CHARACTERIZATION OF SOIL MINERALOGY IN RELATION TO SOIL FERTILITY FUNCTIONAL PROPERTIES FOR SELECTED COUNTRIES IN AFRICA

KAMAU MERCY NYAMBURA

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DECLARATION

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Signature____________________________ Date____________

Mercy Nyambura KAMAU

Department of Agricultural Resource Management
Kenyatta University, Kenya

This thesis has been submitted with our approval as the university supervisors

Signature____________________________ Date____________

Prof. Benson MOCHOGE

Department of Agricultural Resource Management

Kenyatta University, Kenya

Signature____________________________ Date____________

Dr. Keith SHEPHERD

World Agroforestry Centre (ICRAF)

DEDICATION

This work is dedicated to my beloved husband David and daughters: Diana, Barbara and Enede for their understanding, sacrifice, patience and support during the period of this study.

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LIST OF ABBREVATIONS AND ACRONYMS

XRD- X-ray diffraction

SSA- Sub-Saharan Africa

AfSIS- Africa Soil Information Services

ISFM- Integrated Soil Fertility Management

ICRAF- International Centre for Research in Agroforestry

AGRA-Alliance for a Green Revolution in Africa

JHI- The James Hutton Institute

LDSF- Land Degradation Surveillance Framework

RTS Razor Tampered Surface

OM- Organic Matter

ICDD- International Centre for Diffraction Data

PDF- Powder Diffraction File

RIR- Reference Intensity Ratio

IR- Infrared Spectroscopy

PSI- Phosphorus Sorption Index

PCA- Principal Component Analysis

ICP- Inductively-Coupled plasma spectroscopy

ABSTRACT

Africa's development depends heavily on soil ecosystem services. However current soil degradation coupled with increasing pressure on land is threatening the soil resource base. There is an urgent need to establish soil health surveillance systems to guide investments and monitor trends in soil health status and impacts of interventions. Surveillance systems require appropriate and rapid, low cost methods that directly measure soil functional properties and can be applied at larger scale. Spectroscopic methods that directly measure organic and mineral composition hold promise for fulfilling this role. Infrared molecular spectroscopy (IR) is one method that has shown promise for predicting many soil functional properties. X-ray diffraction spectroscopy (XRD) is another promising method, which directly determines soil mineral composition, but has been little researched as a tool for quantitative prediction of soil functional properties. However a comprehensive knowledge of soil mineralogy in Africa is lacking due to poorly and fragmentally coordinated scientific investigations coupled with the limitations in the traditional analytical techniques. The aim of this study was to develop a rapid XRD measurement protocol and evaluate the ability of X-ray diffraction technique to rapidly predict soil functional properties based on mineral composition. Geo-referenced samples associated with the Africa Soil Information Service (AfSIS), taken from a set of 10 sentinel sites randomized over sub-Saharan Africa, were used for characterization. A total of 160 topsoil samples taken from 16 randomized points of ten 100-km^2 sites: Tanzania (3 sites), Malawi (2 sites), Mali (1 site), Burkina Faso (1 site), Kenya (2 sites) and Ghana (1 site) were characterized for chemical properties, particle size distribution, engineering properties and bulk mineralogy. Variation of the mineralogy within and between sites was explored using principal component analysis using the R statistical software, as a precursor to exploring relationships with directly measured soil properties and soil fertility diagnostics. The clustering of individual minerals and the distributions of the soil fertility variables identified across the sites appeared to relate to differences in mineralogical functional groups, supporting the hypothesis that mineralogical data could be used to predict functional properties. The findings therefore suggest opportunity for improving soil assessment using information on soil mineralogy. For instance XRD information on mineralogy can be combined with information from soil physico-chemical properties, to provide powerful diagnostic capabilities, for low cost and rapid prediction of soil functional properties. Further work should aim to develop direct quantitative predictive relationships between soil functional properties and mineralogical composition using the full set of AfSIS reference samples.

Key words: Spectral diagnostics, soil mineralogy, soil fertility.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Importance of Africa's soil resources

More than 70 % of Africa's rural poor depend on agriculture for their livelihoods as it directly affects economic growth, social improvement and trade in Africa. Africa's soils are important for food production to feed a population that continues to grow rapidly, outpacing the growth rate in other regions of the world. Apart from food production, improper soil management practices have serious consequences on other natural resources essential to Africa's livelihoods and development. Soil provides essential ecosystem services and plays a key role in sustaining them. For example, soils are a key resource in the production of foliage, fuel and fibre. Soils store and cycle water from rainfall, filter toxic substances through clay sorption and precipitation process that determine surface and ground water quality. Soil organisms on the other hand decompose organic materials, cycle nutrients and regulate gas fluxes to and from the atmosphere. Other benefits people derive from ecosystems include provisioning services that affect climate, pests and diseases; supporting services such as soil formation and photosynthesis; and cultural services (Millennium Ecosystem Assessment, 2005).

However, nutrient depletion, land degradation and deteriorating agricultural productivity is seriously undermining efforts to bring about food security and strengthen the foundations of sustainable economic growth in sub-Saharan Africa.The state of the soil system is constantly changing, driven by small changes in individual soil properties, natural and human-induced activities. The fertility of Africa's soil is being depleted at a rate that threatens to undermine the continent's attempts at eradicating hunger through sustainable agricultural development. Low inherent fertility of Africa's soils is caused by lack of volcanic rejuvenation, resulting in various cycles of weathering, erosion and leaching; leaving soils poor in nutrients (Smaling and Braun, 1996). In addition, Africa's soil nutrient balances are often negative, indicating that farmers mine the soils. This form of soil fertility degradation has been described as the single most important constraint in food security in Africa. Africa loses $4 billion per year due to soil nutrient mining (Smaling, 1995). During the last 30 years, soil fertility depletion has been estimated at an average of 660 kg N/ha, 75 kg P/ha, and 450 kg K/ha from about 200 million ha of cultivated land in 37 African countries (Smaling 1998). As a result of the inherent low fertility of Africa's soils and subsequent land degradation, only 16% of the land has soil of high quality and about 13% has soil of medium quality resulting to 55% of the land being unsuitable for agricultural use (Eswaran et al., 1997). Population pressures combined with limited access to fertilizers threaten the future of farming in Africa. Sub-Saharan Africa's (SSA) population is likely to double over the next 25-30 years, rising from 1.1 billion in 2010 to an expected 1.75 billion people by 2050. This new population will demand more services from soils and ecosystems as a whole leading to a rapid loss in the capacity of soils to deliver essential ecosystem services and increased conflicts over land.

Building soil fertility to meet future demands on soils will require an increase in use of nutrient inputs. However, adoption of fertilizers in SSA is limited due to a number of factors but including highly variable response to standard nitrogen and phosphorus fertilizer applications due to high variability in soil mineralogy, resulting in frequent meso- and micro-nutrient deficiencies and imbalances (Voortman, 2003). The situation is exacerbated where soil organic matter levels have become critically low due to unsustainable soil management practices (Vanlauwe et al., 2010).

1.2 Statement of the problem

In order to manage Africa's soil resource base for development there is need for reliable spatial information on soil functional properties. Agricultural accessing and monitoring the state and trends of soils will be critical for understanding the complex processes affecting soil productivity, soil degradation and overall soil condition and for targeting appropriate fertilizer and soil fertility management strategies. However, practical systems for soil health surveillance are lacking (Shepherd and Walsh, 2007; Kibblewhite et al., 2008; Robinson et al., 2009).

Governments need soil health surveillance systems to provide information on soil functional properties at fine spatial resolution and to guide planning and assessment of intervention programs and safeguard the soil resource base. However to implement surveillance approaches, there is need for the development of low cost, rapid screening methods that can be used to assess soil functional properties on large numbers of samples, so as to be able to adequately characterize the large soil spatial variability. For example, variables affecting a soil functional property, such as soil nutrient capacity, include mineralogy, total elemental concentrations, texture and organic matter. There are prospects for rapidly assessing such properties using spectroscopy techniques that measure absorbance of electromagnetic energy from the X-ray to visible wavelength ranges. Shepherd and Walsh (2007) have proposed infrared spectroscopy as a key tool for measuring soil functional properties in soil health surveillance systems that are expensive or time-consuming to measure. Infrared spectroscopy is now being implemented as the principal screening tool for soil health in the Africa Soil Information Service (AfSIS, 2012). Another potential technique that has so far received little attention as a tool for prediction of soil functional properties is the use of X-ray diffraction spectroscopy (XRD) to analyse soil mineralogy.

1.3 Justification of the study

Soil mineralogy is the study of the composition of the solid inorganic phases that control the physico-chemical processes in soils. It is one of the principal soil forming factors (Jenny, 1941) and therefore a key determinant of basic soil functional properties. Soil mineralogy has a profound influence on the dynamic behavior of soils namely the gains, losses, transformation and translocation of inorganic and organic substances. Therefore understanding soil mineralogy is important for assessing functional soil properties, such as interactions with nutrients, nutrient quantity (stock) and availability (intensity or strength of retention by soil), sorption of metals, organics and nutrients to mineral surfaces, fertilizer response, water storage, erosion susceptibility, and provision of sites for microbial and faunal activities. These properties in turn determine soil agricultural, environmental and engineering qualities.

Until recently soil infrared spectroscopy has been used as the key soil screening tool in soil health surveillance systems (Shepherd and Walsh, 2002; 2007). However given the importance of soil mineralogy as a determinant of all soil functional properties which include soil fertility and fertilizer response in particular, the new developments in instrument capability for high- throughput X-ray diffraction (XRD) could provide a powerful complementary tool for soil screening. New instrumentation developments in high-throughput X-ray diffractometry (XRD) and steady improvements in mineral identification databases and software have opened up new opportunities for semi-quantitative determination of mineral phases on large sample numbers (Omotoso, 2006). The recent launch of bench-top XRD technology opens up the technology as a routine high throughput technique in soil science. Until recently, use of XRD has been largely confined to detailed analysis on small sets of samples (Dixon and Schulze, 2002; Dixon and Weed, 1989) and the links between soil function and soil mineralogy have remained largely descriptive (Cornu et al., 2009; Andrist-Rangel et al., 2006). This thesis will explore the use of XRD as a direct quantitative analytical method for the prediction of soil functional properties of African soils. It takes advantage of the availability of a diverse set of soils being sampled using a sub-Saharan African wide sampling frame under the Africa Soil Information Service (Vagen et. al., 2010).

1.4 Study objectives

The main objective of this study was to develop a rapid XRD measurement protocol and to evaluate the ability of X-ray diffraction (XRD) technique to rapidly predict soil functional properties of Africa's soils.

Specific objectives were:

1. To develop a protocol for rapid direct analysis of soil mineralogy using a bench top x-ray diffractometer.
2. To measure, identify and quantify the amounts of individual soil mineral phases and their distribution in ten sampling locations in Africa.
3. To investigate the relationships between soil mineralogy and conventional soil functional properties with emphasis on soil fertility variables.
4. To classify Africa soil mineralogy in terms of weatherable and nutrient rich soil minerals, and soil fertility potential for the ten sampling locations.

1.5. Hypotheses

1. High quality x-ray diffractograms can be obtained from whole soil samples using rapid and simple sample preparation methods providing semi-quantitative mineralogical data.
2. Mineralogical compositional fingerprints of Africa's soils fall into distinct clusters or patterns that can be used to distinguish soils of different soil fertility potential.
3. Soil functional properties of African soils can be quantitatively associated with soil mineralogical composition.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Overview

As predicted by Jenny (1941), human activities have dramatically altered the state of climate, organisms and the contingent factors on a global scale, and the rates of human-driven change processes are expected to accelerate over the next 100 years, particularly in Africa. In many parts of Sub-Saharan Africa (SSA), positive feedback dynamics between growing populations, land cover and climate change have led to a rapid loss in the capacity of soils to deliver essential ecosystem services. These highly undesirable changes are not easily reversible and are major challenges to prospects of a better future for Africans. Very little is known about the condition and trend of soil functional capacity in Africa. Land resources' surveys have focused on assessment of soil classification based on diagnostic soil horizons and have largely failed to provide relevant information to decision makers on soil management (Young, 1998). Some attempts have been made at developing indices for soil condition by using relatively novel approaches to the analysis of multivariate data and soil spectroscopic techniques (Vagen et al., 2006). Variables affecting soil nutrient capacity such as clay mineralogy, total elemental concentrations, texture, and parent material can be related to absorbance spectral signatures to provide a more accurate assessment of soils' nutrient capacity. This involves use of new approaches to soil analysis, namely soil spectral diagnostic techniques, which include soil infrared spectroscopy and X-ray diffraction among others, as well as a range of multivariate statistical methods for multivariate calibration, pattern recognition and machine learning.

2.2 Soil properties

Soil properties in their environmental setting result from soil formation processes which are governed by the factors such as climate, topography, parent material, vegetation and time (Jenny, 1941). Three classes of properties can be defined according to the degree to which they show dynamic properties and to which they are influenced by management: Slow, management insensitive properties that change only slowly with time, primarily in relation to soil forming factors, and are key determinants of soil functional properties and therefore important to measure in order to describe spatial variation in soil functional capacity. Examples are mineralogy and particle size distribution. Slow, management sensitive properties are key indicators or determinants of soil functions that are responsive to management over periods of several years (Vagen et. al., 2010). Soil organic matter content is a good example. These are the most useful variables for long-term monitoring of soil functional capacity as reliable estimates that can be obtained from a single measurement point in time. Fast, management sensitive properties are important for some soil functions but fluctuate rapidly (e.g. within a year) in response to climatic, hydrological and management conditions. They require frequent monitoring to develop an understanding of their behaviour and to obtain reliable estimates of average values. It is generally difficult and expensive to conduct such measurements in large area surveys. Examples are mineral nitrogen, microbial activity, and topsoil macro-aggregation.

2.3 Basic soil fertility variables

A number of properties that are related to soil fertility and other functional properties related to agricultural, environmental and engineering applications have been defined by AfSIS (Vagen et. al., 2010). The soil fertility variables are largely based on the Fertility Capability Classification (Vagen et. al., 2010). The availability of N is assessed through soil organic C measurements since C: N ratio of soil organic matter varies between relatively narrow limits around 10:1 in agricultural soils and wide limits of above 30:1(Richards, 1978). Carbon saturation deficit has been proposed as a biological indicator, where organic carbon levels are compared with undisturbed or semi-natural reference sites under the same soil type (Sanchez et al. 2003). Soil acidity not only determines the availability of most nutrient elements, but high level of acidity is a major constraint to crop productivity due to aluminium toxicity.

