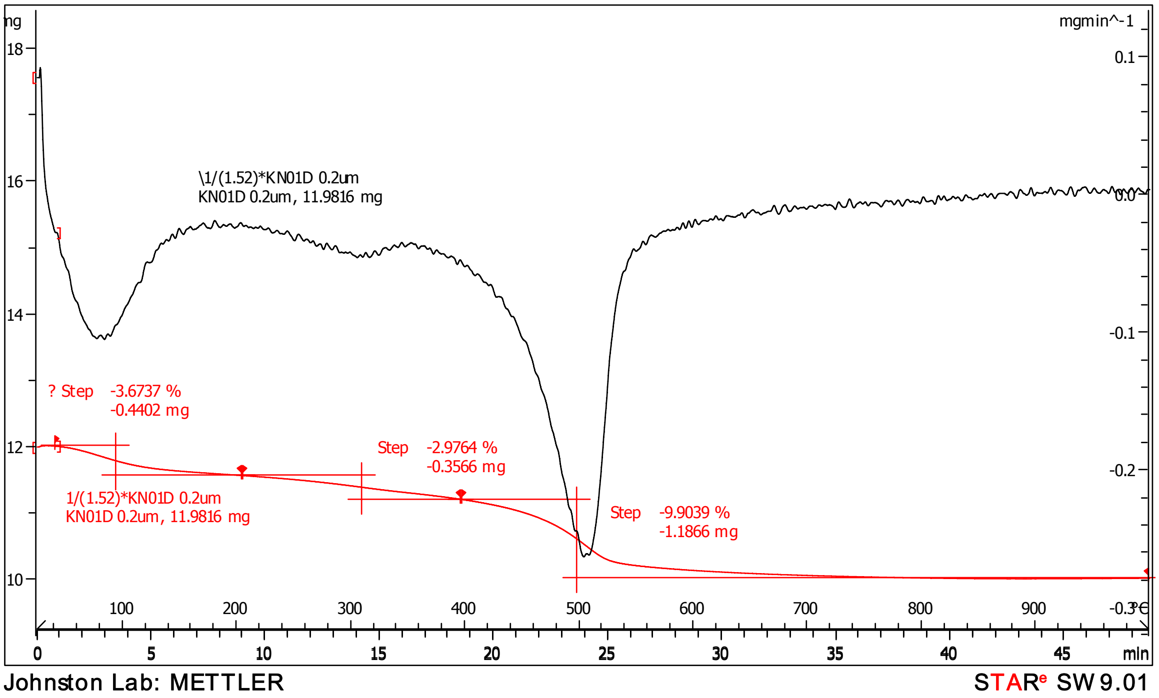

T4A1 < 2μm
Counts
80000
60000
40000
20000
0
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))
Mg-Gly
K25° C
K100° C
K300° C
K550° C


T5A1 < 2µm
Mg-Gly
K25° C
K100° C
K300° C
K550° C
Counts
0
20000
40000
60000
80000
10
20
30
40
50
Position (°2Theta, [Cobalt] (Co))