Stocks of soil P are divided between soil organic matter assessed by soil organic C and sparingly soluble minerals and inorganically sorbed components, their availability being determined by phosphate sorption characteristics of soil Fe and Al oxides and amorphous minerals in tropical soils (van Straaten, 2002). The sorption of phosphate (P) is an important factor controlling the fate and effectiveness of P added to soil from mineral and organic fertilizers. Bache and Williams (1971) proposed a single-point "P sorption index" (PSI) of soil that is calculated from the P remaining in solution after addition of only one P concentration. It has been found to be correlated well with the soil P buffer capacity. A review of global literature has shown that this PSI, along with closely related variations, has been widely useful as a quick means of assessing P sorption across different soil types, pH values and with fertilizer P sources of both high and low solubility and mineral and organic origins. There are mineralogical modifiers (low nutrient capital reserves modifiers) for K, reflecting the fact that K availability is often determined by a moderately slowly available "fixed" pool particularly in feldspars and mica minerals.

The amounts of exchangeable bases largely dictate basic soil fertility. The Mehlich 3 extraction method (Mehlich, 1984; Ziadi and Sen Tran, 2008) is used for cation and micronutrients analysis as it allows multiple elements to be analysed from one extractant using inductively-coupled plasma spectroscopy (ICP). These methods of soil test levels correlate well with other commonly used methods that use different extractants (e.g. Bray P, ammonium acetate) and have also shown to perform well in both alkaline and acidic soils across a broad range of soil types, despite the possibility of soluble P being precipitated by CaF_2, a product of the reaction between NH_4F and $CaCO_3$ (Kleinman and Sharpley, 2002).

Physical condition of the soil can affect important ecosystem processes such as infiltration of water, erosion, aeration and growth of plant roots. A good understanding of physical condition of the soil is a prerequisite to identifying appropriate management practices and also to evaluating effect of management on dynamic changes in the soil properties and soil health. Several indicators such as texture, bulk density, moisture holding capacity, strength and shrink-swell properties are used to characterize the physical health of the soil. Soil particle size distribution is a fundamental soil property that is used as a covariate in predicting or conditioning soil functional properties, such as nutrient retention, tillage properties and hydraulic properties. Dispersed, non-dispersed particle size distribution measurements and dry aggregate size distribution though sensitive to weather and short-term land management have been used as indicators of soil erodibility (Leys et al., 2002). However, these indicators may have value in diagnosing soils that are susceptible to erosion, even though erodibility may be affected by a number of fast variables (Bryan, 2000). There is therefore emphasis on rapid and repeatable measures rather than accurate measures of particle size distribution determination. In AfSIS, a procedure for determining dispersed and non-dispersed particle size distribution is used to index potential erodibility in both wet and dry state (Vagen et al., 2010). The procedure measures micro-aggregate (<0.25 mm) stability, which is a slow variable, and less sensitive to management than macro-aggregate (>0.25 mm) stability. Response of particle size distribution to different levels of ultrasonic energy can be used to derive absolute measures of soil stability (North, 1976).

Measuring the energy status of the soil water (soil water potential) is important because it reflects how hard plants have to work to extract water. Soil water release curves are curves that express the relationship between matric potential and water content of a soil. Soil moisture is determined using disturbed soils (2 mm sieved) in pressure plates apparatus (Cresswell, 2002). The less the water content the more the suction. At a given suction, finer-textured soils retain more water (larger number of small pores). The shape and position of the curve determine hydraulic properties, such as infiltration rate, plant available water holding capacity, and aeration. In this procedure matric potential of the soil, Also called soil water potential represents the force with which water is held within the soil and how much energy is needed to overcome this force to extract water from the soil.

Soil mechanical properties that are important for many engineering decisions such as road construction and earthworks also determine structural stability and tillage properties (e.g. workability) of soils. On the basis of ease of use and ability to infer many other engineering properties, atterberg limits, linear shrinkage tests, and hygroscopic water content are selected as a set of test for engineering purposes (Bell, 2000; Hazelton and Murphy, 2007; Vargen et al., 2010). The atterberg limits are used to estimate the strength and settlement characteristics of soils. They characterize and define the behavior of soil by measuring shrinkage limit, liquid limit and plastic limit. The limits are also linked to erodibility of the soil and their properties depend on the amount of clay, silt, organic matter and type of minerals. Soils that have a high liquid limit have the capacity to hold a lot of water while maintaining a plastic or semisolid state. A low plastic index (0 to 10) indicates silt, while a high Plastic index (more than 35) indicates clay.

Shrink-swell potential is the potential for volume change in a soil with a loss or gain in moisture. Volume change occurs mainly because of the interaction of clay minerals with water and varies with the amount and type of clay minerals in the soil. The size of the load on the soil and the magnitude of the change in soil moisture content influence the amount of the swelling of soils. Shrink-swell potential classes are based on the change in length of an unconfined clod as moisture content is increased from air dry to field capacity. The classes are low, a change of less than 3 percent; moderate, 3 to 6 percent; and high, more than 6 percent. Very high, more than 9 percent is sometimes used (McGarry, 2002).

2.4 Soil mineralogy

Soil minerals play a significant role in dictating the suitability and behavior of soil for various land uses. They provide physical support for plants, contribute to soil structural formation, are sources of many soil nutrients, and can act as sorbents of several environmental pollutants. Therefore, understanding soil mineralogy is essential to understanding many facets of land use and is often a key to solving specific agricultural and environmental problems. The most common methods used for soil mineral characterization include X-ray diffraction, thermal elemental and optical analysis. Through these techniques unique mineral features, which are essential in predicting their impact on the overall soil behavior are identified and quantified. X-ray diffraction (XRD) is a rapid, low cost and non-destructive technique for qualitative and quantitative analysis of crystalline compounds; about 95% of all solid materials in the soil are crystalline (Moore et al., 1997). For mineral identification (silicates, clays, carbonates, oxides and some organics components), phases as little as 1-3% sample weight can be identified independent of crystal type.

An XRD diffractometer works on the principle that when X-rays interact with a crystalline substance or powder, the angle and intensity of the diffracted beam recorded by a detector forms a diffraction pattern, called a diffractogram which provides information about a sample. Results are commonly presented as peak positions at 2θ (theta) angle and X-ray counts (intensity) in the form of a table or an x-y plot. Peak position (angle 2θ), the interplanar atomic spacing or d-spacing provides information about atoms arrangement within the crystalline compounds. Peak width gives the crystallite size. Peak intensity or counts (I) relates to the nature of the atoms and their concentration. A measurement procedure that ensures high peak/background ratios, low sensitivity to sample density variations, and a good counting statistics, while the strongest peaks of 0.334 nm quartz stay within the linearity range of the counter, and the beam stays within the preparation for the lowest 2θ angle, meets the optimal conditions for XRD analysis. Linear one line detector (1D) diffraction scans have good resolution and less noise as shown in in Figure 1.

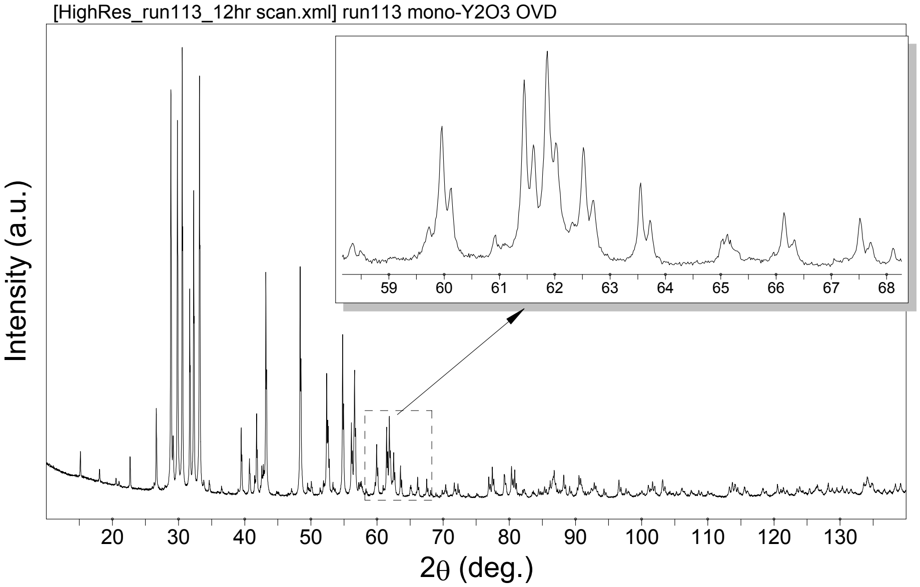


Figure 1: *Example of a diffractogram with good resolution and less noise (inset), (center for material science and Engineering at MIT).*

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study approaches and sampling sites

The African Soil Information Services (AfSIS) aims to develop a practical, timely and cost-effective soil health surveillance system to improve the assessments of soil conditions, enable mapping of soil functional properties, set a baseline for monitoring changes, and provide options for improved soil and land management. The system will facilitate the identification of areas at risk of soil degradation and corresponding preventive and rehabilitative soil management interventions. AfSIS builds on recent advances in digital soil mapping, infrared spectroscopy, remote sensing, statistical analysis, and integrated soil fertility management (ISFM), an approach that has presented the opportunity to improve soil assessments using information on soil mineralogy. AfSIS uses a sampling frame that is based on a set of 60 sentinel sites, each of 100 km^2, stratified by climate and randomized over sub-Saharan Africa (Figure 2). As such it provides an unbiased sample of Sub-Saharan soils.

A subset of ten sentinel sites was selected for this study (the first sites that were sampled and available at the time that this study started). The samples represented a wide variety of landscape positions, parent materials, and land uses as described in Table 1. A total of 160 soil samples from ten 100-km^2 site which include: Tanzania (3 sites), Malawi (2 sites), Mali (1 sites), Burkina Faso (1 site), Kenya (2 sites) and Ghana (1 site) were taken.

Figure 2: *Geographic coverage of AfSIS. Yellow circles represent the sampling locations (**AfSIS, 2012**). Green dots show the full set of AfSIS sentinel sites.*

Table 1: *Description of the soil forming factors for each site. Soil = (climate, organisms, relief, parent material, time). Aw= tropical savanna climate, Bsh = warm semi-arid climate. (Kottek et. al., 2006, Wilkenson et. al., 2010, LDSF * field observation)*

Country	**Site**	**Average Elevation**	**Average Slope**	**Landform Description**	**Climatic Zone**	**Native Vegetation**	**Parent Material**
Tanzania	Mbinga	1000	9.8	Medium gradient hill	AW	Miombo	Granitic
Tanzania	Bukwaya	1197	1.7	Dissected plain with medium gradient hills	AW	Miombo	Granitic
Tanzania	Chinyanghuku	901	15	Medium gradient hills	AW	Miombo	Granitic
Kenya	Mpala	1714	2.8	Plateau/escarpment	AW	Savanna	Lateritic
Kenya	Moiben	2000	1.5	Plateau/escarpment	AW	Savanna	Lateritic
Malawi	Thuchila	700	1.6	Level plain	AW	Miombo	Granitic
Malawi	Nkata bay	660	7.2	Medium gradient hills with wetlands in the valley	AW	Miombo	Granitic
Ghana	Lambussie	200	2.8	Plateau with medium gradient hills	AW	Grassland with scattered trees	Granitic
Burkina Faso	Bondingui	300	2.4	Relatively flat with few isolated hills	AW	Shrub wooded savanna	Granitic
Mali	Koloko	300	0.83	Level plain	Bsh	Woodland	Lateritic

*LDSF: Land degradation surveillance system

3.2 Soil sampling

This study took advantage of the AfSIS field method employed in the soil health component of the AfSIS project developed at the World Agroforestry Centre (ICRAF), and referred to as the Land Degradation Surveillance Framework (LDSF) (Shepherd et al., 2008; Vagen et. al., 2010). This method is designed for understanding ecological metrics and their dynamics at different spatial scales, and a monitoring and evaluation framework for assessing processes of land degradation and the effectiveness of rehabilitation measures over time. It employs a sampling methodology that attempts to understand and quantify factors affecting soil conditions.

The framework is built around a hierarchical field survey and sampling protocol using sentinel sites that are 100 km^2 (10×10 km) in size. The basic sampling unit was a cluster (1 km^2) consisting of 10 plots (1000 m^2) and 4 Sub-Plots (100 m^2). Each sentinel site was stratified into 16 Clusters (16 grid cells), and sampling cluster centroids randomly located within the grid cells (Figure 3). The sampling plots were then randomized around each cluster centre-point, resulting in a spatially stratified, randomized sampling design. Alternative sites were also identified in case the identified site had areas that were not accessible. Randomizing the plots in the cluster was extremely important as it minimized any local biases that may arise from convenience sampling. At the plot level, each sampling plot 1000 m^2 area referred to as LDSF radial arm plot (Figure 3) had 4 subplots. Top- and subsoil samples were corrected from the geo-referenced centre of each subplot at 0-20 cm and 20-50 cm depths respectively. For this study only topsoil samples from one selected plot per site were used. These were the sites that had samples already collected at the start of this study. Topsoil samples from all the 4 subplots per plot were then pooled (composited) into one sample. These resulted in a total of 160 standard soil samples per sentinel site. All 160 topsoil samples taken from 16 randomized points at each site were characterized for chemical properties, particle size distribution, engineering properties and bulk mineralogy.

3.3 Soil sample preparation

Soil samples were air dried and then crushed to pass a 2 mm sieve. Soil fines were sub-sampled using corning and quartering to obtain a representative sample which was stored in a strong paper bag. Part of the sub-sampled fines were further finely ground to a grain-size powder of less than 75 micron with a mechanized agate and pestle motor (Retsch MM 200 mixer mill, Gmbh & co, Haan, Germany). These were used for organic carbon analysis. The remaining soil fines were used for physico-chemical and mineralogical analyses.

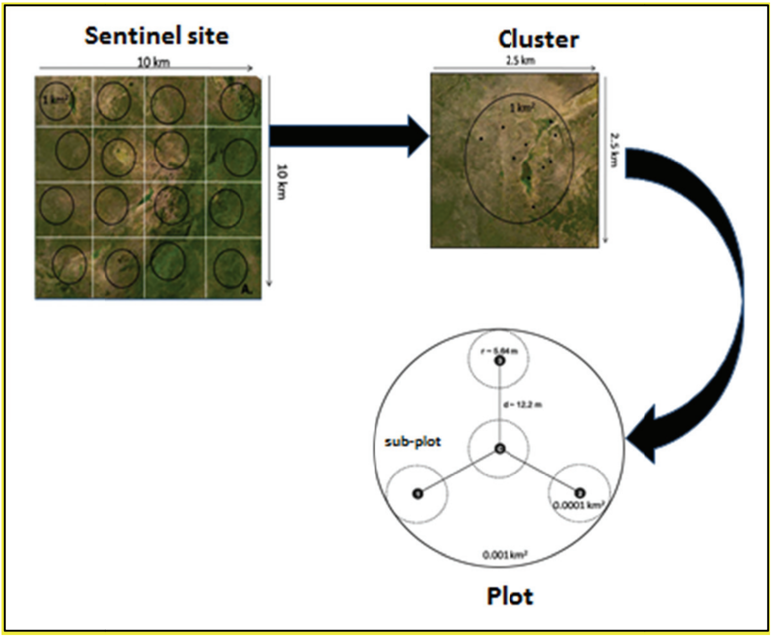


Figure 3*: An AfSIS site containing 16 clusters (16 grid cells) and sampling cluster centroids 1km*^{2}*. The inner circles represent 0.01 ha sub-plots.*

A protocol for preparing and analysis using a benchtop X-ray diffractometer was developed (Appendix 2). The developed procedures aimed at achieving three goals: randomness, homogenization and reduction in size of coarser- grained samples in order to assure good reproducibility of peak intensities, taking care not to cause measurable damage to the layer structure during size reduction. The required reduction in size and homogenisation of soil samples for mineralogy analysis was achieved by 12 minutes wet milling of 3 g air-dried and 2 mm sieved soil sample in a McCrone micronizing mill (McCrone microscope and accessories) with ethanol as a grinding fluid. The mixture was then centrifuged for 10 minutes and decanted. Hexane was added to the sample in the ratio of 0.5 ml hexane to 1 g of soil sample. After mixing, the sample was dried at 80^{o} C in an oven and sieved through a 250 µm sieve (S'rodon' et al., 2006). This provided a harmonized powder with many crystallites in random orientations, meeting the condition for XRD soil mineralogy. Powder crystals in random orientations allow the goniometer to swing through many angles ensuring necessary quantity of crystals and diffraction angles to determine mineralogy. A portion of the randomly prepared samples were mounted onto low background sample holders using the razor tampered surface (RTS) method, which prepares a powder mount by tamping the loose powder with the sharp edge of a razor blade (Guoping et al, 2003). This ensured as much as possible, a similar degree of packing, important for reproducibility of XRD patterns and reduction of peak displacement and broadening due to variations in sample density.

3.4 Laboratory Measurements

3.4.1 X-ray pattern acquisition, phase identification and quantification

The XRD analysis was performed using a Bruker benchtop, D2 phaser diffractometer system with Ni-filtered, Cu-Kα radiation (30 kV and 10 mA). The developed optimal condition for measurement was reached by using a 0.6 mm divergence slit, a 1 mm anti-scatter slit, and a 2.5 mm axial solar slit. The XRD patterns were recorded at a variable rotation of 15^o/min in the angular measurement range of 3 to 75^o 2Theta with an accuracy of 0.02^o throughout the measurement range, and at 0.5 sec/step. The intensity of diffraction of a given mineral in the sample under investigation was continually recorded as the sample and detector rotated through their respective angles as a peak. This resulted into a 30 minutes measurement time with scanned of good quality, high resolution and good data reproducibility (Appendix 2). This procedure ensured high peak/background ratios, low sensitivity to sample density variations, and a good counting statistics, while the strongest peaks of 0.334 nm quartz stayed within the linearity range of the counter, and the beam stayed within the preparation for the lowest 2Theta angle, from which the analysis was performed.

The diffraction pattern obtained for every phase is as unique as a fingerprint. Phases with the same chemical composition can have drastically different diffraction patterns. Using the Powder Diffraction File (PDF) database (containing over 200,000 diffraction patterns of crystalline phases) from the International Centre for Diffraction Data (ICDD), the Bragg angles for the peaks were determined to calculate d – spacing using the Bragg equation

$$\lambda = 2d_{hkl} \sin \theta$$

Where: d = lattice interplanar spacing of the crystal

θ = X-ray incident angle (Bragg angle)

λ = wavelength of the characteristic x-rays

The position and relative intensity of a series of peaks was used to match experimental data from the diffractogram to the reference patterns in the database. The relative abundance of the mineral compositions of the bulk soil samples were determined semi-quantitatively by peak heights (I) and were calculated using the methods of Shultz (1964) and Hillier (2003). The ratio of peak intensities (I) varies linearly as a function of weight fractions for any two phases in a mixture. This gives semi-quantitative results by extracting the reference intensity ratio (RIR) from the PDF reference database to quantify the mineral phases.

3.4.2 Soil Characterization

Soil characterization was conducted using standard laboratory measurement methods that are rapid and of low cost and can be applied on large numbers of samples. Using the AfSIS prioritized modular approach to soil measurements as described in the AfSIS technical specification for soil health surveillance (Vagen, et al, 2010), reference analysis were conducted using the standard soil fertility module.

3.4.2.1 Reference measurements

Basic chemical properties were undertaken to investigate clustering of conventional soil fertility variables and mineral profiling. The Mehlich 3 extraction method (Mehlich 1984) was used as it allows multiple elements to be analysed from one extractant using inductively-coupled plasma spectrometry (ICP). A summary of the soil chemical properties reference analysis is as shown in Table 2.

Table 2: *Soil chemical properties reference analysis*

Analysis	Method
Exchangeable acidity	KCl extraction, unbuffered
Extractable Al, Ca, Mg, P, K, Na, S, Fe, Mn, Zn, Cu, B and other bases	ICP analysis of Mehlich 3 extract
pH	Calorimetric analysis of 1: 2.5 volume water extract using an electrode probe and meter

Soil organic carbon (C) was measured from fine ground samples. Inorganic carbon dissolution was done by acidification of 15 mg soil within a silver capsule. Carbonates evolved as carbon dioxide upon sample acidification. The material was then dried and wrapped with a tin capsule and analyzed by the flash combustion method using a thermal scientific flash EA 112. Soil pH was determined by a standard method that uses a soil to water ratio of 1:2.5 using buffer solutions that bracket the expected pH values of the soil samples.

Basic soil physical properties module in AfSIS includes particle size analysis and soil moisture release curves. The total sand, silt and clay content were determined using a laser diffraction particle size analyzer (LDPSA) (Laser Diode Company: Sanyo Electric Compny Ltd.). This is an automated, rapid low cost technique for measuring particle sizes using light diffraction patterns. A particle passing through a collimated laser beam scatters light over a range of angles that are directly related to their sizes. To disperse the soil, a deflocculating agent was added to the water (Sodium hexametaphosphate – 40 g/L) and further dispersion was obtained by use of ultrasonic agitator incorporated in the equipment. The information was converted into particle size information.

Soil moisture characteristics were determined based on a desorption procedure that uses suction and pressure. The 0.3 bars determination was recorded as the field capacity (Whc) and the 15 bars determinations were recorded as the wilting point (Wp). The soils were saturated and subsequently balanced with respect to the changing values of the moisture tension. The moisture tensions were obtained by creating a series of under and over pressures. The water retention is defined as the soil water content at a given soil suction by varying the soil suction and recording the changes in soil water content (weighing of the samples after each balance adjustment) a water retention function is determined. The water retention function is dependent on particle size distribution, clay mineralogy, organic matter and hysteresis.

3.4.2.2 Engineering Properties

In addition to the determination of basic soil physical properties, soil engineering properties; atterberg consistency limits and soil linear shrinkage test, were determined to exploe the relationships that these properties have with soil mineralogy. The liquid limits of samples were determined by the fall cone test illustrated in the Australian Standards Association (McGarry, 2002). This test uses a standard cone with a 30^{o} apex angle and a total mass of 80 g. A dish (55 mm diameter by 40 mm deep) is filled with soil in the consistency range of the liquid limit. The cone is then released so the 80 g mass produces some penetration for 5 seconds. The liquid limit is defined as the water content at which 20 mm of cone penetration occurs in the 5 s test time. Plastic limits were determined by the rolling thread test based on Australian Standards Association (McGarry, 2002). A sample of ~10 mm^3 was taken and rolled in the palm of the hand on a glass plate into a thread of ~ 3 mm diameter. The moisture content was adjusted until the 3 mm thread just began to crumble. The moisture content was then measured, as this is the plastic limit. The plasticity index (I_p) of a soil is the numerical difference between the liquid limit and the plastic limit. The I_p is usually proportional to the clay content and indicates the rate of water contents over which a soil has plastic properties.

Soil shrinkage was determined by putting wet soil used in the liquid and plastic limits tests into a clean and lightly greased shrinkage mould trough. Air bubbles or voids were removed by lightly tapping the base of the mould on a flat rubber mat and the excess soil was levelled off with a palette knife. The mould was allowed to air dry slowly at room temperature for 12-24 hours after which was dried to constant weight in an oven at 105^o C. After cooling the mean length of the soil bar was measured to the nearest millimetre. Soil shrinkage (LS) is the limit to which a soil material contracts as it loses water on drying.

3.5. Statistical analysis

All calculations and statistical analysis were done using the R statistical software package version 2.14.1(R Development Dore Team, 2008). Data processing and visualization were performed using KNIME workflows (http://www.enotes.com/topic/KNIME). Patterns in soil mineralogy and physico-chemical data arrays were adjusted by a centered log-ratio transformation (Aitchison, 1983, 1986), followed by a normalization of the same, which overcomes the closure problem produced by constant-sum data that are composition in nature. Log-ratios were used to open the data into the full range of the real number space. These transformations were applied before statistical analysis with attempts throughout the analyses made to identify the first two principal components within a causal framework that illustrates the influence of soil forming factors, such as climate and topography.

Variation of the mineralogy within and between sites and the clustering of minerals in the XRD diffractograms was explored using multivariate analysis, including principal component analysis, as a precursor to exploring relationships with directly measured soil functional properties and their prediction. Patterns in soil fertility and major nutrients, basic cations, extractable micronutrients, engineering properties, pH, and soil particle size distribution and soil organic C variables were investigated using principal components analysis (PCA). Principal components bi-plots were used to identify closely associated variables. From each group of closely associated variables, one variable with the highest principal component loadings was taken as an indicator variable for that group and used in further analyses.

CHAPTER FOUR

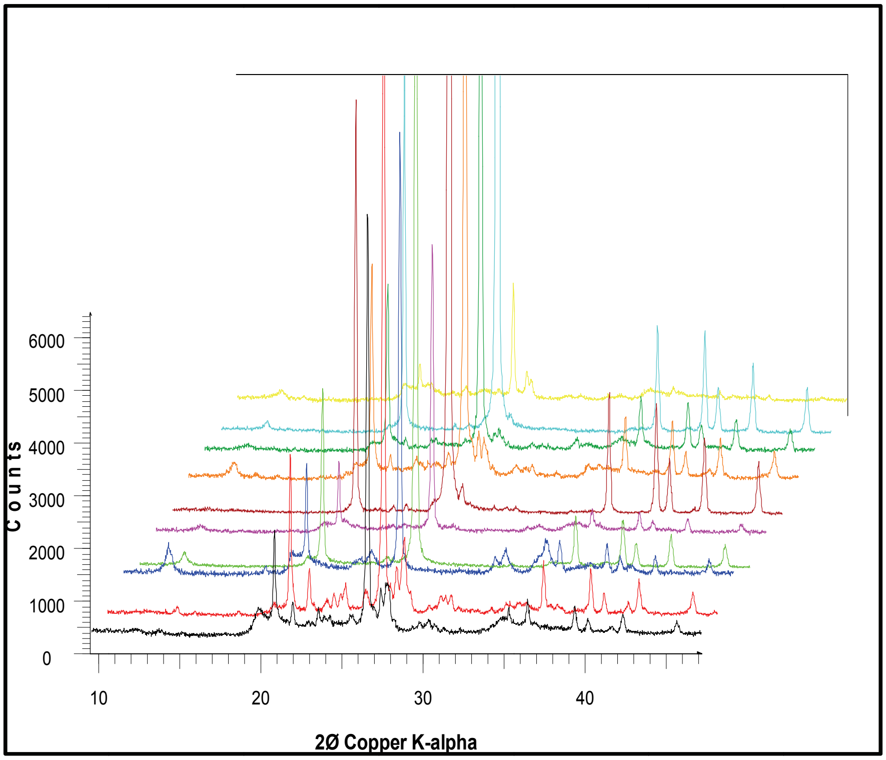
4.0 RESULTS AND DISCUSSION

4.1 Soil mineralogy

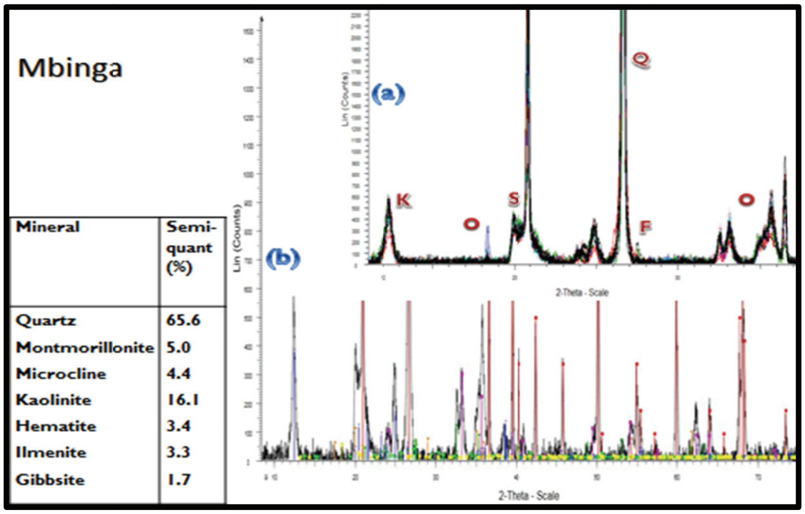
The developed XRD sample preparation and scanning protocol resulted in high quality diffractograms with only a half-hour scanning time. The quality of the results from this bench top instrument, which operates on normal power and does not require an external cooler, is comparable with diffractograms obtained on much larger instruments. This development takes XRD from what has been a largely qualitative and very time consuming and specialized measurement, to a method that can be used in quantitative mode as a routine analytical tool by soil testing laboratories. A protocol for rapid soil mineralogy analysis using X-ray diffraction technique (XRD) is presented in Appendix 2.