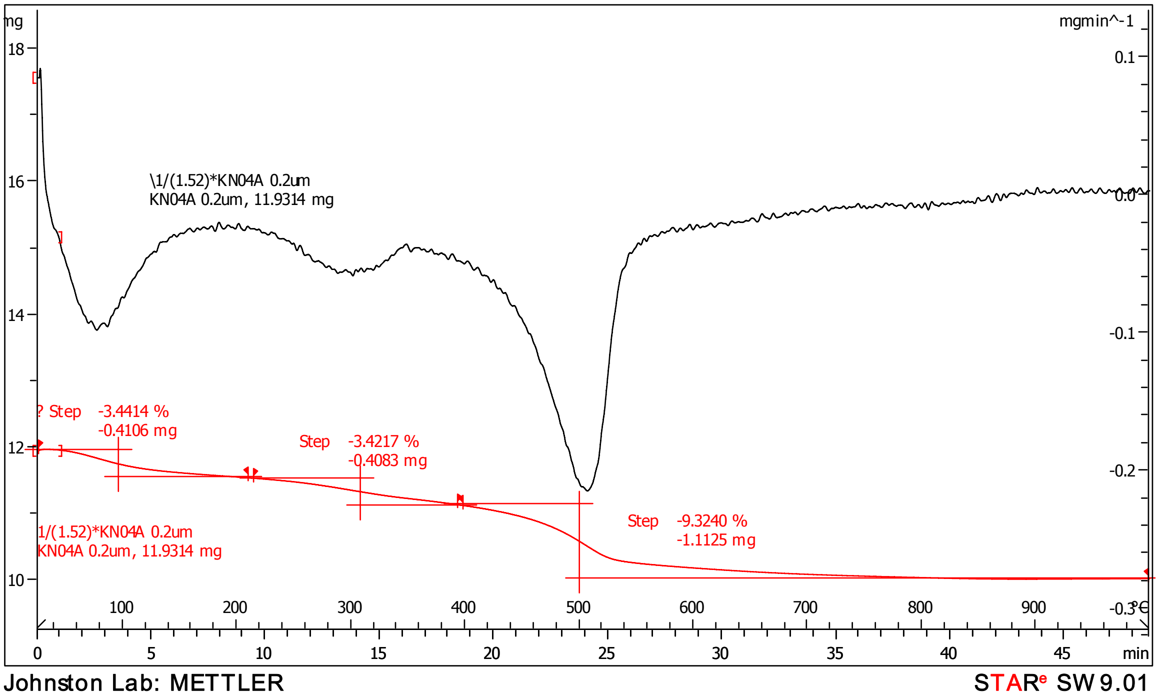
Appendix L. TGA curves of selected Kenyan clays.



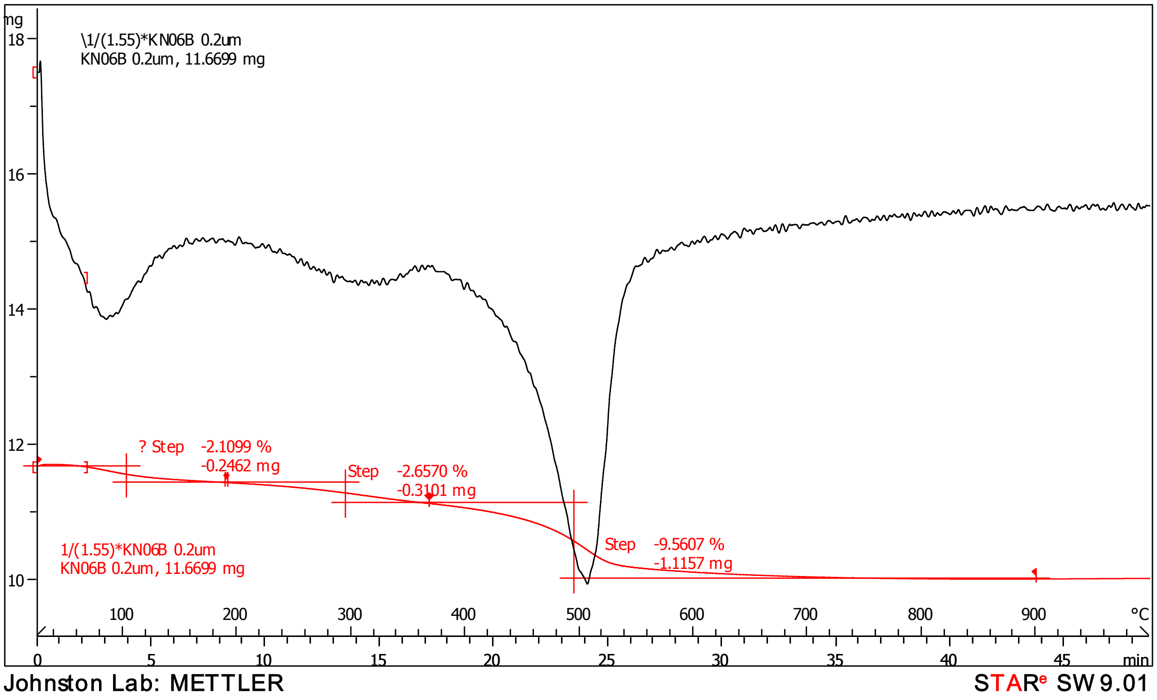
TGA curve with derivative weight loss and approximated weight loss for the KGa-1b