All the 160 soil samples from the ten different locations had a mixed mineral composition typical of most natural samples. The mineralogical composition and semi quantitative estimation of the mineral content of soils investigated based on XRD analysis from the ten locations varied as reflected in the X-ray diffractograms in Figure 4. Figure 4 shows the X-ray diffractogram of Mbinga site as an example of the other ten sites (find others in Appendix 1). Mineral phase identification using the Powder Diffraction File (PDF) database revealed the content of each of the randomly oriented bulk samples across the sites to be composed mainly of quartz, K-feldspars (microcline), plagioclase feldspars (albite), carbonate minerals (calcite, and dolomite), amphibole (hornblende and tremolite), magnetite, hematite, goethite, anatase, diopside, ilmenite, clay minerals halloysite, kaolinite, gibbsite, muscovite, smectite/montmorillonite, vermiculite, and chlorite/clinochlore (Table 4).

a)



b)



Mineral	Semi-quant (%)
Quartz	65.6
Montmorillonite	5.0
Microcline	4.4
Kaolinite	16.1
Hematite	3.4
Ilmenite	3.3
Gibbsite	1.7

Figure 4: *a) Examples of XRD patterns of samples from the ten sites. b) X-ray diffractogram of top soils from Mbinga site (inset a) Mean from 16 top soil samples, (inset b) An example of one sample from the site (Q=quartz, S=smectite, K=kaolinite, F=feldspar, O=Oxide), all un-labelled peaks = quartz.*

To minimize the number of minerals used for this study, minerals with limited occurrence such as calcite, anatase, vermiculite and tremolite were dropped and others with natural affinities and paragenesis in soils were grouped together as described by Drew et al, (2010). Quartz being a ubiquitous mineral, present in soils was not grouped. It is highly resistant to weathering, and an initial, inherited percentage of quartz in soils tend to increase by the weathering and dissolution of other minerals. Plagioclase feldspar (albite) and k-feldspar (microcline) are primary minerals in soils derived from weathered igneous, metamorphic, and feldspathic sedimentary rocks. Referring to the ratio of tetrahedral to octahedral components in the clay structure, halloysite and kaolinite were grouped together as 1:1 clays; 2:1 clays smectites (montmorillonite), chlorites (chlinochlore), and illite/mica (muscovite) were grouped separately. Kaolinite clays are Al-rich and typically form by the weathering of felsic rocks and feldspars. In contrast, smectite contains Ca and Na, and illite contains K, and both may form by weathering of mafic rocks which are rich in magnesium and iron as well as silicate minerals, including micas and feldspars. Carbonates minerals (dolomite) formed from limestones and are easily weathered were grouped as primary minerals. Iron oxides (hematite, magnetite and goethite), aluminium oxides (gibbsite) and titanium oxides (ilmenite) were grouped together as primary and secondary oxides due to their ability to release $Al^{3+,}$ Fe^{2+} and Ti^{2+}. Also the colour of Fe oxides is determined for that of soils with the most colouring agents in soils being goethite and hematite. The ratio of hematite (red) to goethite (yellow brown) seems to be controlled by the pH of the soil (Schwertmann and Taylor, 1989; Scheinost and Schwertmann, 1999). Minerals that may have unique occurrences, such as amphibole and diopside were not grouped. Also listed is the dominant paragenesis for mineral and mineral groups in soils are primary minerals which persist in the weathered parental materials, while others are formed secondarily from weathering of primary minerals. For instance, some clay developed from the weathering of feldspars, or goethite formed by weathering of iron-bearing minerals such as magnetite. Table 3 gives the list of minerals and mineral groups along with abbreviations used in subsequent analysis, tables, figures and text.

Table 3: *Transect mineralogy with minerals grouped by natural affinities and dominant paragenesis in soils. Abbreviations are used in table 4.*

Mineral group name/ Abbreviation	**Mineral(s)**	**Dominant paragenesis in Soils**
Quartz/Qrtz	Quartz	Primary
K-feldspar/K-fp	Microcline	Primary
Plagioclase/Plag	Albite	Primary
Amphibole/Amph	Hornblende	Primary
Pyroxenes/Pyrox	Diopside	Primary
Carbonate/Carb	Dolomite	Primary
Oxides	Hematite/goethite /gibbsite/Magnetite/ Ilmenite	Primary/secondary
Kaol/ Clays 1:1	Kaolinite/Halloysite	Secondary
2:1 clays/Clays 2:1	Montmorillonite/Muscovite/ Clinochlore	Primary/secondary

Estimation of relative abundances of the different minerals identified in the different soil types were made based on the intensity of X-ray diffraction peaks for the different minerals. The bulk soil samples showed that the mineral compositions within the soil sites were relatively uniform, but there was notable difference across sites as shown in Figure 5. The sole commonality was the dominance of quartz mineral. The hypothesis that high quality X-ray diffractograms can be obtained from whole soil samples using rapid and simple sample preparation methods providing semi-quantitative mineralogical data as explained by Hillier, 2003 agree with the current findings. Relative abundances of all the 16 clusters in each site were averaged as presented in Table 4.

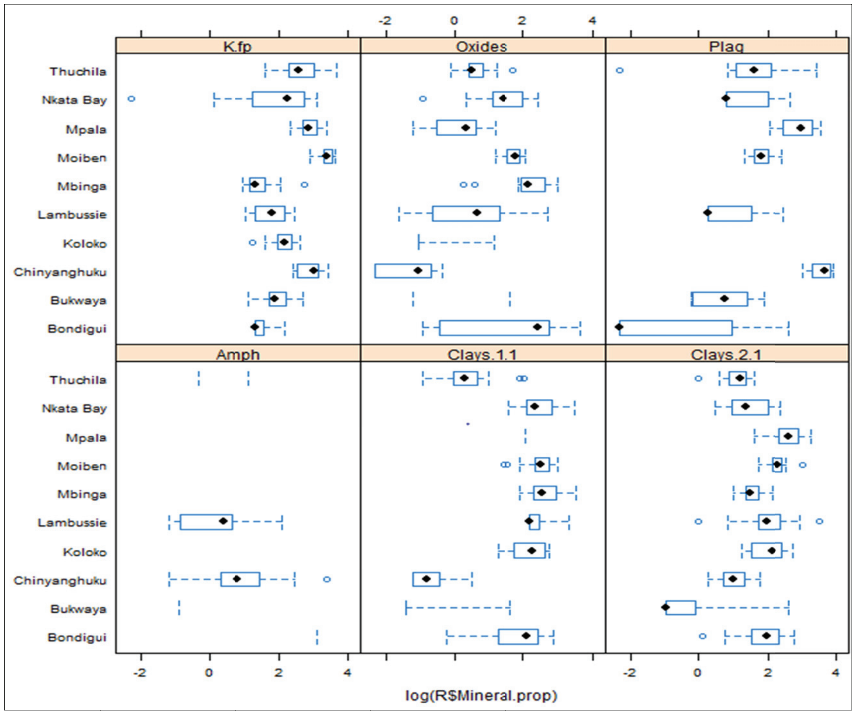


Figure 5: *Box plot illustrating dominant mineral variations within and across sites.*

The mineralogy trends reflected different parent materials but suggested that much of the soils mineral suite was dependent on weathering, a soil-forming process that can influence soil mineralogy at all scales (Dixon and Weed, 1989; Valde and Barre, 2010). All the soil samples were quartz- rich with (38–87%) contents, except Moiben soils which had moderate amounts of quartz (28%). The main iron minerals in the soils were magnetite (Fe_3O_4), goethite (FeO (OH) and hematite (Fe_2O_3), with Bondigui and Mbinga soils having the highest ferric oxide content (10-11%). These oxides are frequently present in small amounts, in all weathering stages of soils, and are associated with different types of clay minerals; nutrient rich 2:1 (Valde and Barre, 2010) in the initial stages of weathering and 1:1 clays in the final stage of weathering where they become dominant.

Table 4: *Relative abundance of the identified minerals phases in the soils (averaged across 16 clusters in each site).*

Country	**Soil location (Site)**	**Qrtz**	**Kfp**	**Plag**	**Amph**	**Oxides**	**Pyrox**	**Carb**	**1:1 clays**	**2:1 Clays**
Tanzania	Chinyanghuku	††††	†††	††††	††	†	Nd	nd	†	††
Mali	Koloko	††††	††	Nd	nd	†	Nd	nd	††	††
Tanzania	Bukwaya	††††	††	††	nd	†	Nd	nd	†	††
Burkina Faso	Bondigui	††††	††	††	††	†††	†	†	††	††
Tanzania	Mbinga	††††	††	Nd	nd	†††	Nd	nd	†††	††
Kenya	Mpala	††††	†††	†††	nd	††	††	nd	†	††
Malawi	Thuchila	††††	†††	††	†	††	††	††	††	††
Kenya	Moiben	†††	††††	††	nd	††	††	nd	†††	†††
Ghana	Lambussie	††††	††	††	††	††	Nd	†	††	††
Malawi	Nkata bay	††††	††	††	nd	††	Nd	nd	†††	††

Mineral symbols as in Table 1 or in the text.
†††† = Abundant (> 30%), ††† = Moderate (10 – 30 %), †† = Minor (1 – 10 %), † = Trace (< 1 %), nd = not detectable (0).

They are also important in the distribution of iron in soils. Mbinga, Nkata bay and Bondigui had moderate amounts of 1:1 clays as the dominant clay minerals representing the effects of weathering in the soils. Predominant in these highly weathered soils was ilmenite in association with magnetite. Chinyanghuku, Mpala and Moiben were rich in either Na- or K-feldspars with minor to moderate amounts of 2:1 clays as the dominant clay minerals, reflecting less weathering and leaching. The ineffective leaching characteristic in these soils may contribute to retention of Na, K, Ca, Mg, Fe and silica nutrient cations. The presence of amphiboles in Chinyanghuku soils displayed a characteristic of silt and clay fractions in young soils. Thuchila, Lambussie, Koloko and Bukwaya soils had moderate to minor amounts of K-feldspars appearing to be associated with quartz and clay minerals. The presence of K-feldspars in association with these minerals represent a transition from less weathered to more weathered material. Quartz is commonly the predominant primary mineral occurring in the sand size fraction of highly weathered soils. Accordingly, quartz presence is generally thought to have little influence on, or relationship to, the nature of the secondary minerals present in highly weathered soils which are oxides of iron and aluminium, and kaolinite (Drew et. al., 2010). Its persistence in these soils is attributed to its extreme chemical inertness and its abundance with secondary minerals suggests that the effects of weathering have increased the percentage of quartz especially through ferralization and ferrugination (Drew et. al., 2010). The trioctahedral chlorite (clinochlore) mineral present in Mpala and Thuchila soils indicate special chemical conditions of a basic Fe- and Mg-rich source rock of clay rich material in the absence of alumina or a situation of low alumina activity with minimal alkali activities.

Principal component analysis (PCA) of the mineralogy data of soils from all ten locations was carried out to determine the major clustering of the mineralogy as a function of the soil forming factors (Figure 6). The first two principal components respectively accounted for 20.4% and 17.9% of the variation in the mineralogical data. There was a considerable overlap in the center of the scatter plot among the ten locations, especially for Koloko, and Bukwaya sites and some samples from Lambussie and Thuchila sites. Chinyanghuku, Mpala and Moiben sites were generally distinct from the others, and Mbinga, Bondigui and Nkata bay sites had some samples that trended away from the larger cluster from the center of the plot. Lambussie and Thuchila had some samples clustering towards the distinct sites. The overlap and distinctness among the sites was apparent of the different weathering stages of the soils as illustrated by their mineralogy compositions (Woodruff et. al., 2009).

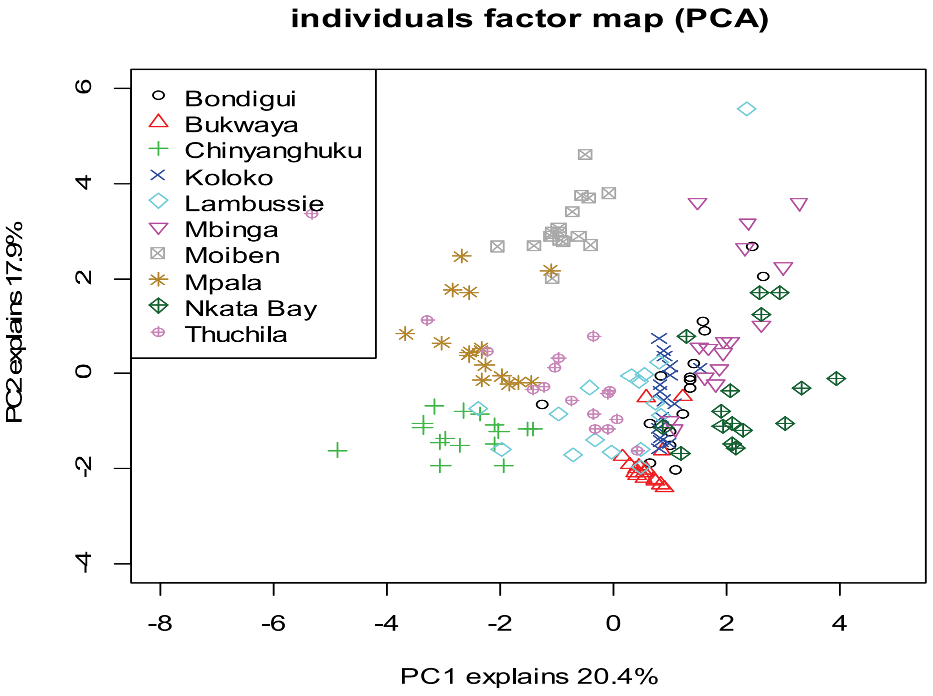


Figure 6: *Scatterplots of principal components 1 and 2 for the mineralogy of soils from all ten locations.*

In this study, Mbinga, Nkata bay and Bondigui soils were classified as highly weathered with low nutrient level kaolinite minerals or 1:1 clays with its relative abundance varying across sites. Kaolinite has no significant cation exchange capacity, where useful cations can be attracted for plant uptake. Further soils dominant with kaolinite minerals are devoid of potassium (Valde and Barre, 2010). There is also a problem of P fixation in soils that are high in 1:1 type of clay mineralogy. Phosphorus in these soils is found in the forms adsorbed on Fe-Al hydrous oxides and clay edges (van Straaten, 2002). Chinyanghuku, Mpala and Moiben soils were classified as nutrient rich soils dominated by 2:1 minerals. These minerals as discussed by Valde and Barre (2010), have a significant amount of cation fixation capacity, and can fix potassium and other base cations (Ca; Mg), major nutrients and probably also ammonium based on their local conditions of chemical potential or chemical activity of different ions in solution. These properties enable them to be reservoirs of these precious elements in soils. Thuchila, Lambussie, Koloko and Bukwaya all had some amounts of nutrients but weathering was causing an inexorable loss of alkalis and alkaline earth elements. These findings by Valde and Barre (2010) supported the hypothesis that mineralogical compositional fingerprints of Africa's soils fall into distinct clusters or patterns that can be used to distinguish soils of different soil fertility potential.

4.2 Soil physico-chemical properties

All soils exhibited a wide range of physico-chemical properties corresponding to their parent materials properties. The results were grouped into sections according to families of associations. Soil chemical properties included exchangeable bases (ExBas), Mehlich-3 extractable phosphorus (P) and potassium (K), exchangeable calcium (Ca) and magnesium (Mg), also Mehlich-3 extractable boron (B), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), sulphur (S) and aluminium (Al). Organic matter status included organic carbon (C). Soil physical properties included particle size distribution (sand, silt and clay); water holding capacity (Whc), atterberg limits (PI), linear shrinkage (lshrink), and wilting point (Wp). The mean and standard deviation values of the physico-chemical data of the 160 soil samples in the study areas are shown in Table 5.

Table 5: *Descriptive statistics of the physico-chemical properties of the different soils.*

Properties		Soil locations (sites)																			
		Chinyanghuku		**Koloko**		**Bukwaya**		**Bondigui**		**Mbinga**		**Mpala**		**Thuchila**		**Moiben**		**Nkata Bay**		**Lambussie**	
		Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
PSA (%)	Sand	53.9	15.8	18.6	11.6	81.6	25.4	35.9	23.7	26.3	11.6	36.4	9.3	25.7	15.0	30.1	4.1	33.6	16.6	37.2	18.5
	Silt	20.4	8.6	27.8	7.9	4.2	3.2	21.3	7.3	17.3	5.9	30.2	5.6	19.0	4.3	37.3	4.7	30.5	12.2	23.4	10.2
	Clay	25.7	12.9	53.6	18.3	14.2	22.5	42.9	18.7	56.4	13.6	33.3	11.6	55.4	16.2	32.6	5.6	36.0	10.8	33.2	19.0
Moisture retention	Whc	11.3	4.8	24.0	4.4	6.4	6.6	21.4	8.8	27.0	6.5	25.4	13.1	9.6	3.9	29.9	5.5	28.4	14.4	16.3	7.2
	Wp	5.5	2.5	11.5	4.0	3.4	4.7	9.9	5.2	12.3	3.5	13.3	9.8	5.2	2.4	19.9	4.5	10.1	6.1	7.5	4.8
Plasticity index %		6.4	5.1	7.7	3.1	9.8	5.1	7.3	3.2	8.4	2.4	8.6	5.8	5.6	5.4	8.0	1.6	7.9	3.6	4.9	3.1
Linear shrinkage %		5.1	1.2	4.4	1.8	5.9	3.2	5.2	2.3	7.0	0.9	7.4	3.6	3.6	0.7	7.9	1.6	5.9	1.3	4.1	2.1
pH-H_2O		7.2	0.5	6.1	0.6	7.0	0.8	6.7	0.4	5.8	0.4	6.4	0.5	6.2	0.2	5.7	0.2	5.6	0.5	6.3	0.6
Exchangeable cations (cmol/kg soil)	Ca	10.7	9.8	5.8	2.2	9.4	9.4	7.8	5.9	3.3	2.6	9.9	6.5	4.8	2.8	6.4	2.2	3.1	2.4	5.8	7.3
	Mg	2.8	1.1	2.7	1.6	2.9	3.1	2.4	2.1	1.1	0.6	3.8	1.7	1.4	1.1	2.5	0.6	1.5	1.0	1.7	1.6
	Na	0.1	0.0	0.2	0.1	0.3	0.3	0.2	0.1	0.2	0.0	0.3	0.5	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.0
	K	0.7	0.2	0.3	0.1	0.4	0.4	0.2	0.1	0.4	0.2	1.4	0.6	0.3	0.2	1.3	0.4	0.4	0.2	0.2	0.3
	Ex-Bas	14.3	10.4	9.0	3.6	12.9	12.6	10.7	7.9	4.9	3.4	15.4	8.7	6.6	4.0	10.5	3	5.1	3.3	7.8	9.0
Exchangeable acidity (Ea)		682	105	1357	590	592	339	0.6	0.2	2176	395	0.1	0.0	795	293	1227	222	1619	258	672	260
Organic Matter (% C)		1.1	0.8	1.0	0.4	0.6	0.3	1.4	1.0	3.1	1.6	1.2	0.5	1.0	0.5	5.7	0.2	1.5	0.8	1.0	0.7
Extractable phosphorus (P) (cmol/kg soil)		21.3	17.6	4.6	2.5	50.0	79.9	7.0	10.7	15.6	22.9	7.5	6.2	27.1	19.2	17.2	8.3	13.1	15.7	26.7	85.1
Mehlich 3 (Micronutrients) (cmol/kg soil)	Fe	120	45	149	95	140	64	1312	95	96	32	103	16	210	65	160	116	224	159	105	36
	Cu	1.5	0.6	1.7	0.9	2.4	2.5	2.3	1.4	2.4	1.1	1.2	0.4	2.7	1.8	1.3	0.3	1.3	0.8	2.0	1.8
	Zn	2.6	1.0	1.4	0.3	4.4	8.9	2.6	1.2	2.2	1.1	2.	2.1	1.6	0.5	3.8	2.5	1.8	1.0	2.3	.7
	Mn	118	41	55	27	143	101	143	102	284	180	235	80	129	87	262	60	104	78	143	83
	B	0.7	0.4	0.1	0.1	0.4	0.4	0.2	0.2	0.1	0.1	o.4	0.2	0.2	0.2	0.4	0.1	0.1	0.1	0.3	0.4
	S	14.0	4.2	9.3	4.7	8.4	3.5	6.0	.6	6.6	0.7	13.	4.7	6.7	3.1	14.4	3.4	9.8	3.7	5.9	2.4
	Al	682	105	1357	590	592	339	800	281	2176	395	927	140	795	293	1227	222	1618	258	672	260

Principal components analysis of the physical-chemical data was carried out to examine the major trends in their composition. The pattern of clustering of the properties (Figure 7) of the different soils revealed that some had very similar and some quite different chemical and physical compositions, which were reasonably consistent with the principal components, scatter plots of the mineralogy as shown in Figure 6.

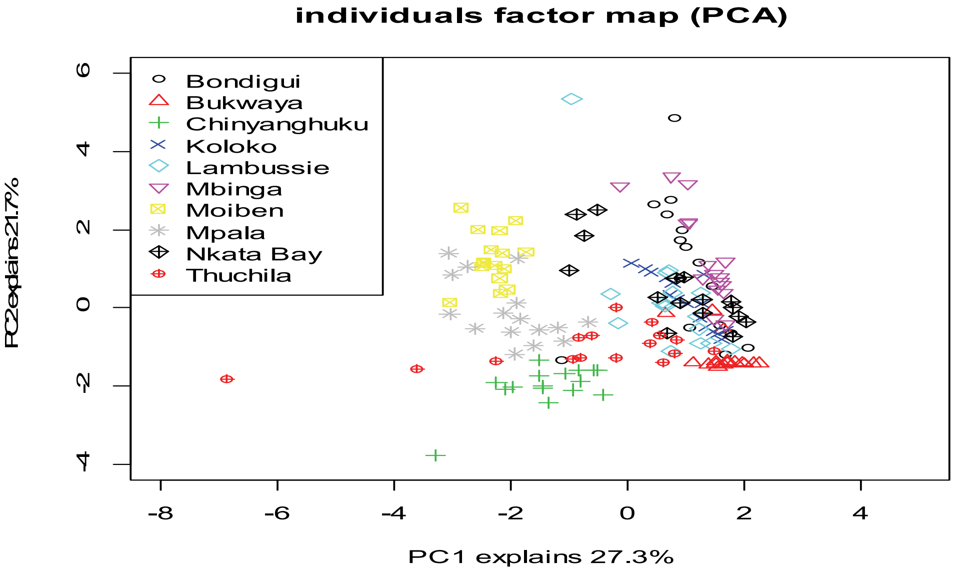


Figure 7: *First and second principal components individual factor map for the physico-chemical properties of soils from all ten locations.*

Principal components bi-plots of all 23 soil properties were conducted to identify close associations of the soil variables in (Figure 8). The first two components, respectively, accounted for 25.1% and 15.2% of the overall data variation. The sorting of the properties along the positive dimension in one axis is apparent. Properties such as Ca, Mg, K and exchangeable bases have been reported to have strong correlations in soils apparently caused by their mutual occurrence in clay minerals (Cannon and Horton, 2009). At low soil pH, there is strong soil acidity and high aluminium in soils which constraints the availability of most nutrient elements. The consequent acidity mobilizes potentially toxic levels of Al and causes intense leaching of nutrient cations such as Ca^{2+}, Mg^{2+} and K^{+} (Rimmer, 2008).

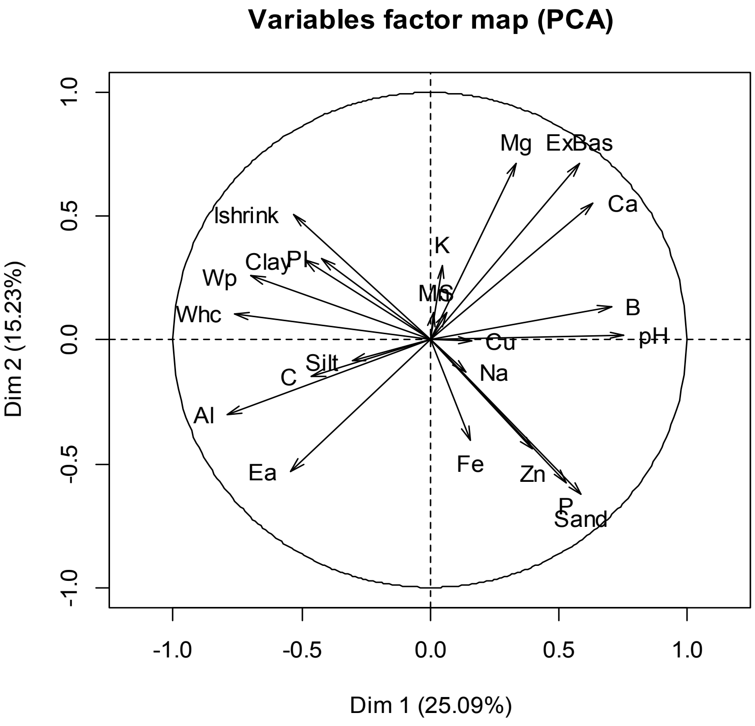


Figure 8: *First and second principal components computed from all soils from all locations*

The organic–mineral relationship is fundamental to the environment that plants grow in. Organic matter has a major influence on soil physical quality by increasing the retention of water, aggregating mineral particles and thus contributing to a favourable soil structure and preventing soil erosion. Soil organic matter also has a major and prolonged role as a reserve for nutrients such as N, P and S which are its constituent's elements and are released with mineralization (Rimmer, 2008; Valde and Barre 2010). Removal of plant biomas impoverishes the soil in its organic content and destabilizes the aggregate structure, which leads to more difficult conditions of plants growth and to a loss of clays due to erosion by water. A high base status (exchangeable bases) indicates low acidity levels an indicator of overall high soil fertility and presence of soil nutrient cations. Very low levels of exchangeable K indicate a high probability of K deficiency. Soils with high clay content will have low sand content and high water holding capacity and linear shrinkage characteristics.

The uniqueness of closely associated properties indicated in the bi-plots of Figure 8 was further demonstrated by the results of loading factors of the first two principle components which are illustrated by arrow sizes that are proportional to the "initial" variability in the elements present.The loadings indicated the properties that had significant contributions to the separation of the property associations. pH, ExBas, K, Al, C, Sand, Clay, Whc and Lshrink that had influential loadings (arrows closer to the circle line or with the longest line) in their cluster groups were chosen as indicator properties for that group and taken forward into further analyses. Positive loading values indicated significant interrelatedness. The correlation analysis (Table 6) suggested significant relationships in which a larger positive or negative correlation co-efficient indicated the importance of a soil property on the differences among the cluster groups (Aitchison, 1983).

Table 6: *Correlation coefficients of soil properties that significantly influenced or contributed to differences among the variables associations in the PC bi-plots.*

Soil property	pH	Ca	Mg	B	Mn	S	ExBas	K	Al	Ea	C	Silt	Sand	P	Zn	Fe	Cu	Na	Clay	Whc	Wp	Lshrink	PI
pH	1	0.5	0.2	0.3	-0.04	-0.2	0.4	-0.2	-0.6	-0.5	-0.24	-0.1	0.5	0.3	0.2	-0.03	0.1	0.2	-0.2	-0.5	-0.6	-0.4	-0.3
ExBas	0.4	0.9	0.7	0.5	-0.1	-0.01	1	0.1	-0.6	-0.6	0.14	-0.3	-0.1	-0.1	-0.1	-0.1	0.1	0.02	-0.1	-0.03	-0.2	-0.01	0.38
K	-0.2	-0.1	0.1	0.2	0.2	0.5	0.1	1	-0.2	-0.3	0.19	-0.01	-0.1	-0.1	0.1	-0.3	-0.4	-0.2	-0.2	-0.05	-0.1	0.2	-0.1
Al	-0.6	-0.6	-0.4	-0.6	-0.1	-0.5	-0.6	-0.2	1	-0.2	0.59	0.04	-0.3	-0.2	-0.3	-0.2	-0.1	-0.1	0.4	0.4	0.3	0.3	0.3
C	-0.24	0.12	0.14	0.12	0.27	0.09	0.14	0.19	0.59	0.46	1	0.33	-0.44	0.01	0.11	0.07	0.19	0.08	0.39	0.58	0.53	0.5	0.4
Sand	0.5	-0.01	-0.2	0.2	-0.1	-0.02	-0.13	-0.1	0.3	-0.2	-0.44	-0.2	1	0.6	0.4	0.3	0.01	0.3	-0.6	-0.6	-0.5	-0.5	-0.4
Clay	-0.2	-0.1	0.1	-0.4	-0.01	-0.2	-0.1	-0.17	0.4	0.1	0.39	-0.02	-0.6	-0.4	-0.3	-0.3	0.2	0.02	1	0.4	0.3	0.2	0.3
Whc	-0.5	-0.3	-0.2	-0.6	-0.1	-0.2	-0.3	-0.05	0.4	0.2	0.58	0.4	-0.6	-0.4	-0.2	-0.01	-0.2	-0.03	0.4	1	0.8	0.3	0.2
Lshrink	-0.4	-0.1	0.2	-0.3	0.1	0.1	-0.01	0.21	0.3	0.1	0.5	-0.04	-0.5	-0.5	-0.4	-0.3	-0.1	-0.2	0.2	0.3	0.4	1	0.5

4.3 Relationships between soil mineralogy and soil physico-chemical properties

The implications of the mineralogy clusters were investigated in relation to the distributions of the soil fertility variables by the principal component bi-plots (Figure 9).