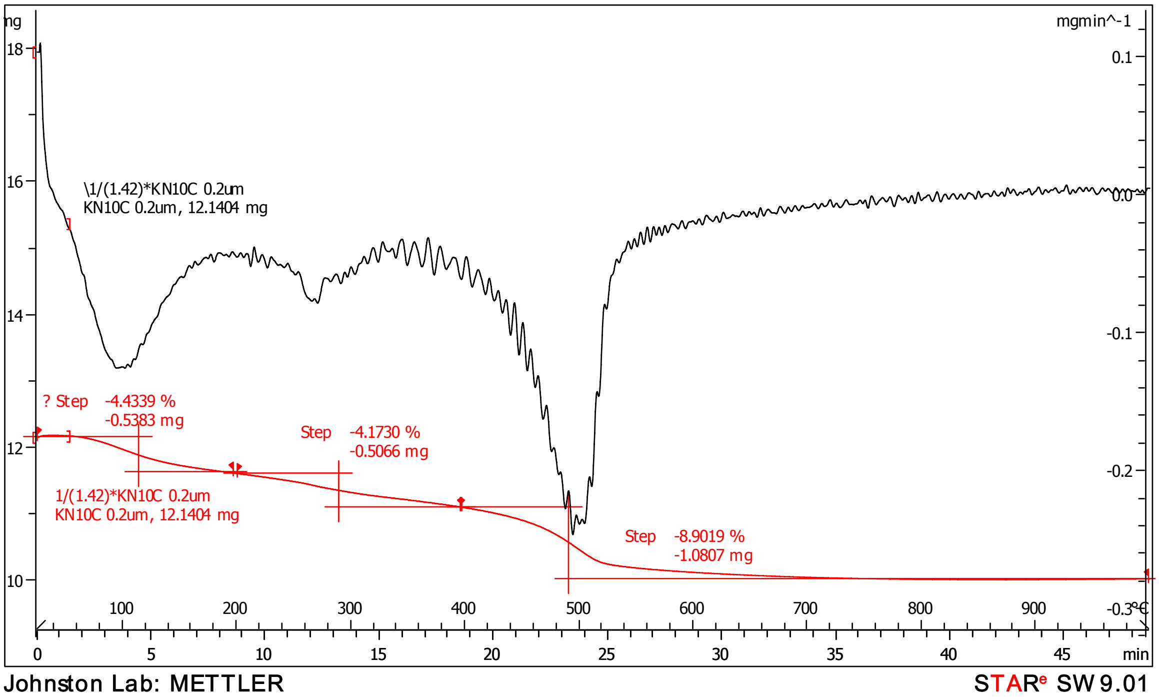
TGA curve with derivative weight loss and approximated weight loss for the KN01D



TGA curve with derivative weight loss and approximated weight loss for the KN04A



TGA curve with derivative weight loss and approximated weight loss for the KN06B



TGA curve with derivative weight loss and approximated weight loss for the KN10C.

VITA

VITA

Pamela Achieng Obura was born to Mariko Obura Kayi and Grace Atieno Obura, in Nyamware village in Kisumu, Kenya. She completed primary and secondary education at Nyamware Primary (1987) and Migingo Girls’ Secondary (1991) schools, respectively. Pamela earned a BSc. degree in Agriculture (1997) from the University of Nairobi, and a Masters degree in Soil Science (2001) from Moi University, Kenya. Between 2001 and 2003, Pamela worked with Madiany Community Development Programme (MCDP) in Bondo district, Kenya as a Programme Coordinator before resigning to pursue a doctorate degree at Moi University. In 2004, Pamela joined Purdue University in pursuit of a doctorate degree in agronomy through a Collaborative Crop Research Program of the McKnight Foundation. Pamela is married to Thomas Ochuodho. Pamela and Thomas have one daughter: Lyne-Nicole Aluoch.