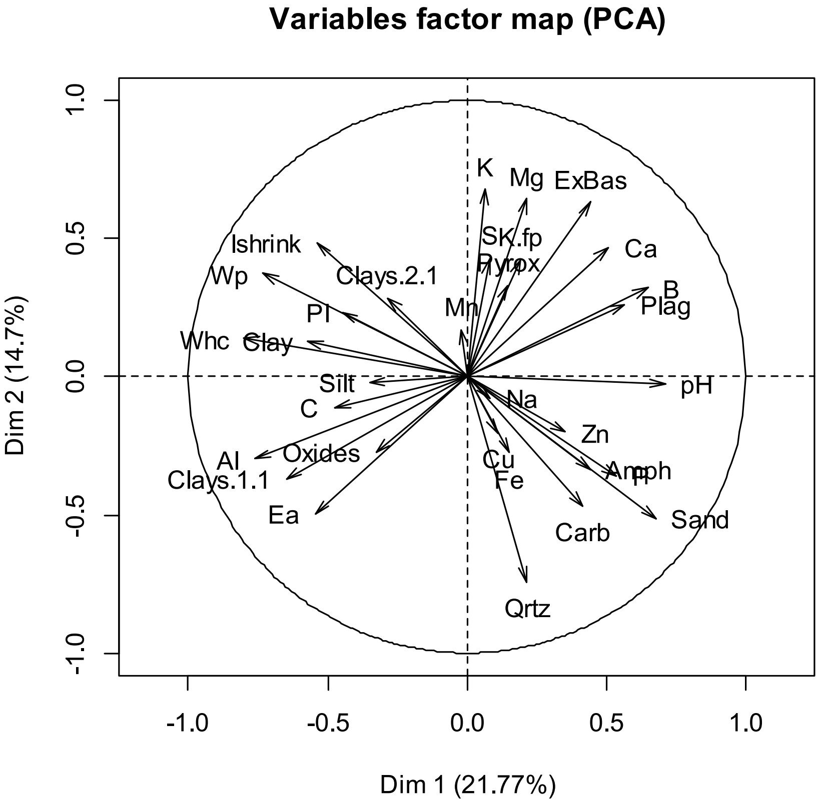


Figure 9: *First and second principal components computed from all soils from all locations showing the relationships of soil mineralogy and soil physico-chemical properties.*

On the positive side of PC1 axis in figure 9 are ExBas and pH as well as micronutrients such as Mn, B, elements typically contained within either feldspars or clays. Negative PC1 and positive PC2 in figure 9 quadrant contains clays grouped with strong linear shrinkage and water holding characteristics, properties typically contained in heavy clay soils. Positive PC1 and negative PC 2 in figure 9 quadrant contains P, grouped with Fe, Zn, Cu and Na, which are elements typically contained within either Fe-oxides or Fe-Mg silicate minerals reflecting a geochemical link related to long term phosphate fertilization, known to enhance Fe on surface soils (Mulla et.al., 1980). OC, EA, and Al lie within the negative PC1 and negative PC2 quadrant and denote an Al influence and characteristics of soils dominant in highly weathered minerals. The relationships between mineralogy and the indicator soil fertility variables were illustrated using the correlation coefficient (r) for pairwise associations (Table 7).

Table 7: *Correlation coefficients between indicator soil variables and grouped soil mineralogy.*

Mineralogy / Soil properties	Clays 2:1	Clays 1:1	K-fp	Plag	Qrtz	Oxides	Amp	Carb	Pyrox
Clay	0.57	0.42	-0.07	-0.14	-0.24	0.33	-0.05	-0.18	-0.002
Sand	-0.58	-0.52	-0.06	0.10	0.36	-0.31	-0.12	0.22	-0.05
L shrink	0.43	0.34	0.25	-0.001	-0.41	0.24	-0.01	-0.21	0.20
Whc	0.49	0.59	0.22	-0.18	-0.40	0.34	-0.13	-0.20	0.18
ExBases	0.24	-0.19	0.20	0.29	-0.27	-0.08	0.17	-0.05	0.09
K	0.40	-0.16	0.59	0.27	-0.54	-0.09	-0.01	-0.16	0.50
pH	-0.16	-0.44	-0.07	0.38	0.05	-0.22	0.22	0.00	-0.16
ExAl	0.20	0.63	-0.10	-0.30	-0.10	0.35	-0.17	-0.17	-0.07
C	0.15	0.48	-0.02	-0.05	-0.30	0.45	0.12	-0.13	-0.01

The mineralogy composition of soils from Chinyanghuku, Moiben, Mpala, Thuchila, Lambussie and some soils from Koloko and Bukwaya had higher exchangeable bases and organic matter content which guarantees higher retention of plants nutrients. In addition they had high clay content which implies more stable aggregates and consequently lower rates of erosion. The opposite is true for Mbinga, Nkata Bay and Bondigui soils where their physico-chemical properties such as Exbas, P and K are low and the mineralogical composition high with Kaolinite which encourages erosion (Ben-Hur et. al., 1985). This study has observed that soil functional properties of African soils can be quantitatively associated with soil mineralogical composition.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

A method was developed for rapid benchtop X-ray diffraction characterization of mineral composition on whole soil samples. The method provided good quality diffractograms enabling mineral identification and semi-quantitative analysis, with potential for full quantitative composition analysis. This development enables quantitative mineral composition analysis as a routine analytical tool in soil science.

Using principal component analysis, characterization and classification of the physico-chemical and the mineralogical data from the soils collected across the ten locations was conducted , enabling to recognize geologic controls and soil forming processes, including soil parent material and weathering. All soils exhibited a wide range of relationships between the physico-chemical and mineralogical properties as illustrated by the first and second principal components bi-plots. The clustering of individual minerals and the distribution of the soil fertility variables identified across the sites appeared to relate to differences in mineralogical functional groups, supporting the understanding of the pedologic environment differences and similarities. The variations revealed by the first and second principal components individual factor maps for the physico-chemical properties and the mineralogy data of soils from all ten locations emphasized the control exerted by weathering effects.

The relationships obtained in this study demonstrated the potential that analysis of soil mineralogy using the X-ray diffraction technique can allow for the determination and prediction of soil functional properties such as water holding capacity, organic matter retention, soil nutrients, fertilizer response among others. In addition, the findings presented the opportunity to improve soil assessment using information on soil mineralogy. For instance XRD information on mineralogy can be combined with information from infrared spectroscopy, which characterizes soil mineral and physio-chemical properties, to provide powerful diagnostic capabilities, and be used as a complementary input to pedo-transfer functions for low cost and rapid prediction of soil functional properties. Improved prediction of soil functional properties through the use of XRD combined with spectroscopy has potential to aid implementation of surveillance frameworks for soil fertility diagnosis and other agricultural, environmental and engineering applications

5.2 Recommendations

The results of this study provide an analytical method and data analysis framework for interpreting the physico-chemical and mineralogical processes in soils that can be used as a routine measurement in the AfSIS. Further research should seek to establish pedo-transfer functions for individual soil functional properties using XRD data both directly and combined with MIR spectral data. The use of raw diffractograms should be compared with fully quantitative estimation of mineralogical composition as an input to pedo-transfer functions. Further development of the interpretation methods is required to provide fully quantitative mineralogical determination. This quantification work may be aided by further work on mineralogical analysis of clay fractions, as opposed to whole soil samples, to build up mineral libraries.

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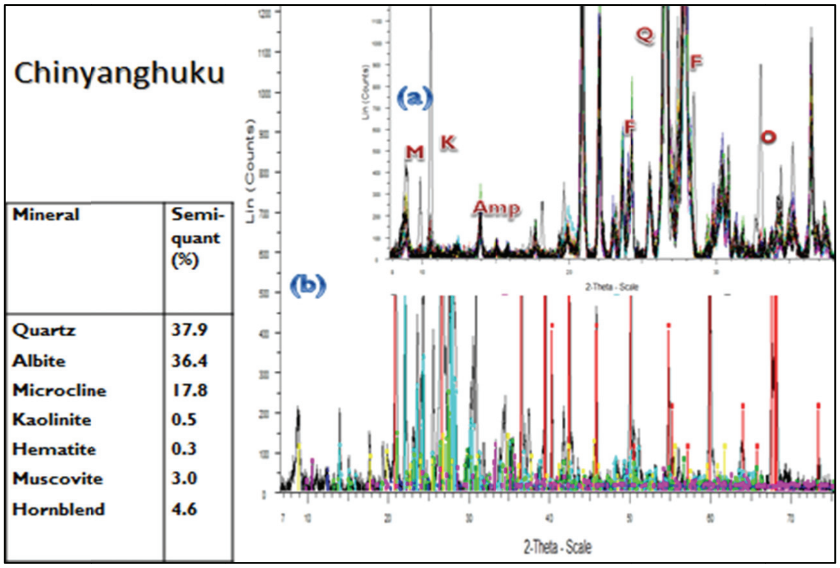
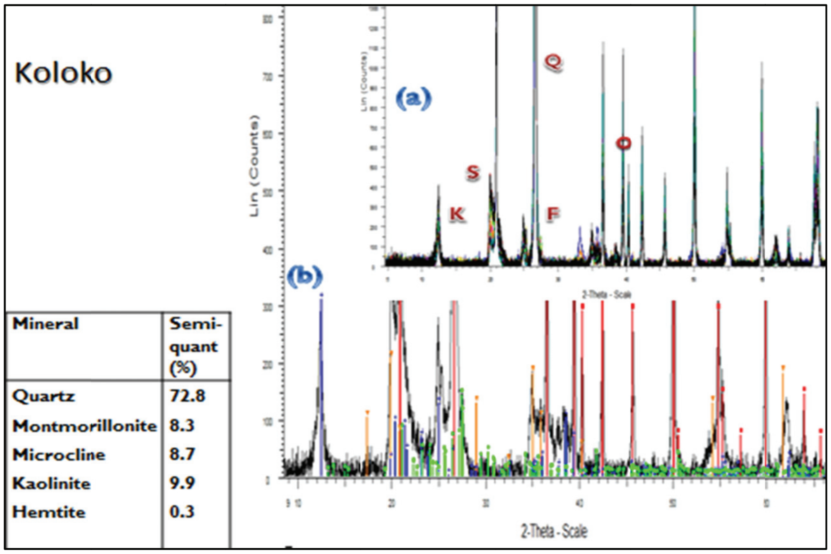
APPENDICES

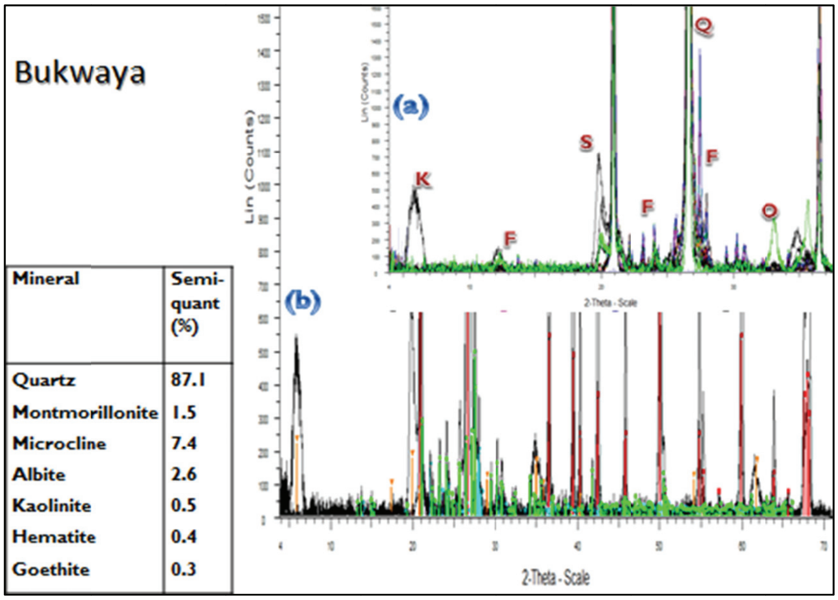
Appendix 1: *X-ray diffractograms for other sites.*



Mineral	Semi-quant (%)
Quartz	37.9
Albite	36.4
Microcline	17.8
Kaolinite	0.5
Hematite	0.3
Muscovite	3.0
Hornblend	4.6

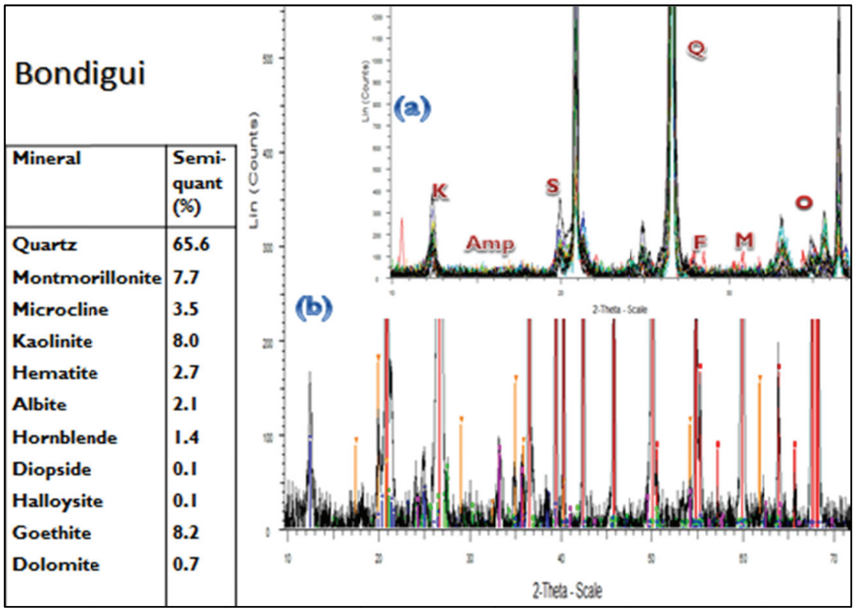


Mineral	Semi-quant (%)
Quartz	72.8
Montmorillonite	8.3
Microcline	8.7
Kaolinite	9.9
Hemtite	0.3



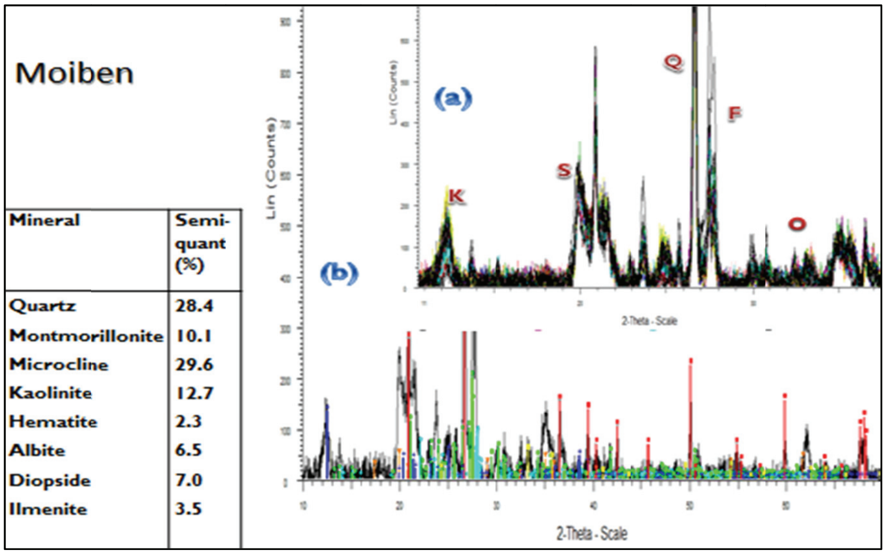
Bukwaya

Mineral	Semi-quant (%)
Quartz	87.1
Montmorillonite	1.5
Microcline	7.4
Albite	2.6
Kaolinite	0.5
Hematite	0.4
Goethite	0.3



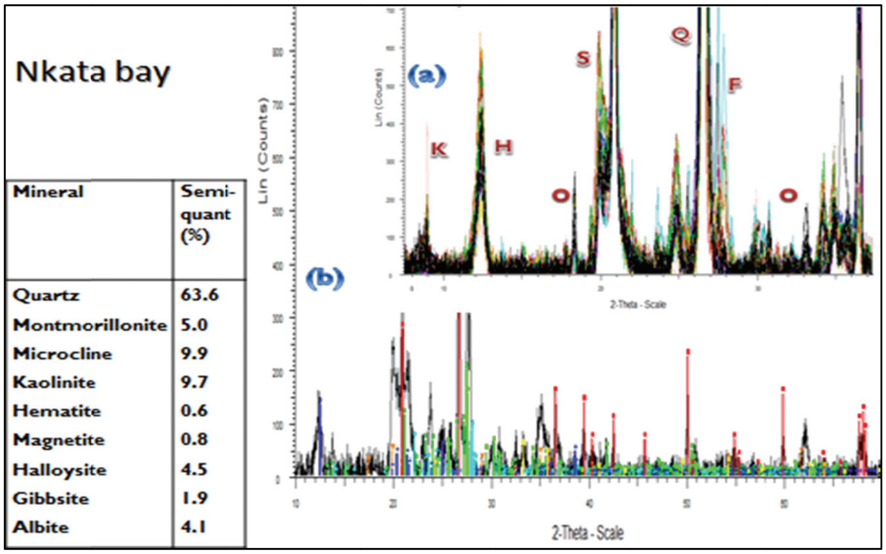
Bondigui

Mineral	Semi-quant (%)
Quartz	65.6
Montmorillonite	7.7
Microcline	3.5
Kaolinite	8.0
Hematite	2.7
Albite	2.1
Hornblende	1.4
Diopside	0.1
Halloysite	0.1
Goethite	8.2
Dolomite	0.7



Moiben

Mineral	Semi-quant (%)
Quartz	28.4
Montmorillonite	10.1
Microcline	29.6
Kaolinite	12.7
Hematite	2.3
Albite	6.5
Diopside	7.0
Ilmenite	3.5

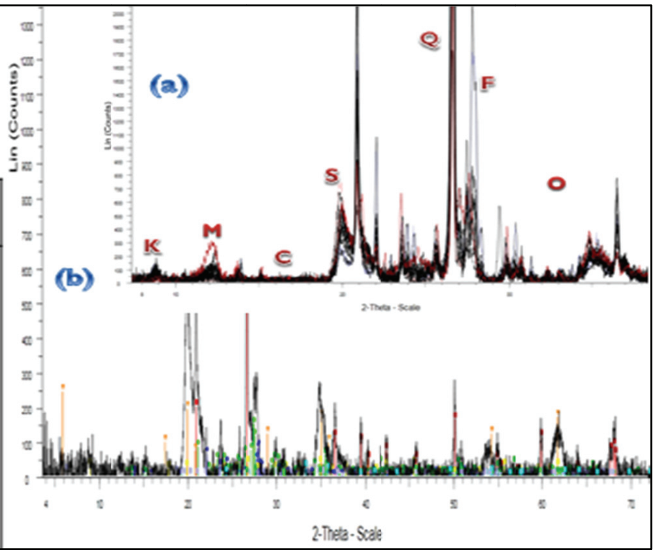


Nkata bay

Mineral	Semi-quant (%)
Quartz	63.6
Montmorillonite	5.0
Microcline	9.9
Kaolinite	9.7
Hematite	0.6
Magnetite	0.8
Halloysite	4.5
Gibbsite	1.9
Albite	4.1

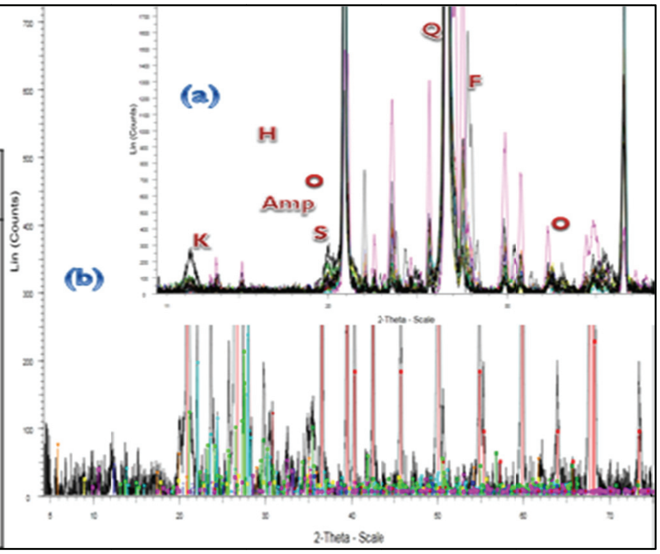
Mpala

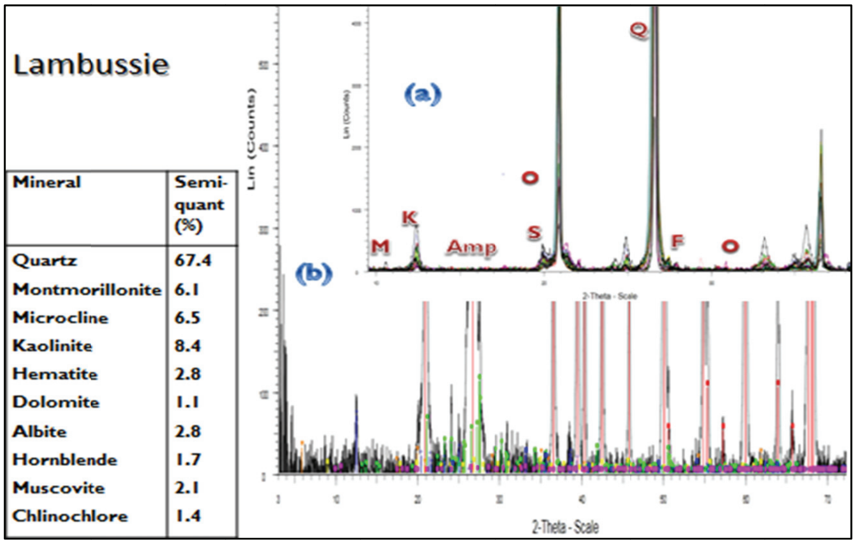
Mineral	Semi-quant (%)
Quartz	38.4
Montmorillonite	10.2
Microcline	18.7
Chlinochlore	2.0
Kaolinite	1.0
Hematite	0.6
Ilmenite	0.8
Albite	19.1
Diopside	5.8
Muscovite	2.5



Thuchila

Mineral	Semi-quant (%)
Quartz	59.5
Montmorillonite	2.5
Microcline	15.5
Kaolinite	2.0
Hematite	0.5
Ilmenite	1.5
Hornblende	0.5
Albite	7.5
Diopside	4.4
Muscovite	0.7
Dolomite	6.2





Mineral	Semi-quant (%)
Quartz	67.4
Montmorillonite	6.1
Microcline	6.5
Kaolinite	8.4
Hematite	2.8
Dolomite	1.1
Albite	2.8
Hornblende	1.7
Muscovite	2.1
Chlinochlore	1.4

Appendix 1: *X-ray diffractograms of top soils from all site (a) Mean from 16 top soil samples, (b) An example of one sample from the site (Q=quartz, S=smectite, K=kaolinite, F=feldspar, O=Oxide), all un labeled peaks = quartz.*

Appendix 2: Soil mineralogy (XRD) laboratory protocol

1. Introduction

The determination of the types and relative amounts of the minerals present in soil (soil mineralogy) is determined routinely because of its strong influence on soil behavior, its use in soil classification, and its relevance to soil genetic processes. At ICRAF I developed an X-ray diffraction (XRD) technique protocol for qualitative and quantitative clay mineral analysis in soils, with emphasis on methods using mineral intensity factors in combination with the so-called 100% approach. XRD is the principle tool and most powerful technique used for analysis of minerals and offers mineral phase's identification and quantification. It takes two types of approaches namely (1) Clay fraction approach; clay fractions are physically separated from the rest of the rock or material and made into an orientated layer of clay supported by a substrate and (2) Whole rock approach; sample is prepared into a random powder which helps in analysis of total amounts and identification of non-clay minerals present. These analyses provide information about the clay minerals present in a sample and also the abundance.

1.1. X-ray Diffraction technique for soil mineralogy

Powder diffraction is routinely used as a finger-print identification technique of various solid materials in the laboratory. It is a high-tech, rapid, cheap and non-destructive technique for qualitative and quantitative analysis of crystalline compounds; about 95% of all solid materials in the soil are crystalline (Moore t al., 1997). For mineral identification (silicates, clays, carbonates, oxides and some organics components) phases as little as 1-3% sample weight can be identified independent of crystal. XRD in our labs is done using a shown in (Figure 1).

1.2. Basic Features of Bruker bench top X-ray diffractometer (XRD)

- Ceramic **Cu source** X-ray tube KFL Cu-2K (0.4mm * 12mm **source of X-rays**) with line focus, housing and mount
- Incident-beam optics(primary optics components): condition the X-ray beam before it hits the sample
- The goniometer: the platform that holds and moves the sample, optics, detector, and/or tube
- The sample & sample holder
- Receiving-side optics (secondary optics components): condition the X-ray beam after it has encountered the sample
- 1dimensional-linear LYNXEYE silicon strip detector: counts the number of X- rays scattered by the sample and records diffraction pattern at varied angles
- Slide up front cover for sample loading and integrated computer

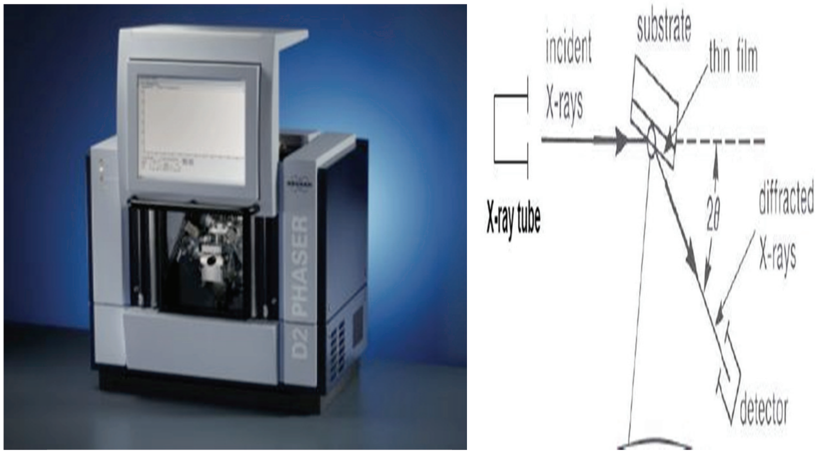


Figure1: XRD spectrometer with slide up front covers for sample loading and an integrated computer

1.3. Working principle

When X-rays interact with a crystalline substance or powder, a diffraction pattern called a diffractogram is produced and can be quantified. Information obtained from this patterns include phase composition of a sample, types and nature of crystalline phases (minerals) present, crystal structure, amount of amorphous (OM) content, microstrain, size and orientation of crystallites. XRD has become an indispensable method for materials investigation, characterization and quality control. The angle and intensity of the diffracted beam recorded by a detector forms a diffraction pattern, which provides information about a sample. Results are commonly presented as peak positions at 2θ and X-ray counts (intensity) in the form of a table or an x-y plot as shown in (Figure 2). Peak position (angle 2θ) and interplanar atomic spacing (d-spacings) provides information about atoms arrangement within the crystalline compounds. Peak width gives the crystallite size. Peak intensity (I) gives the type and nature of the atoms. A good instrument resolution resolves overlapping diffraction peaks in complex patterns. Linear one line detector (1D) diffraction Scans have better resolution and less noise as shown in (Figure 3).

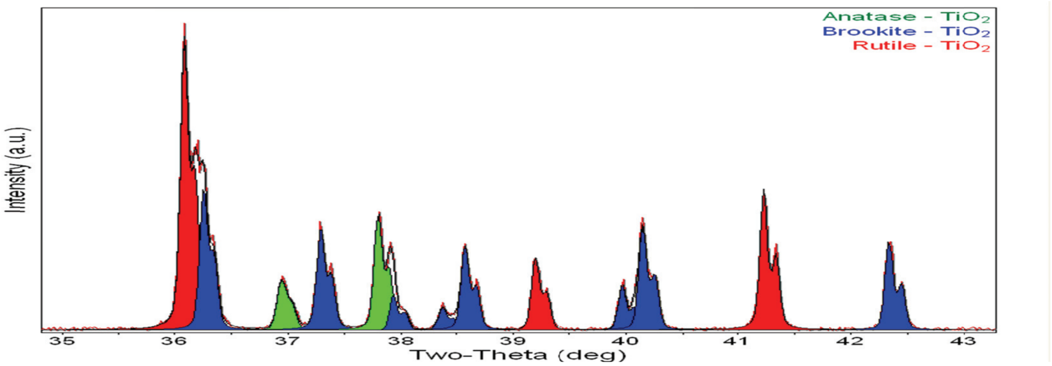


Figure 2: Example of a diffractogram produced during an X-ray scan

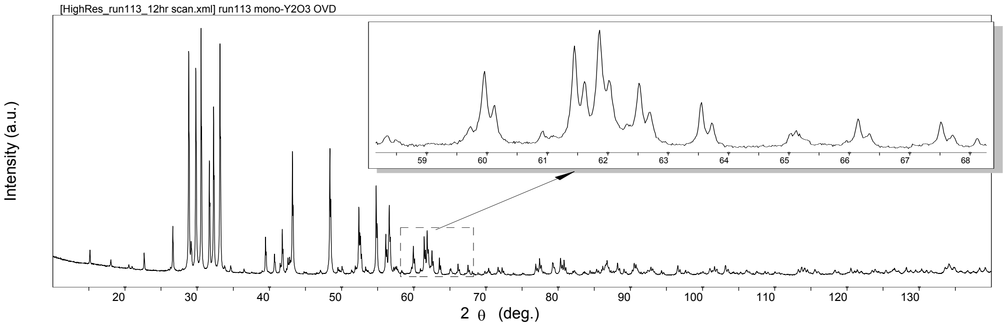


Figure 3: Example of a diffractogram with better resolution and less noise (inset)

The diffraction pattern for every phase is as unique as a fingerprint. Phases with the same chemical composition can have drastically different diffraction patterns. Use of the position and relative intensity of a series of peaks is used to match experimental data to the reference patterns in the database such as the Powder Diffraction File (PDF). The PDF contains over 200,000 diffraction patterns of crystalline phases. Modern computers have automated search/match programs that determine what phases are present in a sample by quickly comparing the *d*s of the unknown to those of known materials in the International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF). Phase composition and quantitative phase analysis is obtained by determining the d-spacing of each peak and then using the Bragg equation

$$\boldsymbol{\lambda = 2d_{hkl} \sin \theta}$$

Where: d = lattice interplanar spacing of the crystal

θ = X-ray incident angle (Bragg angle)

λ = wavelength of the characteristic x-rays

The (d) and (I) information will be used to 1) identify the type of material by comparing patterns obtained in standard databases, and 2) to quantitatively estimate the amount of that phase in a multi-component mixture.

The data will be collected using a measurement procedure that will ensure high peak/background ratios, low sensitivity to sample density variations, and a good counting statistics, while the strongest peaks of 0.334 nm quartz stay within the linearity range of the counter, and the beam stays within the preparation for the lowest 2theta angle, from which the analysis will be performed. These conditions will be met by using a Bruker AXS, D2 phaser diffractometer system operating at 30 kV and 10 mA using Ni-filtered Cu-Kα radiation, at variable rotation of 15^{o}/Min in the angular measurement range of 3 to 75^{o} 2Theta with an accuracy of 0.02^{o} throughout the measurement range, at 0.5 sec/step to obtain the X-ray diffractogram.

The intensity of diffraction of a given mineral in the sample under investigation will continuously be recorded as the sample and detector rotates through their respective angles as a peak (figure 4). The angle and intensity of the diffracted beam forms a diffraction pattern, which provides information about a sample.

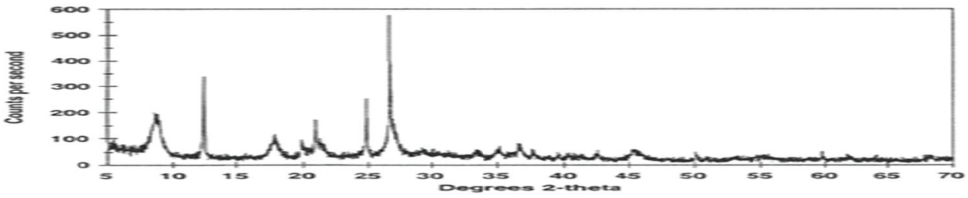


Figure 4: Example of an XRD data diffractogram

1.4. Applications

XRD has a wide range of applications in geology, material science, environmental science, chemistry, forensic science, and the pharmaceutical industry, among others. In Agriculture it has application in qualitative and quantitative analysis of actual minerals in top soils and sub soils, in classification of soils in terms of weatherable and nutrient rich minerals to measure soil fertility potential and use of mineralogical data in pedo-transfer functions to directly predict soil functional properties.

Caution!

Please read the 'D2 PHASER systems control and laboratory safety manual' before operating the D2 PHASER equipment and carrying out any XRD experiments!

Please refer to the XRD manual on safety and systems control.

2. Requirement:

2.1. Equipment

D2 PHASER Diffractometer with the following components:

1. A D2 PHASER Diffractometer with appropriate software
2. McCrone micronising mill
3. Weighing balance
4. Centrifuge
5. Oven
6. Ultra-sonic probe
7. Vacuum pump
8. Millipore filtration apparatus vacuum tubing

2.2. Supplies and consumables

1. Corundum and quartz standard reference material
2. Standard 55mm sample discs made from PMMA
3. Innovatek cooler fluid
4. glass microscope slides
5. Soft brush
6. Weighing paper
7. PH-indicator strips (non bleeding)
8. weighing paper (4"x4")
9. mortar and pestle
10. 250 µm mesh sieve
11. spatulas
12. carbide or diamond glass scriber or marker pen
13. Squeeze bottle with distilled water, ethanol and hexane
14. lab tissues
15. thermometer
16. Timer
17. 500 ml beakers
18. Stiff brush or stop cork no. 43
19. Uniform set of sedimentation cylinders (measuring cylinders) with internal depth of 340 ± 20 mm and capacity of 1 L.
20. Millipore HA, 47-mm, 0.45-micron nominal pore opening cellulose filters
21. Desiccators with desiccator shelf
22. Tongs
23. Hexane
24. Ethanol
25. Deionised water
26. Forceps

3. PROCEDURE

3.1. Sample preparation

3.1.1. Definitions:

Rock: Rock is an aggregate of one or more minerals. It may also include organic remains. Soils washed away and deposited become sandstones and siltstones. The structure of the original rock is replaced by a new one. This alters the mineralogy composition but the bulk chemical composition may not be different. Other chemical composition changes may occur due to high pressure with heat and movement.

Samples: Sample is the material supplied for analysis. Sample preparation is carried out according to sample receipt, preparation and storage procedures. An air-dried 2mm sieved soil sample is sub sampled to 10g by conning and quartering. The 10g sub sample is oven dried at 40^0C and then put in a labeled zip-lock polythene bag and transferred to the XRD laboratory

Specimen: specimen is the portion of the sample that is prepared and presented to the instrument and is a statistically infinite amount of randomly oriented powder with crystallite size less than 10 µm, mounted in a manner in which there is no preferred crystallite orientation. How a specimen is prepared will determine whether it is representative of the sample as a whole, and if the resultant data is similarly representative and is usually the most critical factor influencing the quality of XRD analytical data.

Specimen preparation procedures will generally aim at achieving three goals: randomness, homogenization and reduction in size of coarser- grained samples (desirable particle size, orientation,
thickness) in order to assure good reproducibility of peak intensities. Size reduction should not cause measurable damage to the layer structure to avoid destroying micas and the soil crystals. Careful preparation, loading and packing of specimen is important to reduce preferred orientation. Different specimens will produce different kinds of analytical errors, and it is important to understand these errors, how they may be recognized in your data, and how they can be minimized. Good sample preparation helps minimize errors and ensures good statistical representation. A measurement on a single sample must give the same result as an average measurement on a number of the same samples. Inadequate sample preparation can lead to significant variation, which is difficult to correct following analysis.

3.1.2. Principle

X-ray Powder Diffraction (XRPD) requires that a sample be prepared such that the particles in the sample are randomly oriented powder. An ideal powder sample should have many crystallites in random orientations such that the distribution of orientations should be smooth and equally distributed amongst all orientations. If the crystallites in a sample are very large, there will not be a smooth distribution of crystal orientations and a powder average diffraction pattern will not be obtained. Crystallites should be <10mm in size to get good powder statistics. Large crystallite sizes and non-random crystallite orientations both lead to peak intensity variation where the measured diffraction pattern will not agree with that expected from an ideal powder and the measured diffraction pattern will not agree with reference patterns in the Powder Diffraction File (PDF) database.

3.2. Whole rock approach Procedure

Here randomly oriented powders and mounts are prepared. The random orientation insures that the incident X-rays have an equal chance of diffracting off any given crystal lattice face of the minerals in the sample.

3.2.1. Randomly oriented powder

1. Using a loading device for McCone Mill load the forty-eight cylindrical agate grinding elements into the sample cup. This helps produce both line contact blows and planar shearing, in contrast to the random contact blows of a conventional ball mill.

2. Tare the weight of the sample cup with agate elements and weigh in 3 grams of soil sample. Using a wash bottle make to 12 grams with ethanol as a grinding fluid.

3. Cap the cup and mill with a McCrone Mill for 12 minutes. The unique grinding action of the mill rapidly reduces particles to submicrometer sizes and mixes for homogenization required for quantitative and qualitative analytical methods (Approx. 10 µm). A longer milling time lowers the intensity of the peaks. Making the particles too small can cause damage to crystal structure or alteration of phases making it difficult to identify or quantify the actual phases present in the sample.

4. After milling shake the cup just in case milling had stopped a few minutes before and stayed in the milling position. Wash out all the milled soil into a 50 ml centrifuge tube with ethanol making sure to collect as much of it as possible.

5. Turn on the power switch of the centrifuge and press Stop/Open to release the safety latch and allow the cover of the centrifuge to be opened. Place the tubes in the centrifuge. Be sure that the centrifuge is balanced by having opposite tubes filled equally with ethanol; 2, 4, 6, or 8 tubes may be used. Close cover. Centrifuge for 10 minutes at 4000 rpm.

6. Remove tubes from the centrifuge, pry off caps, and pour off the supernatant liquid into the sink. Be careful that the sediment on the bottom of the tubes is not poured off. (NB: we loose a little of the fine clays when decanting, if this is of interest then it would be better to evaporate ethanol in an oven instead of centrifuging.)

7. Add Hexane to the sample in the ratio of 0.5 ml hexane to 1 g of soil sample. Using a vortex mixture, mix to re-suspend the sample in hexane and then dry at between 80^{o} C to 105^{o} C in an oven for one hour.

8. Using a spatula to loosen any sample that has stuck to the centrifuge bottle, brush the dried material into from the tube to a 250 µm sieve.

9. Brush the powder sample through the sieve into a weighing paper. A plastic stop cork can also be used to push the powder through the sieve. The purpose of the brushing is to obtain a harmonized powder with many crystallites in random orientations.

10. Pour the sieved powder sample into a glass vial and cap. The sample is ready for loading and measurement.

3.2.2. Randomly oriented mounts

This involves preparing a powder mount that ensures as much as possible, a similar degree of packing, which is important for reproducibility of XRD patterns (peak displacement and broadening due to variations in sample density). It also gives a smooth flat surface with a random distribution of all possible h, k, l planes. Only crystallites having reflecting planes (h, k, l) parallel to the specimen surface will contribute to the reflected intensities. If we have a truly random sample, each possible reflection from a given set of h, k, l planes will have an equal number of crystallites contributing to it

1. Pour a fraction or portion of the randomly prepared samples into the well of a low background sample holder. Tap the holder on a bench or on the side to help fill and properly pack the sample to avoid sample displacement which causes peak shifts.

2. Using a sharp razor tap the sample surface slowly into either direction pushing excess sample slowly to the end of the well and finally scrapping it off the holder. Repeat this procedure until the well is completely filled and the sample surface flat with excess sample on the disk brushed off. Correct sample height to the lip is critical since error in height will cause peak displacement. After measurement the disc can be off loaded and washed with tap water and then re-used. Concern on trace contamination is not necessary

4. Sample measurement procedure

4.1. Instrument performance Verification and other maintenance checks

These are performance verification tests on the D2 Phaser diffractometer to check the functionality of all relevant components, precision and alignment of the diffraction system. These are:

Daily, Weekly and Monthly check: Performed routinely to check if the instrument is operating within specified limits. Instrument verification is done by measuring an in house quartz standard reference material delivered with the system. A Glasspalt kpl standard is also supplied for Customer acceptance tests. Other checks include checking the level and pH of the cooling fluid and daily initializing the drives of the D@ PHASER.

Please refer to the Instrument verification and maintenance manual.

4.2. Inserting the sample

Samples are placed in the sample holder of the diffractometer. The sample holder is factory aligned so that the goniometer centre coincides with the surface of the sample. The sample holder is mounted with four screws which must not be loosened to avoid the sample holder’s alignment being lost. It also has a spherical handle used to lift the sample holder into measurement position. The steps for inserting the sample are as follows:

1. Switch off the high voltage to open the door
2. Open the instrument door by sliding it up
3. Drop down the spherical handle of the sample holder lift

4. Take the sample and insert it into the sample position of the sample holder
5. Lift the sample back into the sample measurement position by pulling up the spherical handle
6. Close the instrument door by sliding it down and lock by putting the high voltage on

The sliding front door of the instrument is routinely opened to insert and change samples

Notes:

1. Do not forget to lift the sample back to sample measurement position by lifting up the spherical handle

2. The D2 PHASER difractometer is fitted with fans that provide its interior with fresh cooling air from the environment. When the front door is opened air flows from inside to outside the housing through the front door; hence only solid compressed powders and samples should be inserted into the sample holder to avoid sample being blown into the face or inside the instrument.

4.3. Measurement procedure

The data is collected using a measurement procedure that will ensure high peak/background ratios, low sensitivity to sample density variations, and a good counting statistics, while the strongest peaks of 0.334 nm quartz stay within the linearity range of the counter, and the beam stays within the preparation for the lowest 2theta angle, from which the analysis will be performed. These conditions will be met by using a Bruker AXS, D2 phaser diffractometer system operating at 30 kV and 10 mA using Ni-filtered Cu-Kα radiation, at variable rotation of 15^o/Min in the angular measurement range of 3 to 75^o 2Theta with an accuracy of 0.02^o throughout the measurement range, at 0.5 sec/step to obtain the X-ray diffractogram.

The intensity of diffraction of a given mineral in the sample under investigation will continuously be recorded as the sample and detector rotates through their respective angles as a peak

4.3.1. Instrument parameters settings:

Recommended settings for Bragg-Brentano systems to guarantee an optimum resolution at maximum intensity are as follows:

Instrument parameter	**Value**
Radiation Anode	Cu ($Cu_{k\alpha 1}$ = 0.154060nm)
Generator settings	30 kV, 10mA (recommended)
Divergence slit	0.6mm
Axial Soller slit module	Primary 2.5mm, Secondary 2.5mm
Anti scatter screen	1.0mm
Monochromatisation kβ - filter	0.5 Ni filter
Linear LYNXEYE detector	5^0 detector opening and 0.5% Ni-filter Upper and lower discriminator window at 0.240^o and 0.160^o

4.3.2. Measurement parameters settings:

For LynxEye detector all reflections are measured in one uninterrupted range. Other recommended settings for Cu radiation are as follows:

i) Method name: Quartz reference standard

Measurement parameter	**Value**
Rotation	15 rpm
Scan type	Locked coupled (Coupled $\theta/2\theta$ scan)
Two Theta (2θ)	1 range start 25^0, increment 0.004^0, stop 27^0
Time per step (s)	0.500s

ii) Method name: Soils and clay scans

Measurement parameter	**Value**
Rotation	15 rpm
Scan type	Locked coupled (Coupled θ/2θ scan)
Two Theta (2θ)	1 range start 3^0, increment 0.002^0, stop 75^0
Time per step (s)	0.500s
Run time	30 minutes

iii) Method name: Reference samples scans

Measurement parameter	**Value**
Rotation	15 rpm
Scan type	Locked coupled (Coupled θ/2θ scan)
Two Theta (2θ)	1 range start 3^0, increment 0.002^0, stop 75^0
Time per step (s)	3s
Run time	3 hours

4.4. Start measurement with commander

1. Close door and switch on HV to set generator to 30kV and 10mA.

2. Initialize 2θ and Phi motor using the initialize button on the commander screen.

3. Entervalue for sample rotation in rpm as per methods above and press ‘set’ button to start rotation.

4. Select scan type, scan mode, increment and time as per method being run. Start measurement by pressing the start button.

5. After the measurement is complete save the raw scan file in the appropriate folders of the D2 PHASER computer.

5. Reference:

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